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SCUOLA DI INGEGNERIA INDUSTRIALE
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EXECUTIVE SUMMARY OF THE THESIS

Grease-resistant and water-resistant coating solutions for paper-based food packaging materials

MASTER THESIS IN FOOD ENGINEERING

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ACADEMIC YEAR: 2020-2021

1. Introduction

Food packaging is one of the most important aspect linked to the food industry.
It is aimed at product's protection, being solid during transport and it can be also a driver for advertising. Therefore, in the last decades food packaging has increased its role and importance in the supply chain.
Plastics, as one of the most used material in the packaging industry, represents a problem for their end-of-life treatments. although looking for a versatile and processable alternative with overall good mechanical and barrier properties is challenging
[1][2].
Plastics waste management is the main aspect that has moved companies towards the production of new packaging solutions based on alternative materials.
One of the main materials that is increasing its role in the food packaging industry is paper. Paper is easy to produce and use, but does not possess great barrier properties, in fact, when put in contact with water or grease tends to be permeated easily [3].
In order to improve these properties paper-based packaging are usually coupled with plastics, biomolecules and bioplastics in the form of films or coating. Paper has a great importance in terms of recyclability, moreover, if coupled with other compostable or biodegradable materials such property can be preserved [4].
This relevant feature has moved the market to develop sustainable materials, able to protect the packed products and able to be treated after their usage in a way that does not affect the environment [5].
As mentioned before, two of the main substances that could affect paper structurally are water and oil, therefore, in order to increase the resistance of paper against them, several materials can be added to enhance both grease and water resistances.
The idea of this project work is to deliver a paper-based food packaging materials, which possesses improved performances, recyclability and, if possible, compostability.
Chitosan and sodium alginate, as commonly used biomolecule, may represents a serious alternative to plastic film [6]. However, their hydrophilic nature must be taken into consideration.
Zein, a corn's protein, due to its hydrophobic nature, has been chosen as well to be tested when applied on paper-based substrate. Nonetheless, zein tend to be expensive, but possesses good barrier property against the permeation of gases [7].
Lastly, Poly-L-Lactic Acid (PLLA) which is a stereoisomer of Poly Lactic Acid (PLA), due to its water repulsion capabilities has been selected to be tested [8].

2. Experimental section

In this study, film and coating from the selected materials have been produced and characterized to understand if they will fit as a packaging solution for paper-based substrate.

2.1 Materials and methods

All materials have been developed by Sigma Aldrich:

- Chitosan: deacetylation degree 85%, medium molecular weight.
- Sodium Alginate: the one extracted from algae.
- PLLA: stereoisomer of PLA, developed in flakes.
- Zein.

Preparation of solutions.
Chitosan solution, 2% (w/v), dissolved in aqueous solution of acetic acid 1% (v/v) by means of magnetic stirring for 24h at 23°C. Sodium Alginate solution, 2% (w/v) in deionized water, magnetically stirred for 24h at 23°C. PLLA solution, 6% (w/v) in acetone solution, agitated for 24h at room temperature. Lastly, Zein, 20% (w/v) have been dissolved in ethanol solution, 95% (v/v) dissolved with magnetic stirring for 24h at 23°C.

Coating deposition.
A study of the interaction between the developed solutions and paper was carried out, in order to preliminarily select the best performing materials for our application.
Solutions were deposited by pasteur's pipette on previously made paper sample, cut in squares of 6 cm x 6cm [9].

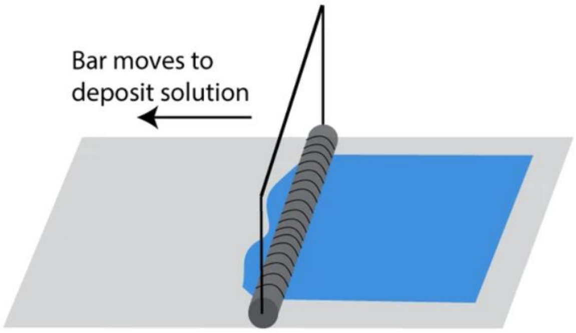

Figure 1: Rod coating method [9].

Film casting.
Separated film specimens with 50 μm thickness have been prepared by solvent casting inside petri dishes, in order to further analyze the materials emerged as promising from interaction with paper.

Coating configuration.
Starting from the development of single layer based on chitosan, alginate, PLLA and Zein, multilayer materials were built layer by layer to increase packaging properties.
The materials were coupled as follows:
- Alginate and chitosan: to create a packaging solution able to protect food products from grease penetration.
- PLLA and chitosan: to increase PLLA own grease resistance while increasing water repulsion of chitosan.
- Zein and PLLA: since the former has a better barrier properties against oil, the latter can increase water resistance.

Figure 2: Multilayer solution characterization.

In this work tri-layer and multilayer solutions have been studied due to results come out by testing single and bi-layer. The goal was to look for solutions which are not already present in the market.

3. Characterization

Thickness and grammage increment.
Using an electronic micrometer and an electronic scale, thickness increment and g/m^2 increments can be measured.
Thickness is an aspect of relevant importance because films and coatings must fit in specific thickness requirements in order to enter in the market. Have been taken 8 measures, and then averaged them.

Droplet's test.
To qualitatively understand the behaviour of the deposited coatings, water and olive's oil droplet was dropped above the designed packaging configurations, checking at predetermined timepoints the diameter's increment.
Droplet's diameters have been measured using ImageJ at the t0, time at which droplets are deposited on materials, and after 120min.

ASTM F119: grease penetration.
To assess the penetration time of a grease substance through the deposited coatings. A frosted glass plate has been placed underneath the specimen, then a cotton's patch, wetted with olive's oil, was compressed with a 50g weight on top of the

setup. Then, at predefined timepoints, it was observed the penetration time needed for the oil to reach the glass plate was measured [10].

ASTM E96: water vapor transmission rate.

Water Vapor Transmission Rate (WVTR) of the designed configuration has been measured following the ASTM E96. The test allowed a quantitative measurement of water vapor amount penetrated through the sample. The test's setup included a stainless-steel cup, filled with deionized water, in which the specimen is fixed by vacuum and sealed by an interlocking closure. The cups have been arranged inside a plastic container filled with $CaCl_2$, generating a proper driving force due to the different RH % between the cup (100%) and the container (0%). The test was conducted at 37.5 °C for 24h [11].

ASTM D570: water adsorption.

Water absorption of a material is a fundamental property that needs to be evaluated when its application may lead to direct contact with water.

Samples of specified dimension have been prepared and dipped in a becker filled with water for 24h. Then, to assess the structural conditions of the materials], the specimens were weighed and left drying under hood at room temperature [12].

ASTM D3985-02: oxygen transmission rate

The oxygen transmission rate (OTR) test was used to assess barrier properties of the selected materials against the oxygen permeation. The specimens were fixed between two distinct chambers which composed a standardized permeation chamber (Oxygen Permeation Cell, Precision Sensing GmbH). Filling the lower chamber with pure oxygen and the upper one with nitrogen, it was possible to creates a strong driving force due to the gradient of O_2 concentration [13]. The OTR values have been calculated following the equation Eq_3

3.1. Equations

$WVTR = G/(t * A)$ [Eq_1]

In which:

G= weight change [g] .

t= time during which G occurred [h]

G/t= slope of the straight line, [g/h]

A= test area (cup area),[m^2]

WVTR= water vapor transmission rate in [$g/m^2/d$]

$increase\ in\ weight, \% = (Wa - Wb)/Wa * 100$ [Eq_2]

In which:

W_a= weight after immersion [g].

W_b= weight before immersion [g.]

$OTR = (p_{o2} * Vcell)/(p_{std} * A) * (T_{std}/T_M) * p_{std}$ [Eq_3]

In which:

P_{o2}= increase in oxygen partial pressure in the upper test chamber [hPa/d]

V_{cell}= volume of the upper test chamber [cm^3].

P_{std}= standard pressure of the test [hPa].

T_{std}= standard temperature of the test [k].

OTR= oxygen transmission rate [cm3/ m^2/d].

ΔP_{02}=difference in pressure between lower and upper chamber.

A= permeation area [m^2].

4. Results and discussion.

The first part of the experiments has been focused on the characterization of the single layer structure deposited upon paper specimens, so as to discard materials resulting in being inadequate for our purpose. Both droplet tests and grease penetration tests confirmed the typical behavior of chitosan and sodium alginate films as good barrier against grease, while less interesting performances have been detected for PLLA and zein turned out to be a less efficient alternative. On the contrary, when looking at the barrier properties, zein provided the best protection against water vapor if compared to other materials which also holds true for its performance on paper . On the other hand, chitosan and alginate coating provides good protection in case of oxygen permeation.

Consequently, the number of layers deposited on paper was increased to test the efficiency of the above-mentioned materials in further enhancing paper's properties when combined together. Therefore, different multi-layer configurations have been selected through an optimization process in which the number of deposited layers has been gradually increased. Firstly, bilayer configurations slightly ameliorated grease protection, which was already satisfied by single layer of chitosan and sodium alginate. Secondly, tri-layer solution showed little improvements of the water vapor permeability in case of Zein and PLLA based solutions. As a final effort, four layers configuration provided interesting results, described in more detail below.

Grammage and thickness results.

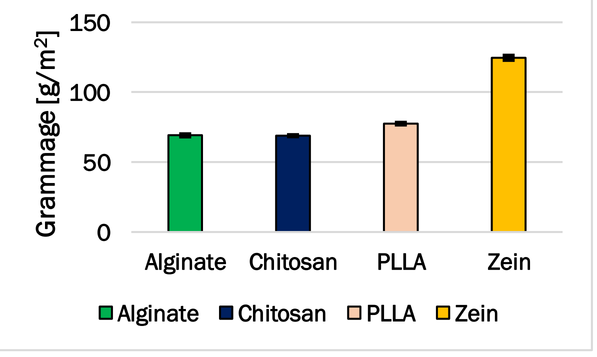

Figure 3: increase in grammage.

As shown in Figure 3, an increment in g/m^2 can be detected. Grammage increase of Alginate and chitosan coated paper was of 69.14 ± 0.79 g/m^2, and 68.91 ± 0.42 g/m^2. PLLA increase by 77.51 ± 0.64 g/m^2, while zein turned out to be the heaviest coating with an increment of 124.61 ± 1.51 g/m^2.

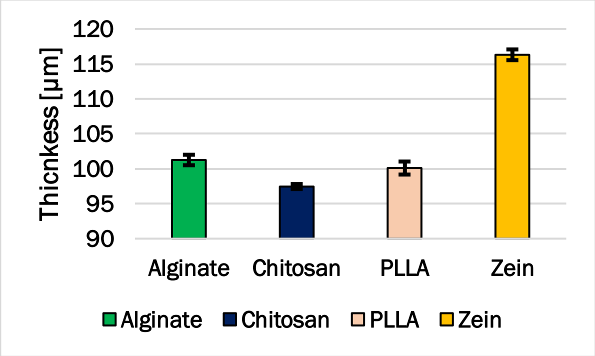

Figure 4: Thickness of single-layer configuration, values are expressed as paper + coating.

Starting from paper (90μm), increments in layer thickness for each single coated material are shown in Figure 4.
Alginate increase in thickness was 21.3±0.75 μm, chitosan increase was 17.45±0.36 μm, whereas PLLA increase was 20.1±0.93. The most relevant thickness increase was that of Zein, by 36.3±0.77 μm.

Droplet's test results.
From this test also a quantitative analysis can be develop based on increment of droplet's diameter according to time.
Results have been shown in Figure 5.

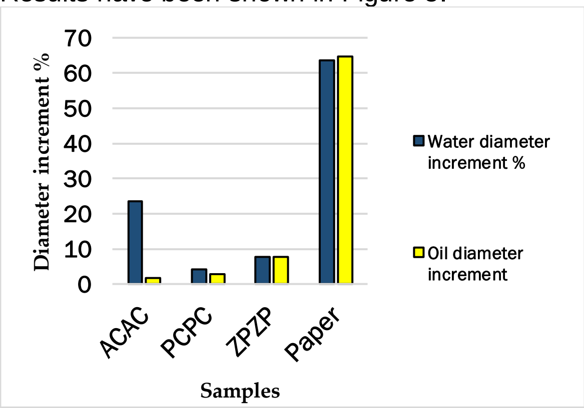

Figure 5: Diameter increment after droplets test

ACAC solution is the one that has the best response to grease penetration (2%), while it has problems considering water permeation (23%). PCPC is good at both reagents, water (4%), oil (3%). ZPZP responds similarly to water (8%) and oil (8%).

ASTM F119: grease penetration results.

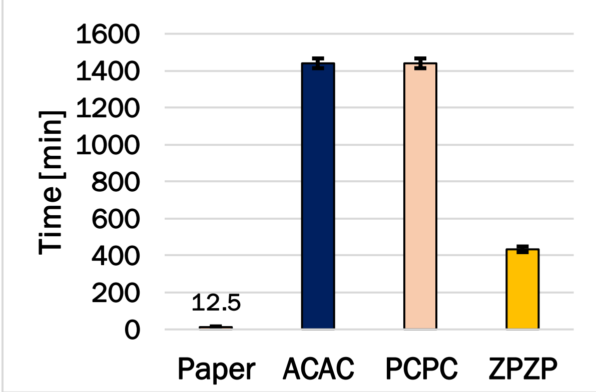

Figure 6: ASTM F119 multilayer results

Figure 6 shows time of grease penetration. ZPZP solution shows halos after 7.30h±15 min, while PCPC and ACAC solution are able to protect from grease penetration for the entire test duration, 1440min±26. ASTM F119 carried out with olive oil has underlined the ability of all the solutions not to be not penetrated after different times. Halos created by the possible penetration of oil through materials have been made at constant interval of time up to 24 h. According to [10] tests shall be run for a longer period of time and with different type of grease.

ASTM E96: WVTR results.

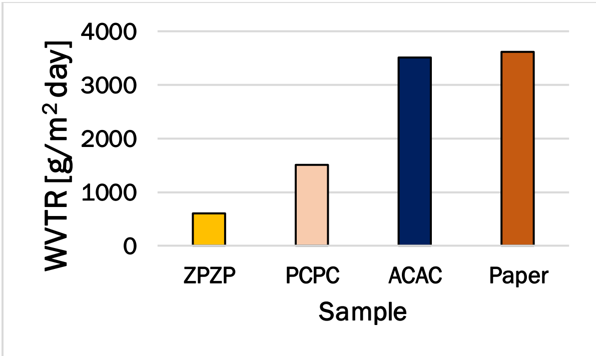

Figure 7: WVTR multilayer results

As shown in Figure 7, ZPZP was the best solution to significantly improve barrier property against water vapor: this may be the complementary action of both the hydrophobicity of zein and PLLA. On the other hand, ACAC is the worst one, providing no significant enhancement if compared to pristine paper's performance, as expected from hydrophilic materials such as chitosan and sodium alginate. PCPC configuration provides some improvement, although less outstanding than ZPZP, the main protection of this designed is given by the two layers of PLLA. The obtained results were difficult to properly compare to the literature, since parameters such as the type of paper, the solution's composition, thickness and deposition technique, highly affect the barrier properties. However, some agreement with similar studies can be found, for example in [14] where similar performances have been shown by chitosan coated print paper.

ASTM D570 water adsorption results.

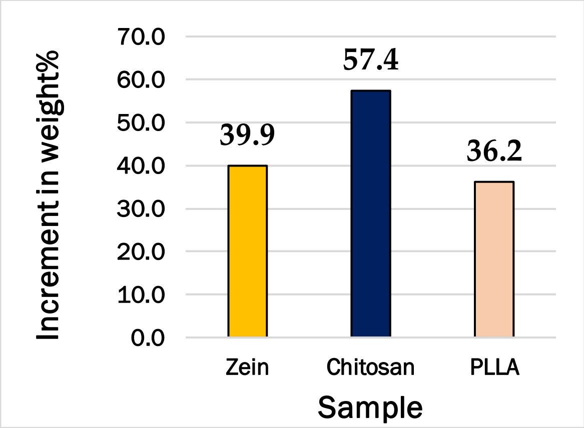

Figure 8: Increment in weight % after 24h immersion.

Chitosan, due to its hydrophilic nature, reported the highest value of water absorption among the selected materials. On the other hand, both PLLA and zein showed similar behaviour during the test, increasing the starting weight around 40%.
Sodium alginate, absent in Figure 8, was totally dissolved during the test, providing no opportunity to quantify the data. Such result was expected, according to [15].

ASTM D3986-02: OTR results.
Oxygen transmission rate of the synthetized film of chitosan, sodium alginate and PLLA have been measured by means of an oxygen permeation chamber. Both OTR value of chitosan and Alginate have been compared to those found in recent literature while PLLA film has been bought from a supermarket in order to compare the values (articles which analyze PLLA OTR were not found). Unfortunately, a proper zein film was difficult to be prepared due to the high stiffness of the synthetized material, which will inevitably influence the test's results. Measured OTR values have been shown in Figure 9.

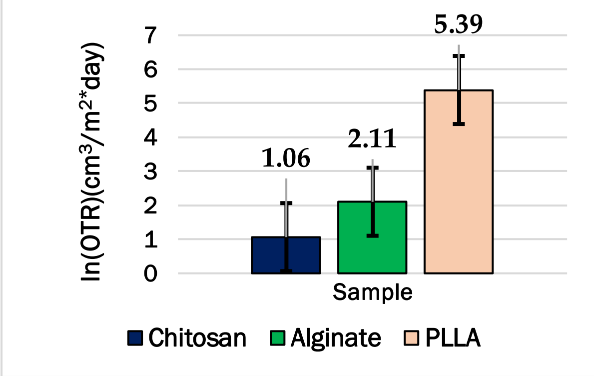

Figure 9: OTR logarithmic path of single layer materials films

Firstly, OTR measurements detected from the chitosan films, around 3 cm^3/m^2/day, were in good agreement with current literature [16]. Similarly, sodium alginate specimens showed comparable values to [17]. Surprisingly, the oxygen transmission rate of PLLA film, was lower than the one measured from a PLA-based packaging, acquired from a local supermarket and used as a comparison.
Lastly, considering paper's OTR 918 cm^3/m^2/day [18], an increase in Oxygen Barrier can be seen if coupled with films.

5. Conclusion.

During this study, different packaging configurations have been developed in order to provide an optimal solution, both in terms of biodegradability and performances, for paper-based packaging. Preliminary results obtained from single layer, bi-layer and multi-layer configurations showed a significant improvement in terms of grease protection as well as water and oxygen permeability. However, some of the reported results found some differences to similar evaluation presented by the scientific community. This is mainly connected to substantial differences between test's parameters, such as the type of paper used as substrates, the chemical composition of the synthetized solutions, thickness and grammage of the coatings. For example, Kraft Paper [19], is a thicker and more compact material then the paper used in this study. Therefore, the comparison between the two types of paper needs further attention. Single layer configurations provided the enhancement of grease penetration and oxygen barrier properties, in case of chitosan and alginate while zein and PLLA were useful to improve the WVTR of the packaging.
Bi-layer configurations followed similar trends to those observed previously during the preliminary analysis on single layer coatings. However, some improvement in WVTR was achieved by the

combination of PLLA and chitosan as well as zein and PLLA.

Lastly, both tri-layer and multi-layer structured configurations slight strengthened the benefits highlighted during preliminary analysis. In conclusion, PCPC configuration, was the best choice to provide the overall best performances to paper substrate. This results, underlined the importance of combining complementary materials such as chitosan (for grease protection) and PLLA (as a hydrophobic layer), to create a solution suitable to different tasks.

However, considering the water vapor transmission rate test, PCPC had a minor impact than ZPZP configuration. Nevertheless, due to the inconsistencies in the film structure and the studied properties, zein based packaging solutions were not the best options.

On the other hand, PLLA-chitosan multi-layer can be destinated as a food packaging solution in order to enhance the barrier properties of paper-based substrate. The best target for this packaging can be products that possess a great water activity and must be protected from gasses permeation, such as fruits and vegetables [20].

Considering the solutions developed in this work, and the trends of the food packaging industry, all materials can be produced as card coated vessel with different type of products, like ready-to-eat meat, fish, fresh fruits and vegetables and then sealed with film to increase barriers against oxygen and water which are, considering food packaging, the worst enemies [21].

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List of figures

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Grease-resistant and water-resistant coating solutions for paper-based food packaging materials.

TESI DI LAUREA MAGISTRALE IN FOOD ENGINEERING

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Academic Year:	2020-21

Abstract

Paper-based materials are increasing their importance in the packaging industry. Paper possesses great properties such as recyclability and ease of usage, moreover, can be coupled with biomolecules, plastics, and bioplastics to realize more versatile packaging solutions.
New paper-based packaging solutions have been designed to improve the grease and water resistances of the base material. Typically, the best strategy consists in coupling paper or cardboard with another material as a coating or film.

In this work different materials, namely Chitosan, and Sodium Alginate, Poly(L)Lactic Acid (PLLA), and Zein, have been used to improve the barrier properties of paper. Chitosan and Sodium Alginate were selected to enhance the grease resistance, PLLA to prevent water penetration, and Zein as biopolymer to achieve both oil and water resistances. After the preparation, the selected solutions have been deposited by mean of rod coating technique on paper samples.
The prepared specimens were then characterized by standard tests to evaluate their performances in terms of grease resistance, water resistance, and barrier against oxygen and water vapor.

Results show that these solutions respond properly against oil penetration and water penetration. Solutions developed in this work have the aim of being fully recyclable and push the market through sustainability. New trends in the food industry make clear that the development of this kind of materials can helps in preventing food and materials waste.

Keywords: paper board, coating, grease resistant, water resistant, biopolymers.

Abstract in lingua italiana

I materiali a base carta stanno aumentando la loro importanza nell'industria degli imballaggi. La carta ha grandi proprietà come riciclabilità e facilità d'uso e può essere accoppiata con biomolecole, plastiche e bioplastiche per essere più efficiente.

Nuove soluzioni di imballaggio a base di carta sono state progettate per migliorare la resistenza al grasso e all'acqua del materiale di base. In genere, la migliore strategia consiste nell'accoppiare carta o cartone con un altro materiale come rivestimento o film.

In questo lavoro diversi materiali, vale a dire chitosano e alginato di sodio, acido poli(L)lattico (PLLA) e zeina, sono stati utilizzati per migliorare le proprietà barriera della carta. Il chitosano e l'alginato di sodio sono stati selezionati per migliorare la resistenza al grasso, PLLA per prevenire la penetrazione dell'acqua e Zein come biopolimero per ottenere resistenze sia all'olio che all'acqua. Dopo la preparazione, le soluzioni selezionate sono state depositate mediante tecnica di rod coating su campioni di carta.

I campioni preparati sono stati poi caratterizzati da test standard per valutarne le prestazioni in termini di resistenza al grasso, resistenza all'acqua e barriera all'ossigeno e al vapore acqueo.

I risultati mostrano che queste soluzioni rispondono correttamente contro la penetrazione dell'olio e la penetrazione dell'acqua. Le soluzioni sviluppate in questo lavoro hanno l'obiettivo di essere completamente riciclabili e spingere il mercato attraverso la sostenibilità.

Le nuove tendenze nell'industria alimentare chiariscono che lo sviluppo di questo tipo di materiali può aiutare a prevenire lo spreco di cibo e materiali.

Parole chiave: carta, oleorepellente, idrorepellente, biopolimeri, film e coating.

Index

Introduction

Paper-based packaging materials are increasing their importance in the food packaging industry. The main properties of paper such as recyclability versatility and processability, have facilitated its application as a packaging material.

The main drawback in using paper-based packaging resides in its poor barrier properties, however, paper and cardboard can be coupled or laminated with different materials in order to achieved as a composite material, extending its application to the food industry, protecting the products from spoilage and reagents.

Nowadays plastics is the most used material coupled with paper due to ability of preventing food spoilage by increasing water and oil repulsion. To deliver a packaging solution focused on recyclability and sustainability, paper can be laminated with biopolymers.

Biopolymers, like bio molecules and bioplastics, are used to increase paper properties against water, oil and gases permeation. Paper can be coated both with films, and coating solutions, using different methods, and delivering different materials.

Paper-based materials and biomolecules, due to their nature as a recyclable and compostable solution, found great interest by the current market, as governments demand concrete changes by industries and companies [0].

1. Food packaging.

Food packaging is essential and pervasive: essential because without packaging the safety and quality of food would be compromised, and pervasive because almost all food is packaged in some way.

Food packaging fulfills several functions: it protects the food from contamination and spoilage; makes it easier to transport and store foods; and provides uniform measurement of contents. By allowing brands to be created and standardized, it makes advertising meaningful and large-scale distribution and mass merchandising possible. Food packages with dispensing caps, sprays, reusable openings, and other features make products more usable and convenient[1].

Usually, packaging can be distinguished between primary, secondary and tertiary. A primary package is one that is in direct contact with the contained product. It provides the initial, and usually the major, protective barrier.

A secondary package contains several primary packages, for example, a corrugated case. It is the physical distribution carrier and is sometimes designed so that it can be used in retail outlets for the display of primary packages.

A tertiary package is made up of a multiple of secondary packages, the most common example being a stretch-wrapped pallet of corrugated cases.

Food packaging is one of the most important aspects that belongs to the food supply chain. Packaging is proper discipline that works simultaneously with the production site, to give to customers' products that are fresher, that have an extended shelf life, and bring with them also an emotional factor. Packaging is not only what protects, prevent, and facilitates the transportation; it is also important to sell the product, as an advertising vehicle, to bring with it community needs in terms of sustainability, thus making a company more important in the food market because of its attention to materials employed in packaging [1].

To design a food packaging, a very broad range of materials can be used; it’s easy to see glass used for bottles of wine, or plastics in every shelf of a supermarket. In the last year, also considering the claim for a plastic-free world paper and paperboard packaging materials have increased their usage in the food industry.

Choosing which material the product will be made of is a crucial aspect, since this decision can determine if the final product will be successful or not.[2].

In particular, if the material will be able to achieve its goal, how much it will last and its economical and industrial feasibility. In brief, can be said that the three main players (Figure 1) involved in the design procedure of a generic product are:

- The product itself;
- The material it is made of;
- The manufacturing processes;

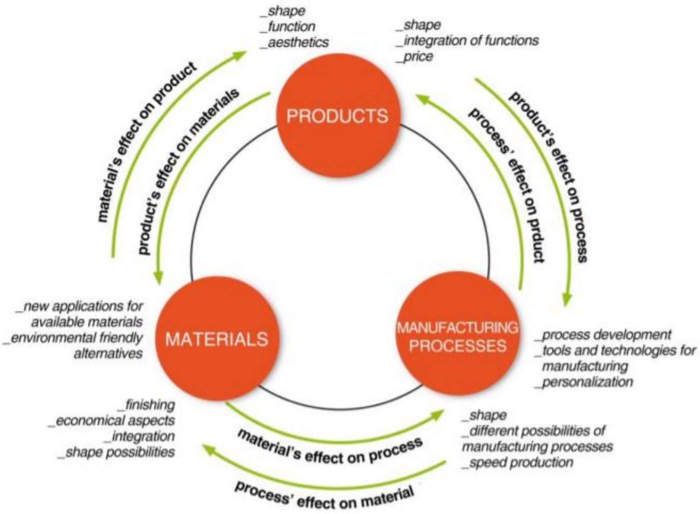


Figure 1: Relationship among Products, Materials and Manufacturing Process, with their relative effects on each other. [2]

All three aspects must be considered because they are strictly interdependent and could help in designing the correct solutions. No less relevant is the analysis of the solution already present in the market, which could help in understanding in which direction to focus attention, and what can be added to the already existing typologies.

Food packaging is one of the most important aspects of the food industry and considering all the materials which it can be made of, a benchmark analysis of what it can be found in supermarkets must be done.

The most widely used materials all over the world are obviously plastics. Considering their importance in preventing food spoilage, and their ease of processing.

The main plastics which can be found in the food industry are Polyethylene (PE), Polypropylene (PP), Polyethylene Terephthalate (PET) and Polystyrene (PS). All of them can protect food from contamination and are also great barriers against water and oil. However, considering their distribution worldwide, and the misuse people make of them, the recyclability of these types of packaging is a huge problem.

Plastics are mainly produced as films, extruded, and then laminated on paper; this process allows paper to increase its properties against oil, water vapor and liquids. Considering a PET film, Water Vapor Transmission Rate, and grease repulsion can be increased [3]. Another important type of plastic is PS, it is a great moisture repellant, is easy to use, and is considered also in big markets like the US one [4].

Plastics represents one of the best materials to have been invented but there is a great problem considering their impact on the environment.

Posing the attention on the environmental problems is mandatory to find and analyze different solutions, which can be useful for both their properties, as well as been eco-friendly, fully recyclable and, biodegradable. Considering alternatives to plastics biopolymers can be analyzed. These materials are mainly used in solution, like chitosan, a biopolymer that comes from shrimps,[5], but also some components that are produced by animals like beeswax [6] or proteins that come from whey or molecules that come from starch [7].

Each of this biopolymer is interesting because can increase paper properties by being coated on it. Chitosan and beeswax, for example, are grease repellants, [5,6], while proteins and starch are considered for their ability to repulse water [7]. Considering their end of life, it can be surely said that they are completely biodegradable [6], because they come from the biosphere, but they are able to decay naturally and without harming the environment; so, they could bring important aspect linked to sustainability that can help industry in reaching a better waste utilization.

Bioplastics, such as Polylactic acid (PLA) or Polybutylene succinate (PBS), represent a particular class of materials which is raising its position into the market.

These types of material are respecting the request of more biodegradability of the market. Something that can protect and store the products but that also respects the environment and does not produce relevant waste. Materials that are specialized in a specific property, like water repulsion [8], and can be implemented using other solutions in order to create a specific packaging are already used in industry and can be found in well-known supermarkets.

They are biodegradable but to produce them is used a close exploitation of natural resources, and this means that the industry paradigm cannot be changed [8].

1.1 The plastics substitution's problem.

When a food package is put into market, it is of relevant importance to write on the package which is the end-of-life treatment of the material intended for the use. It is mandatory according to the law to write on a package where the customer must throw it out after the consumption of the product [9]. Nowadays with the rise of initiatives guided by more developed countries, there is an increasing attention on packaging waste, and on plastic waste.

Plastics is a problem due to its wasting after consumption. Nations have decided to take decisions and try to build programs that could solve this specific problem for the environment.

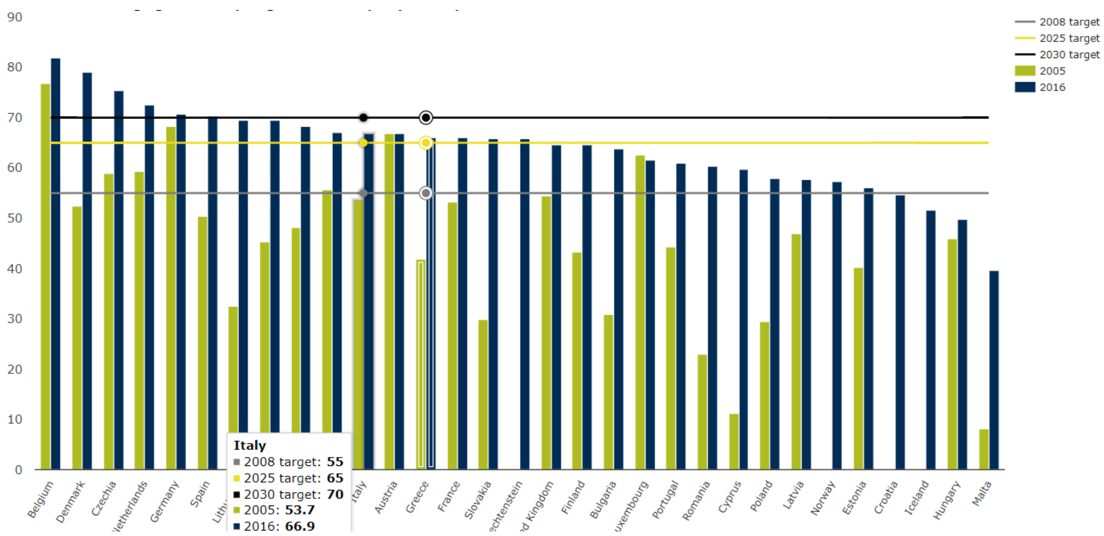


Figure 2: Packaging waste recycling rates by country in Europe.

[10]

In 2015 the United Nations decided to subscribe to the Agenda 2030: “This Agenda is a plan of action for people, planet and prosperity. It also seeks to strengthen universal peace in greater freedom.”

Agenda 2030 recognizes that eradicating poverty in all its forms and dimensions, including extreme poverty, is the greatest global challenge and an indispensable requirement for sustainable development.

All countries acting in collaborative partnership, will enact this plan; freeing humans from the tyranny of poverty and to heal and secure the planet. Nations are determined to take the bold and transformative steps which are urgently needed to shift the world on to a sustainable and resilient path. [11]

This program entails 17 sustainable different goals the ones that are more relevant considering packaging solutions are: responsible consumption; protect the planet; life below water, and renewable energy.

A similar direction has been taken at the European 2020 Strategy, which poses at it center the Research and Development using a Sustainable Growth. The European Plastics Pact brings together leading companies, Non-Governmental Organizations, and governments, who are together committing to realize common goals by 2025 and go beyond the current legislation. The European Plastics Pact targets include:

- Reducing virgin plastic products and packaging by at least 20%.
- Raising collection and recycling capacity in Europe for plastic packaging by at least 25%.
- Boosting the use of recycled plastics in packaging to an average of at least 30%.

The signatories of the European Plastic Pact, will be committed to several objectives to be achieved by 2025, such as:

:

- Designing all plastic packaging items placed on the market to be reusable, and recyclable;
- Moving towards more responsible use of plastic packaging and Single Use Plastic (SUP) products, aiming to reduce items and packaging made of virgin plastics by at least 20%, with half of this reduction coming from an absolute reduction in plastics;
- raising the collection, sorting, and recycling capacity by at least 25% and reaching a level that corresponds to market demand for recycled plastics;
- increasing the use of recycled plastics in new products and packaging, with manufacturers achieving an average of at least 30% recycled plastics by weight in their products and packaging;

According to the European Parliament [12] less than 1/3 of European plastics is recycled.
Even if Europe is one of the most involved continents in Sustainability, [12], it is not nowadays able to reuse alle plastics produced by itself.
The inability of Europe in recycling its own plastics has not only increase plastics rejection in young people and NGOs that pretend a plastic-free World but has also created a problem for food industry that is trying to reach packaging solutions that follow this direction.
Protecting food, respecting law, and preventing spoilage are the aim of the packaging industry, but trends of markets must be considered when designing a food package.
Trying to reach this condition it has been decided to decrease the plastics usage to give to customer something that is not only good as a food packaging, considering all the aspects linked to product's protection, but also that can be reutilize, or thrown in separate waste collection, without hurting the environment, and without create a problem of recyclability.

1.2 Paper usage and recyclability constraints.

1.2.1 Paper usage.

Papers and cardboards are widely used in the packaging industry, providing outstanding properties such as good mechanical strength, light weight, barrier to light, ease of converting and printing. On top of that, paper-based materials are characterized by good recyclability, and they came from renewable resources, making them a sustainable solution in most applications. On the other hand, paper-based packaging exhibits several drawbacks, including poor barrier properties against water, oil, and grease compounds due to the porous structure and hydrophilicity of the paper [12,13]

Paper is made of natural fibers of bleached or unbleached cellulose. Chemical additives are needed in the manufacture of paper and boards to achieve different technical functionalities like grease resistance and mechanical strength. They are either added to the pulp during production or coated onto the surface afterwards. Additives can be mainly categorized into functional additives and processing aids. The first group of additives is used to modify the properties of the paper. They typically remain in the paper and include sizing agents, wet and dry strength resins, softeners, dyes, and pigments. Common processing aids are defoamers, biocides, felt cleaners, and deposit control agents.
As mentioned before paper and carton are permeable barriers due to the nature of their microstructure. Consequently, low molecular weight and volatile additives, but also non-volatile compounds and external contaminants can migrate from and through the packaging into the food. Well-known migrants from paper and cardboard include mineral oils. [13,14,15].

To improve paper's properties, films and coatings can be created. Films and coatings are placed on paper and can significantly improve spoilage's barrier.

Paper can be laminated with plastics or other materials to increase paper properties. For its utilization after consumption there are recyclability constraints that underline and describe every single situation that can be found by consumers and producers. In this way it's easy for every component of the Food Supply chain, to understand which the best way is to treat paper, or paper laminated with plastics, in order not to waste it, and giving later another possibility of life.
These constraints are governed by standards, and one of the most important considering Italian legislation is UNI 11743:2019. [16]

1.2.2 Aticelca's system of evaluation.

Following the analysis made by UNI 11743:2019 on processes that can create or recycle paper, ATICELCA, has developed an evaluation's system that helps every single character of the Food Supply Chain in understanding what it has to do when using a paper-based material [16].

This evaluation system is made only for materials that are for the most made of paper, or materials that are predominantly cellulosic; and it allows one to create a classification based on recyclability, giving to each single material a specific class, to understand what degree of recyclability it has.

To better understand ATICELCA, some important definitions need to be clarified:

- **Paper or cardboard to be recycled**: products consisting predominantly of paper and board, which may include other constituents which cannot be removed by dry separation such as coatings and laminates, spiral bindings, etc. [UNI EN 643]
- **Use of paper and cardboard to be recycled (recycling process in the paper mill)**: all the processes applied in the recycling of paper and cardboard to be recycled by the paper industry. Such processes mainly include the pulping of paper and cardboard to be recycled and the subsequent purging of the paste obtained from non-cellulosic components and use different types of plant in the nature of the paper and cardboard to be recycled and the desired final product. [UNI 11743]
- **Material predominantly cellulosic based:** paper and cardboard in need of further transformation to become final products (e.g., rolls and sheets of paper intended for printing or papermaking, sheets of corrugated board intended for the production of packaging, rolls of tissue paper intended for the production of tissues). This material may contain other non-cellulosic constituents not more than 50% by weight. [UNI 11743]
- **Product predominantly cellulosic based:** final objects (such as, for example, packaging, printed matter, household items) consisting of more than 50% by weight of materials with a cellulosic prevalence. [UNI 11743]
- **Recyclability**: ability of the product to be processed effectively and efficiently from the point of view of technological and economic view, in order to reuse the cellulosic fibers contained in it through the currently most widespread paper production technologies for paper processing to be recycled. [UNI 11743]

The evaluation of products recyclability is based on those parameters that can affect the recycling processes.
This analysis is made following the constraints giving by UNI 11743:2019; the procedure used in this type of analysis is briefly described below:

- **Sampling and sample preparation:** sampling is made by choosing a determined quantity of material, preserving its characteristics and proportions between components.
- **Determination of dry matter content:** the sample is tested in the oven (80°C) to eliminate the moisture present and determine the dry matter content at which point subsequent measures will be reported on.
- **Squeezing and dilution:** then proceed with the pulping in a laboratory pulper of the material, to obtain a sample of dough for subsequent analysis. The squeezing takes place in conditions that simulate typical industrial pulpers. The dough sample is then diluted for subsequent tests.

- **Measurement of the coarse waste and preparation of the first accepted sample:** the coarse waste is determined through a process of mechanical separation of the different components found in the diluted dough. The waste coarse is measured from the solid fraction that does not pass through the cracks. The first accepted sample is represented by the dough that passes through the perforated plates on which subsequent tests are conducted.
- **Measurement of the flakes**: the flakes are determined by a mechanical separation of the different components using plates with grids of smaller width than those used for the coarse waste. The solid fraction that is retained by the plate represents the flakes.
- **Measurement of macro stickies**: macro stickies are determined utilizing a mechanical separation of different components using even thinner cracks, the subsequent preparation of specimens and the use of a system image analysis capable of distinguishing adhesive particles with an equivalent diameter between 0.1 and 2.0 mm. The total surface area covered by particles is then measured.
- **Preparation of the second accepted mixture and laboratory sheet formation:** the accepted mixture of the size of the adhesive particles is homogenized, the fiber consistency and test slips are formed.
- **Adhesion test:** the adhesion test is conducted by verifying that the leaflet does not adhere to support and cover sheets after the assembly has been pressed between two metal plates and subjected to high temperatures. Adhesiveness is considered absent if the sheet can be separated without showing damage and breakages. Traces of fibers are allowed on the substrate and / or on the cover. Scraps of paper are not allowed on the support and / or cover.
- **Evaluation of optical inhomogeneities**: optical inhomogeneities are evaluated by observing the leaflet on both sides and assigning a judgment by comparison with the references reported in the UNI 11743: 2019 standard. The result is reported on a scale of 1 to 3 where the level 1 represents a weak or absent optical inhomogeneity (on a white or brown basis), level 2 a medium inhomogeneity and level 3 a high one.

The results evaluation is made considering Figure 3. With the worst parameter that characterizes the product.

Evaluation's system of recyclability* Aticelca 501:2019	Recyclable with paper				Not recyclable with paper
	Level A+	Level A	Level B	Level C	Not recyclable wiht paper
Coarse waste (%)**	< 1.5	1.5 - 10.0	10.1 - 20.0	20.1 - 40.0	> 40.0
Area of adhesive particles ø < 2000 µm. (mm²/kg)	< 2.500	2.500 - 10.000	10.001 - 20.000	20.001 - 50.000	> 50.000
Flakes (%)***	< 5.0	5.0 - 15.0	15.1 - 40.0	> 40.0	-
Adhesiviness	absent	absent	absent	absent	present
Optical inhomogeneity	level 1	level 2	level 3	level 3	-

Figure 3: Aticelca's system of evaluation. [16]

Notes:

* With recyclability it’s describe the ability of the product to be worked in an efficient manner, both from the technological and economical side, with the aim of reusing cellulosic fibers following standards [UNI 11743].

If the paper sample is classified as not recyclable, this material cannot be collected with separate waste collection; it can be used in other industrial processes or used in energetic recover.

** If samples are observed that are resistant to crushing or not coupled with plastics or metals; if, after test samples for 10 minutes, the coarse waste is more than 40% a new test can be done for 20 minutes. After the second test, if coarse waste is under 40% the material can be admitted and classified with level C.

*** If there is a prevalence of flakes in the material that is not paper based, the result for flakes is not considered but it is added to coarse waste value, calculated on first weight.

Figure 4: Different classes of Aticelca's classification for paper-based materials.

Every single code has a specific meaning in paper recycling. Here it has been tried to describe in a proper way what the letter stands for:

Figure 5: A+ class in Aticelca's classification.

Figure 5 classified packaging recyclable with paper efficiently and effectively from a technological and economic point of view when mixed with other secondary fibers, obtained from the separate collection of paper, through the predominantly paper production technologies. The waste obtained during the recycling process is less than 1.5%.

Figure 6: A class in Aticelca's classification.

Figure 6 classified packaging recyclable with paper efficiently and effectively from a technological and economic point of view when mixed with other secondary fibers, obtained from the separate collection of paper, through the predominantly paper production technologies. The waste obtained during the recycling process is less than 10%.

Figure 7: B class of Aticelca's classification.

Figure 7 classified packaging recyclable with paper efficiently and effectively from a technological and economic point of view when mixed with other secondary fibers, obtained from the separate collection of paper, through the predominantly paper production technologies. The waste obtained during the recycling process is less than 20%.

Figure 8: C class of Aticelca's classfication

Lastly Figure 8 classified packaging recyclable with paper when used mixed with other secondary fibers, obtained from the separate collection of paper, through the predominantly paper production technologies. Its recycling process results in up to 40% waste and a considerable contribution in terms of macro stickies and cellulose fibers agglomerates.

1.2.3 C/PAP system of evaluation [17,18].

Another important law regarding recyclability has been developed by the EU Parliament.

In 1997 the European Commission (EC), delivered a system of codification in order to establish a shared classification to understand materials that are used for packaging as well as the connected waste.

The European Commission has delivered this set of codes explaining the meaning but also the reason why, using several articles:

- **Article 1:** this Decision, which covers all packaging covered by Directive 94/62/EC aims to establish the numbering and abbreviations on which the identification system is based, indicating the nature of the packaging material(s) used and specifying which materials shall be subject to the identification system.
- **Article 2:** For the purposes of this Decision:
  —the same definitions set out in Article 3 of Directive 94/62/EC shall apply where relevant,
  — composite: means packaging made up of different materials, and which cannot be separated by hand none exceeding a given percent by weight which shall be established in accordance with the procedure laid down in Article 21 of Directive 94/62/EC. Potential exemptions for some materials may be established by the same procedure.

- **Article 3:** the numbering and abbreviations of the identification system are as laid down in the Annexes. Their use shall be voluntary for the plastic materials mentioned in Annex I, the paper and fiberboard materials mentioned in Annex II, the metals mentioned in Annex III, the wood materials mentioned in Annex IV, the textile materials mentioned in Annex V, the glass materials mentioned in Annex VI, and the composites mentioned in Annex VII. A decision whether to introduce on a binding basis the identification system for any material or materials may be adopted in accordance with the procedure laid down in Article 21 of Directive 94/62/EC.
- **Article 4:** this Decision is addressed to the Member States.

The annex cited in the articles can be listed in Figure 9 to understand better what is used in everyday life. It is important for the study of this work, codifications regarding plastics-based materials, paper-based materials, but also composite materials that are predominantly made of paper.

ANNEX VII

Numbering and abbreviation system (¹) for composites

Material	Abbreviation (*)	Numbering
Paper and fibreboard/miscellaneous metals		80
Paper and fibreboard/plastic		81
Paper and fibreboard/aluminium		82
Paper and fibreboard/tinplate		83
Paper and fibreboard/plastic/aluminium		84
Paper and fibreboard/plastic/aluminium/tinplate		85
		86
		87
		88
		89
Plastic/aluminium		90
Plastic/tinplate		91
Plastic/miscellaneous metals		92
		93
		94
Glass/plastic		95
Glass/aluminium		96
Glass/tinplate		97
Glass/miscellaneous metals		98
		99

(*) Composites: C plus abbreviation corresponding to the predominant material (C/).

(¹) Only capital letters shall be used.

Figure 9: Codes for recyclability identification divided by materials [17].

Every packaging material that is a composite has a different number of codifications, this means that for every single material, can be applied a code, that helps costumer in understanding where that specifical packaging material must be thrown. Increasing in this way the ability of costumer to be self-confident on recyclability and more responsible for what can lead to environment problems.

This normative made by EC, is important not only in Europe, but a can be used as an international code of identification that could help all the state in recycling and managing food packaging waste, trying to reach the best from each single life of materials.

1.2.4 Biodegradability.

Biodegradability is an important aspect linked to paper. Paper is compostable and building a food packaging based on paper and biomolecules can increase its properties without affecting biodegradability.

Biodegradability is the ability of organic substances and materials to be broken down into simpler substances through the action of enzymes from microorganisms [22]. If this process is complete, the initial organic substances are entirely converted into simple inorganic molecules such as water, carbon dioxide and methane [19].

Biodegradation is part of the earth's natural life cycle, which is based on carbon. Thanks to photosynthesis by plants and algae, carbon dioxide is absorbed from the atmosphere to synthesize sugars and other substances used by plants to grow and develop. The flow of substances and energy passes through the food chain from plants to herbivores and from herbivores to carnivores. When plant and animal organisms die, microorganisms present everywhere in the environment feed on organic material through biodegradation processes and release water and carbon dioxide into the atmosphere, thereby closing the cycle.

This means that biodegradation is strongly influenced by the chemical nature of the substance or material and by the environment in which this process takes place. The environments in which biodegradation occurs at a consistent pace, and in which it can be managed industrially, are those of composting and anaerobic digestion. In these systems it is therefore possible to process solid organic waste, including man-made substances (such as biodegradable plastic) for which the speed of biodegradation is compatible with these processes. Composting will produce mature compost (which is a fertilizer) while anaerobic digestion (followed by stabilization through composting) will produce biogas (and therefore energy) as well as compost. Another biologically active environment is soil: some materials can be completely biodegraded in soil, and this property can be exploited in specific applications such as mulching [20]

Considering this aspect paper can be considered a bio-waste [23].

Bio-waste is defined as biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers and retail premises, and comparable waste from food processing plants. It does not include forestry or agricultural residues, manure, sewage sludge, or other biodegradable waste such as natural textiles, paper, or processed wood. It also excludes those by-products of food production that never become waste [21].

Following the continuous research for a better waste management but also responding to the article 22 of Waste Framework Directive (2008/98/CE), which put the attention on: collection, separation, composting and digestion of bio-waste; the management of those substances have a great role in an environmental perspective. The European Commission already presents some project which could help Member States to reach predefined targets:

- Recycling and preparing for re-use of municipal waste (including bio-waste) to be increased to 70 %.

- Phasing out landfilling for recyclables (including plastics, paper, metals, glass and bio-waste) waste in nonhazardous waste landfills – corresponding to a maximum landfilling rate of 25%.
- Measures aimed at reducing food waste generation by 30 % by 2025.
- Introduction of a separate collection of bio-waste.

Composability is another important characteristic that is increasing its importance in the last year.
Composability is the capacity of an organic material to be transformed into compost through the composting process. This process exploits the biodegradability of the initial organic materials to transform them into a finished product called compost. Compost is therefore the result of disintegration and aerobic biodegradation (occurring in the presence of oxygen): mature compost is like fertile soil and its high proportion of organic substances means it can be used as a fertilizer. Composting can be conducted at a domestic-amateur level on a very small scale, or at an industrial level [19].

1.3 Paper modifications

Paper modification is the process of modifying paper or applying to it materials, to increase properties of packaging material. There are several types of paper modification. Additives can be added in the making of paper, or a film or a coating of different materials or solutions can be applied, after having produced paper [24].

This process is important in the Food Packaging industry. Firstly, because it can be developed to give customers a type of packaging that is based on paper, so as said before, fully recyclable, but also because it can be a solution that overcomes plastics, giving a different protection to a product but with the same objectives.

Paper-based materials are nowadays ubiquitous in the food industry. However, considering paper modification, these types of materials can give a push towards sustainable solutions to the market that can lead a company to the top of the market.

1.3.1 Technologies

Coating paper is the process of creating a film of a specific material, and then gluing or applying it to paperboard itself. Considering the actual packaging industry panorama, there are two main coating processes: film production and coating production, both with the same goal to improve the base material properties, thus expanding its applications and functionalities.

Film production consists in the production of a uniform sheet, and then to laminate it on paper-based substrate. Adhesives or high temperatures can be used to ensure the coupling with the paper, bonding them together and creating the desired composite material.

To produce a uniform film, different processes are currently available. Typically, the first step of such processes requires a calender or reactor in which different compounds like plastics resins and auxiliary materials are mixed at a determined temperature (200°C~300°C) [24]. Consequently, different methods can be used to develop the finished films.

Firstly, is the T-die extruder that is a machine that using an extruder, as shown in Figure 10, which is set at a temperature that can melt granules of biopolymer that are then solidified and extruded as a bobbin that can be divided in films [25]

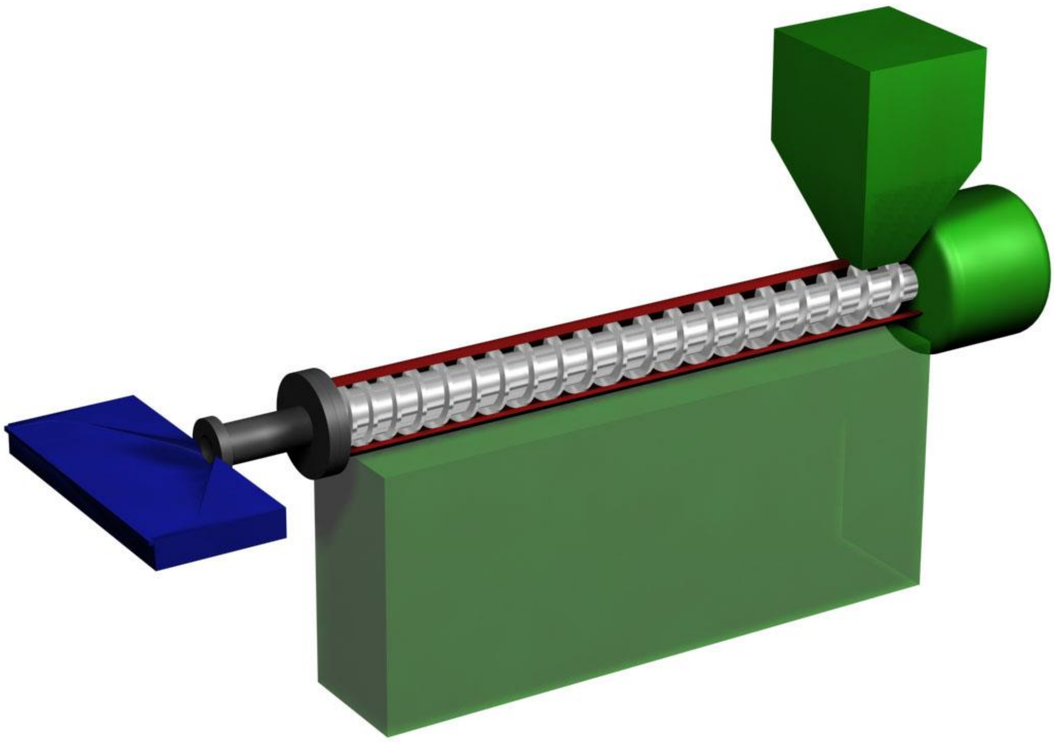


Figure 10: T-die extruder example. [26]

The second method to produce a uniform film is casting, schematized in Figure 11. This industrial process requires a circular machine that rotates at constant speed, and which has some metallic plates. Plastic emulsion after being mixed is put on these plates. The machine rotating and helped passing below air sprayers, is able to dry films that are of the required measures.

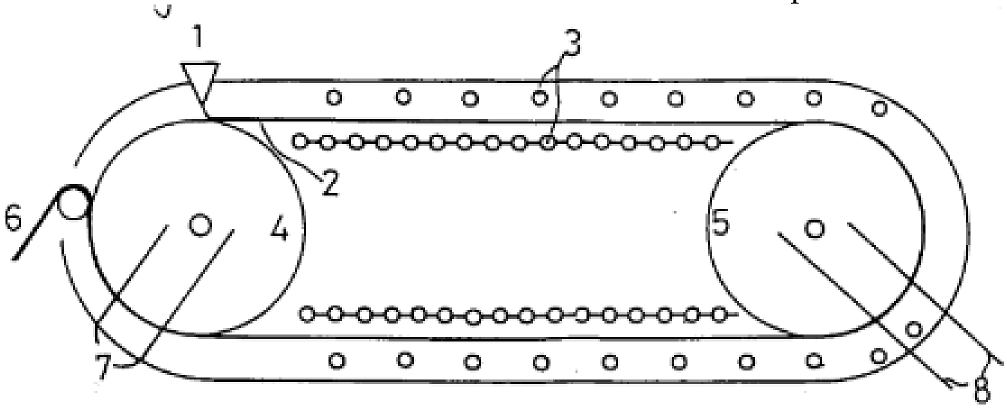


Figure 11: Film casting method scheme. [27]

A third process to realize uniform and thin films is the blowing method also known as the film blowing process [28,29]. In this case the extrusion die is shaped as a circle, as represented in Figure 12, and air pressure is used to expand the molten matter exiting the extruder. After the mixture is expanded to achieve the desired dimensions, is cooled down and to solidify by the action of rolls which then shape the polymer to form the film.

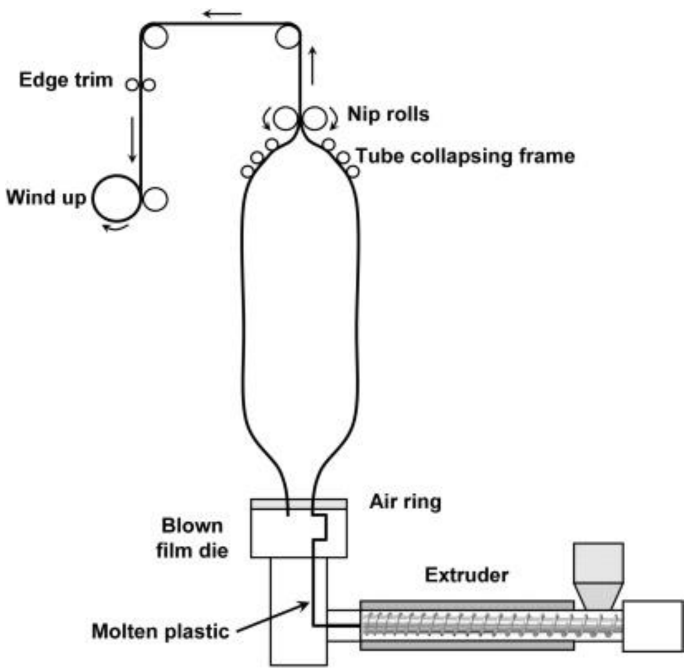


Figure 12: Film blowing method scheme.[30]

There are two different methods to apply the produced films on paper-based substrates, namely dry compounding, and lacquering. This step is fundamental since is the last one, which will shape the final products and gives to the market the desired packaging.

Dry compounding is the most used process. It consists in smearing a water based adhesive, on the paper, and making a thermocompression. This process helps the two materials to laminate each other and give to the producer the packaging [31,32].

Solvent free compounding does not involve an increase of temperature, but using a non-organic adhesive extrudes the two layers together, completing in this way the packaging solution [33].

Lacquering is another way to produce films. Lacquer production or coating production, has the aim to produce a mixture of the material and coat it on paper to increase barriers or specific properties.

The emulsion can be produced into a reactor or a calender. Usually, materials are slowly added to the water solution in order to facilitate the dissolution, so that could be smeared on paper. This procedure is totally different from film production, because it does not have an adhesive or a compound that bonds together paper and film. On the contrary, the coating solution, is smeared onto paper without adhesive and dried for a specific period.

Two main types of solutions depositions techniques are mainly used to develop a paper-based composite material, bar coating and spray coating.

The first process, also used in the laboratory, is the bar coating method. Using a wire rodbar, the solution can be deposited and then smeared on a paper sheets in a homogeneous way , after dropped some solutions on paperboard. [34,35].

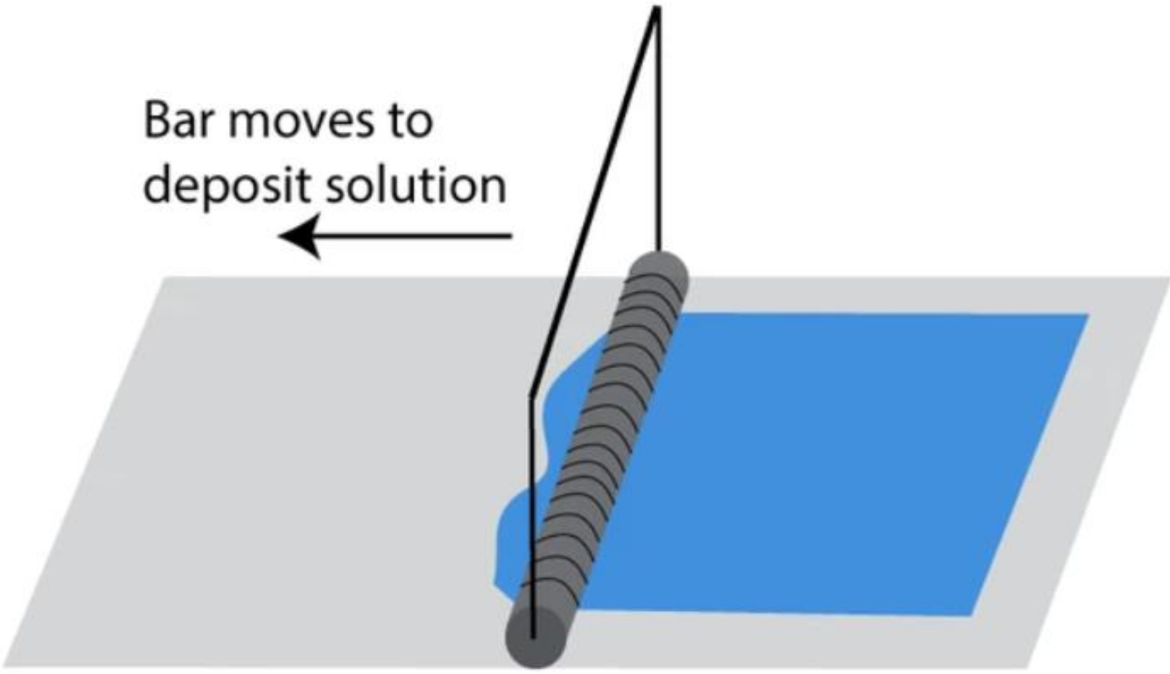


Figure 13: Bar coating method scheme. [34]

The second method is the spray coating technique, where an airbrush is used to deposit a thin layer on the paper. This procedure is able to smear the solution in a more homogenous way and can be checked in a better way according to the bar coating method [34].

1.3.2 Materials

To improve paper's barrier properties, a coating or a film must be made, not only to fit paper with product requests (if a product must be covered from oxygen permeation it needs a protection from this type of hazard) but also to bring to packaging a positive and an important characteristic that increases not only the value of the product but also the shelf life of it [36].

Several solutions can be found that help paper on enhancing its properties for satisfying the market needs.

1.3.2.1 Plastics

One of the most used solutions nowadays is undoubtedly lamination with plastics [37]. A very different range of plastics are used.
The coupling can be made in different ways. As seen before, the market tends to create films that are then glued on paperboard to increase properties. Plastics more used are Polyethylene (PE), both samples High Density (HDPE) and Low Density (LDPE); Polyethylene Terephthalate (PET); Polypropylene (PP) and Polystyrene (PS). All these

types of plastics are used in huge amounts in order to develop food packaging materials which can help paper to be more protective for products.

Plastics are good materials because they are easy to work with, can be found everywhere and can be recycled. [17]

Plastics are not only used as films to be coated on paper, but through extruding them with special types of paper there can be created special packages that are used to pack fried food, hot liquid drinks and special food [37].

Plastics, although they tend to be poor on oxygen permeation regarding barriers, are materials which can protect food from water permeation, oil permeation and liquid permeation. This ability underlines the reason why plastics are used all over the world and with a huge frequency: they are cheap, easy to work, and able to protect foods.

Plastic film, the most widely used technology to coat paper, is made using a reactor where plastics and resins are mixed to be then extruded on a desired shape. To apply these films on papers the industry tends to utilize high temperature extrusion, or glues that help materials to be attached together.

The objective of laminating together plastics and paper is to realize a material which is able to be oil-proof, water resistant and heat sealable [38].

An important aspect linked to plastics coated paper is the recyclability cycle. Considering C/PAP and Aticelca regulations, plastics coated paper is completely recyclable, but it is important to understand in which waste disposal category the packaging solutions must be placed.

1.3.2.2 Biobased materials.

Biobased materials represent an intriguing material class that can be used to create coatings and films to improve a paper-based solution.

Polymer’s packaging materials originated from naturally renewable resources such as, polysaccharides, proteins, lipids or a combination of those components, offer favorable environmental advantages of recyclability and reutilization compared to conventional petroleum-based synthetic polymers [40].

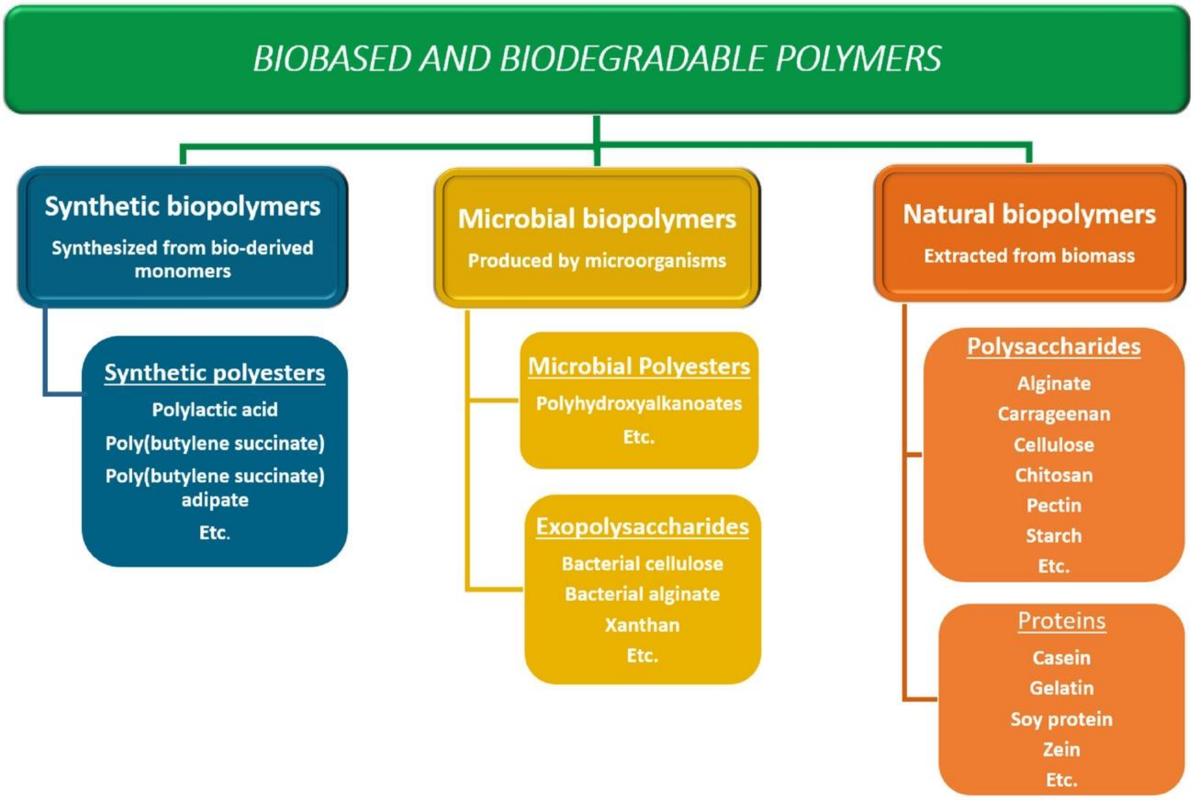


Figure 14: "Current status of biobased and biodegradable food packaging materials: Impact on food quality and effect of innovative processing technologies". [39]

Biomolecules-based films and coatings may also serve as solute barriers and complement other types of packaging by minimizing food quality deterioration and extending the shelf life of foods [41]. Moreover, biopolymer-based films and coatings can act as efficient vehicles for incorporating various additives including antimicrobials, antioxidants, coloring agents, and nutrients [42].

These types of biopolymers bring interesting properties to be investigated while keeping the characteristics of the material totally recyclable and environmentally friendly.

1.3.2.3 Biopolymers

Biopolymers can be protein, like casein or zein, that are able to be filmed on paper packaging, and give to paper an improvement in its oxygen barrier, and mechanical properties, even if do not respond properly against water vapor [44].

Polysaccharide's derivatives can be filmed forming good samples, but because of their hydrophilicity tend to not create a barrier to Water Vapor; instead, they can be used as grease resistance materials.

Two of the most used polysaccharides are: chitosan, an edible and biodegradable material, and alginates, from alginic salt. Both materials tend to increase fat resistance of paperboard [45].

Lipid coatings are another important biomolecule-based material that can bring to paper different properties. Fatty acids can give to paperboards a more significant moisture repellency thanks to their hydrophobicity. These types of molecules are used typically with drinks to protect food from water [46].

Biomolecules can be combined to deliver different food packaging materials. To increase properties these are mixed or applied in different moments to bring improvements to packaging paper-based solutions.

Beeswax is used in great amount according to literature, sometimes applied with chitosan, and sometimes with saccharose [47,48]. A mixture of petroleum-based plastics and beeswax is done to increase water's barrier [49].

1.3.2.4 Bioplastics

Bioplastics are biopolymers that start to be used in the packaging industry.

This type of materials has increased its importance in the current market due to its nature since it can be considered as fully compostable. Moreover, bioplastics in general possesses similar properties if compared with the most used plastics. However, a drawback is connected to the poor gas barrier properties [39]. One of the most important bioplastics is Poly-lactic-acid (PLA), which is characterized by a great water repellency, although that, PLA tends to be permeated by gases [50]. Another interesting bioplastic is Polyhydroxyalkanoates (PHAs). Specifically, PHA have been compared in its application to commonly used plastics, such as PP, PE, and PET. PHA as their petroleum-based counterparts, is characterized by a high hydrophobicity, processability and versatility [51].

Aim of the work.

The aim of this thesis is the development of paper-based packaging solutions possessing by an enhance water resistant and grease resistant, if compared with the bulk material. Different solutions have been designed and synthetized by selecting four distinct biopolymers, namely Chitosan, Sodium Alginate, PLLA and Zein. The prepared solutions have been applied upon paper samples, creating single and multi-layers composites. The specimens have been characterized and compared by means of standardized tests.

A particular focus has been posed on recyclability of the prepared materials, delivering packages that can be considered totally recyclable, or fully compostable, potentially bringing to market solutions able to answer the sustainability claim from costumers.

It was fundamental to gain a deep understanding of the behavior of each single material employed when placed in contact with oil, grease and water. Particular attention has been given also to the barrier properties of the composites by studying both water vapor and oxygen transmission rate.

Figure 15 shows the thinking and optimization processes followed during the experimentation in laboratories.

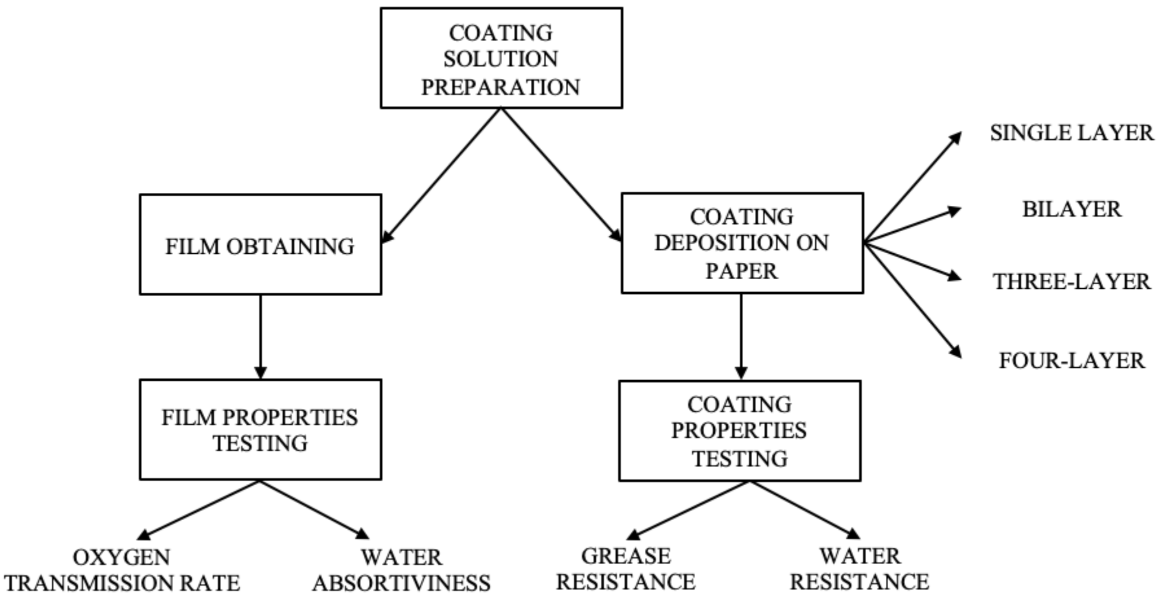


Figure 15: Scheme of laboratories activities.

After having prepared the solutions, they have been deposited on paper to create coating solutions, in multilayers configuration, and then tested against water and grease resistance following standards.
Later the solutions have been deposited in petri dishes to create films, then tested against oxygen permeation and water adsorption.

2. Materials and Methods.

2.1 Materials.

Chitosan (C) is a biopolymer obtained from the deacetylation of chitin, a carbohydrate that is obtained from the hard outer skeleton of shellfish, including crab, lobster, and shrimp. It is used for medicine and in bio engineering, but it is also used as a grease resistant material [44]. The structure of chitosan is shown in Figure 16.

The solution was prepared starting from chitosan, with medium molecular weight and 85% of degree of deacetylation and acetic (from Sigma-Aldrich, St Louis, MO, USA). Coating solution was prepared by dissolving 2.0% (w/v) of chitosan in an aqueous solution of acetic acid (1.0 % v/v) by means of magnetic stirring for 24h at room temperature.

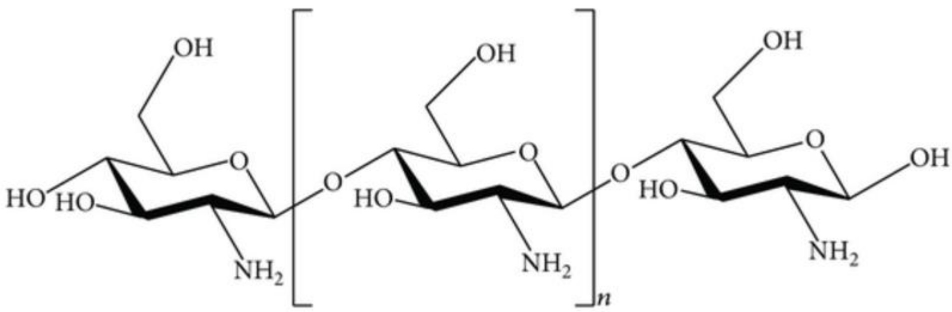


Figure 16: Chitosan's structure. [52]

Sodium alginate is a biopolymer obtained by algae. It is grease repellant and tend to be a great barrier against oxygen. [40]

Sodium alginate (A) was purchased from Sigma-Aldrich (St Louis, MO, USA). Sodium alginate solution was prepared by dissolving it in sterile distilled water (2% w/v) under magnetic stirring at room temperature for a total of 24h. The typical structure of

Sodium Alginate is provided in Figure 17.

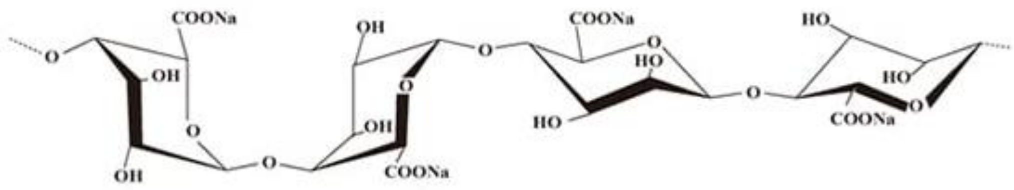


Figure 17: Sodium Alginate's structure. [53]

Poly lactic acid (PLA) is a polyester made with two possible monomers or building blocks: lactic acid and lactide. Lactic acid can be produced by the bacterial fermentation of carbohydrate source under controlled conditions. In the industrial scale production of lactic acid, the carbohydrate source can be corn starch, or sugarcane, making in this way the process sustainable and renewable.

PLA has great advantages and some disadvantages. It gives to the final materials a great resistance to water penetration, moreover it can be considered as a sustainable solution. On the other hand, at high temperature, PLA losses stability since it possesses a low melting point (180°C) [54] Therefore, its application in packaging where higher temperatures are mandatory, is limited.

Poly (L-lactic acid) (PLLA) is a biodegradable polymer which has attracted the attention of both the scientific community and companies due to its classification as an eco-friendly material. The main reason behind its classification resides in the obtaining process by means of fermentation of oils and carbohydrates, as well as from plants. The chemical structure of PLLA(P) is schematized in Figure 18.

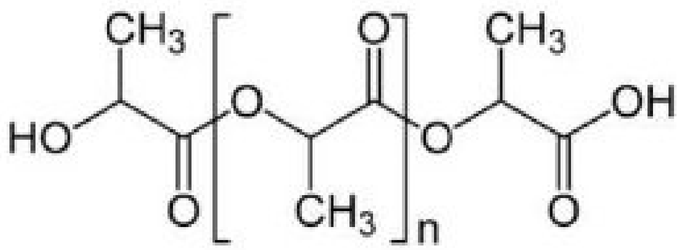


Figure 18: PLLA's structure. [55]

Zein (Z) is a component of corn, is a protein that can be found in three different classes, α, β and γ. It has great properties against water and oil, and as a protein is good in protecting from Water Vapor [39].

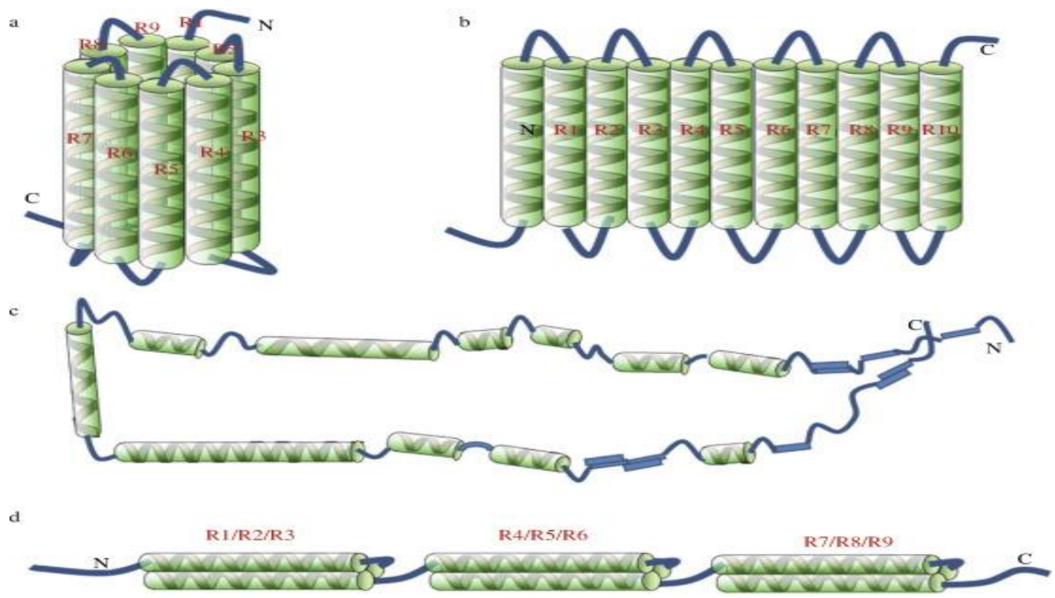


Figure 19: Zein's structure.[56]

It has been decided to design a Zein-based coating solution to better understand the properties that this biomolecule can provide to paper-based packaging since the information available in the literature were limited if compared to the other materials selected in this work.

Zein was purchased from Sigma-Aldrich (St Louis, MO, USA); 20% (w/v) of Zein was dissolved in ethanol aqueous solution (85% v/v).

2.2 Methods

Chitosan-based coating solution was prepared by dissolving 2.0% (w/v) of chitosan in an aqueous solution of acetic acid (1.0 % v/v) by mean of magnetic stirring, the agitation at room temperature lasted for 24h.

Subsequently, a visual evaluation of the prepared solution highlights a yellowish tone: color on the tone of yellow, viscosity, and some particles not at all completely dispersed.

Sodium alginate solution was prepared by dissolving sodium alginate powder (2%, w/v) in a sterile distilled water solution under magnetic stirring at room temperature, the reactants were kept under agitation for 24h. The final solution was characterized by a less intense yellow tone, if compared to the previous solution as well as a completely dispersion of the reactant.

PLLA solution was prepared by dissolving PLLA powder (6% w/v) in acetone. The PLLA particles were added slowly and in small parts to let the dissolution happening. Magnetic stirring was used, keeping the solution at room temperature for 24h.

Zein solution was prepared by dissolving 20%w/v of zein powder in ethanol-water solution (85% v/v). The final solution was characterized by a very high viscosity if compared with the previous ones, therefore its application on paper sample by mean of rod coating was difficult. As a result, zein-based solution was added directly on the prepared specimens using a Pasteur pipette.

To reduce the high viscosity reached in the first solution, a new formulation have been tried out following the instruction provided in [57]. Therefore, zein powders (20% w/v) have been dispersed by slowly adding them to a 95% ethanol solution under vigorous stirring and leaving under hood for 24 h.

2.3 Coating deposition.

To deposit the prepared solutions, two methods were used depending on the achieved viscosity. The Rod coating technique was performed to deposit a uniform layer of the less viscous solutions upon paper samples. In case high viscosity preparation, the deposition has been performed by means of Pasteur's pipettes by carefully cover up the entire sample, following that, a wire rod has been used to distribute the solution uniformly. Paper was fixed on polystyrene supports using tape scotch. Approximately, for each prepared sample, 2 ml of solution have been used to achieve a complete cover. After the coating procedure the specimens were leaved under hood to dry.

To better understand the improvement given to the deposited film to the paper substrates, both single and multi-layer solutions have been designed through an optimization process. Presented below, from Figure 20 to Figure 23, are shown the distinct multi-layered structure designed during the experiments.

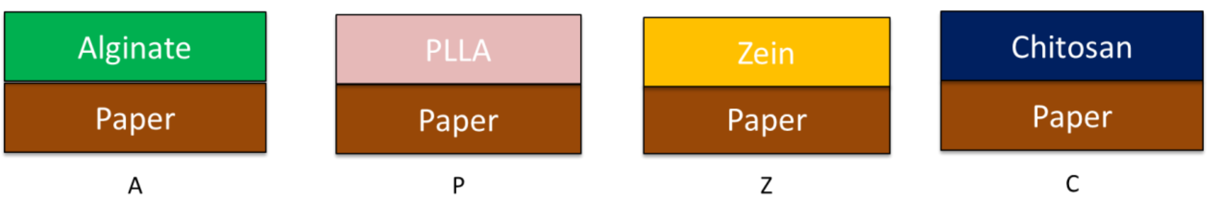


Figure 20: Single layer solutions tested scheme

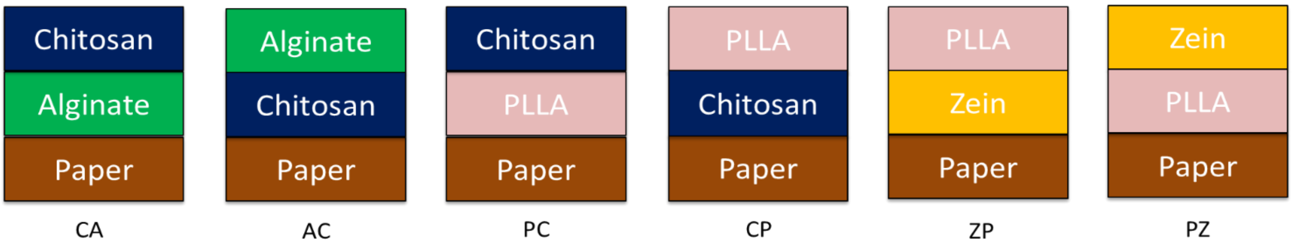


Figure 21: Bi-layer solutions tested scheme.

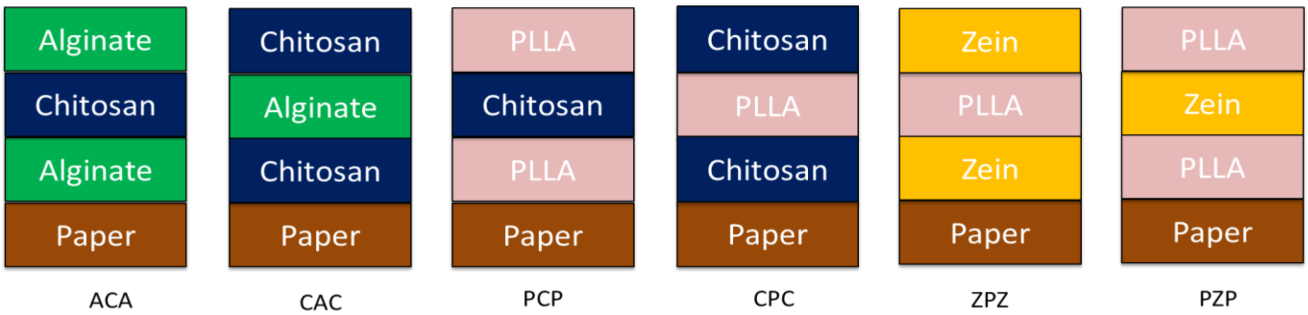


Figure 22:Tri-layer solutions tested scheme.

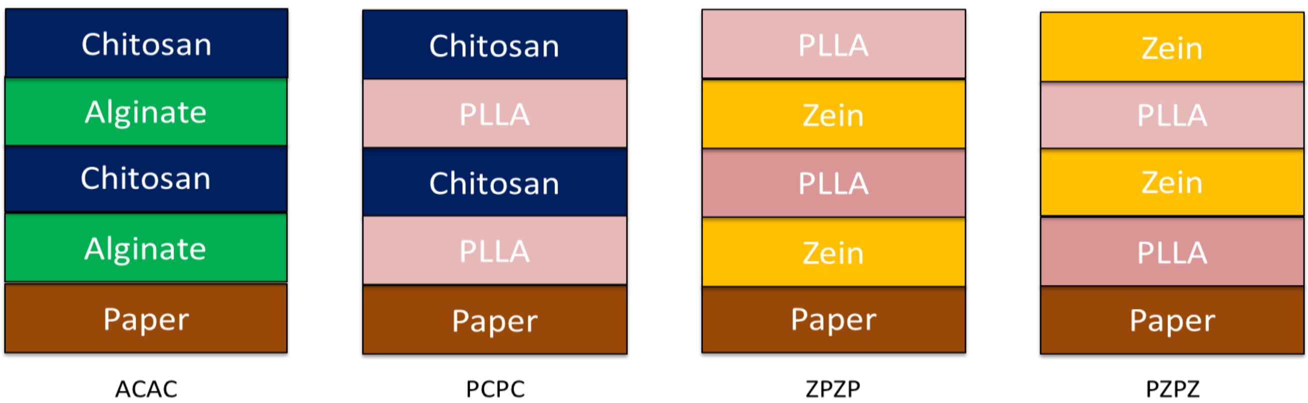


Figure 23:Multilayer solutions tested scheme.

To assess both the water adsorption and oxygen transmission rate (OTR) of the developed materials, several films have been prepared by casting 20 g of solution inside petri dishes. The casted solutions have been left drying at room temperature for 24 h under ventilated hood. Following this procedure both thickness and weight have been measured.

2.4 Characterization

The first step in the characterization process was investigate the enhancement provided by a single layer coating on paper sample and compare their properties to the bulk material. Therefore, a qualitative analysis has been carried out by measuring the weight and thickness of the deposited film as well as by droplet tests, which has underlined the behavior of each single film against water and oil penetration. Film obtained by solvent casting were used to investigate the oxygen transmission rate and the water adsorption.

The weight of the coatings has been assessed by measuring the specimen before and after the deposition, while the thicknesses have been measured by means of a micrometer.

The preliminary results of this analysis led to the design of multi-layered structure to achieve further improvement

2.4.1 Droplets Test.

The droplets test is a qualitative analysis made on sight, that helps in understanding the behavior of the materials investigated when placed into contact with different substances such as oil, soy sauce or water.

After placing a droplet for each testing liquid on the prepared specimens, several images were analyzed. The photos have been taken starting from the the moment at which oil and water droplets have been deposited, and, monitoring the situation with photos every 15 minutes, for a total of 2 hours.

This qualitative evaluation has provided precious information regarding the protective properties of the coatings, however, since the goal was to achieve a significative improvement compared to the bulk material, a layer-by-layer (LbL) design have been theorized and produced. Afterwards, the newly made multi-layer structure have also been tested.

2.4.2 ASTM F119: grease penetration.

The ASTM F119 is a standard developed by American society for standard and testing material (ASTM) that provides the information necessary to study the grease resistance of flexible barrier materials. The standard is built in a simple way, that can be easily replicated in a laboratory with cheap tools. A specimen of material must be cut into square of 50mm x 50 mm. The tested sample specimen must cover completely the glass surface, this to avoid any creep failure occurring on the edges. Subsequently 6 droplets of oil need to be dropped inside a cotton patch and placed upon the tested sample. Lastly, a 50 g weight is positioned on top of the setup to ensures and accelerates the migration of the oil from the patch to the sample.

At periodic timepoints, the specimen needs to be lifted and separated from the rest of the setup to provide firstly a visual evaluation and secondly, in case of oil penetration a more accurate analysis by mean of a stereo microscope. The time needed for the oil to penetrates the sample and reaching the glass surface need to be recorded [58].

2.4.3 ASTM D570: water adsorption.

The ASTM D570, standard test method for water vapor adsorption, provides all the necessary information to measure the amount of water adsorbed by a material in a specified condition. This test has two main functions, first of all, it provides the quantitative measurement of the water absorbed by a material, additionally it can assess the influence of the moisture content on different material's properties, such as mechanical, electrical and geometrical [49]. Moreover, in some cases, the water adsorption method can be applied to determine the uniformity of a given product, which is useful when performed on a finished product.

The test's specimen needs to be cut in the form of a bar with dimension of 76.2 mm x 25.4 mm and conditioned at 37°C in an oven for 24h to be dried.

The conditioned specimens shall be weighted and then placed inside a container filled with distilled water and kept at a temperature of 23 ± 1°C, the samples must be completely cover with water for a total of 24 h. Following that, the specimens shall be removed from the water one at time, all the water on the surface wippedo off with a dry cloth and weighed for the second time. [59]
The report shall include:

- Dimensions of the specimens before test, and reported to the nearest 0.025 mm
- Conditioning time and temperature,
- Immersion procedure used,
- Time of immersion (long-term immersion procedure only)
- Percentage increase in weight during immersion, calculated to the nearest 0.01 % as in Equation 1 :

$$increase\ in\ weight\ \% = \left(\frac{Wa-Wb}{Wa}\right) * 100 \quad \text{[Equation 1]}$$

In which:

Wa= weight after immersion in grams.

Wb= weight before immersion in grams.

2.4.4 ASTM E96: water vapor transmission rate.

The ASTM E96/E96M, standard test method for water vapor transmission rate, cover the determination of water vapor transmission rate (WVTR) of materials. Such properties are fundamental in all the application in which the permeation of water vapor have a key role. In particular, in the food industry, the presence of water on the surface of the package may be detrimental from a marketing point of view, while taking into account the preservation of the food products, moisture may induce spoilage or another unwanted phenomenon. The ASTM E96 cover two distinct methods to evaluate the WVTR, the desiccant method and the water method. For this study it has been decided to use the water method.

The cups are the placed inside a container in which $CaCl_2$ is used to obtain a relative humidity (RH) of 0 % to generate the driving force between this confined space and the inside of the cup (100 % RH). The whole setup is then placed inside a ventilated oven at a constant temperature of 37° C. Lastly, at predetermined timepoints, starting from the very start of the test, the cups are weighted [60].

The WVTR is calculated following [Equation 2]:

$$WVTR = G/(t * A) \text{ [Equation 2]}$$

In which:

G= weight change in grams.

t= time during which G occurred in h

G/t= slope of the straight line, grams/h

A= test area (cup area), m^2

WVTR= water vapor transmission rate in ($g/(m^2day)$)

2.4.5 ASTM D 3985-02: oxygen transmission rate.

The ASTM D 3985-02, standard test method for oxygen transmission rate (OTR), provide all the necessary information to measuring the OTR upon specimen of a given material and specified condition. can be determined based on ASTM D 3985-02 method. The test's setup includes an oxygen permeation chamber (Fibox 4 & Fibox 4 trace, PreSens Precision Sensing) connected to two sensors used to monitoring the temperature and O2 partial pressure increment. The specimens need to be cut into circular disk with a diameter of 10 mm and fix between the two chambers of the setup.

Films have been sealed between two chambers, each one having two channels. Prior the start of the measurement, both chambers were filled with nitrogen in order to tare the instrument, once the no fluctuation of the Oxygen level were detected in the upper chamber, the lower one was filled with Oxygen. In this way a driving force between the two distinct chambers were created by the different O2 concentration, thus starting the actual test. OTR is calculated using equation 3:

$$OTR = \frac{\dot{P}_{O_2} * V_{cell}}{p_{std} * A} * \frac{T_{std}}{T_m} \qquad \text{[Equation 3]}$$

In which:

$\dot{P}_{O_2}$= increase in oxygen partial pressure in the upper test chamber [hPa/d]

V_{cell}= volume of the upper test chamber [cm^3]

p_{std}= standard pressure of the test [hPa]

T_{std}= standard temperature of the test [K]

OTR= oxygen transmission rate [cm^3/ m^2/d]

A= permeation area m^2

From OTR (cm^3/m^{2*}day) can be calculated also Oxygen Permeability (OP) (cm^3/m^2/d/bar) [61]

2.4.6 Data analysis.

Data have been expressed following two main forms.
If possible, series of measurements have been made and then an average value with a standard deviation.

Where it has not been possible to carry out the tests in triplicate, results shall be expressed as individual values.

3. Results and discussion.

3.1 Thickness and grammage.

Every single coating, deposited using the rod coating technique, obviously increase the total thickness of the samples. However, this information is fundamental since in the food packaging industry tolerance and the global weight of the packaging matter especially in terms of laws and legislation. Together with the thickness measurements, another important aspect is the grammage, which is defined as the amount of weight of a given substrate or coating per unit area, expressed as g/m^2.

All the single layer and multi-layer solutions have been analyzed by this point of view, putting in relationship every single layer with the increase in thickness and weight.

Thickness has been measured on at least eight different points using a digital micrometer, while weighing has been made using an electronic scale. The results of such characterization have been categorized and analyzed.

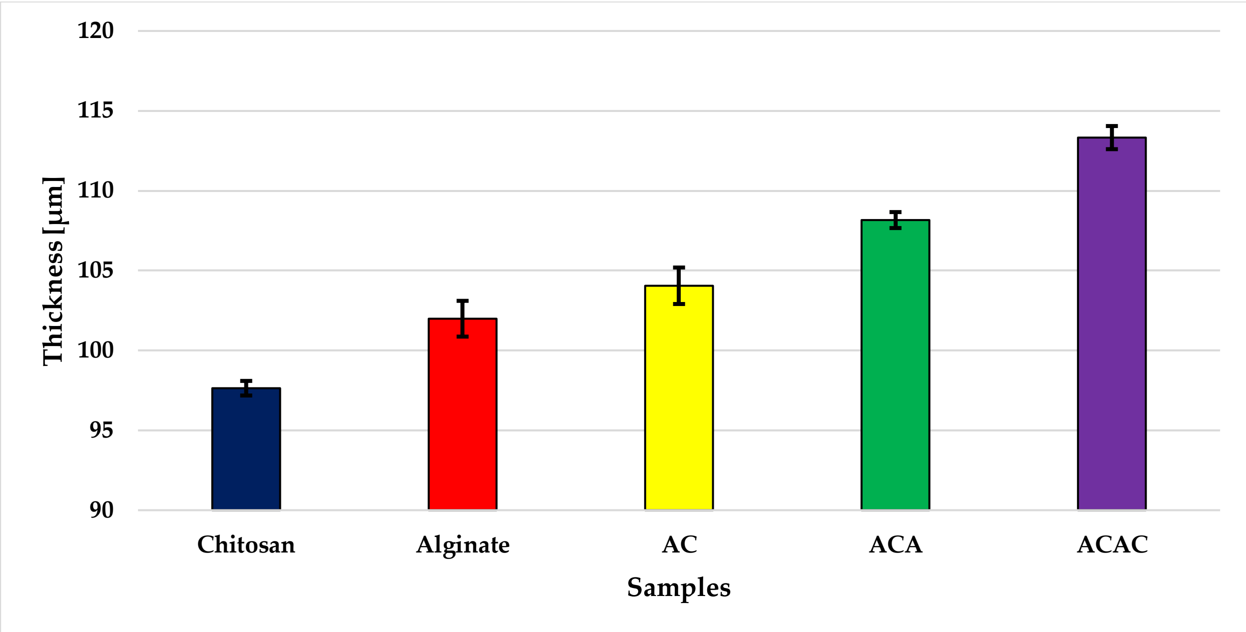


Figure 24: Layer by Layer thickness increment of ACAC solution. Thicknesses have been expressed as paper + coating.

Chitosan and Alginate have been chosen for their great grease resistance [39] and their ability to be a good barrier against oxygen [63]. This coating solution is focused on grease resistance.

Paper's thickness has been measured before coating deposition; its value is: 90µm.

Figure 24 shown the increment in thickness, obtained from Alginate (A) and Chitosan (C) solutions and their combination in multi-layer structure, upon paper substrates. The reported values are expressed as paper substrate plus the deposited coating thicknesses. By adding more layer the thickness increases consequently with the higher one obtained by ACAC multi-structure, with 13.7 ± 0.83µm.

These values can be compared to those found in literature.

If we consider alginate's single layer thickness, 11.25µm, at 2%w/v in water solution, is less than 21.1µm proposed by [62] but differences of concentration, 5% w/v in [62], can underline good relationship between w/v% and thickness.

Considering chitosan's single layer thickness, 7.45µm, in [63] chitosan solution (4% w/v) increases thickness of paper by 3.65µm. This difference is linked to a coating method which involves a deposition of 6g/m² for each deposition layer, while increment in g/m² is higher in this work.

Considering rod casting method, as the one proposed in this work, results are like articles that enhance grammage in chitosan coated paper samples [65].

For the case of bilayers, the attention must be put on solutions which are different from the one proposed by this work and with different coating solutions configuration; 13.75µm is less than 30µm but also in this situation must be taken in account differences between solutions formulations. [63]

Thickness increment is not proportional to the deposition of the layer. In fact, if chitosan thickness is 7.45 ± 0.36µm and alginate one is 11.25 ±0.75µm, the bi-layer thickness must be the sum of these values. Instead, AC solutions has an increment in thickness of 23.75±1.14µm.

Differences can be linked to the substrate on which coating solutions are deposited. The first one meets paper, which tends to adsorb a part of the solution, while creating coating. Next layers find different substrate, which adsorb in a different way, creating different coating.

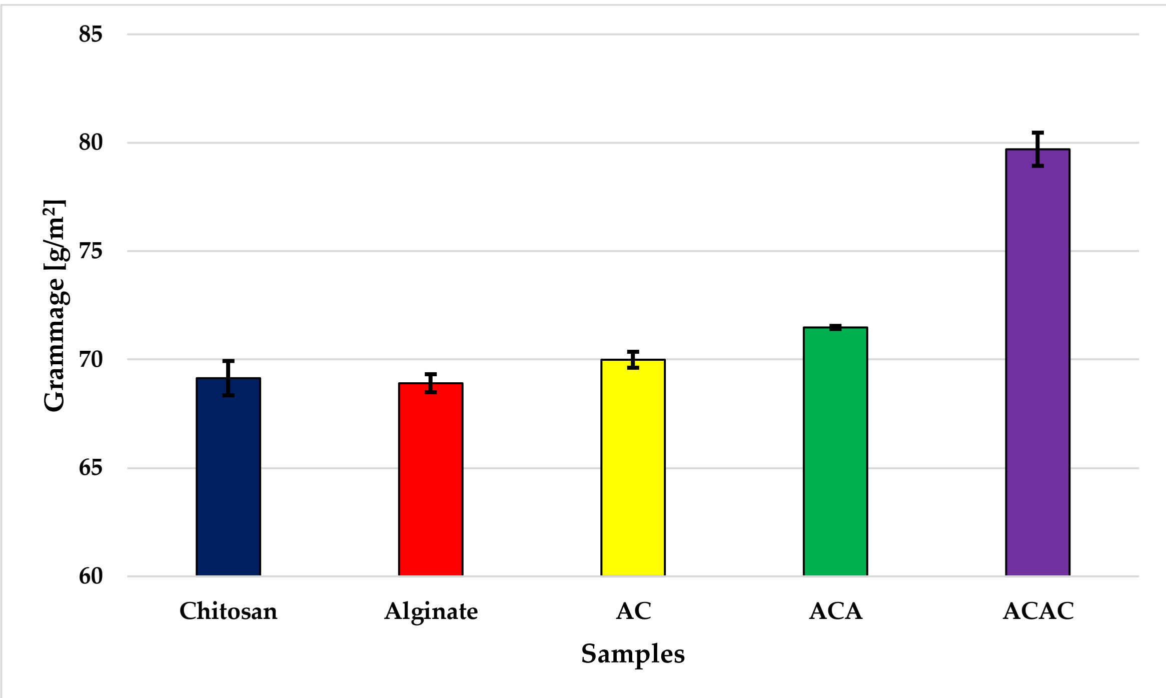


Figure 25: Layer by layer g/m² increment of ACAC solution.

Weight's increment underlines the increasing of g/m^2 of paper, when it has been coated with different materials. The weighing has been made after having dried the solutions.

Starting from the single layer solution, as shown in Figure 25, there is a trend that underlines the increasing in weight at every addition of layer, reaching maximum express by the multilayer solution which is: 79.69 ± 0.77 g/m^2.

The results presented in scientific articles which investigate the enhancement of single layer deposition above paper has shown differences. 69.14 g/m^2 and 68.91g/m^2 are lower than results in [63]; this gap underlines differences in coating solutions concentration. [63] delivers a 4% (w/v) coating solution instead of 2% (w/v), utilization of different type of paper, [63] uses a paper made by primary fiber instead a pristine one, influences results.

Grammage increment in g/m^2 is not proportional to layer deposition. AC and ACA underline this situation, first layer is probably penetrated in paper, while the second and the third ones find a different substrate on which dry in a different way.

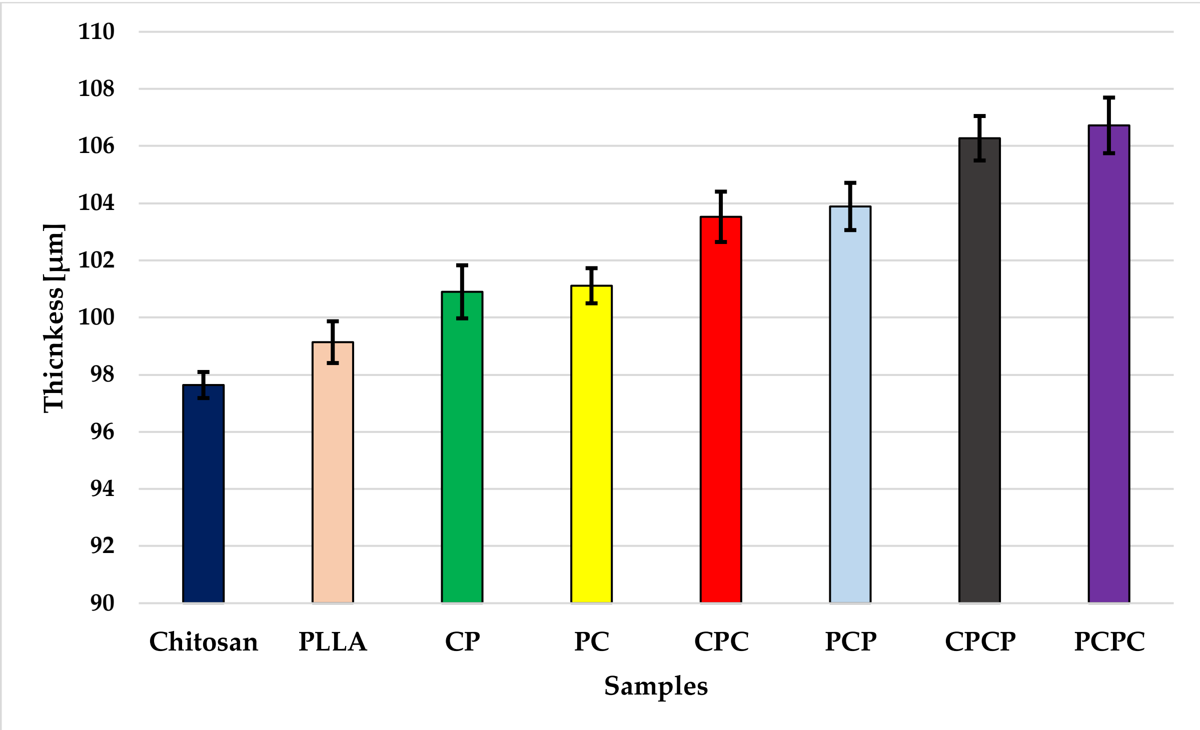


Figure 26:Layer-by-layer thickness increment of PCPC solution. Thicknesses have been expressed as paper + coating.

PLLA has been chosen for its great water repellency even if responds badly against oxygen permeation [39, 67]. Chitosan for its great grease repellency, and great barrier against oxygen [39,63]. To develop a coating solution made by chitosan and PLLA, instead of using Alginate as a grease resistant, comes from the differences between these two grease repellants in responding to oil permeation in droplets test.

Figure 26 describes the trend observed in terms of thickness increment for the single and multi-layer structure achieved with Chitosan and PLLA solutions. The maximum is represented by PCPC solution with an increase in thickness of 16.72 ± 0.97µm.

Considering chitosan coupled with paper a thickness of 97.64µm is little bigger than 85µm found in literature [54], due to the fact that in [64] coating solutions has a concentration of 1%w/v instead of 2% w/v presented in this work.

For PLLA single layer coating is set a range between 1-12µm [66]. 8.85µm respects this range and underlines the relationship between w/v % in solution and thickness of films or coatings.

Bi-layer thicknesses 20.9±0.92µm, and 21.15±0.61µm, are less thick than composite solution found in literature that expresses a value of 47.1µm,[67], in this case must be considered that solutions are made in different way.

In this work a balanced presences of both biopolymers have been set, while in [67] for composite films has been decided to use 70% by weight of chitosan and 30% by weight of PLLA [67].

PLLA and Chitosan increase thickness not in a proportional way linked to layer deposition. Bi-layer thicknesses is not the sum of single layer. This means that a part of coating deposition is penetrated in paper while the second one has found a substrate different, that does not leave permeation.

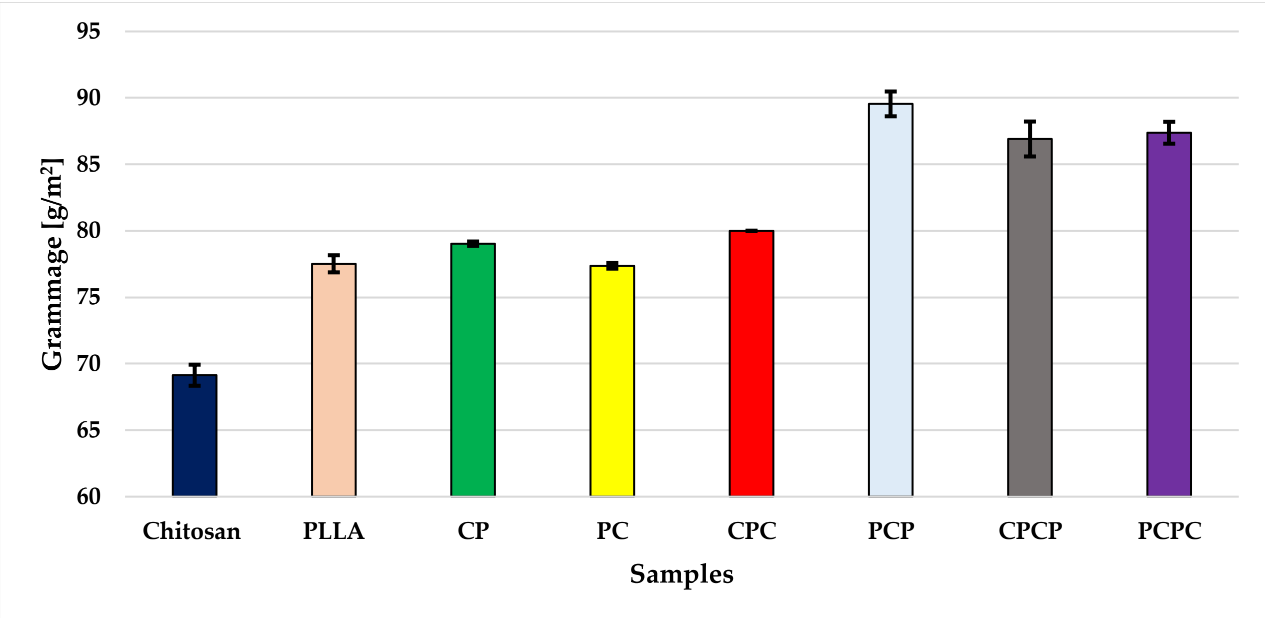


Figure 27: Layer-by-layer g/m² increment of PCPC solution.

Figure 27 shows that PLLA has a specific weight bigger than Chitosan. There is a trend that explains in a clear way a path of increment according to number of layers built on paper. PLLA has an important role in increasing weight. 77.52±0.64 g/m² is a result that follows the ones presented in literature [68]. Combining chitosan and PLLA gives to paper a great increasing in weight, 87.38±0.82 g/m^2 for PCPC and 86.9±1.31g/m^2 for CPCP are values bigger than those found out with ACAC solution.

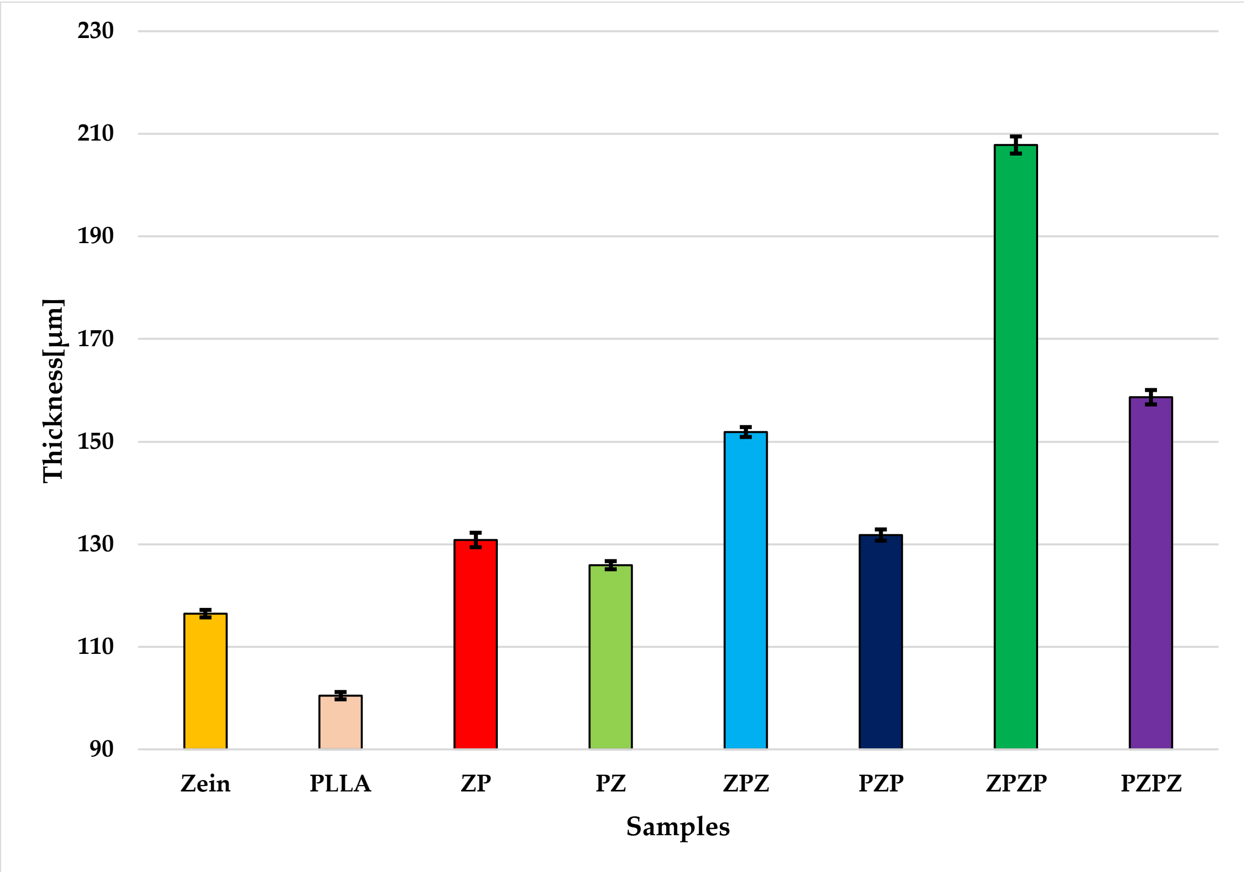


Figure 28: Layer-by-layer thickness increment of ZPZP solution. Thicknesses have been expressed as paper + coating.

Zein and PLLA has been coupled for their properties to deliver a packaging solution focused more on water repellency. PLLA as a great water repellant [39, 68] needs zein in order to increase its grease repellency [73,74], even if Zein is a material that responds in a good way to both reagents.

Figure 28 underlines the differences between coating zein or PLLA in different position. Zein, after being dried, increase in a relevant way thickness till 107.62±1.67µm talking about ZPZP solution; while if PLLA is coating as first layer it can be seen an increasing in thickness but less compared to the previous solution. In fact, PZPZ increases by 68.65 ±1.41µm.

This condition is present due to differences of materials in permeating paper. Zein tends to remain on the surface of paper without migrates, while PLLA migrates increasing in minor way thickness of packaging solution.

As seen before PLLA respects the range 1-12μm, here is zein that increases in a very important way thickness of paper-based packaging materials. Zein tends to stay between 25μm and 35μm according to measures taken [69], there are changes in coating receipt, that do not influence thickness results.

Even in this case increment's proportionality must be analyzed. Considering ZPZP solution a sort of trend is respected. Layer deposition increasing is respected in bi-layer, while tri-layer and multilayer do not respect values' sum.

This situation can be present due to differences in substrate that coating solutions find when are cast.

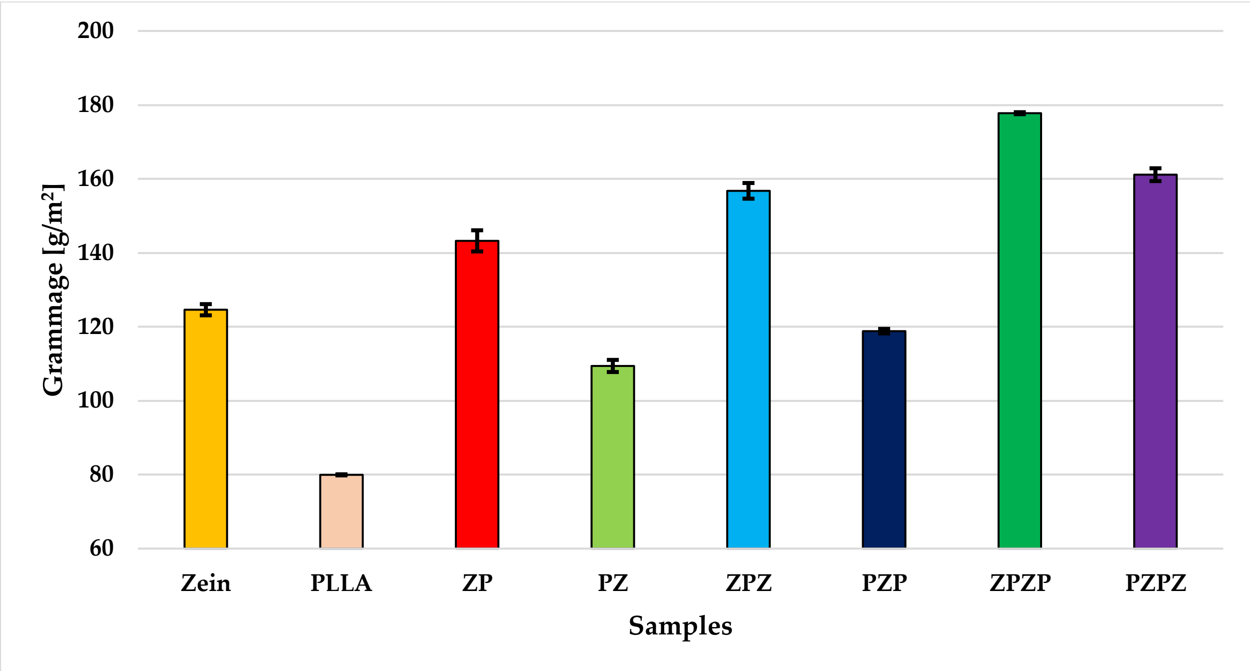


Figure 29: Layer-by-layer g/m² increment of ZPZP solution.

Increasing in weight follows increasing in thickness, Figure 29 shows that according to different set of layers there is a different increment of weight. If PLLA is chosen as first layer there is an increment in weight that is less than the solution with Zein as first layer, 161.35±1.73 g/m² vs 177.76±0.26g/m².

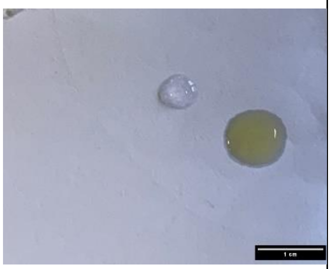
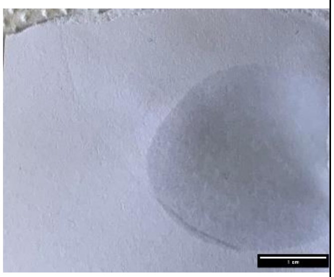
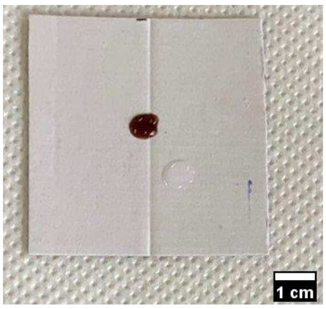
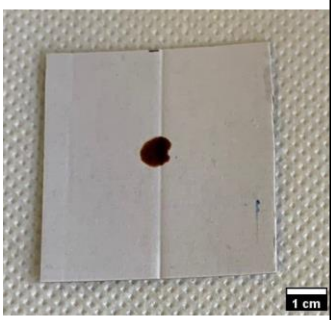
As said before PLLA has an average of 80 g/m² so is zein to be the heaviest component. 123.53 g/m² is a little bit different from range between 145.10-167.21g/m² found in literature [70], due to differences in coating deposition method and w/v%. Zein according to results is the material which increases more thickness and grammage of packaging solutions.

3.2 Droplet's test.

Droplet's test has been made to understand behavior of each single coating material when it comes in contact with grease and water.

The depletion of drops on coating surface can help in understanding which is the reaction of materials according to reagents put on it.

The droplet test has been used to gain both a qualitative and a quantitative analysis by visually evaluate the layer-by-layer structure, observing the increment in the diameter of the halos left by the liquid dropped on the specimens. The ImageJ software was used to define the values reported in Figure 30.

Sample	t_0=0min	t_{fin} =120 min	$Ø_0$ H2O [cm]	$Ø_{fin}$ H_2O [cm]	$Ø_0$ grease [cm]	$Ø_{fin}$ grease [cm]
Paper			0.41	1.27	0.65	2.16
Alginate (A)			0.47	0.67	0.57	0.59

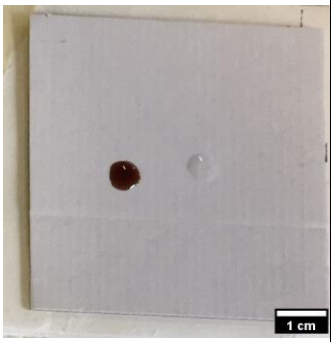
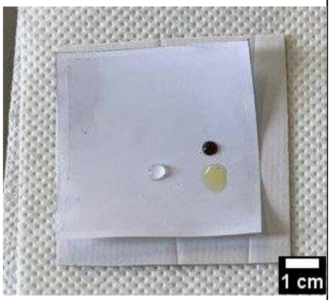
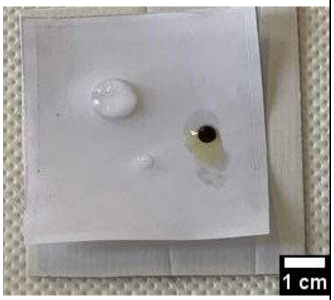
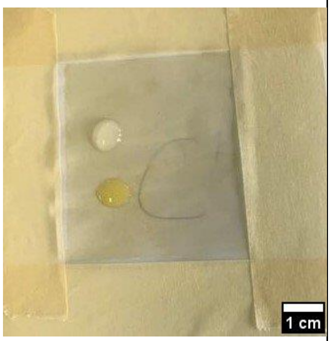
Chitosan (C)			0.44	0.56	0.40	0.45
PLLA (P)			0.44	0.47	0.58	0.81
Zein (Z)			0.53	0.71	0.63	0.69

Figure 30: Droplets test results single layer.

Qualitatively, it has been confirmed that chitosan and sodium alginate are great grease repellants, while tend to adsorb water, PLLA responds in a better way against water if compared to alginate and chitosan, while tends to absorb grease; zein responds in a better way against water if compared to alginate and chitosan, considering, instead grease permeation responds in a better way if compared to PLLA.

This qualitative observation is supported by a quantitative analysis made on measurements of halos diameter.

This helps in understanding the behavior and the ability of a single material to adsorb or repulse grease or water. Diameters' increments are shown in Figure 31.

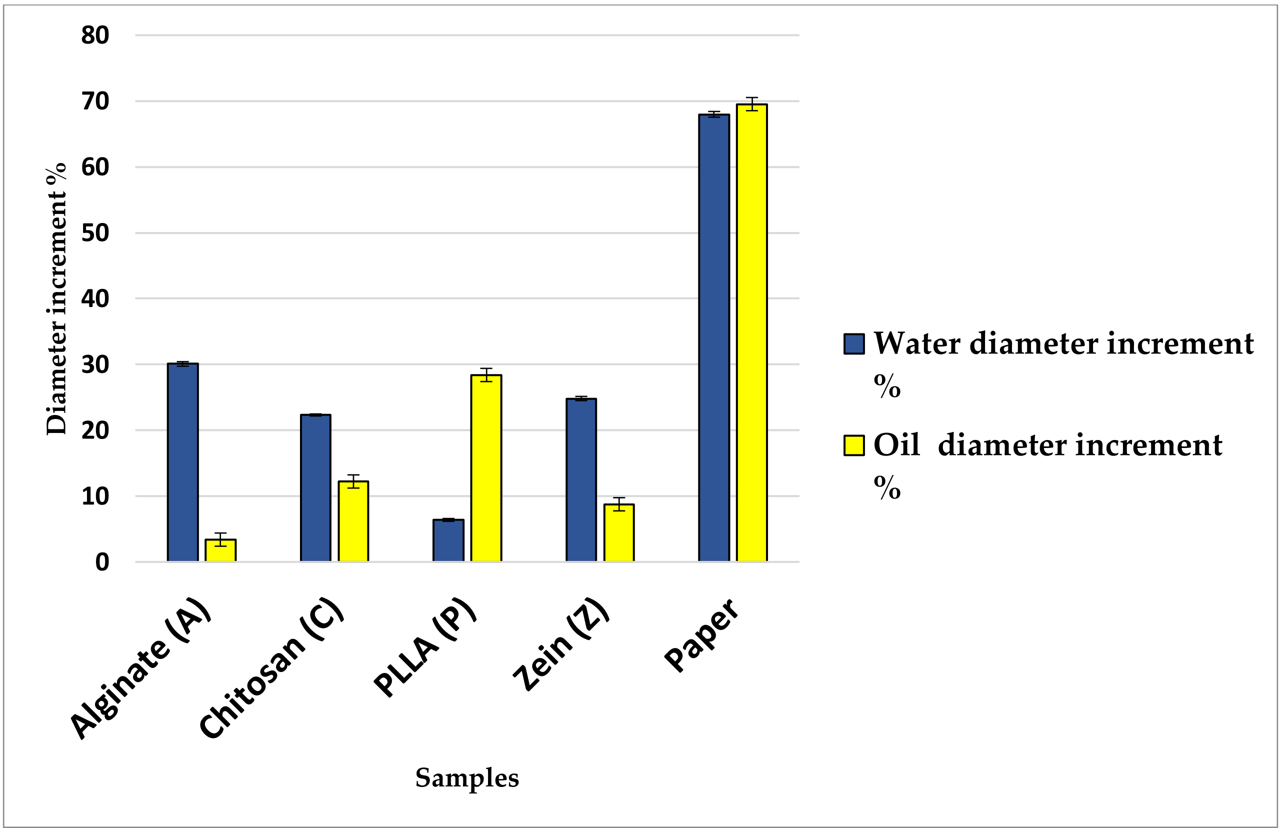


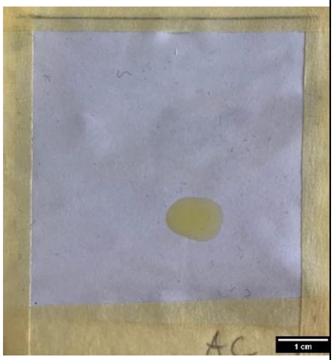
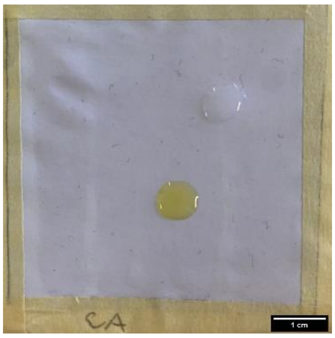
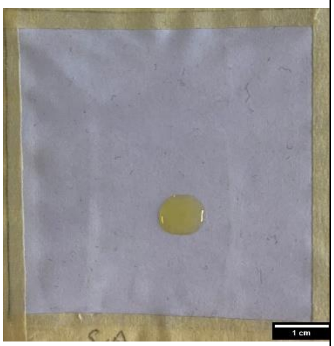
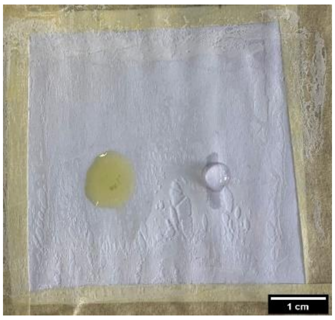
Figure 31: Diameter 's increment in % single layer vs paper.

This first droplet test analyzed the behavior of each single materials used in this work. Alginate and Chitosan provided a barrier to oil and grease penetration, underlined also by [71]; the diameter increases for alginate just 3.38±0.4%, while for chitosan 12±0.05%. A different behavior has been obtained for water, where alginate increases its diameter of 30±0.34%, while chitosan 22.3±0.15%. Chitosan has been studied in similar way in [69], where is underlined chitosan's great oil repulsion, and the spot of water that remains on chitosan's coating without permeating paper. PLLA has a great barrier against water, increment of 6.38±0.22%, also detected by [72] that underlines increasing in water barrier due to PLLA coating on paper; while tends to be penetrated by grease, 28.4±0.29% bigger. Zein has a good barrier to oil, 8.75±0.42% of increment, while tends to be penetrated by water, 24.8±0.28%. This zein's characteristics is also detected in [69] even if have been used a different test based on contact angle.

Pristine Paper underlines its bad results with a 68% of increment considering water and 69% considering oil.

Given these preliminary results, it was decided to couple together the selected materials in different combinations to achieve a significant improvement on the base properties of paper substrates. First of all, Chitosan and Alginate where selected to be coupled due to their nature as complementary materials [63]. Secondly, since PLLA showed great performances against water penetration, was combined separately with Chitosan and Zein, to improve consistently the grease resistance.

In Figure 32 are shown the results and images collected from the droplet test upon bi-layer structured specimens.

Sample	t_0=0min	t_{fin} =120 min	Ø$_0$ H2O [cm]	Ø$_{fin}$ H_2O [cm]	Ø$_0$ grease [cm]	Ø$_{fin}$ grease [cm]
AC			0.35	0.54	066	0.78
CA			0.56	0.67	0.52	0.58
CP			0.44	0.49	0.61	1.13

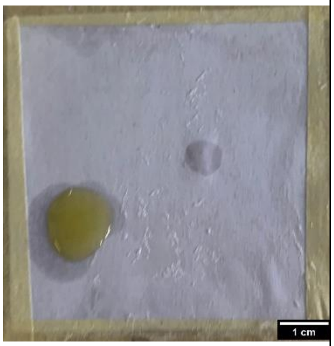
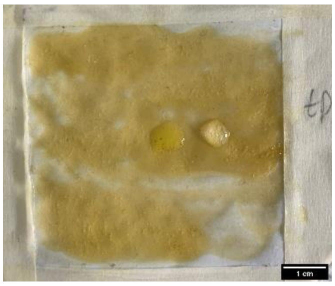
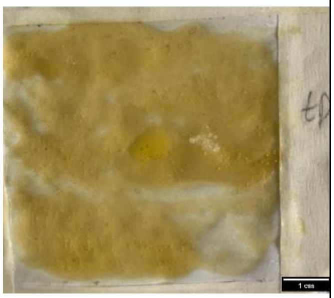
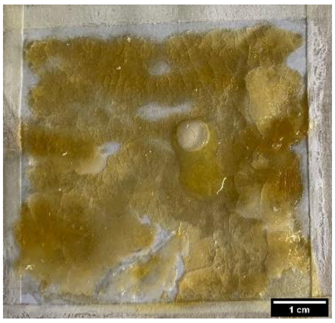
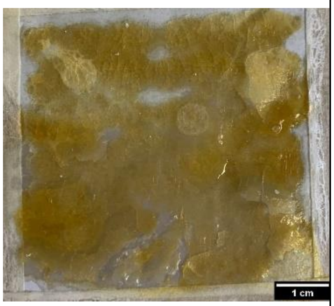
PC			0.44	0.51	0.79	1.04
ZP			0.50	0.57	0.53	0.68
PZ			0.48	0.55	0.57	0.64

Figure 32: Droplets test results bi-layer.

Diameters' increments are shown in Figure 33.

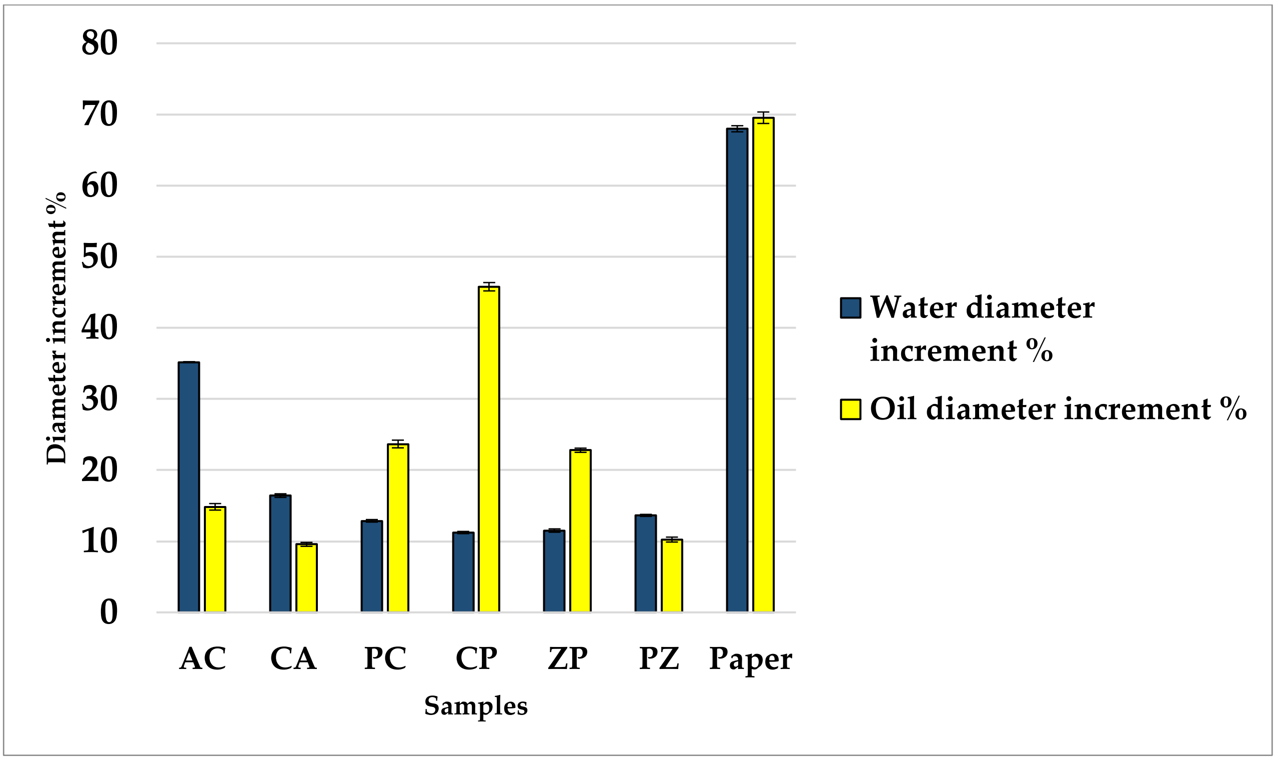


Figure 33: Diameter's increment in % bi-layer vs paper.

Considering the results obtained from bi-layer coatings, some interesting consideration can be made. Starting from Chitosan and Alginate, the better performances were detected by firstly applied a layer of Chitosan followed by Sodium Alginate (CA) if compared to the other counterpart (AC). Very similar resistances were achieved by the combination of PLLA and Chitosan (PC) if compared to the single materials weaknesses. Once again, the opposite configuration, CP, failed to obtain an improvement, especially in case of oil resistance, showing a diameter's increment of over 40%. This probably due to some reaction between the chitosan layer applied first and the PLLA one.
Adding PLLA to Zein (ZP) increase water repulsion, from 24.8% to 11% (in terms of diameter's increment), while decreasing oil repulsion, from 8% to 22%, on the other hand adding Zein to PLLA (PZ) decrease water repulsion, from 6% to 13%, while increasing oil repulsion from 28% to 10%. This behavior may be connected to the Zein layer inhomogeneity, clearly showed in the images in Figure 28.

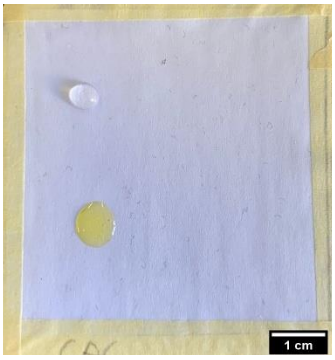
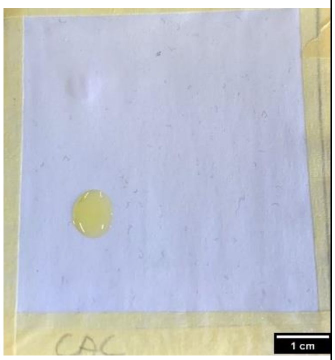
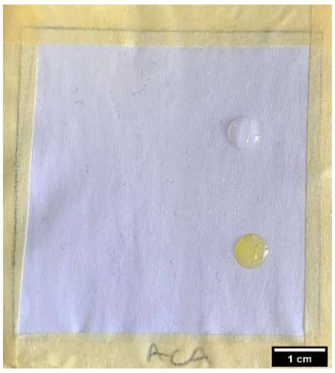
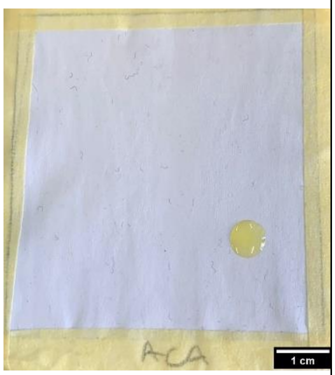
After the droplets tests made on bilayers, the best configuration achieved were CA, PC and PZ. Going more into details, the layer-by-layer structures obtained from the combination of chitosan and alginate respond in a great way to oil, however, further improvement against water remains a major challenge to tackled.

Chitosan and PLLA solution performed better against water most of the water's droplet seems to evaporate instead of permeates through the layers. On the other hand, oil permeates in an unwanted way; considering PLLA and Chitosan bilayer (PC), seems to leave penetrates water by the first layer while blocking oil.

Zein and PLLA solutions responds both in a good way to both liquids. During the experiments with Zein, it has been seen that water tend to solidify it, consequently inducing the formation of several cracks [56]. This condition underlines the necessity of building a new layer to add further protection.

Once again, the results obtained from the droplet tests let to the decision of adding a new layer to solidify the enhancement obtained.

In Figure 34 are categorized the results achieved during the experiments of the new layer-by-layer structure.

Sample	t_0=0min	t_{fin} =120 min	$Ø_0$ H2O [cm]	$Ø_{fin}$ H_2O [cm]	$Ø_0$ grease [cm]	$Ø_{fin}$ grease [cm]
CAC			0.44	0.61	0.48	0.52
ACA			0.48	0.72	0.50	0.53

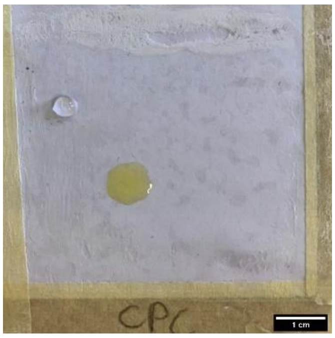
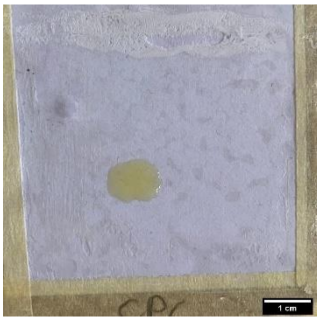
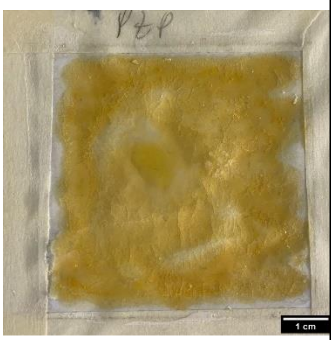
PCP			0.45	0.52	0.88	1.00
CPC			0.43	0.49	0.63	0.89
ZPZ			0.60	0.94	0.52	0.55
PZP			0.42	0.81	0.69	1.33

Figure 34: Droplets test results tri-layer.

Tri-layer diameters' increments are shown in Figure 35.

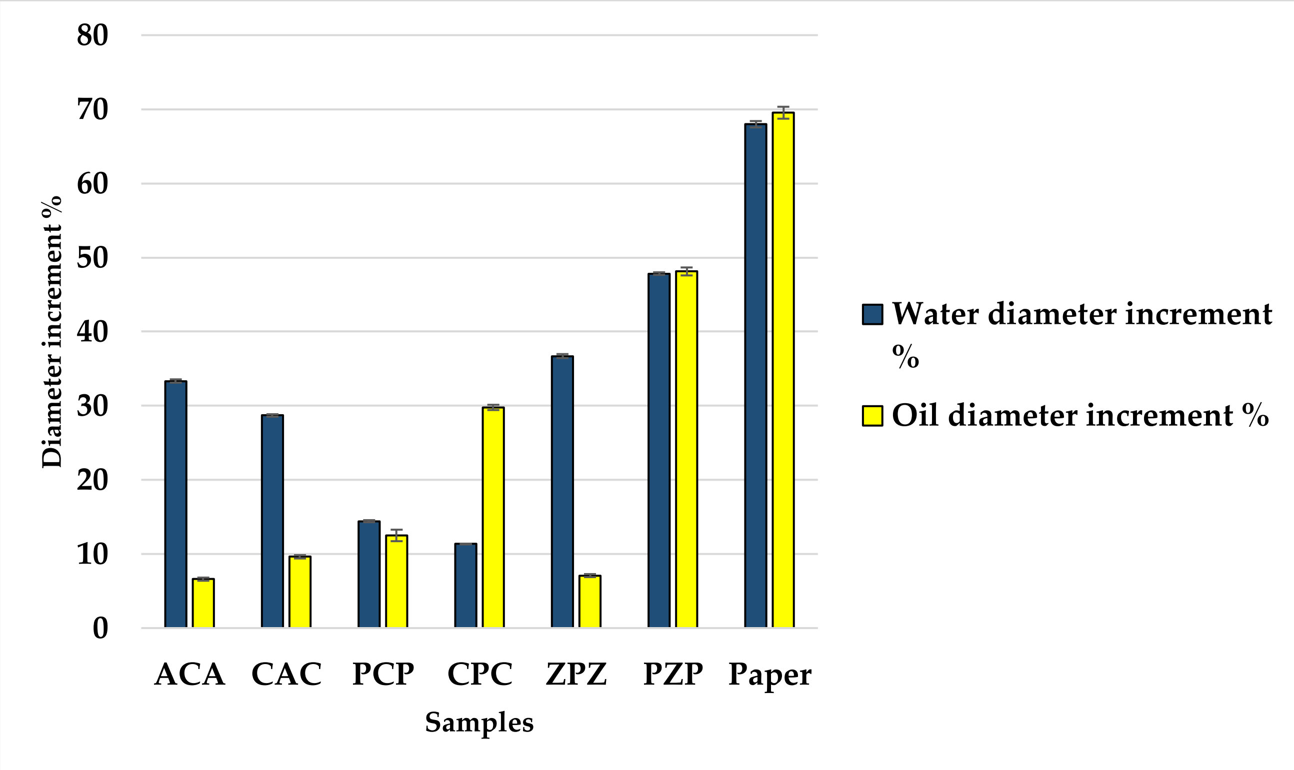


Figure 35: Diameter increments in % tri-layer vs paper.

Considering the results gained from testing the tri-layers configurations, a great inconsistency with tests made previously. Starting with ACA (two layer of Sodium Alginate separated by one Chitosan layer) and its counterpart CAC, it was assumed that Sodium Alginate layer was the main responsible for the oil protection. However, it seems that adding only layer was not sufficient to gain any improvement to both water and grease resistances. Moreover, it is easy to underline the difficult of Chitosan layers to repulse water due to its hydrophilic nature.

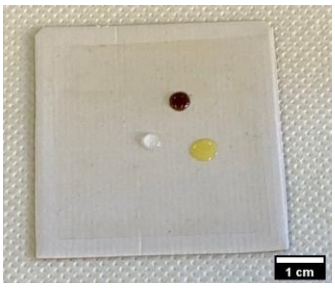
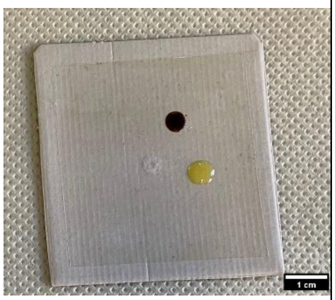
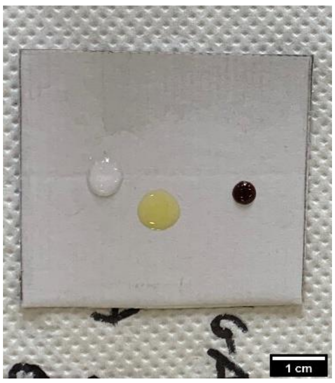
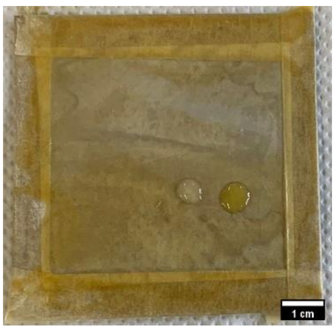
PCP configuration (two layers of PLLA separated by one layer of Chitosan) demonstrates a good barrier to both liquids, with a diameter's increment of 14% for water and 12.5% for oil. On the other hand, CPC (two layers of Chitosan interrupted by one layer of PLLA) presents comparable water resistance but far worst oil resistance.

Considering the structure in which Zein-based solution has been used, a significant deterioration of the coating was observed upon the prepared samples. The presence of uneven structure and cracks led to very poor performances, with the only exception of the oil resistance for ZPZ (two layers of Zein separated by one layer of PLLA).

Considering the results discussed above and to complete this study, a multi-layer structure comprising of four layers was tested. For the solution made by Alginate and Chitosan according to the droplet tests, a multi-layer configuration composed of Alginate-Chitosan-Alginate-Chitosan (ACAC) was created. Secondly, For PLLA-

Chitosan solution it has been decided, according to the previous tests, to realize a structure organized as follow, PLLA-Chitosan-PLLA-Chitosan (PCPC). Lastly, for the Zein-PLLA solutions, in a final attempt to stabilize the inconsistent results obtained with such difficult biomolecule, two distinct configurations have been selected, both composed by two layers of Zein and two layers of PLLA, respectively ZPZP and PZPZ.

All solutions presented above have been analyzed using ImageJ software and presenting them in Figure 36.

Sample	t_0=0min	t_{fin} =120 min	$Ø_0$ H2O [cm]	$Ø_{fin}$ H_2O [cm]	$Ø_0$ grease [cm]	$Ø_{fin}$ grease [cm]
ACAC			0.37	0.48	0.46	0.47
PCPC			0.54	0.58	0.52	0.55
ZPZP			0.48	0.54	0.52	0.55

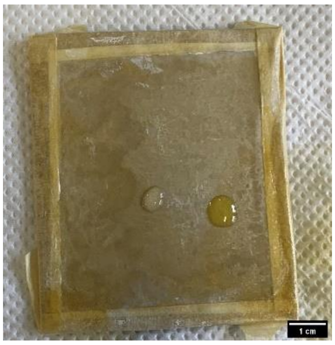
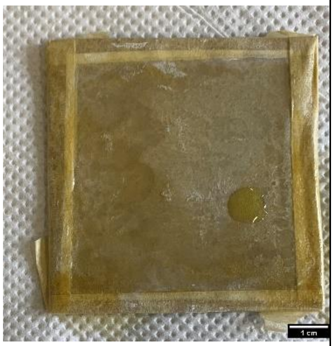
PZPZ			0.58	0.81	0.54	0.58

Figure 36: Droplets test result multilayer.

Droplets test results on diameters' increments are shown in Figure 37.

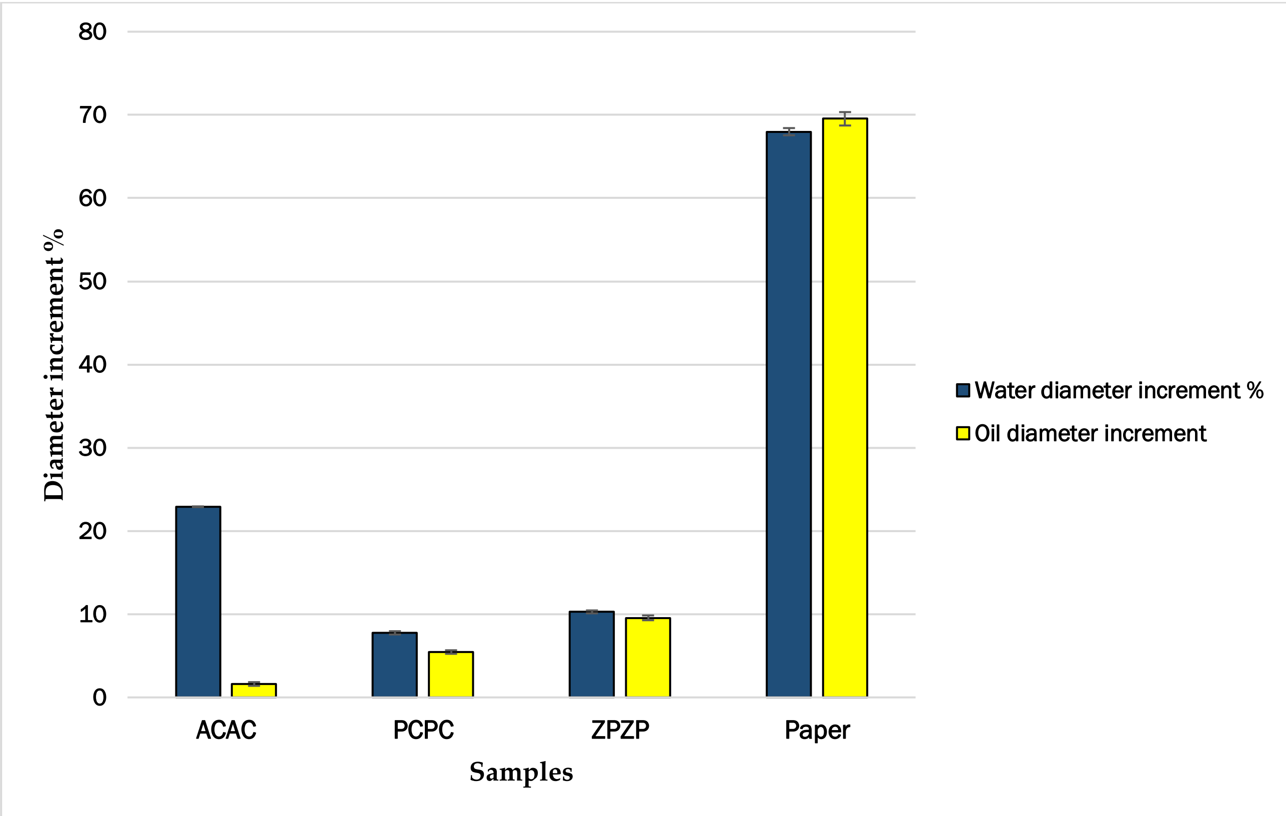


Figure 37: Diameter increment in % multilayer vs paper.

ACAC tends to respond in an outstanding way to oil, as expected from the combination of more than one layer of Sodium Alginate [60,71,79]. However, some issues have been highlights during the droplet test against water. On the other hand, PCPC configuration showed the best results so far to both oil and water. Lastly, for the multi-layer sample comprising Zein (ZPZP) was observed overall good performances.

In Figure 37 can be seen that, comparing the designed solutions to pristine paper, a significant improvement in both water repulsion and oil repulsion.

Moreover, this achievement underlines that the differences between the three solutions can be useful also in delivering specific products. For example, ACAC solution is the best considering oil repulsion, it can be used to pack grease food like ready to eat fruit and vegetables, fried food, roast chicken; PCPC can be used with food that has a big water activity, and tend to pull out liquids, like fruits and vegetables [86]. ZPZP is useful for food and beverages, in fact it has a great repulsion both to liquids and oil, and both materials are not hydrophilic so tend to repulse water [69].

3.3 ASTM F119: grease penetration results.

This test helps in understanding the time at which grease start to penetrate through the deposited coatings. Paper has been coated with the different designed solutions prepared as described in 2.4.2. After predetermined timepoints, a visual observation has been made to check the liquid penetration.

Results have been divided according to the number of layers of the investigated configuration and compared with pristine paper.

The test duration was set to a maximum 24 hours, in future investigations, such limit could be further prolonged to verify the coating behavior.

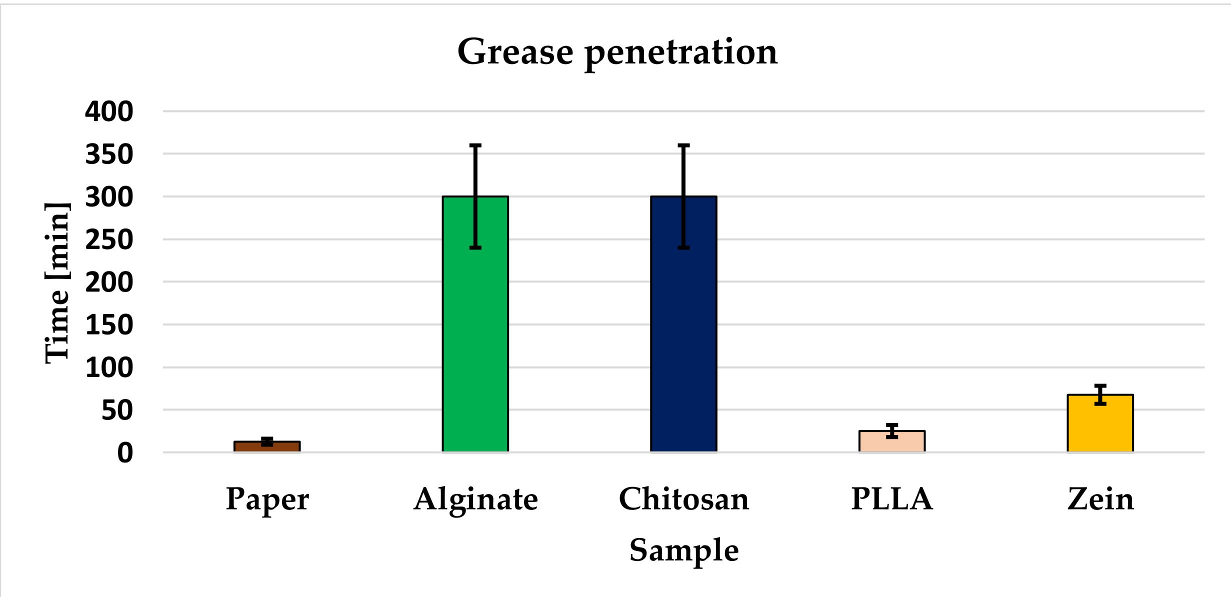


Figure 38:ASTM F119 results single layer vs paper.

Paper has been penetrated shortly after the start of the test. Alginate and Chitosan do not present any penetration before 300 ± 60 min of test, showing good performance, especially compared to the literature [63]. PLLA, is penetrated after 15-30±7 min, [75] describes PLLA as a bad grease resistant material, as expected in this project. Zein coating showed better performance if compared to PLLA and pristine paper, presenting the formation of evident halos after 60 ± 10 min.

These results have confirmed the previous hypotheses made from the droplet test. In particular, the ability of a specific material to provide grease protection can be qualitative assessed by the oil penetration time. Generally, PLLA layer was the worst coating considering this aspect, while Chitosan and Sodium Alginate provided the highest protection of all.
Once more, Zein confirm the previous trend as a material with medium performances against grease. In Figure 39, the measured time for the grease penetration for bi-layer configuration have been reported.

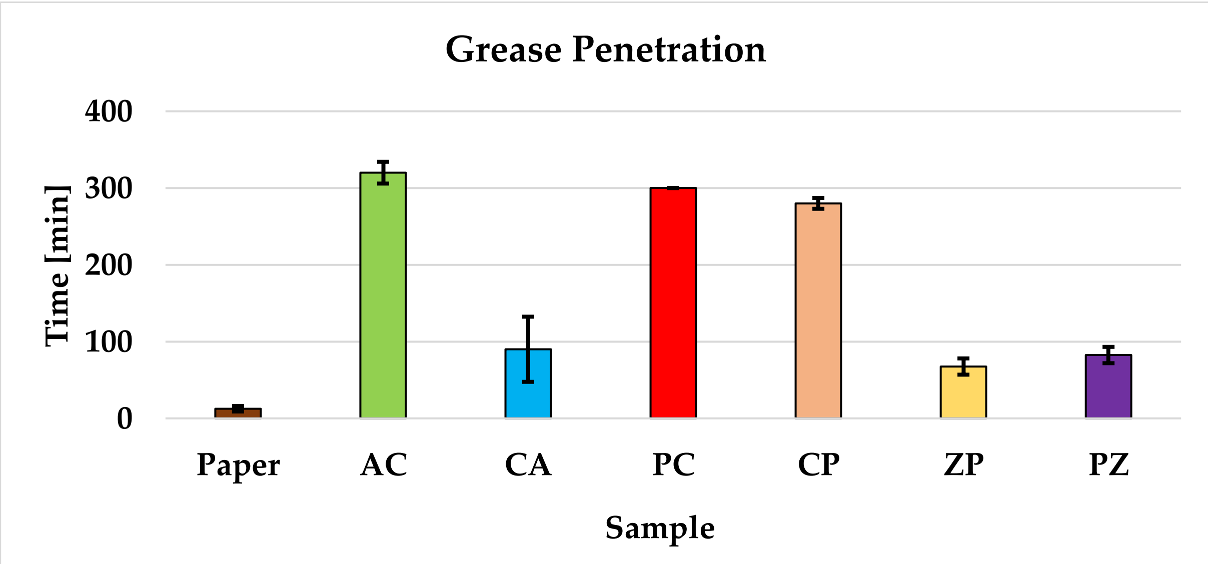


Figure 39: ASTM F119 results bi-layer vs paper.

Bi-layer configurations were designed to further improve the protection provided by the single layer materials in case of contact with grease. Analyzing the results, significant improvement was detected by adding a Chitosan layer to PLLA (on both the selected configurations, PC and CP), as well as in case of the combination of Zein and PLLA layers (PZ and ZP) although the latter was less interesting.

These combinations underline only the great grease repulsion of Chitosan-based coating, as also presented in [68], in which chitosan no present grease penetration even against worse greases. CA configuration (Chitosan layer and Sodium Alginate layer) presents variable performances, this can be correlated to some inhomogeneity in the coating structure of the produced samples. Basically, no real improvement over the results gathered in the first assessment were measured. Clearly this is connected to the fact that only one layer was added to the previous configurations, therefore, the improvements were connected only to its influence. Following the same pattern as done in the droplet tests, it has been studied the grease penetration also for the tri-layer solutions. The results obtained were presented in Figure 40.

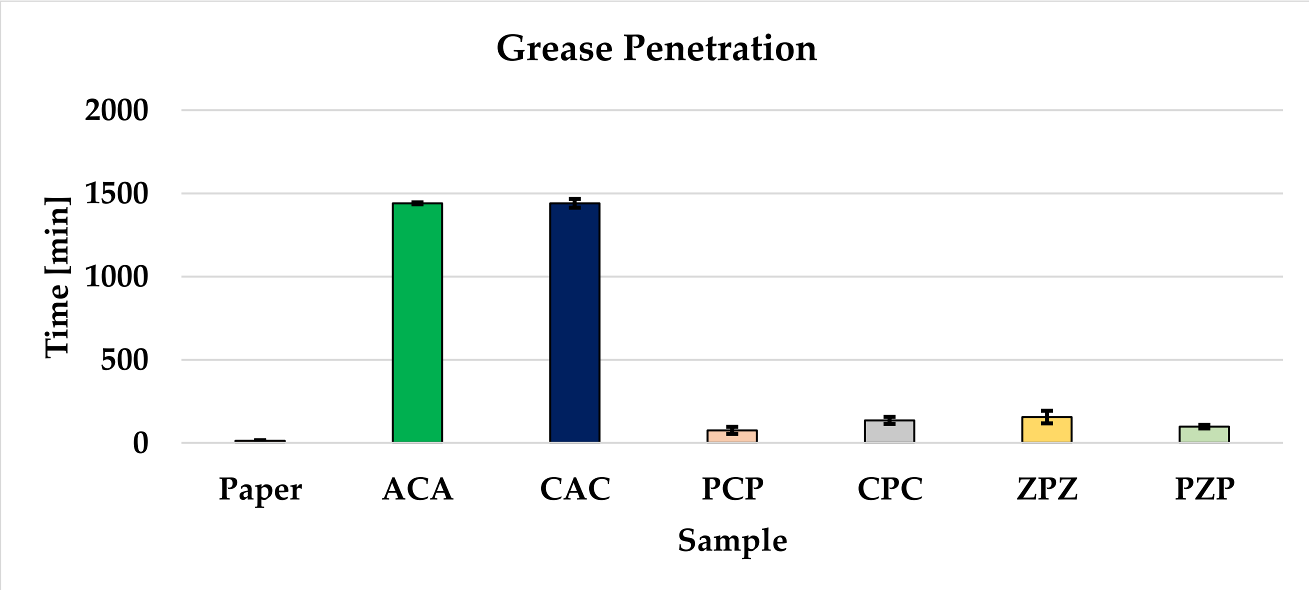


Figure 40: ASTM F119 results tri-layer vs paper.

Considering the reported times in Figure 40, almost all the packaging solutions can provide a solid protection against oil permeation, with the sole exception of PCP (two layer of PLLA separated by a layer of Chitosan).

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ACA and CAC solutions do not present halos before 1440 ± 30 min, with significant increment compared to previous solution. PCP configuration confirms the limit of PLLA to be grease repellant, [71], thus, the needs coupling it with materials which provide a better grease repulson, such as Chitosan.
In PZP solution (two layers of PLLA and one layer of Zein) no significant improvement were achieved if compared with the previous configuration (PZ). It is worth noting that several difficulties were encountered when using the viscous Zein-based solution, thus, generating a uniform coating was not always possible.

CPC (two layer of Chitosan interrupted by one layer of PLLA), slight improve the protection provided previously in PC and CP configurations. Lastly, ZPZ (two layer of Zein and one layer of PLLA) is penetrated after 155±38 min. The last tests were brought upon the multi-layer configuration selected; the data collected are shown in Figure 41.

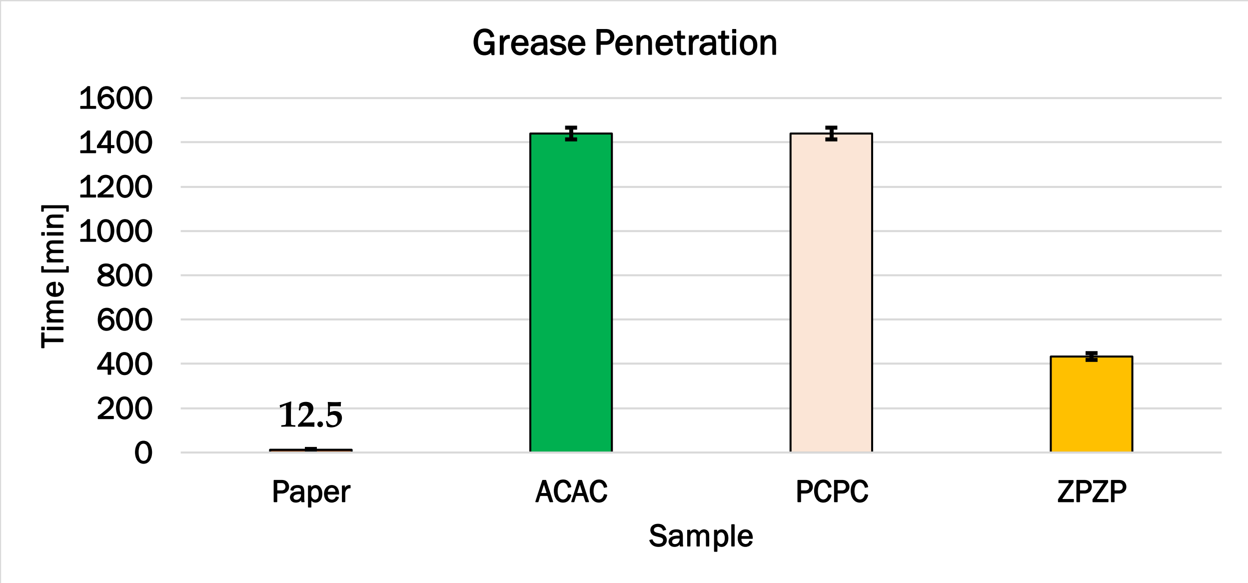


Figure 41: ASTM F119 results multilayer vs paper.

Figure 41 analyzes multilayer coating solutions, ZPZP solution presents halos after 430±15 min increasing in a relevant way three-layer solutions made with Zein and PLLA confirming behavior detected in droplets' test; ACAC solution and PCPC solution do not present halos before 24h±26min. These results explain the good resistance to grease penetration of all the multilayer and underlines the importance of creating a four-layer solution.

The multi-layer solutions designed in this study were the results of an optimization process in which the objective was the achievement of the better performances given by the selected materials. In fact, no four-layer solutions have been tested or presented in current literature, as more commonly coated paper was characterized with only one or two layers. Moreover, some differences can be found in the development of the grease penetration test. For example, [63][71][75] delivered this kind of test for more than 6h and not only with olive oil but utilizing different types of grease like toluene, castor oil, etc. Analyzing in this way also different type of grease that could affect materials.

Simultaneously with the qualitative evaluation reported previously with the penetration time, a quantitative analysis was conducted by measuring the areas left by the penetrated oil upon the opaque glasses, named halos.

These measures have been made using a Stereomicroscope (Leica, model S9i) to photograph glass square at $t_0 = 0$ min and at different timepoint each one after 30 min. The test lasted at least two hours for most of the selected solutions, while longer time was needed for both the tri and four-layer configuration.

The images acquired with the stereomicroscope, were analyzed by means of ImageJ software [91]. Figure 42 represents an example of the photos taken at the start and at the end of the quantitative evaluation.

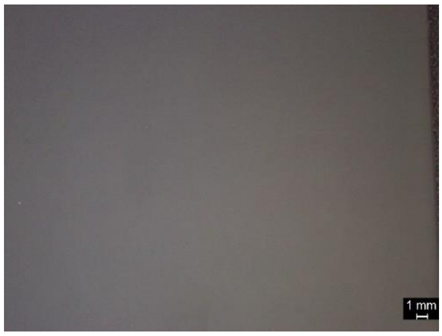
Sample	t0=0min	tfin=120min
Zein		
ACAC		

Figure 42: Sample of differences between glass square before and after the test.

In figure 43 results of grease test penetration categorized according to grease's area penetrated are shown. Knowing that square's area is 2500mm^2 using Image J software can be measured areas of olive oil penetrated trough material.

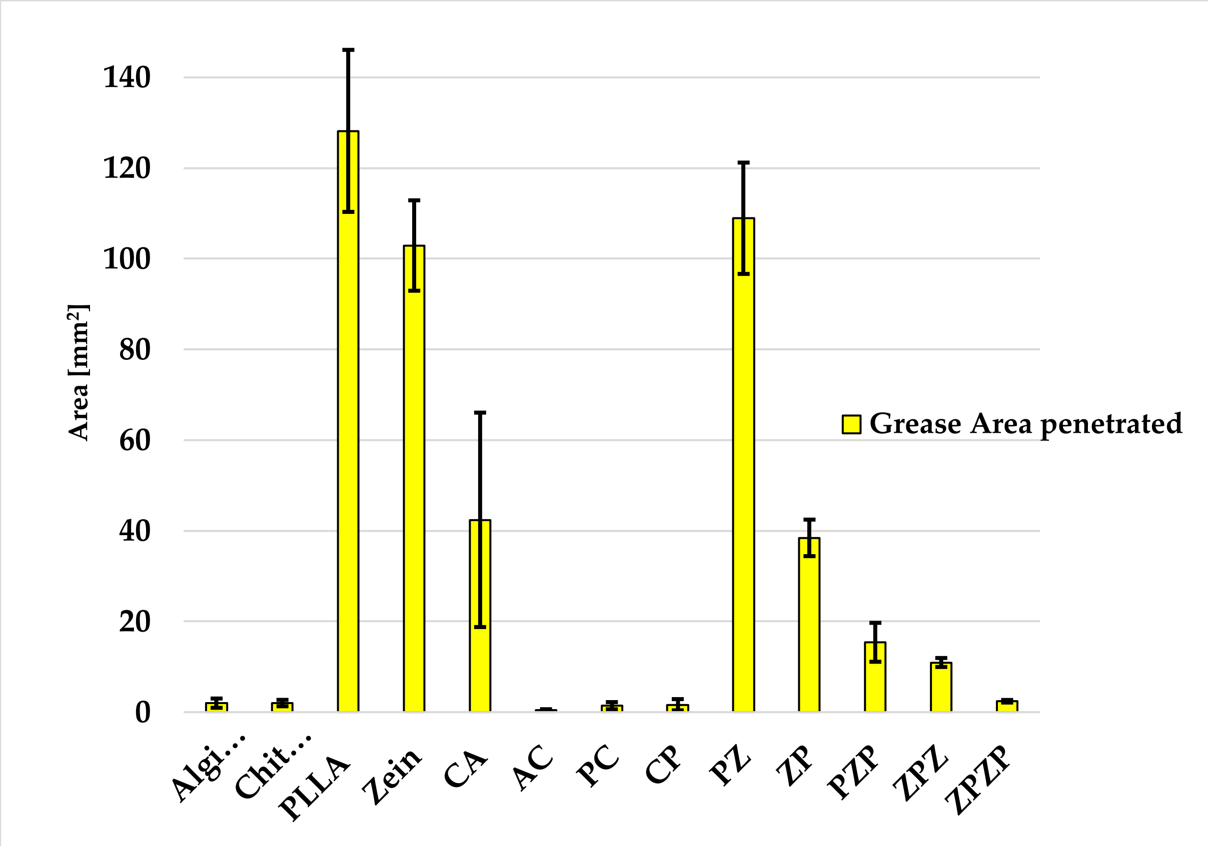


Figure 43: Grease's area in samples affected by penetration.

Figure 43 has been developed to make a comparison between packaging configurations which have been penetrated by oil. The other not presented in Figure 43, have not present halos before 24h, time after which the test has been stopped.

Paper is penetrated instantly by 750mm^2 of oil.

Have a look to single material layer. PLLA is the worst one. Through it penetrates 128±17.86 mm^2 of oil while for Zein halos area is 102.92±9.97mm^2. CA as said before presents halos due to errors occurred during casting phase.

3.4 ASTM D570: water adsorption results.

Materials film have been cut following the instruction mentioned in 2.4.3. After preparing and weight the samples, beaker have been filled with distilled water. The specimens have been then placed in the containers, completely immersed in the water for 24 h under ventilated hood, the temperature was kept constant at 23 °C during the entire experiment. Once the 24 h have passed, the samples have been weighted again after being dried with cloth to measure the increasing in weight due to the water absorbed.

Sodium Alginate sheets has been totally dissolved in water, due to its hydrophilic nature [63]. Alginate tends to be dissolved in water without catalyst, this property is shown also in [39]. However, Chitosan, PLLA and Zein, samples were in a better shape, reaching the end of the test without being dissolved.

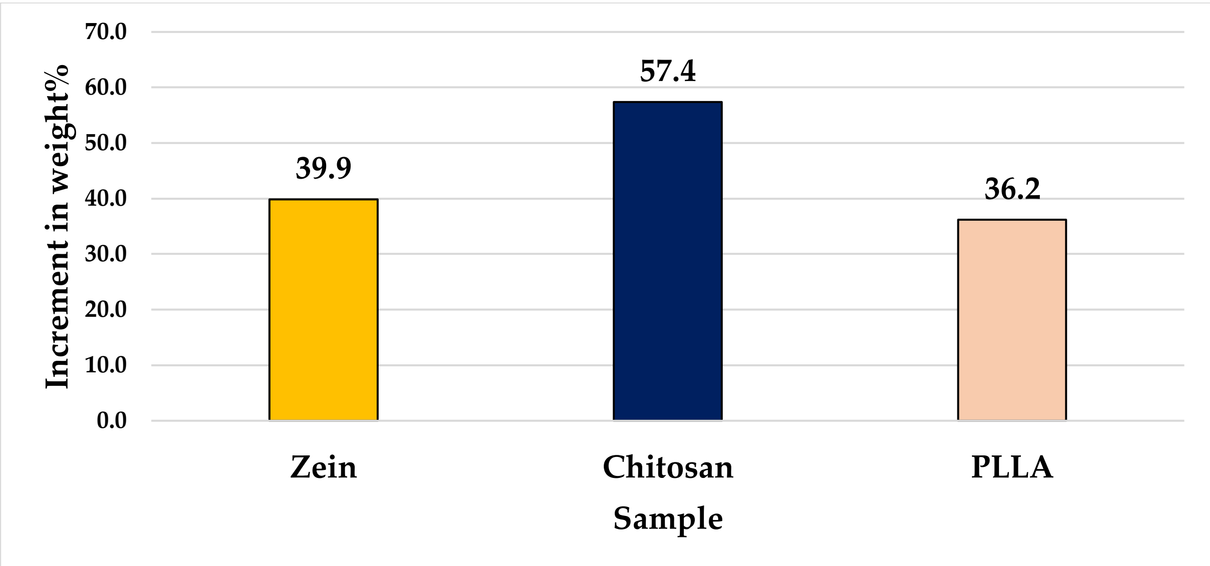


Figure 44:Increment in weight after 24 h of immersion in water solution.

The worst material was, as already mentioned, Sodium Alginate (not presented in Figure 44), that has been totally dissolved in water, not giving the opportunity to be analyzed. These bad properties against water considering Sodium Alginate have been discussed widely in the literature [71][39]. Chitosan, as shown in figure 44, is the worst materials in terms of water absorptiveness. Chitosan layer adsorbs water and increases its weight by 57.4%. PLLA and Zein confirm their good water repellency with a weight increment of 39.9% for Zein and 36.2% for PLLA.

These results can be compared with behavior that have been detected using droplets' test. PLLA is the best one due to its ability of being filmed and plasticized as PE, PET. [40]

Cobb's test is the one that is used in a constant way in literature, there are differences between this test and the Cobb's one, and comparison is slightly difficult [61,75,76,79]. Developing materials after having utilized this type of test can close the gap between this work and articles already present.

3.5 Water Vapor Transmission Rate (WVTR) results.

The different Packaging configuration designed in this work, have been tested, starting from the single layer to the multi-layers ones, using pristine paper as a control sample.

Using the [Equation 2], provided by the ASTM E96, was possible to measure and better understand the behavior of packaging solutions when the permeability toward water vapor has a key role. For example, in the food industry, the water vapor permeability of a material is of fundamental importance when dealing with fruits and vegetables [86]. In Figure 45, the values of the WVTR of the single layer configuration have been reported.

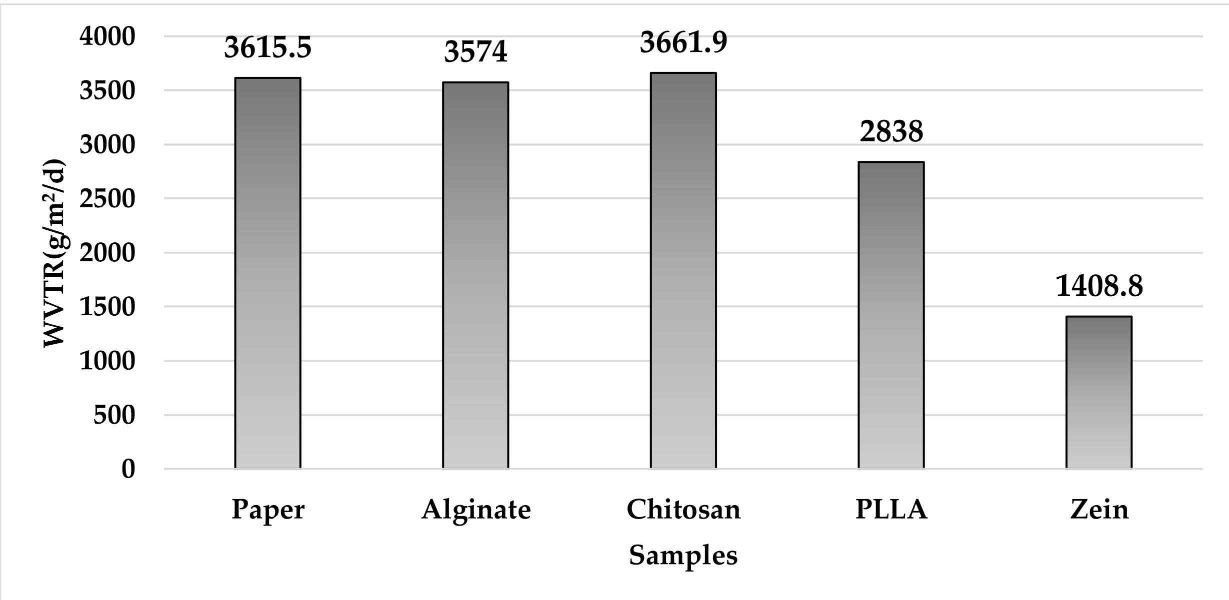


Figure 45: WVTR single layer vs paper.

As shown in Figure 45 paper sample, coated with Alginate and Chitosan, do not provide a significative protection against water vapor, if compared to paper. This is a worse situation considering literature, [53], where even the paper coated by a single layer was characterized by a WVTR less than the configurations proposed by this work. The differences between the two studies may be explained by the differences between the substrates. Kraft paper was thicker, resulting in better starting performances and providing a different structural substrate for the deposited solution. In [63] sodium alginate has a completely different WVTR 2000 g/(d*m^2), this result can be linked to different type of coating percentage by w/v. The differences between the two studies may be explained by the differences between the substrates. In particular [71] detects a WVTR of 1550 g/(d*m^2) against 3574 g/(d*m^2), this gap can be given by differences in casting alginate's film similar to plastics one and alginate's coating films, deposed on paper substrate.

A relevant barrier in comparison to Paper's WVTR is given by PLLA that decreases grams of water vapor permeated by 21.5 %. [74] expresses WVTR of PLLA for film casting in petri dishes, around 208g/d/m^2, due to differences between casting a film and coats solution on paper. Another work expresses PLLA WVTR as 600g/d/m^2,[75], this value is lower than the one expresses in this work. Although the differences between those values may be correlated to several parameters, such as casting method, percentage of w/v in solutions and thickness.

Zein layer increases significantly the WVTR of the paper, which was unexpected if compared to the results discussed in [76], where the protection given by the zein coating was less impactful.

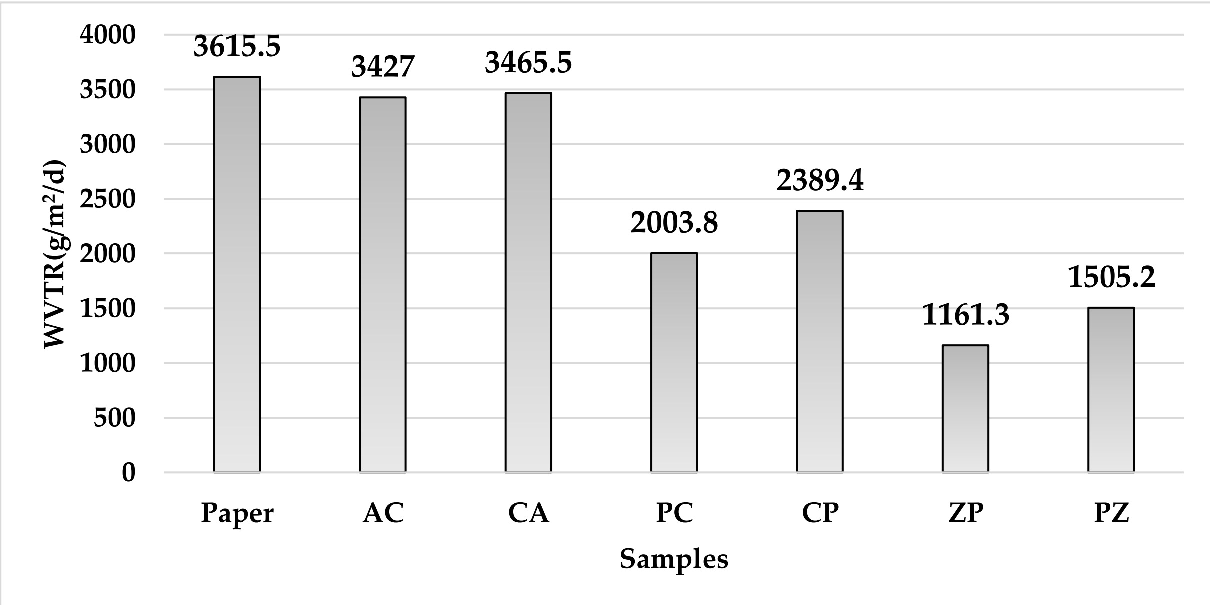


Figure 46: WVTR bi-layer vs paper.

As shown in Figure 46, coupling together specific materials help in increasing the global WVTR, the best result has been detected from ZP (first layer of Zein and second layer of PLLA) solution, 1161.3 g/(d*m^2), and PZ solution, 1505.2 g/d/m^2). A comparison can be made with solutions found in [66], even if zein is not coupled with PVOH, can be seen that increasing barrier against Water Vapor Permeability can be considered a property specific of corn protein. Zein and PLLA were the two materials that responded in a better way, to Water Vapor Permeability (WVP), coupling them together is a good idea to improve this specific property. AC and CA solutions, as explained in [6], even if delivered as bi-layer solutions do not increase WVTR of paper in a consistent way. PLLA is material that, if coupled with chitosan, brings to paper an increasing in WVP. [6] explains that chitosan increases water vapor barrier property by a maximum of 100 g/(d*m^2), creating PLLA and Chitosan based multilayer solutions can brings advantages to paper-based packaging solutions against water vapor permeation.

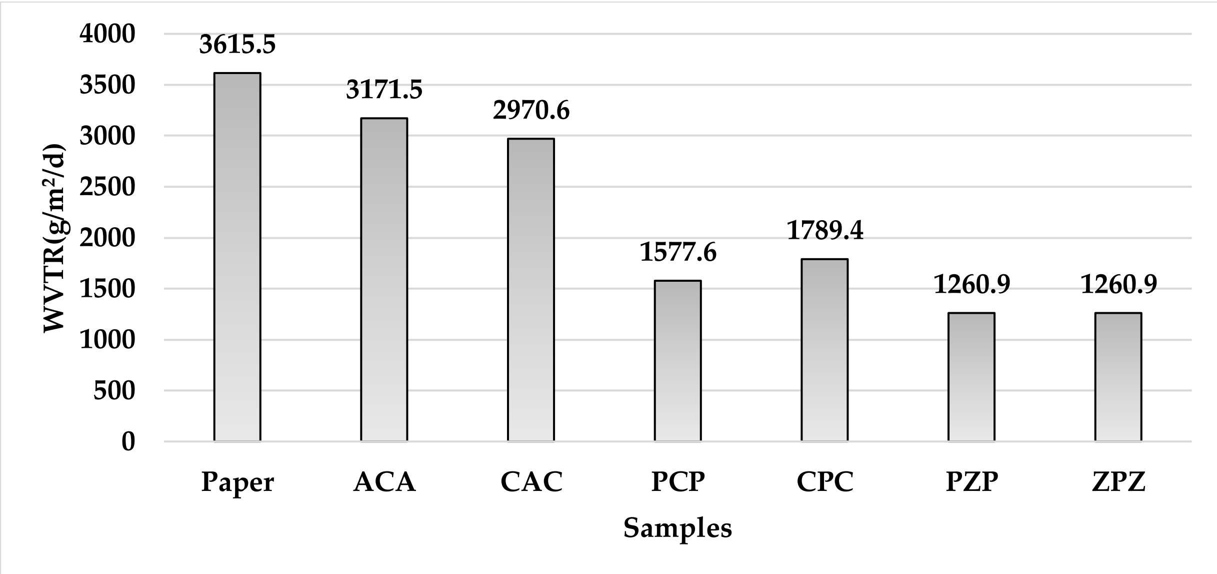


Figure 47: WVTR tri-layer vs paper.

This can be seen in CAC solution, where an additional chitosan layer from 3465.5 g/d/m^2 to 2970.,6 g/d/m^2 , PCP solution, from 2003.,8 g/d/m^2 to 1577.,6 g/d/m^2, in CPC from 2389.,4 g/d/m^2 to 1789.,4 g/d/m^2 , and in ZPZ, from 1505.,2 g/d/m^2 to 1260.,9 g/d/m^2. Tri-layer structured paper packaging were difficult to comment with respect to the current literature since more commonly only single or bi-layer are studied.

Multilayers have been considered as last packaging solution to be tested.

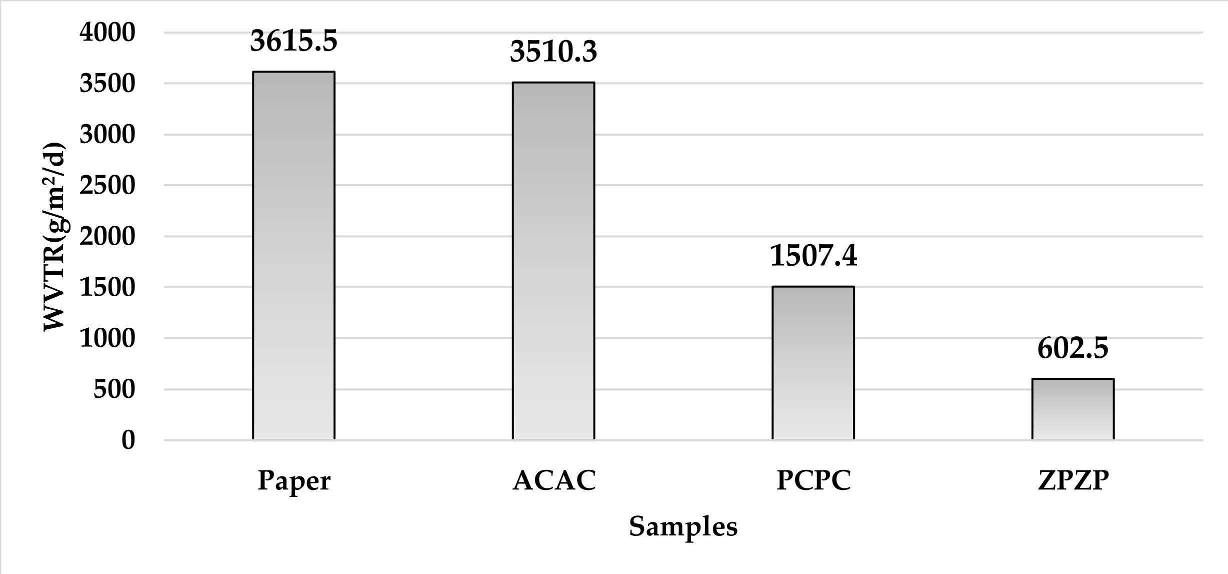


Figure 48: WVTR multilayer vs paper

Lastly, in figure 48, can be seen that it's possible to compare the WVTR of uncoated paper with the multi-layer configuration designed at the end of the optimization process of this study. PLLA and Zein were, once again, the main players in reaching the best performances as water vapor barrier. The lowest value determined during the experiments was obtained by ZPZP (two layers of zein and two layers of PLLA) while PCPC (containing chitosan and PLLA) was in line with what was experienced with previous configurations.

As expected, Alginate and Chitosan, thanks to their hydrophilicity do not any sort of protection against water, as also detected in [63].

3.6 ASTM D 3985-02: oxygen transmission rate (OTR) results.

Oxygen transmission rate have been calculated using films of Alginate, PLLA and Chitosan. Casting Zein film has been difficult, in fact, putting film into the OTR machine it did tend to crack and break itself.

Films thickness has been measured using electronic micrometer: Chitosan, 45-50±1.57µm, Alginate 25-35±3.47µm; and PLLA 50-57±2.45µm.

Since the measured values between the investigated films were very different from each other, it has been decided to use a logarithmic scale to provide a better comparison. The reported values presented in Figure 49, are expressed as mean and standard deviation of at least three repetitions.

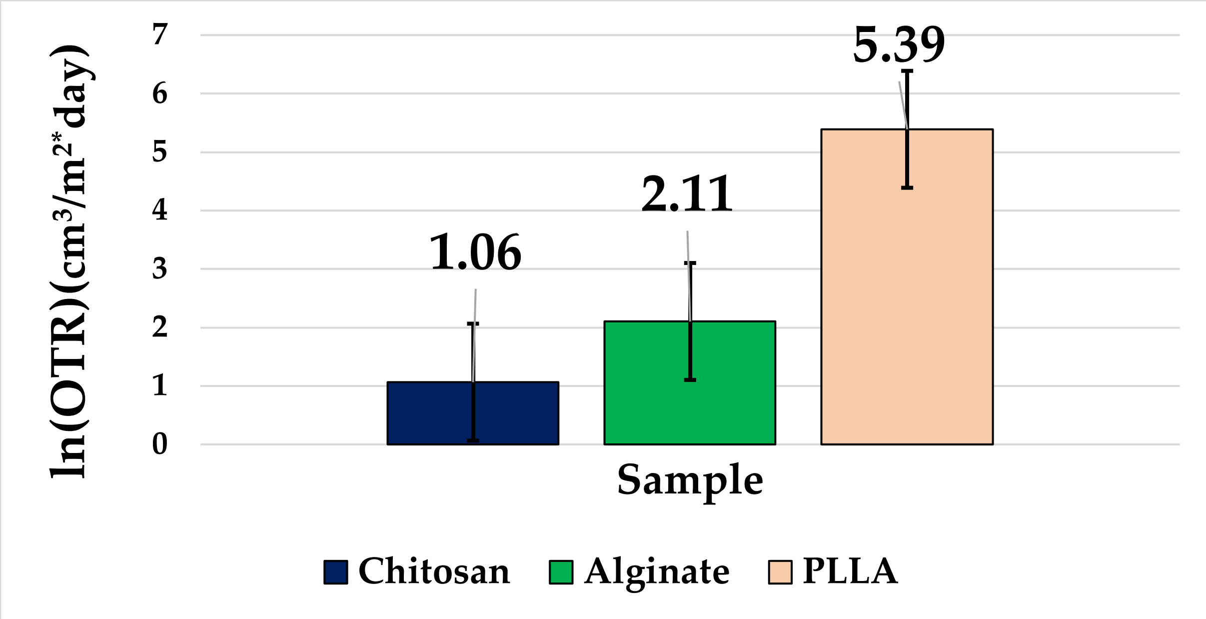


Figure 49: OTR logarithmic graph of single material films

The oxygen transmission rate data collected found good agreement to several scientific papers. In particular chitosan can be considered as a material able to protect products from oxygen permeation, as detected in [79] and [69], the reported value of 2.90 ± 0.44 μm was perfectly in line to the author's findings. The same could be said also for sodium alginate films, which possess less outstanding OTR of around 8.00 cm3/m2/day, as underlined in [69].

For PLLA it has been decided to buy in supermarket a film of PLA, to analyze it and compare the already present solution to the one delivered by this work.

To provide a more consistent comparison for the result obtained from PLLA film, a commercially available PLA packaging has been bought at local supermarket. However, the performance showed by the PLA film, was lower than the synthetized specimen of PLLA, respectively 400 cm3/m2*/day and 220 cm3/m2/day. This difference may be partially explained by the different film's thickness.

The uncoated base material was not analyzed through the oxygen transmission rate test to the difficulties encountered during the experiments fixing the specimen in the permeation chamber, with or without the necessary vacuum grease, led to some leaks, which inevitably affects the measurement. Because of that, it was decided to consider as a starting point the value reported in the literature, which was defined around 900 $cm^3/m^2/day$, [81][82]. It was then clear how the materials used in this study, provided a considerable enhancement to the oxygen barrier property of pristine paper, fundamental in food packaging.

4. Conclusions and future perspective.

During this study, different packaging configurations have been developed in order to provide an optimal solution, both in terms of biodegradability and performances, for paper-based packaging. Preliminary results obtained from single layer, bi-layer and multi-layer configurations showed a significant improvement in terms of grease protection as well as water and oxygen permeability. However, some of the reported results found some differences to similar evaluation presented by the scientific community. This is mainly connected to substantial differences between test's parameters, such as the type of paper used as substrates, the chemical composition of the synthetized solutions, thickness and grammage of the coatings. For example, Kraft Paper [83], is a thicker and more compact material then the paper used in this study. Therefore, the comparison between the two types of paper needs further attention. Single layer configurations provided the enhancement of grease penetration and oxygen barrier properties, in case of chitosan and alginate while zein and PLLA were useful to improve the WVTR of the packaging.

Bi-layer configurations followed similar trends to those observed previously during the preliminary analysis on single layer coatings. However, some improvement in WVTR was achieved by the combination of PLLA and chitosan as well as zein and PLLA.

Lastly, both tri-layer and multi-layer structured configurations slight strengthened the benefits highlighted during preliminary analysis. In conclusion, PCPC configuration, was the best choice to provide the overall best performances to paper substrate. This results, underlined the importance of combining complementary materials such as chitosan (for grease protection) and PLLA (as a hydrophobic layer), to create a solution suitable to different tasks.

However, considering the water vapor transmission rate test, PCPC had a minor impact than ZPZP configuration. Nevertheless, due to the inconsistencies in the film structure and the studied properties, zein based packaging solutions were not the best options.

On the other hand, PLLA-chitosan multi-layer can be destinated as a food packaging solution in order to enhance the barrier properties of paper-based substrate. The best target for this packaging can be products that possess a great water activity and must be protected from gasses permeation, such as fruits and vegetables

[86].

Considering water absorptiveness can be developed more tests on coating solutions presented in this work. Cobb60 [84] and Contact Angle [85] test can help in understanding coating solutions water repulsion.

ASTM F119 can be developed utilizing different types of grease like castor oil, toluene and peanut oil, and extending timing of test as done in [92].

Differentiation in multilayer solutions is a possibility that can be considered. Building different types of materials and testing them according to presented solutions can be a future development for this project.

Considering the solutions developed in this work, and the trends of the food packaging industry, all materials can be produced as card coated vessel with different type of products, like ready-to-eat meat, fish, fresh fruits and vegetables and then sealed with film to increase barriers against oxygen and water [87].

Figure 50: Paper coated vessel example [88].

Figure 51: Paper coated vessel example [89]

Following the recent change of trends in the food industry, these packaging solutions could represent a serious alternative to the classic plastic-coated paper packaging.

It is interesting in discussing this work, that all the packaging solutions that have been proposed are fully recyclable, and completely compostable also in accordance with Aticelca's system of evaluation explained in 1.2.2. This must be a plus because of the needs of industry to help governments in reducing waste, emissions and increasing recycling.

Biodegradability and recyclability of these packaging solutions is easy to understand for customers. Italy has already reached the percentage of recycled paper goal posed for 2030 today, underlining the possibility of getting into the market these kinds of packaging solutions, before other nations, thanks to attention and responsiveness of Italian industry. [90]

This work aims to highlight and present new packaging solutions to the contemporary problems of sustainable and reliable packaging. This concern is what has driven this project and is embedded within all the solutions proposed in this project. The possibility where packaging can be fully used, recycled, or biodegraded is hopefully feasible in the near future.

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