CHARACTERIZATION OF GREEN COMPOSITES FILMS FROM AGAR AS A POTENTIAL PACKAGING MATERIAL

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CHARACTERIZATION OF GREEN COMPOSITES FILMS FROM AGAR AS A POTENTIAL PACKAGING MATERIAL

by

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LIST OF SYMBOLS

^{o}C	Degree Celsius
%	Percentage
µ	Micro
F	Fahrenheit
g	gram
GPa	Giga Pascal
L	liter
mm	millimeter
MPa	Mega Pascal
s	second

LIST OF ABBREVATION

B_d	Weight of Dry Sample
Bw	Weight of Wet Sample
Ca^{2+}	Calcium Ion
$CaCl_2$	Calcium Chloride
C_3H_8	Nitrate
CO_2	Carbon Dioxide
COOH	Carboxyl Group
DFT	Dry Film Thickness
EDX	Energy Dispersive X-Ray Spectroscopy
H_2O	Water
Mo	Initial Weight
M1	Final Weight
MT	Metric Tone
OH	Hydroxyl Group
PEG	Poly Ethylene Glycol
PEG 200	Poly Ethylene Glycol 200
PEG 1000	Poly Ethylene Glycol 1000
PEG 2000	Poly Ethylene Glycol 2000
St	Percent of Water Absorption

SEM	Scanning Electron Microscopy
Tg	Glass Transition Temperature

PENCIRIAN FILEM KOMPOSIT HIJAU DARIPADA AGAR BERPOTENSI SEBAGAI BAHAN PEMBUNGKUSAN

ABSTRAK

Agar ialah biopolimer yang diekstrak daripada alga merah. Filem daripada agar yang lut cahaya telah menarik minat ramai pengkaji sebagai alternatif untuk bahan pembungkusan berasaskan plastik. Agar mempunyai kekuatan gel yang tinggi pada konsentrasi yang rendah, kelikatan yang rendah dan juga keboleh prosesan berbalik. Namun demikian, filem yang dihasilkan adalah rapuh dan mempunyai daya serapan air yang tinggi kerana sifat semulajadinya yang hidrofilik. Oleh yang demikian, filem daripada agar memerlukan penambahan agen pemplastikan untuk mengurangkan sifat kerapuhan filem. Empat jenis agen pemplastikan (Gliserol, PEG200, PEG 1000 dan PEG 2000) dengan variasi penambahan 10%, 20%, 30% dan 40% (berat/berat) telah dikaji. Berdasarkan keputusan yang diperolehi, agen pemplastikan PEG 1000 pada penambahan 40% dipilih untuk kajian penambahan agen paut silang iaitu kalsium klorida dan resin akrilik. Bagi mengurangkan sifat hidrofilik filem agar, penambahan resin akrilik 40% (w/w) berjaya mengurangkan kadar serapan air pada 38.64% berbanding penambahan kalsium klorida dan filem agar tanpa agen pemaut silang pada 73.63%. Disamping memberikan sifat yang lebih hidrofobik, penambahan resin akrilik pada 40% (w/w) juga meningkatkan sifat mekanikal dan memberikan kekuatan tensil filem agar 47.85 MPa dan pemanjangan takat putus pada 1.76%. Manakala filem dengan penambahan $CaCl_2$ 2% dan masa rendaman 4 minit menunjukkan kekuatan tensil 57.54 MPa dan pemanjangan takat putus adalah 1.20%. Filem agar dengan penambahan 1000 PEG 40% menunjukkan kekuatan tensil 29.02MPa dan pemanjangan takat putus 3.19%. Ini menunjukkan penambahan resin akrilik sebagai agen pemaut silang bukan sahaja mengurangkan sifat hidrofilik filem agar malahan meningkatkan kekutan tensil. Walau bagaimanapon keputusan pemanjangan takat putus pula menunjukkan penurunan selepas penambahan akrilik resin. Daripada Analisis Pembelauan Infra Merah (FTIR) membuktikan kewujudan resin akrilik didalam filem yang dihasilkan dengan kehadiran puncak 1728.32 cm^{-1} menjelaskan kewujudan kumpulan karbonil (C=O). Termogravimetrik pula menunjukkan kestabilan termal bagi komposit filem berasaskan agar dengan penambahan akrilik resin meningkat dari 313.63 ^{o}C hingga 386.52 ^{o}C. Manakala ujian kadar penyerapan air menunjukkan filem dengan resin akrilik mengalami kadar serapan air yang paling rendah pada penambahan 40% resin akrilik, iaitu hanya 35.95%. Seterusnya, kajian diteruskan dengan ujian biodegradasi, filem yang dipaut silang oleh kalsium klorida telah mengalami pengurangan berat, perubahan warna, pengecutan dan terurai dengan ketara pada 14 hari sehingga 28 hari ujian penguraian. Manakala filem dengan penambahan agen paut silang oleh resin akrilik mengambil masa yang lebih lama untuk terurai sepenuhnya, iaitu memerlukan masa lebih dari 28 hari untuk terurai sepenuhnya. Berdasarkan keputusan dalam kajian ini, filem dengan penambahan agen pemplastikan PEG 1000 pada 40% menunjukkan ciri-ciri yang sesuai untuk kajian selanjutnya. Berdasarkan permerhatian keputusan yang diperolehi dengan penambahan agen paut silang resin akrilik telah menunjukkan ciri-ciri fizikal, mekanikal, terma, morfologi dan biodegradasi yang lebih baik berbanding filem dengan penambahan kalsium klorida dan juga tanpa penambahan agen paut silang.

CHARACTERIZATION OF GREEN COMPOSITE FILM FROM AGAR AS A POTENTIAL PACKAGING MATERIAL

ABSTRACT

Agar is a biopolymer extracted from certain red algae. The transparent film made from agar gum is becoming a common and renewable alternative for plastic-based food packaging materials. Agar have speciality in properties such as, high gel strength at low concentration, low viscocity and riversible process.. However, the film produced has poor properties such as brittle, high moisture permeability, and poor thermal stability. Hence the effect on addition of four types of plasticizers (Glycerol, PEG 200, PEG 1000 dan PEG 2000) with variation (10, 20,30 and 40%) has been done. Based on the results obtained, the plasticizing agent PEG 1000 at an addition of 40% was selected for the study of addition of crosslinking agents namely calcium chloride and acrylic resin. To reduce the hydrophilicity properties of agar composites based film, the addition of 40% (w/w) acrylic, whereas the film with the addition of 2% $CaCl_2$ and an immersion time of 4 minutes showed a tensile strength of 57.54 MPa and a breaking point elongation of 1.20%. The agar film with the addition of 1000 PEG 40% showed a tensile strength of 29.02 MPa and a breaking point elongation of 3.19%. This indicates that the addition of acrylic resin as a cross linking agent not only reduces the hydrophilic properties of the film in order to increase the tensile strength. However, the break point elongation results showed a decrease after the addition of acrylic resin. From the infrared diffraction analysis (FTIR) proved the presence of acrylic resin in the film produced with the presence of a peak of 1728.32 cm^{-1} explains the existence of carbonyl group (C = O). Thermogravimetric, on the other hand, showed that the thermal stability of agar -based film composites with the addition of acrylic resin increased from

313.63 °C to 386.52 °C. While the water absorption rate test showed that the film with acrylic resin experienced the lowest water absorption rate at the addition of 40% acrylic resin, which is only 35.95%. Next, the study was continued with biodegradation testing, the calcium chloride cross -linked films underwent significant weight reduction, discoloration, shrinkage, and decomposition at 14 days to 28 days of decomposition testing. Whereas films with the addition of cross -linking agents by acrylic resins take longer to fully decompose, it takes more than 28 days to fully decompose. Based on the results in this study, films with the addition of PEG 1000 plasticizing agent at 40% showed suitable properties for further study. Based on the observations the results obtained with the addition of acrylic resin crosslinking agents have shown better physical, mechanical, thermal, morphological and biodegradation properties than films with the addition of calcium chloride and without the addition of crosslinking agents

INTRODUCTION

1.1 Background

Packaging material dominated 40% of all plastic production in which 50% consumed by single use food packaging as reported by (Swarup Roy, 2021). Packaging functioned to preserve, protect from oxidative and microbial spoilage and extend the shelf life of the packaged materials. Increased use of synthetic packaging films has led to serious ecological problems due to their non-biodegradability, hard to be recycled and the emergence of microplastics. The growing concern towards environmental problems and the urgent need for more versatile environmental friendly materials has led to increasing attention about polymer composites, fillers/reinforcing materials coming from renewable sources and biodegradable, especially from the nature.

Biodegradable plastic food packaging has been introduced to mitigate the adverse impacts of petroleum-derived synthetic plastic. In recent years, promising formulations of biodegradable polymers with superior material properties have been developed to replace incumbent synthetic plastic (Din et al., 2020).

Biopolymeric, biodegradable and green materials, which are obtained from renewable resources, are intended to replace synthetic polymers in the future having the biodegradable properties. Nevertheless, their production costs and properties (especially barrier and mechanical performance) need to be improved in making it competitive as food packaging materials (Martínez-Sanza et al., 2019). Currently, different biodegradable packaging materials such as drinking cups, plates, cutlery, overwrap, and lamination films are produced and distributed at food stores showing the demands are increasing (Anshu et al., 2017; Fatemeh, 2020). Green composite is defined as composite materials in which at least one of the constituents is derived from natural resources (AL-Oqla, 2014). This includes a combination of natural fiber reinforced petroleum-derived polymers, which are non-biodegradable. While (Mohanty and Misra, 2002), discussed biopolymers reinforced synthetic fibers such as glass and carbon are not fully environmentally friendly. According to (Antoniou et al., 2014), biopolymers reinforced by natural fibers, which commonly termed as “green bio-composites”, are more environmentally friendly.

To create a sustainable environment and avoid the possible disposal of recalcitrant waste, green composites have gained a lot of attention as promising alternatives to the traditional ones, particularly for their potential biodegradability. Typically, a green composite is a material being manufactured entirely by bio-based constituents or a mix of synthetic and bio-based constituents at a flexible percentage. The efforts towards green composites were focused on the production and characterization of systems based on recyclable polymer such as polyolefins filled natural filler, for instant fibre and particle from plant (Amir and Inamuddin, 2020) .

Another important constituent of green composites is biodegradable polymers that act as a matrix or continuous phase and play an important role in determining the green composite's demanding properties. It protects the composite against environmental and chemical attack, and holds and binds the reinforcing materials together and transfers load and stress to the reinforcement (Karim et al., 2016 and Thakur et al., 2014). There are a few criteria for the formation of such films whereby at least one film-forming agent and plasticizer are to be added to a solvent to form a film-forming solution.

The term biodegradable bio-composites are those in which the polymeric matrix is biodegradable. Matrix includes two different families, which is bio-based and petroleum-based. Biodegradable polymers are different from biopolymers in the raw material. Biodegradable polymers can be created from bio-based or petroleum-based and can be classified as green polymeric matrices. In addition, bio-based bio-composites or sometimes called fully biodegradable green composite, are terms used when both the fiber and matrix are from renewable resources such as starch, polysaccharides (agar), polylactic acid, polyhydroxybutanoate and many more. These bio-composites have a less environmental impact (Omari, 2016).

Polysaccharides and proteins that are mainly synthesized from renewable biomass are attractive alternatives to replace petroleum-based plastic polymers (Spierling et al., 2018). Polysaccharides are abundantly available, low-cost and environmentally friendly biocompatible polymers that are useful and suitable raw materials for food packaging applications (Kumar and Tamilarasan, 2013; Awadhiya et al., 2018). Films based polysaccharides or blend of polysaccharides with several compounds including other polysaccharides, proteins, lipids and additives, have been applied to extend the shelf-life and preserve the quality of foods (Patricia et al., 2017). The development of polysaccharide-based films brought a significant increase in their applications and in the number of products that can be treated for extending the shelf-life. For example, polysaccharide films have good mechanical properties. However, their hydrophilic nature makes them poor barriers to moisture (Falguera et al., 2011)

Among the polysaccharides, agar commercially harvested from seaweeds is one of the most common base materials that has been studied extensively (Ali et al., 2017). Agar films have attracted significant attention for several film applications in the agriculture and packaging industry. Agar composites based films typically show good mechanical strength, as they are transparent and homogeneous. These properties make it suitable for the fabrication of composites based films and coatings for food packaging applications (Orsuwan et al., 2016). But, they are very hydrophilic in nature and brittle. These two features are seen as less attractive for food packaging applications. Agar composites based films are brittle and crack during handling. To overcome these problems, plasticizers were added to reduce brittleness and increase the flexibility of the films. To increase of agar films' flexibility, different kinds of plasticizers, usually polyols, have been used. Glycerol is one of the most preferred and widely studied (Arham, 2016). Type of the plasticizers play the main role in composites based film making. The plasticizer decreases the intermolecular forces and increases polymer chains mobility, giving the biomaterial more flexibility and less rigidity and brittleness (Chengcheng et al., 2017).

Most edible films made of biopolymers have brittle and stiff structures due to numerous interactions occurring between their molecules (Cazón, 2017). Plasticizers are usually utilized to overcome this challenge. The plasticizers used in the structure of edible films are small non-toxic biodegradable non-volatile molecules. They situate between polymer chains, reduce cohesion forces between them, and effectively decrease brittleness and glass transition temperature of the film. They also enhance flexibility, extendibility, processability, and, in some cases, reduce the cost of final dried films. Polyols (such as sorbitol, glycerol, and polyethylene glycol) and sugars (such as glucose, fructose, and sucrose) are different types of food-grade plasticizers. Among these, glycerol is the most common plasticizer that has been applied to the structure of agar-based films (Arham, 2016 and Wardana, 2017).

However, inherent limitations of natural biopolymer-based packaging materials such as low mechanical and water resistant properties are causing a major restriction for their industrial use. These problems have been overcome by blending or reinforcing plasticizers and crosslinking agents into biopolymers. Consequently, natural biopolymer-based packaging materials with multifunctional properties have a high potential for their application in the active food packaging industry (Shankar et al., 2015). To achieve multi-functional properties of biopolymer films, fillers have been used widely in developing food packaging films et al., 2015).

In addition, Agar has strength comparable or even higher than other commonly used natural polymers such as starch that makes it suitable for developing bioplastic. However, excessive water uptake and high price limit its applicability (Zhang et al., 2012; Ankur et al., 2016). The agar composites based films with the selected formulation were then crosslinked with two different types of crosslinking agent calcium chloride and acrylic resin The main reason using these two crosslinking due to green materials and provide excellent properties. The purpose of crosslinking study is to create a new properties of the agar-based films and produce agar-based films with high mechanical properties and low water absorption.

Mechanical properties of agar composites based films for food packaging applications are high interest as they affect the physical integrity of the packaging and consequently better conservation of the food during storage and commercialization. The mechanical properties that are suitable for usage packaging with applications are required. The effect of plasticizers nature on tensile strength, modulus tensile and elongation at break in this research are summarized.

Calcium ion’s ability to bind divalent cations and form hydrogels under mild conditions makes it a widely preferred choice to crosslink agar. The crosslinking between calcium and agar is achieved by the ionic interaction between Ca^{2+} ions and the hydroxyl groups from agar. Calcium chloride is the most widely used as a crosslinking agent because it is nontoxic, and films or beads thus obtained are more compact in nature (Lilinga et al., 2016).

Agar is an abundant and biodegradable polymer with moderate strength making it an excellent candidate for packaging (Ankur et al., 2016). In addition, when molecular bonds break due to the materials inherent instability, chemical degradation may also occur in these blends. All these processes aid in the break-down (degradation) of materials and consequent natural recycling processes. However, one most important reason why some natural polymers are not incorporated into consumer products is their degradation times–that range from months to several years (Freile-Pelegrín et al., 2007).

Acrylic resin is a solution, and dispersion has been developed as alternative wood adhesives and fiber composites. They are non-corrosive and do not emit carcinogenic gases. Compared to most natural plant fibre composites' resins, the acrylic resin has superior tolerance to moisture during composite fabrication may be minimized or eliminated. Many researchers work in fibre composite preparation by using acrylic resin as adhesive and binder. Still, less reported literature on the utilization of acrylic resin as a crosslinking agent in agar composites based films. Since acrylic resin is a water-based system, it offers alternative solvent-based resins. It, therefore, guarantees safe, simple and environmentally compatible with handling. Acrylic resin is considered environmentally friendly because it is water-based and formaldehyde-free cross-linking acrylate resin plus excellent binding properties (Natu, 2015 and Dong, 2016).

Hence, this research was embarked to provide an alternative of biodegradable and environmental friendly green composites with different types and loading of PEG. The optimum loading and type of plasticizer were further enhanced with the addition of various loadings of calcium chloride and acrylic resin. The samples were subjected to different characterization such as physical, mechanical testing and soil buried testing. The optimum formulation of agar-PEG-Acryclic resin is reported with respective characterization.

1.2 Problem statement

The environmental issues created by conventional plastic such as pollution, emergence of microplastic and many more has led an alternative of using green materials in food packaging. The growing interest in using green materials, such as agar, as a raw material to produce a composite film for packaging application is due to their potential values, such as high performance in mechanical properties, environmental problem reason, availability, low in cost and ease of handling. However, the major problem in using agar as material to produce the green film is its brittleness and hydrophilic nature. This creates some limitation by using agar as a material to produce films. Hence, to overcome the brittleness and hydrophilicity of agar composites-based films, the addition of various types and loadings of PEG as plasticizers was proposed in improving its flexibility. However, the excellent interfacial between the constituents materials are crucial in determining the final properties of the obtained biocomposite. Hence, different types of crosslinking agent were added into the films to reduce percentage of water absorption of the films as well as to increase tensile strength, thermal stability and reduce water uptake. During crosslinking two or more polymeric chains are bonded chemically. Chemicals with multi-functional reactive groups are commonly used for crosslinking purposes. Crosslinking agent can reduce water absorption of agar-based film, -OH group from agar which is hydrophilicity in nature create a new bonding with the functional group from the crosslinking agent. These process reduce free -OH group from agar and at the same time reduce the capability water absorption of agar composites based films.

1.3 Objectives of the study

This study's main goal was to obtain the optimum ratio of the agar as a raw material and plasticizers in the producing of agar composites-based films on its physical and mechanical properties. The effect of various types and loadings of plasticizers in agar film was studied by various characterization such as tensile properties, water absorption and soil test. The method applied in producing the agar film via solvent casting method. This research also focused on the effect of various crosslinking on improving mechanical properties and reducing water absorption.

Research on agar composites-based films is expanding to improve the properties of agar-based films to give a wider application in packaging. In this study, the method to produce flexible agar composites-based film by adding different types of plasticizers and concentration, improving mechanical strength, and reducing water absorption of agar film is studied.

The main objectives of this work are:

1. To study the effects of different types and concentration of plasticizers in agar composites-based films on mechanical and physical properties.
2. To investigate effect of crosslinking agents on mechanical properties and water absorption of crosslinked agar composites-based films.
3. To improve properties and functionality of agar composite based films with potential applications as packaging material.

2

LITERATURE REVIEW

2.1 Introduction

Development of the next generation of materials, products, and processes depends on sustainability and industrial ecology. Biodegradable plastics and bio-based polymer products based on annually renewable agricultural and biomass feedstock can form the basis for a portfolio of sustainable, eco-efficient products that can compete and capture markets currently dominated by products based exclusively on petroleum feedstock. Biopolymers are moving into main stream use, and the polymers that are biodegradable or on renewable “feedstock” may soon be competing with commodity plastics, as a result of the sales growth of more than 20–30% per year and improvement in the economics of sales (Mohanty and Misra, 2002; Gurunathan and Smita, 2015). Bio-composites from plant derived from natural are novel materials of the twenty-first century and would be of great importance to the materials world not only as a solution to growing environmental threat but also as a solution to the uncertainty of petroleum supply (Gurunathan and Smita Mohanty, 2015).

Research on innovative bio-based packaging materials is receiving significant attention due to increasing concerns about safety and environmental issues of non-biodegradable plastic packaging waste. One of these innovative packaging technologies, biopolymer-based active packaging, is a sustainable and environmentally-friendly way to improve food shelf life without compromising food safety and quality (Kuorwel et al., 2015). According to (Bhargava et al., 2020), active packaging can be used as an alternative to food additives to preserve food products. Generally, there are two types of methods used for active packaging. First is the chemically active (chemical) method, and the other is the biologically active (biological compound) method, the latter is more beneficial due to its non-toxic, biodegradable, biocompatible, sustainable properties (Sharma et al., 2020; 2021).

The use of materials from renewable resources is attaining increased importance, and the world's leading industries and manufactures seek to replace dwindling petrochemical-based feedstock with composites derived from natural fiber and biopolymers (Mohanty and Misra, 2002). Biodegradable polymers are derived from renewable materials, which are inherently compostable (Tharanathan, 2003). Biodegradable polymers in food contact articles include disposable product such as cutlery, drinking cups, plates, over wrap and lamination film, straws and cups, plates and containers for commercial food establishments.

Plastic films are the most widely used materials in packaging due to their excellent good in mechanical properties and low cost is the most reasonable factor to use plastic films in packaging applications. Plastics such as polystyrene (PS), polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET) have been widely used in packaging and food industries for a few years. However, these materials requires hundreds of years to degrade into their basic components after disposal. In the last twenty years, several studies have focused on alternative methods to produce biodegradable materials (Freile-Pelegrín et al., 2007).

Plastic based materials have been widely used and attract researchers because of a few factors, such as cheap, good aesthetic quality and convenient to use with good processability, and excellent physico-chemical properties such as mechanical, barrier, optical, and surface properties. More than five billion tons of waste from packaging materials is produced annually in the world, 30% of which are plastic compounds. Pollution with synthesized plastics, which is called white pollution, forms a major part of environmental pollution in industrial countries, and also in developing countries like

Iran that have weak plastic recovery systems (Liu et al., 2012). Plastic can cause health problem and large impact on the environment.

Synthetic polymers are important material to the packaging industry but there are few advantages. Most of them are durable and inert or resistant to microbial degradation (Bae et al., 2008), researchers use environmental concerns, particularly with regard to solid waste accumulation problems and the threat to wildlife (Jayasekara et al., 2005). Concept of environmental friendly technology has been applied in the packaging industry. Invention of bio based packaging material reflects the recent evolution of packaging material. Bio based packaging materials is well known as a green and environmental packaging material.

Mostly wrapper for food application especially from synthetic plastics. About 288 million tonnes of plastics were produced worldwide with more than 36% of these plastics being used for packaging in 2012. These synthetic plastics are not biodegradable, effected causing a big problem in terms of overflowing landfills and ocean pollution. Researchers try to find new material that can replace the synthetic plastic. Finding a material alternative to synthetic plastic is the motivation behind agar plasticity.

Environmental concerns and consumer demands for healthy food free from synthetic preservatives, associated with non-degradable plastic packaging wastes that pollute the ecosystem and environment including water bodies have led to the development of alternative bio-based packaging materials. Polysaccharides and proteins are bio-based plastics which mainly synthesized from renewable biomass such as that are attractive alternatives to petroleum-based plastic polymers (Spierling et al., 2018).

Plastics are undoubtedly dominating the market in the food packaging area, which is not surprising, given their low cost, good processability and possibility to adapt their properties to comply with specific food product requirements. However, due to the growing concerns on the severe environmental impact of plastics, associated to the consumption of virgin fossil feedstocks and to the large amounts of non-biodegradable waste generated after disposal, efforts are being focused on the development of sustainable materials (Martínez-Sanza et al., 2019).

Plastics made from synthetic polymers are difficult to be decomposed using biotic components such as microorganisms and abiotic components. It will take approximately 100–500 years to completely decompose plastic in the soil; therefore, plastics are considered as environmental polluters. Due to the growing concerns on the severe environmental impact of plastics, associated to the consumption of virgin fossil feedstocks and to the large amounts of non-biodegradable waste generated after disposal, efforts are being focused on the development of sustainable materials. Biopolymer materials, which are biodegradable and obtained from renewable resources, are intended to replace synthetic polymers in the future. Biodegradable films are prepared from natural and easily renewable materials such as starch, cellulose, proteins, and fats. This compound can be used to replace plastics from synthetic polymers and be biodegraded by microorganisms. Furthermore, biodegradable plastic can be a part of the solution, and it is one of the most critical challenges that must be overcome by the food packaging industries (Mostafa et al., 2018). While (Espitia et al., 2014), said that plastics are being recycled less than 5% leading to a high accumulation of plastics in the environment.

The main advantages of this kind of packaging materials are a reduction of the environmental pollution, increasing the shelf life of food products increase the nutritional value of the foods, maintaining food quality and providing their microbial safety to consumers. The use of biopolymer-based films in food packaging applications depends on several features like cost, availability, functional attributes, mechanical and barrier properties, optical quality, structure resistance to water, sensorial acceptance. Besides, there is also an increased awareness on sustainability, which can in general be achieved on different levels. On the level of raw materials, use of recycled materials or use of renewable resources are two strategies to reduce CO_2 emissions and the dependency on fossil resources.

Biodegradable polymers are capable of undergoing decomposition into CO_2, CH_4, H_2O, inorganic compounds or biomass through predominantly the enzymatic action of microorganisms. A few polymers can compostable, which means decomposition will take place in a compost site at a rate consistent with known compostable materials (Siracusa et al., 2008). The development and application of bio plastics for food packaging interest from the food, packaging and distribution industry toward, it has been increased in the last decade. Based on European Bio plastics organization, plastics based on renewable resources (biobased) can be as defined bio plastics or as plastics which are biodegradable or compostable (Song et al., 2009).

The applications of polysaccharide-based films in food packaging offer new opportunities to develop novel food packaging systems. Biodegradable films also can reduce the environmental problems associated with food packaging. Various application of biodegradable polymers-based natural source in the food industry includes disposable cutlery, drinking cups, lamination films, containers for food dispensed and fast-food establishments (Siracusa et al., 2008). These materials obtained from renewable and natural sources that have been used to produce edible film include mainly polysaccharides and all possible combinations, and sometimes incorporation of additives aimed to improve the properties of the film.

Agar is renewable and non-toxic and has excellent film-forming properties. Microorganisms consume part of the generated agar oligosaccharide after agar degrades. The other part is absorbed by plants, whose growth is promoted by this absorption. Agar has been used extensively as a gelling agent in the food industry and in other applications such as microbiology and molecular biology techniques, this is because of its ability to form very hard gels at very low concentrations. More recent uses of agar include dental moulds, casting of archaeological pieces and sculpture moulds. Packaging films developed using agar as biopolymer matrix has good in physical properties, as they are homogeneous and transparent. These properties make agar suitable for fabrication of films for food packaging applications (Vieira et al., 2016). This polysaccharide constitutes the main structural component in the cell walls of some red seaweed species, such as Gelidium and Gracilaria. Although the industrial production of agar has been mostly destined to microbiology and food industry applications, recent works have also demonstrated its potential for the development of biodegradable food packaging materials (Sousa and Goncalves, 2015).

Agar has a potential for making biodegradable films for packaging applications because good in mechanical properties. Despite its good film-forming capacity, agar still presents several drawbacks for its commercialization as packaging material, such as its relatively high production cost and the great brittleness and moisture sensitivity of the produced films (Martínez-Sanza et al., 2019). Packaging films developed using agar as biopolymer matrix has good physical properties, as they are transparent, homogeneous and flexible. These properties make it suitable for fabrication of films and coatings for food packaging applications (Orsuwan et al., 2016). Materials producers start concentrate on products which are environmentally friendly because the growth of environmentally conscious society. Environmentally friendly and sustainability material can only be realized by considering the entire life cycle of the product. Start from the raw material that used in producing the packaging extraction to the disposal. Thus, materials generally poses no harmful impacts on the environment during their whole life cycle until degradations process. Several factors affected growing growth in the commercialization of biodegradable packaging materials are, greater environmental awareness, petrochemical resources shrinkage, government laws and company policies, and suitable technology.

2.2 Agar

Agar is produced by many red seaweeds as cell-wall polysaccharide. This polysaccharide is important in industry because of its excellent thickening and gelation properties properties. Traditionally, agar has been classified into three different grades on the basis of gel properties: food grade, bacteriological agar, and agarose. Bacteriological agar is usually prepared from *Gelidium* and *Pterocladia*, because the gelling temperature of *Gracilaria* agars is above 40 °C.

Agarose is usually obtained from *Gelidium*, although some preparations of this neutral molecule could be obtained from some *Gracilaria* species. At present, approximately 90% of the agar produced is used for food applications, with the remaining 10% for bacteriological and biotechnology applications (Kim et al., 2017). Although its use in food is increasing, non-traditional uses are still being tested, because the profits from 10% bacteriological agar and agarose may be much higher than those from 90% food-grade agar (Madera-Santana et al., 2009).

In the field of biomaterials, agar, either by itself or in conjunction with other biopolymers, seems to confer excellent properties on plastic films, thus improving its resistance, clarity, and biodegradability (Madera-Santana and Robledo, 2011). However, the application of agar in the field of food or biology not only involves the gel strength of agar but also depends on its other properties, such as high transparency, low gel-formation temperature, and low melting temperature. Obviously, the agar prepared by the current alkaline production technology, with gel strength as a single index, could not meet the diversified requirements, thus restricting the healthy development of agar in food, bacteriological, and biotechnological fields.

Agar can be describe a mixture of gelling polyssacharides made up of from d- and l-galactose which is from red algae. Agar is a mixture of two polysaccharides: (i) agarose, the gelling fraction, which is constituted by β-D-galactose and 3,6-anhydro-α-Lgalactose repeating units and (ii) agaropectin, the non-gelling fraction, which presents the same backbone as agarose but contains substituent groups such as sulphate esters, methyl esters and pyruvate acid ketals (Martínez-Sanza et al., 2019).

Agar is known as a traditionally consumed as a food in Japan for making sweets. Agar was the first phycocolloid discovered and prepared as a purified extract. According to a Japanese legend, the original manufacturing method of agar was discovered in the middle part of the 17th century, presumably in 1658. The method of agar manufacturer was accidentally discovered by a Japanese officer. “A Japanese officer in the winter of that year arrived at a little inn. The inn keeper Minoya Tarozaema ceremoniously received him and offered a traditional seaweed jelly dish as dinner, which was prepared by cooking *Gelidium sp.* with water. After dinner the surplus jelly was thrown outdoors by the innkeeper. The jelly was frozen during the night, thawed and dried in the sun, the jelly leaving on several days a white, porous and dried substance. Tarozaemon found this soft substance and boiled it in water. On setting, he obtained a whiter jelly than the original one." It is known in Japan as "Kanten" meaning "cold weather," in China it is "Dongfen" or "frozen powder." The word "agar" is Malayan and used in the double form agar-agar, originally referred to jellies of certain seaweeds especially Eucheuma muricatum of the East Indies. Figure 2.1 shows sample of agar strips.

Using agar in agricultural films reflects the ecological concept of making full use of resources. From the various study, another major problem in producing agar composites based films is its hydrophilicity nature. Thus, agar is limited to be used in producing films for packaging applications because it can absorb water in high quantity. However, the agar's hydrophilicity nature needs to be transformed into hydrophobic nature to make it suitable for packaging applications (Xu et al., 2016).

Figure 2.1 Sample of Agar Strips

2.2.1 Chemical structure of agar

Agar is a polysaccharide extracted from specific species of marine red algae which belong to the Rhodophyceae class (Martinez-Sanz, et al., 2019). Gelidium sp.

and Gracilaria sp. are the two main commercial sources of this polymer. Agar forms a supporting structure in the cellular walls of the seaweeds. The chemical structure of agar is composed of a mixture of agaropectin (non-gelling fraction) and agarose (gelling fraction). Fig. 2.2 shows the latter is a linear polysaccharide consisting of repetitive units of D-galactose and 3-6, anhydro-L-galactose, linked by alternating α-(1 → 3) and β-(1 → 4) glycosidic bonds. While the former is slightly branched and sulphated (Barros et al., 2013). Agarobioses can be produced in many variable forms by the different agarophytes depending on gender and species which depend on their genetic characteristics. It is influenced by a series of ecological factors such as the nutrient availability, substrate composition on which they grow and the habitat hydrodynamic sulphate content usually below 0.15%. The rest of the fractions are known as agaropectins Strong hydrogen bonds, where random coils associate to form single and double helices, contribute to the formation of the high-mechanical-strength gel (Khanarian et al., 2012).

Agaropectin is usually removed during the commercial manufacturing of agar, therefore, an agar powder with higher gel strength is obtained (Fatemeh, 2020). These 11 agarobioses can be produced in many variable forms by the different agarophytes depending on gender and species which depend on their genetic characteristics. It is influenced by a series of ecological factors such as the nutrient availability, substrate composition on which they grow and the habitat hydrodynamic sulphate content usually below 0.15%. The rest of the fractions are known as agaropectins.

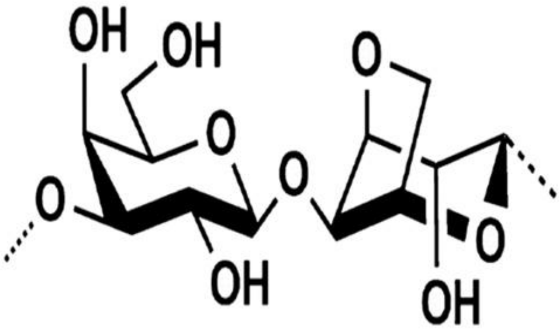

Figure 2.2 Structure of Agarose (Gheribi, 2018)

2.2.2 Gelation of agar

Agar has a unique properties and which is not found in other biopolymers. Agar does not require the presence of any particular ions to form a gel, it may to form very strong gels, and it has a uniquely large hysteresis between its gelling (35–44 ◦C) depends on the concentration of the agar and melting at (85–92 ◦C) temperatures (Armise, 2000). Agar is a hydrophilic colloid which is consisting of polysaccharides group that have the ability to form a gels by cooling a hot aqueous solution and can form a solution when heat it up with water at 90-95 °C.

Despite its good film-forming capacity, agar still presents several drawbacks for its commercialization as packaging material, such as its relatively high production cost and the great brittleness and moisture sensitivity of the produced films (Sousa and Goncalves, 2015). There are various types of agar powders available with specific properties and applications that differ in their algae origins and production technologies. The general industrial process established for extracting agar gum includes (1) soaking of dry algae in boiling water to detach the agar gum, which exists in the cell wall, and dissolving it in water, (2) sieving the liquid extract, and (3) separating the gum from the water with the aid of freezing and thawing techniques (Xiao et al., 2019). Moreover, alkali treatment could be applied to improve the gelation ability of agar. This treatment modifies L-galactose-6-sulphate to 3,6-anhydro-L-galactose being responsible for gel strength (Lee, 2017).

However, alkali treatment might have negative effects on the films made, the properties of the films made form native and alkali modified agar gums compared by (Sousa, 2015). They reported that the native agar was cheaper and safer to extract on an industrial scale. It also provided a higher viscosity as compared to the alkali-modified ones. Furthermore, the films made from native agar gum showed higher elasticity and better water vapor barrier properties; while it appeared more colorful. The continuous film-forming ability of agar is based on its gelling property. A viscous fluid forms by dissolving agar powder in hot water. Decreasing its temperature below the gelling temperature (90–103 °C) can result in the formation of a thermo reversible gel (Fatemeh, 2020).

Agar physical gelation occurs only by the formation of hydrogen bonds between agarose molecules. In the agar gel, a network of agarose double helices is formed and stabilized by water molecules. They aggregate by their external hydroxyl groups. Due to this special gelling ability, agar gels can keep a considerable amount of water inside their network. In the film-forming process, while casting agar solution, the temperature of the casting surface and the film-forming solution is required to be higher than the agar gelling temperature. This prevents premature gelation of the gum solution. After casting, while drying the agar solution, the non-ionic and linear structure of agarose enables its molecules (Xiao et al., 2019).

Figure 2.3 shows the continuous film-forming ability of agar is based on its gelling property. A viscous fluid forms by dissolving agar powder in hot water. Decreasing its temperature below the gelling temperature (90–103 °C) can result in the formation of a thermoreversible gel. Agar physical gelation occurs only by the formation of hydrogen bonds between agarose molecules. In the agar gel, a network of agarose double helices is formed and stabilized by water molecules. They aggregate by their external hydroxyl groups. Due to this special gelling ability, agar gels can keep a considerable amount of water inside their network (Mekonnen, 2013).

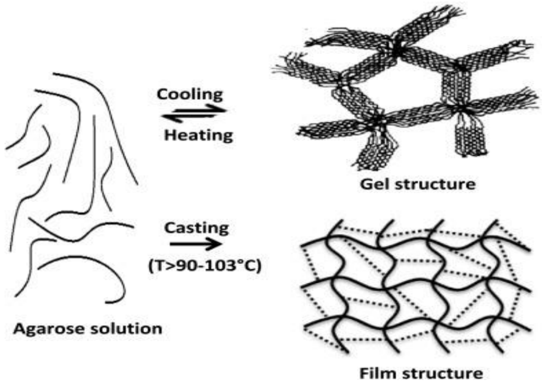

Figure 2.3 Gelling and film forming mechanisms of agar gum (Mekonnen, 2013)

The agaropectin fractions present in agar narrow the reticulum reducing slightly its exclusion limit. Intermediate between the physical and chemical gels, those gels that require the presence of cations to form gel structures as in the case of carrageenans and alginates. In the case of gels formed by alginic acid with di- or tri-valent cations we face totally irreversible gels that will not melt by heating. These are gels that have formed ionic bonds that can be broken only by eliminating the bonding cation, which is normally calcium. It is done with the help of a complexing agent such as EDTA (ethylene diamine tetracetate). Hence, these gels can be considered as ‘ionic chemical gels’ as they from ionic bonds and are irreversible. An important property of agar gels derived from their agarose content is the very high gelling hysteresis, defined as the temperature difference between its gelling (around 38ºC) and melting temperatures (around 85ºC).

These temperatures depend on the presence of agarobioses originally in the agarophyte seaweed from where the agar is extracted. Gel temperature is an indicator to identify the agarophyte used to produce an agar. Based on Table 2.1 the origin of an agar can determine the by identifying its characteristic gelling temperature. It has been proven that the gelling temperature is influenced by the methoxylation degree of the C6 of the agarobioses present in the agar, in such a manner that the more methoxylated corresponds to Gelidiella agaroses and the least to the Pterocladia ones. This is the same as saying that a greater methoxylation in carbon 6 will correspond to a higher gelling temperature. Curiously, the methoxylation of the rest of the carbons reduces the gelling temperature and its gel strength at the same time.

Table 2.1: Typical gel temperatures of agars extracted from several agarophytes (Armise, 2000)

Genus	1.5% solution,gel temperature
Gelidiella	42–45ºC
Gracilaria	40–42ºC
Gracilariopsis	38–39ºC
Gelidium	36–38ºC
Pterocladia	33–35ºC

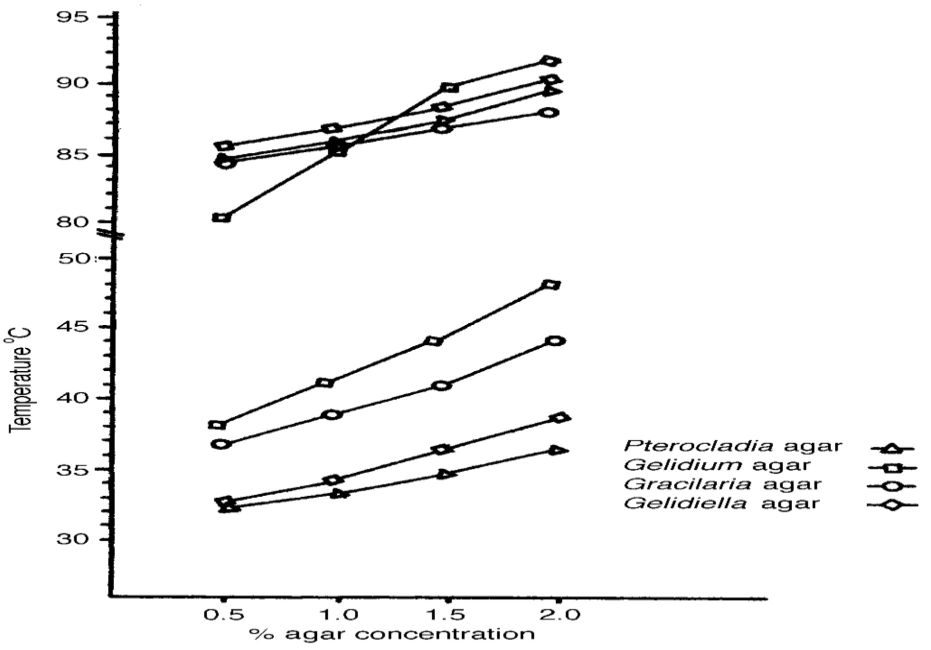

Figure 2.4 Gelling and melting temperatures of agar gels: gelation hysteresis. (Armise´n, R. 1997)

This is due to the inability to establish hydrogen bonds by the hydroxyl group located in C6 because of their position in the gelling helices while the rest of the hydroxyl group are bonding points where hydrogen bridges can be formed. The gelling process of agarose shown in Figure 2., obtained from Medin (1995). This is an exothermic process which develops when agarose molecules are dissolved in water. It can be seen on the left that these molecules are real ‘statistical random coils’ subject to Brownian movements. When cooling down close to the gelling temperature, the next structures start to form gel. According to Rees and Welsh (1997) shows how antisymmetric double helices (**B1**) are formed in their aggregation to form a macroreticulum as pictured in the upper side of **C** and **D**. In the bottom part of Fig. 2.4 and according to Foord and Atkins (1989) shows simple helices **B2** that are joined by hydrogen bridges that produce folded structures (symmetric double helices) that will form the macroreticulum as can be seen in the lower side of **C** and **D**. It seems that both gelling processes can coexist and one or the other dominates depending on the cooling speed. A faster rate favours the first process. Both are based in the formation of hydrogen bridges and produce a macroreticular structure.

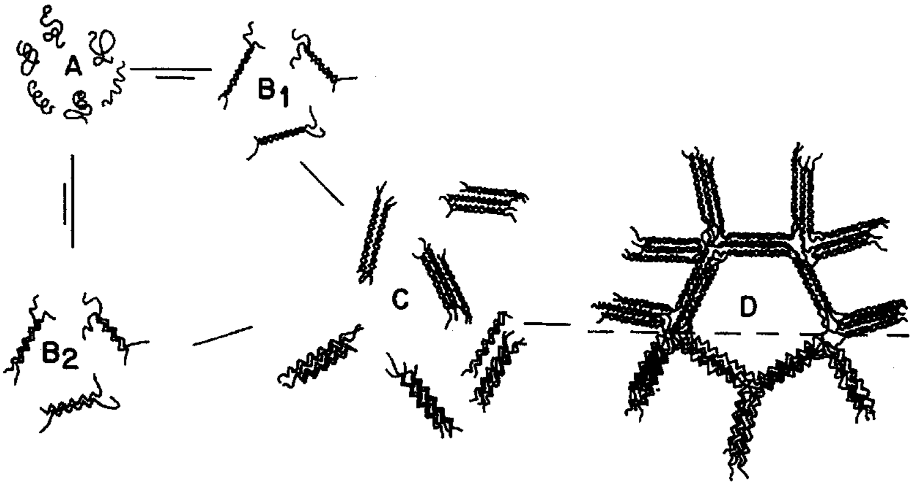

Figure 2.5 Agarose gelation (Medin, A. S. 1995) reference

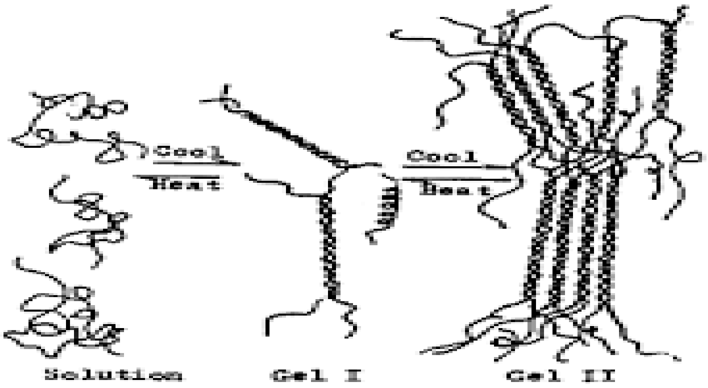

Figure 2.6 Gelling mechanism of agar (Fisheries and Aquaculture Department 2016a)