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Biodegradable Cellulose Films as Alternatives to Plastics

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BIODEGRADABLE CELLULOSE FILMS AS ALTERNATIVES TO PLASTICS

BY

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THESIS ACCEPTANCE PAGE

CECILIA W WANJUU

This thesis is approved as a creditable and independent investigation by a candidate for the master’s degree and is acceptable for meeting the thesis requirements for this degree. Acceptance of this does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Srinivas Janaswamy
Advisor Date

Vikram Mistry
Department Head Date

Dean, Graduate School Date

I dedicate this thesis to my daughter. You are destined for greatness and you can conquer the world because I have faith in you

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LIST OF ABBREVIATIONS

Å	Angstrom
°	Degree
˚C	Degree Centigrade
ΔE	Total color difference
α-	Alpha
β-	Beta
>	Greater- than
<	Less-than
%	Percentage
ANOVA	Analysis of Variance
AOAC	Association of Official Analytical Chemists
$CaCl_2$	Calcium Chloride
$CaCO_3$	Calcium carbonate
cm	Centimeter
FTIR	Fourier-transform infrared spectroscopy
hrs.	Hours
kg	Kilogram

log	Logarithm
LSD	Least Significant Difference
MCC	Microcrystalline cellulose
mins	Minutes
mm	Millimeter
mL	Milliliters
MPa	Mega Pascal
OH	Hydroxy group
Pa	Pressure
p-value	Probability value
RH	Relative Humidity
s	Second
SD	Standard Deviation
T600 %	Transmittance at 600nm
µg	Microgram
µL	Microliters
µm	Micrometer
UN	United Nations

WI	Whiteness Index
WVP	Water Vapor Permeability
w/w	Weight per weight basis
w/v	Weight per volume
YI	Yellowness Index
$ZnCl_2$	Zinc Chloride

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ABSTRACT

BIODEGRADABLE CELLULOSE FILMS AS ALTERNATIVES TO PLASTICS

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Plastics are versatile and have desirable packaging characteristics such as flexibility, durability, and affordability. The production of plastics has increased over the years resulting in concerns about their single-usage and disposal. Since plastics are non-biodegradable, they have been associated with detrimental health impacts due to the leaching chemicals from the landfills and their accumulation in the natural and marine environment. Cellulose obtained from agricultural residues is a viable substitute because of its low density, biocompatibility, biodegradability, low toxicity, and a strong and stiff structure. However, the extraction of cellulose has been less exploited because of its insolubility in water and common organic and inorganic solvents.

The hypothesis is that cellulose is biodegradable and hence products such as cellulose films will be less toxic to the environment. The purpose of this study is to develop biodegradable films from cellulose extracted from corn stover and cassava peels. The cellulose films have been characterized by determining their physiochemical characteristics such as color, thickness, transparency, moisture content, water vapour permeability, tensile strength, and biodegradability. The physicochemical properties of films of binary mixture of starch (corn and potato) and microcrystalline cellulose have been carried out.

The corn stover and cassava peels cellulose extracts (1-3% w/w) were solubilized in 68% w/w $ZnCl_2$ and 20 μL of HNO_3 was added for further dissolution and then thoroughly mixed overnight in a water bath at 85 ℃. The starch-cellulose films have been prepared by mixing 65% (w/v) of $ZnCl_2$, 3% (w/v) of microcrystalline cellulose, 0.2-0.8% (w/v) of starch and 0.1% (w/v) crosslinking agent $CaCl_2$.The films from extract of corn stover and cassava peels are brown in color while those from starch-cellulose blend are white. They are thin, homogeneous, and the opacity, thickness, moisture absorption, and tensile strength significantly depend on the source of starch, cellulose, and amount of crosslinking agent. The films disintegrate in the soil within 30 days. Overall, the cellulose-based films are a sustainable substitute for petroleum-based packages and an economical alternative to help reduce environmental contamination. The use of agricultural residues to develop biodegradable films will expand the utilization of agriculture by-products hence value-addition.

Keywords: Cellulose, starch, stovers, cassava peels, crosslinking,

CHAPTER 1: INTRODUCTION

Since the 1950s, production of petroleum-based packaging materials has outpaced that of almost every other product. The world's largest producers of plastic packages are America, European Union and Japan, while most of the waste is generated in Asia (UN 2018). The plastics are designed for single-use purposes and are disposed almost immediately (North and Halden, 2013; Raman Sharma and Sharma, 2014). Consequently, petroleum-based packages accounts for more than half of the non-biodegradable waste in the world. The environment is already overwhelmed by the ability to cope with these wastes. According to the United Nations (2018), out of the nine billion tons of plastic ever produced, only nine percent has been recycled and the rest ends up in the landfills and marine environment.

The UN predicts that if the currently high consumption patterns and poor waste management practices continue, there will be 12 billion tons of plastic waste in the environment by 2050. The situation is made worse because petroleum-based packages do not degrade. Plastic bags and containers need thousands of years to decompose. They are slowly broken down into smaller fragments known as microplastics and nano plastics that contaminate the soil and water (Smith, Love, Rochman and Neff, 2018; Eriksen, Thiel, Prindiville and Kiessling, 2017). Furthermore, they have been associated with detrimental health impacts due to the leaching chemicals from the landfills and their accumulation in the natural and marine environment (Gallo et al., 2018).

The wastes generated from agribusiness activities are gaining significant interest regarding value addition. Agricultural commodity residues are currently being used in the development of biodegradable films (Arevalo, Aleman, Rojas, Morales, and Galan, 2009). Biodegradability contributes to the alleviation of waste problem, consequently reduction in the production of wastes due to landfill diversion and material recycling (Jeong, Moon, Jeong, Koh and Lee, 2018). Therefore, it is possible to completely switch to homogeneous wastes consisting of biodegradable packaging that are beneficial to the ecosystem (Razza and Innocenti, 2012). Nature produces cellulose and starch in substantial quantities, which are biodegradable. Food wastes are also available as sources of these biopolymers. They could be used as alternatives to develop biodegradable films and packages and hence to reduce non-biological wastes (Xu et al., 2016).

1.1 Justification

Plastics are non-biodegradable and are associated with detrimental health impacts due to chemical leaching from the landfills and their accumulation in natural and marine environment. The growing concerns on environmental sustainability and depletion of petroleum resources demand for green and bio-economic products and resulted in the design and development of biopolymers-based products (Garrison, Murawski and Quirino, 2016). Natural polymers such as starch, and cellulose are attractive owing to their biodegradability, composability, renewability, availability, cost-effectiveness, and ecological functions (Ghanbarzadeh and Almasi, 2013).

The realization of the harm caused by improper disposal of petroleum-based packaging materials has prompted many governments to impose bans along with improving the waste management practices. The enactment of such policies demands further research and development of alternative packaging materials. Polymers from agricultural residues have potential to replace the petroleum-based polymers. These are eco-friendly and available in abundance in nature, hence lower cost of production. Since they are biodegradable, light, biocompatible and less toxic, they are considered “green” and safe (Ghanbarzadeh and Almasi, 2013).

Cellulose and starch can be derived from various sources such as corn stoves, cassava, cotton, wood (hardwoods and softwoods), potato, sisal, kenaf, wood fibers (hardwoods and softwoods), jute, hemp, flax, grasses, rice, bamboo, bagasse, and rye (Yadav, Kale, Hicks and Hanah, 2017). This research provides viable use of biowastes derived from agricultural residues toward developing economically and technically practicable alternatives to plastic packages.

1.2 Hypothesis

Cellulose is biodegradable and hence products such as films will be less toxic to the environment and better alternatives to food packaging, and to address the concerns of petroleum-based materials.

1.3 Research Objectives

1.3.1 Major Objective

To prepare biodegradable films from microcrystalline cellulose and cellulose-extract of agriculture residues (e.g. corn stover and cassava peel).

1.3.2 Specific Objectives

1 To extract and solubilize cellulose from corn stover and cassava peel.

2 To establish the physicochemical properties of cellulose films.

3 To determine the effect of starch on cellulose films.

CHAPTER 2: LITERATURE REVIEW

The world is moving towards the "green environment" to phase out non-biodegradable polymers. The growing demand to replace petroleum-based packages with biodegradable carrier bags significantly allows for the increase in volume production of cellulose-based sheets and films. Polymers such as cellulose and starch have recently gained technological interest because of their availability and biodegradability, hence their potential application in the development of novel renewable materials. The polymers are environmentally friendly and sustainable resources. The successful prospects and application of these polysaccharides depend on their physical, mechanical, and chemical properties, abundance, low weight, renewability, biodegradability, and biocompatibility. Starch and cellulose and their derivatives exhibit the required mechanical strength that is desirable for applications such as pharmaceuticals, textile, tissue engineering, food packaging industries.

Starch and cellulose are made up of α-D-glucose and β-D-glucose, respectively. The starch granule is heterogeneous physically composed of crystalline and amorphous regions, and chemically has linear (amylose) and branched (amylopectin) chains (Bertoft, 2017). Amylopectin is made of α-1,4 glycosidic bonds along with highly branching at the α-1,6 positions (Alcázar-Alay and Meireles, 2015). On the other hand, amylose consists of a linear chain of α-1,4 glucans but the branching points at the α-1,6 positions are limited. Amylose has a molecular weight ranging between 10^5–10^6 and a degree of polymerization (DP) as high as 600. The molecular weight of amylopectin ranges between 10^7 to 10^9. Amylopectin is about 70 to 85%, while amylose is 15-30% of common starches (Bertoft, 2017).

2.1. Cellulose

Cellulose is the most common organic polymer and it is the structural and principal cell-wall component of higher plants. It makes up about 33 to 90% of the plant and high-quality cellulose could be obtained through pulping and purification. It has high-molecular weight with a linear and repetitive β-D-glucopyranose unit of (1,4) glyosidic linkages and is insoluble in water (Kim, Yun & Ounaies, 2006). Due to the stereo regular (flat) and linearity nature, cellulose molecules associate and extend to form long fibrous and polycrystalline bundles. Numerous hydrogen bonds hold the crystalline regions together while amorphous regions connect them in the microfibrils.

2.1.2 Sources of cellulose

Cellulose is the most abundant biodegradable and renewable polymer that has the potential of being applied in various industries. It is naturally available with an annual production estimated to be over 7.5×10^{10} tons (Liew et al., 2015). It exists naturally, either in its pure form as in the case of seed hairs of the cotton plant, or in association with hemicelluloses in the cell wall of higher plants (Varshney & Naithani, 2011). The benefits and versatility of cellulose are more apparent and has been found to be a useful functional and structural material. It is derived from various sources such as cotton, wood (hardwoods and softwoods), sisal, kenaf, wood fibers (hardwoods and softwoods), hemp, flax, ramie, jute, grasses, bamboo, bagasse, corn stovers, rice, rye, and marine algae (Yadav, Kale, Hicks & Hanah, 2017). In addition, it could be obtained from biomass such as agricultural crops, forestry, animal, and industrial residues. The extracted biomass obtained from these resources contains three significant components namely cellulose, hemicellulose and lignin in varying amounts ranging from 40 to 50, 25 to 35, and 18 to 35%, respectively. The percentage of these components depends on the source. The extracted biomass must be processed to separate the different polymers and isolate cellulose. The cellulose percentage in various plant sources is narrated in Table 1 (Menon, Selvakumar, Kumar & Ramakrishna, 2017).

Table 1: The percentage of cellulose present in various plant sources

Source	Cellulose content (%)
Rice husk	94.2
Eucalyptus	76
Wheat straw	43
Rice straw	71
Flax fibers	72
Cotton fibers	85–90
Corn silage	32
Hemp fibers	68
Sisal fibers	65.5
Cassava bran	16.71

Animals and microbes are also good source of cellulose. The bacteria Gluconacetobacter xylinus can synthesize cellulose extracellular pellicles from glucose (Moniri et al., 2017; Khalid, Khan, Ul-Islam, Khan & Wahid, 2017). Some other strains such are Acetobacter, Agrobacterium, Achromobacter, Azotobacter, Salmonella, Sarcina, Escherichia, Pseudomonas, and Aerobaeter, Alcaligene, and those of genera Rhizobium (Khalid, Khan, Ul-Islam, Khan & Wahid, 2017). Azotobacter and agro-bacterium depict flocculent growth because of the formation of cellulose fibrils. Bacterial cellulose has unique properties such as high crystallinity, high water holding capacity, biocompatibility, high water-holding capacity, high tensile strength, and a fine fibre network (Paximada et al., 2016, Sukhtezari, Almasi, Pirsa, Zandi & Pirouzifard, 2017). Another source of cellulose is from marine animals like tunicate which deposits cellulose on its cell walls. The formation of cellulose is a common property of Gram-negative and floe-forming bacteria too.

Despite being abundant in nature, cellulose and its modified forms lack significant nutritional value and only serve as dietary fibre for humans. Consequently, it passes through the digestive system. Nevertheless, it is a functional component of the diet because it adds to the bulk of intestinal contents, lowering the transit time, hence increases the rate of absorption for other nutrients. Cellulose is a source of dietary fiber that contributes to the health of individuals because it reduces absorption of bile salts (Dhingra, Michael, Rajput & Patil, 2011). This is significant because it lowers the concentration of cholesterol in the blood. The bulk also results in the high amounts of hydrophilic molecules in the intestinal content so that individuals could retain a sufficient amount of water resulting in an easier and smooth easier passage into the large intestine.

2.1.3 The Structure of Cellulose

Cellulose is a large polysaccharide having 7,000 and 15,000 degrees of polymerization (DPs). It contains 44 to 45% carbon, 6 to 6.5% hydrogen and the rest consisting of oxygen. The empirical formula is $C_6H_{10}O_5$. The glycosyl forming unit is glucose, hence the polymer is a homoglycan. It is a regular and linear polymer characterized by (1→4) linkages of β-D-glucopyranosyl units. The β-(1→4) configuration in combination with the intramolecular hydrogen bonds result in a rigid structure. The crystalline or aggregate forms are due to the inter-molecular hydrogen bonds found between the hydroxyl groups. This association makes cellulose insoluble in water and hence its limited utility. It forms flat ribbon-like structures that can undergo extensive hydrogen bonding within the chain so that the crystallites are parallel and ordered and separated by amorphous regions. The linear chain crystallization gives cellulose fibers the insolubility, strength, and resistance to breakdown because the regions are inaccessible to enzyme penetration. Another explanation for the insolubility is that the cellulose network which has its adjacent layers separated by around 3.9Å (Nishiyama et al., 2002, 2003; Wada et al., 2006., Xu et al., 2016). This results in a tight arrangement and a stiff and sheet-like molecular structure so that water cannot penetrate.

The molecular structure of the cellulose consists of several repeating domains. The semi-crystalline cellulose polymer can adopt several forms in the plant cell wall. The amorphous regions, also known as the low-order, coexists with high-order crystalline domains. The degree of crystallinity depends on the source or the pre-treatment of cellulose.

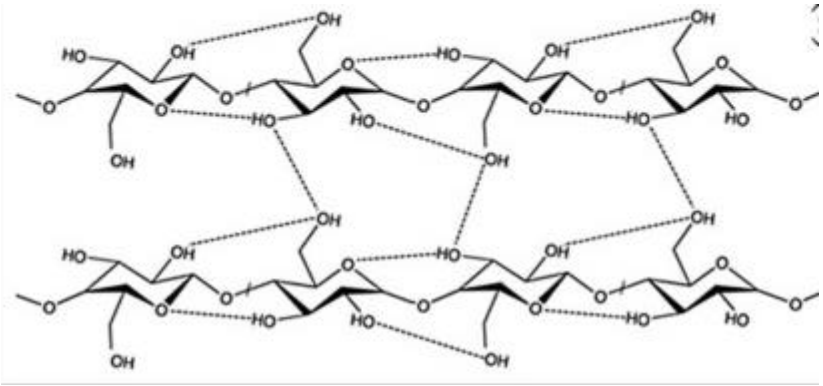


Figure 1: The native cellulose, chains held together through strong hydrogen bonding (broken lines) interactions (adapted from Xu et al., 2016).

In the solid state, the glucose units are rotated by 180° with respect to each other because of the constraints of β-linkage. Every units has three hydroxyl (OH) groups on the C-2, C-3 and C-6 positions. The terminal group at the either end of the cellulose molecule is different in nature from the other. The C-1 OH on one end of the molecule is an aldehyde group that has reducing activity. Aldehyde groups form intramolecular hemiacetal form that result in a 13-pyranose ring. In contrast, the C-4 OH end of the chain is an OH constituent, hence an alcohol borne with non-reducing properties. The glucose ring adopts the $^4C_1$-chair formation therefore exists as a pyranose ring. This formation constitutes the lowest energy conformation.

Native cellulose (I) is a polymorph structure that exists in two crystalline forms which are Iα as in the bacteria and algae and Iβ as in the higher plants. Cellulose I has a sheet like structure that is stabilised by the intermolecular hydrogen bonds (Figure 1). The bonds are aligned parallel to the pyranose rings and the sheets are stacked in equivalent distances to half-glucose rings in the crystalline forms along the axis of the cellulose chain (Nishiyama, Langan & Chanzy, 2002). The difference in the two allomorphs is in the mode of staggering: Cellulose Iα has a continuous staggering while cellulose Iβ has an alternating staggering occurs in. If cellulose I is regenerated from a solvent such as ionic liquids or when it is treated with a strong alkaline solution it adopts a crystal structure polymorph of cellulose II. This new structural form of cellulose has two antiparallel chains.

2.1.4 Solubility of Cellulose

There have been challenges regarding the extraction of cellulose because of the pulping processes or technologies applied previously such as the Kraft processes which significantly degrade hemicellulose and lignin. Other drawbacks include, utilization of high pH and temperature and release of toxic compounds which result in water contamination (Isik, Sardon & Mecerreyes, 2014). Cellulose is insoluble in water and most common organic solvents. The insolubility is due to complexity of the crystalline structure, biopolymeric network and the non-covalent interactions between the molecules, and the strong intermolecular and intramolecular hydrogen bonds in the individual chains (Kayikci et al., 2018; Alves, 2015). Despite its poor water solubility characteristics, cellulose has a wide range of applications such as packaging, netting, composites, coatings, upholstery, and paper. The polymer is chemically modified to obtain cellulose derivatives that can be utilized in different industrial applications. The chemical and reactivity characteristics of cellulose depend on the presence of the hydroxyl groups which are positioned on the equatorial in the glucose unit. It is also attributed to the β-glycosidic linkages in the chain that are susceptible to hydrolytic attacks. The OH groups in the cellulose play critical role in the solubility and reactions with other groups of compounds such as primary and secondary alcohols.

Cellulose is neither soluble nor meltable in most organic solvents or water (Mohd, Draman, Salleh and Yusof, 2017; Alves, 2015). Cellulose dissolution solvents are divided into derivatizing and non-derivatizing solvents. Derivatizing solvents comprise of the dissolution of the system of cellulose that occur through chemical formation of an unstable ester, ether or acetal intermediate (Sen, Martin and Argyropoulos, 2013; Trygg and Fardim, 2011). The common derivatizing method used at large scale is the viscose process (NaOH + CS2). An alternative to this process utilizes urea as an ingredient which forms an intermediate of cellulose known as carbamate. This dissolves in an aqueous sodium hydroxide solution, in the presence or absence of additives such as ZnO (Alves, 2015).

Numerous solvents have been identified to dissolve cellulose. For instance, ethylenediamine was used in the early 19th Century as an alternative to ammonia (Alves, 2015). Other complex solvents such as nickel oxide and cadmium hydroxide in aqueous ethylenediamine were further identified on their potential to dissolve cellulose. Over the years, the significant transition has been characterized by using different metals such as palladium and zinc combined with ammonium or an amine compound (Shen and Hartwig, 2006). However, these systems did not fully achieve the targeted commercial success (Alves, 2015). There are also problems associated with these approaches, such as pollution due to non-biodegradability and toxicity especially if they are disposed into the soil or the aquatic environment. There is a problem of scalability and the implicated costs that make them difficult for solvents to be applied at the industrial level. Ionic liquids (ILs) have also been touted as "green" solvents and have attracted much attention. ILs have the ability to fully or partially disrupt the intermolecular hydrogen bonding present in cellulose network.

Zinc chloride can dissolve cellulose directly without activation or pre-treatment. The liquid has a molar water-salt ratio that is close to the coordination number of the strongest hydrated ion because of the number of closely bonded atoms to each centered ion. The main ions in aqueous $ZnCl_2$ solution are H^+, Zn^{2+} and Cl^-. Cellulose interacts with the cations to form a viscous Zn-cellulose solution (Xu et al., 2016). Though the network is strengthened by the C3…O3H hydrogen bonds which are responsible for the formation of the molecular structure, Zn^{2+} ions can penetrate adjacent cellulose layers, pushing them apart, resulting in the formation of O3H· · ·Zn interactions. The cellulose chain becomes flexible and hence solubilization of the polymer.

2.1.5 Prospects of Cellulose

2.1.5.1 Plastic replacement.

Currently, most governments are encouraging the use of alternatives of petroleum-based packaging materials due to the realization of harms of plastic wastes to the marine and natural environment. Cellulose is a potential substitute to the plastic packages because it has similar properties of plastics in addition to being biodegradable. Cellulose from plant-based materials can be used to prepare coatings and films (Ghanbarzadeh, Almasi & Entezami, 2010). It certainly offers solution to the problem of degradation caused by the non-biodegradable polymers.

Petroleum-based polymers pose a dual threat of environmental pollution and depletion of non-renewable energy. Cellulose is a naturally occurring polymers that has proven to be efficient in its utilization and development of renewable, available, affordable, biocompatible, and biodegradable materials. Since it is available in nature and in abundance it has the potential to meet the current and future demands hence phase out dependence on petroleum-based polymers (UN, 2018). It is regenerated through an environmentally friendly process which avoids the use of harsh chemicals because most of the reagents (coagulants and solvents) can be reused or recycled (Wang, Lu & Zhang, 2016). The functional materials fabricated directly from cellulose solutions are utilized in packaging, textile, water-treatment, biomedicine, and optical/electrical devices, to name a few. The cellulose-based films are densely packed and exhibit good mechanical properties because of homogeneous bulk structure. Such properties show the potential application in food engineering and drug delivery.

2.1.5.2 Health and Medicine

In the medical field, there is a new paradigm shift to use cellulose as a regenerative material that works while in contact with biological surfaces such as cells, tissues, organs, biomolecules, and physiological fluids. The polymer's recent interest and applications focus on designing biomedical devices such as artificial blood vessels and artificial skin. The chemical feasibility of cellulose indeed enables its widespread utility in the health and medical field.

2.1.5.3 Tissue Engineering

Cellulose has a future application in tissue engineering where matrices can be developed to support cells, promote their differentiation and proliferation, and finally form a new tissue. From a physical property aspect, cellulose possess the tensile strength required for soft tissue repair or for an artificial blood vessel and the compressive strength necessary for bone tissue engineering. On a chemical basis, the high water-holding capacity of cellulose is beneficial as it allows anchorage of adhesive protein that promotes cell adhesion hence tissue repair. Therefore, cellulose has the potential to meet the demands for materials that can be used for wound cover, dressing and skin repair especially for burn incidences.

2.1.5.4 Pharmaceuticals

Cellulose can be used in the pharmaceutical industry as a drug delivery system. It is used as a tablet coating for drugs that are administered orally. There is the potential use in various forms of cellulose such as bacterial nanocellulose (BNC), cellulose nanofibers (CNFs), and cellulose nanocrystals (CNCs) in drug-loaded systems based on novel drug carriers or tablet dissolution. The regulation and influence that nanocrystalline cellulose have on drug release, and the interaction between the molecules of the drug are still under investigation**.** Cellulose can be used in bone regeneration. However, studies and application of nanocrystalline cellulose in bone regeneration is still in its fundamental stage.

2.1.5.5 Binary Blends

Another potential application of cellulose and its derivatives is as binary blends. Cellulose could be blended with other polymers such as starch, chitosan and gums to create new materials such as fibers, composite films and sponges. The films made from such blends are expected to have improved properties such as tensile strength, thermo-dynamics, biodegradability, and water sorption than the as compared to that of cellulose film alone (Douglass, Avci, Boy, Rojas & Kotek, 2017). Cellulose has been extensively used in combination with chitosan to produce new blend materials with antibacterial activity (Wu et al., 2004), metal ions adsorption (Liu et al., 2012), odour treatment properties (Twu, Huang, Chang, & Wang, 2003), improved water absorption capacity and mechanical characteristics (Liu et al., 2011), good antistatic and moisture absorption properties (Xu et al., 2010), high porosity and interconnected porous structures (Wang, Zhu, & Zhang, 2014), self-healing characteristics (Duan, Han, Liu, Jiang, & Li, 2016), to name a few.

2.1.5.6 Food packaging

The most significant food preservation method is through packaging because it protects the product from adverse environmental conditions and enhances shelf life. Due to the increased interest in protecting nature and consumer requirements, there is the need to develop active and functional packaging systems (Sanches-Silva et al., 2014; Schaefer & Cheung, 2018). Consequently, packaging industry is utilizing cellulose, along with other biopolymers, to develop bio-nanocomposite films since they are renewable, biodegradable, biocompatible and less toxic. More specifically, nanocomposite films are gaining attention because they are an excellent biomaterial suitable for the conservation and packaging of food.

2.2 The Polymer Starch

Starch is also a plentiful natural polymer found in fruits, leaves, seeds, flowers, stem, and roots of plants. It serves as a carbohydrate reserve for the plants, hence a source of carbon and energy (MacNeill et al., 2017). The synthesis of starch involves a biochemical chain reaction in the chloroplasts of green leaves to produce glucose molecules, a process known as photosynthesis. Organelles are responsible and reserve starch in cereals and tubers (Pfister and Zeeman, 2016). Its production happens rapidly and is performed diurnally in the chloroplasts. Conversely, amyloplasts produce starch that is deposited in the reserves over several days to weeks.

2.2.1 Sources of Starch

Starch is found as granules, each containing millions of amylopectin and a larger number of amylose molecules. The major source of starch is maize (corn). It is also isolated from roots and tubers such as sweetpotato, potato and cassava; and grains such as rice, wheat, and legumes. Fruits contain approximately 70% starch on dry weight basis (Chandrasekara and Josheph Kumar, 2016). In cereals, the main location of starch synthesis and storage is the endosperm. Recently, starch crops are being genetically modified to enhance the development and functionality of starches (Hebelstrup, Sagnelli and Blennow, 2015).

Each botanical species has a unique accumulation pattern of starch granules which varies depending on the plant tissue, composition of molecules, size, shape, and structure. The starch granule is heterogeneous: physically, it has both crystalline and amorphous regions, and chemically, it has linear (amylose) and branched (amylopectin) structures (Bertoft, 2017). Linear chains of glucose units are linked by the α-1,4 glycosidic bonds to form amylopectin. It is highly branched at the α-1,6 positions (Alcázar-Alay and Meireles, 2015). Amylose consists of a linear chain of α-1,4 glucans but the branching points at the α-1,6 positions are limited. Amylopectin ranges between 70 to 85%, while amylose is 15-30% in most of the common starches. The structural units of starch, amylose, and amylopectin are shown in Figure 2, while Table 2 lists the amylose and amylopectin content of different starch sources.

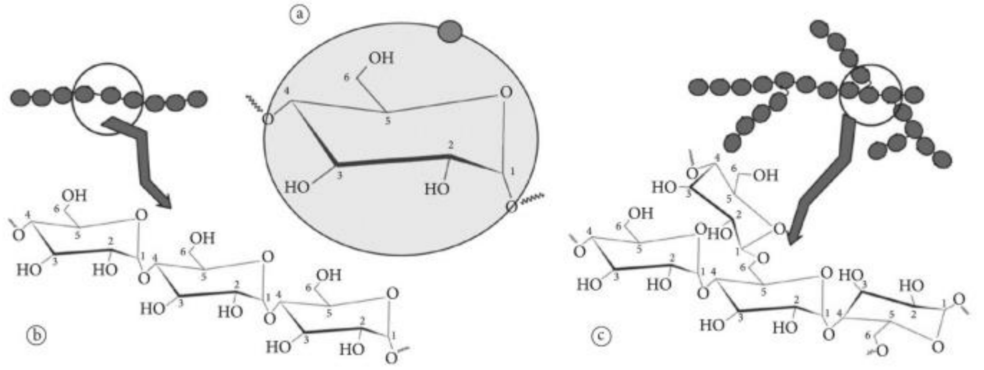


Figure 2: a) the glucose unit; b)Amylose; c)Amylopectin structures (adapted from Bertoft, 2017).

Table 2: Content of amylose and amylopectin in different sources of starch

Source	Amylose	Amylopectin
Corn	21	76
Corn-Waxy	1	99
Corn- high amylose	75	25
Rice	18	82
Rice-waxy	1	99
Potato	23	77
Sorghum	25	75
Banana	17	83

Different sizes, grouping of branch points and polymodal distribution of α-glucans chains in the amylopectin molecule result in the formation of double helical chains. Amylose and amylopectin are arranged in a semi crystalline structure that forms a matrix of starch granules with alternating crystalline (amylopectin) and amorphous (amylose) regions. These are known as the growth rings (Cornejo-Ramírez et al., 2018). Some starches are known as waxy" starches because they contain a minimal amount of amylose (<30%). Consequently, the endosperm tissue appears waxy. The starches may contain other molecules of a different polysaccharide molecules that they exhibit a slight deformation in the granule appearance.

The amylose fraction is associated with lipid molecules in the form of free fatty acids and phospholipids in the cereal grains (Bertoft, 2017; Alcázar-Alay and Meireles, 2015). The lipid complexes within the starch granules are observed as hydrophobic nucleus located in the helices of the amylose chains. The lipid complexes range between 0.15 to 0.55% of the amylose fraction in starches sourced from cereals. The presence of lipids in starch granules, though represented as a small fraction, can significantly lower the swelling capacity of the starch paste (Svihus, Uhlen and Harstad, 2005). Another molecule that could be embedded in the starch matrix is protein, which is approximately 0.6%. The protein and lipids on starch are located on the granule surface and significantly influence starch physical and chemical properties and hence its functionality. For example, in wheat starch, presence of protein in the starch granules results in grain hardness.

2.2.2 Characteristics of starch granules: size, morphology, crystallinity, and composition

Starch granules are microscopic with their diameters ranging between 0.1 and 200 µm. The morphology varies depending on the botanical source to form different shapes, such as ellipsoidal, oval, smooth, spherical, lenticular, and angular (Singh, Singh, Kaur, Singh Sodhi and Singh Gill, 2003). The size distribution could be uni-, bi-, or polymodal. The A-type starch granules are large in size and have a lenticular shape, for example in common cereals such as barley, wheat, and rye. The B-type of starch granules are small in size with a spherical shape, e.g. potato starch (Tetlow, 2010). The morphology of a granule typically contains a central line known as the hilum or “Maltese cross” (Figure 3). A starch granule may contain several Maltese crosses, a characteristic that reduces its birefringence (Cornejo-Ramírez et al., 2018). It is important to consider an isolation method that does not affect the original size of the starch granule.

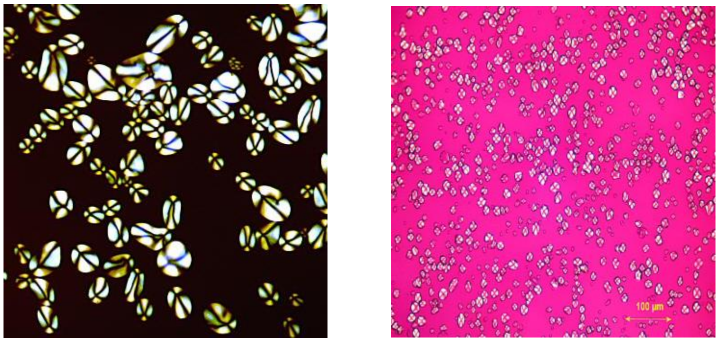


Figure 3: Maltese cross of potato and corn starch in polarized light (adapted from Cornejo-Ramírez et al., 2018).

The functional and physicochemical properties of starch significantly depend on the amount of amylose in the granule. The amylose content varies between same botanical varieties due to differences in environmental, cultural, and geographic origin (Patindol, Siebenmorgen and Wang, 2014; Gao et al., 2014). Amylose plays important role in the swelling and solubility of starch granules. The rate of swelling increases rapidly after amylose molecules are leached. However, if the amylose molecules form lipid complexes, they are not leached and this prevents the swelling capacity (Wang et al., 2018; Singh et al., 2003). Since amylose is amorphous, it is important in the industrial application of film preparation. Films formed by starches with high amylose content are very strong, odorless, colorless, and tasteless, non-toxic, transparent, and biodegradable (Lu, Xiao, and Xu, 2009; Campos et al., 2011).

Non-carbohydrate components in the starch granule also affect starch functionality. For example, monoester phosphates are linked to the amylopectin fraction by covalent bonds are known to increase viscosity and clarity of starch paste. Phospholipids could cause a low viscous and opaque paste (Debet and Gidley, 2006). Wheat and rice starches have high phospholipid content hence produce pastes with low transmittance power. On the other hand, starches from corn and potato have less phospholipid thus yield high transmittance (Singh et al., 2003).

2.2.3 Starch applications in the food industry

Starch serves as a food since it is a significant digestible polysaccharide. Common sources of starches in food include grains and seeds (rice, wheat, corn and barley), roots (cassava) and tubers (potato). Approximately 70-80% of calories consumed by humans are derived from starch. Starch functions as a structural agent because of the modifications introduced during manufacturing. The food industry is the principal utilizer of starch to modify viscosity, texture, adhesion, gel formation, moisture retention and films preparation, to name a few (Waterschoot et al., 2015a). The bakery sector utilizes starch in making bread and cakes which are highly consumed. It is also used in the preparation of extrusion products such as pasta, noodles, fried and instant foods.

Starch is also proven to be important contributor to biobased films. Starch films have received much attention because of their advantages over synthetic films mainly to control pollution as they could degrade faster. They act as barriers that prevent gas exchange, moisture transfer, movement, and oxidation of solutes along with maintaining quality and organoleptic properties (Dhall, 2013). Such films could be functionalized with flavors, plasticizers, colors, sweeteners, antimicrobials, and antioxidants.

2.2.4 Starch used for non-food applications

The increase in demand for renewable and biodegradable resources has highlighted the importance and versatility of starch in new processing techniques. Starch has a chemical feedstock that enables its conversion into numerous products of substantial value. The pharmaceutical industry utilizes starch as an excipient to bond active drugs. The amylose of starch is capable of forming inclusion complex with food ingredients such as fatty acids, essential oils and flavor molecules. Starch is also used as encapsulant and to improve shelf life of products (Kim and Lim, 2009).

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

Microcrystalline cellulose Avicel was obtained from FMC Corporation, USA. Corn stovers were from the Northeast Research station at the South Dakota. Cassava peels were from IITA (Zambia). $CaCl_2$, $ZnCl_2$ and glycerol were purchased from VWR, and Ethanol was from Fisher Scientific.

3.2 Extraction

Dry corn stovers and cassava peelings were ground to 40-mesh size particles and were defatted using a standard Soxhlet hexane extraction. They were washed to remove impurities. Around 30 grams was washed with 1 L of 2-3% NaOH solution with agitation at 90 °C. The resulting solution was washed 3-5 times to remove soluble components and to obtain the pulp. Subsequently, α-amylase treatment was carried out to remove starch, if any, and to obtain cellulose extract that was dried for further use.

3.3 Preparation of Zn-cellulose salts

3.3.1 Zn-Microcrystalline cellulose

A range of $ZnCl_2$ solutions (50–78% w/w) and cellulose (1-3% w/w) were used for the solubilization and dissolution process. The best concentration, which was 68% was selected for further experiments. Initially, cellulose paste was prepared by adding 0.8 g of Avicel to 1.6 mL of distilled water. In a separate beaker, pre-determined weights of $ZnCl_2$ were dissolved in 6.0 mL of distilled water to make solutions with weight percentage of 50–78% and equilibrated at 65(±1) °C in a water bath for about 10 min. Later, $ZnCl_2$

solution will be added to the cellulose paste and mixed thoroughly for 30 mins. This was termed as the control sample. Later, various concentrations of starch (corn and potato) were added to develop starch-cellulose films.

3.3.2 Zn-Corn stovers cellulose

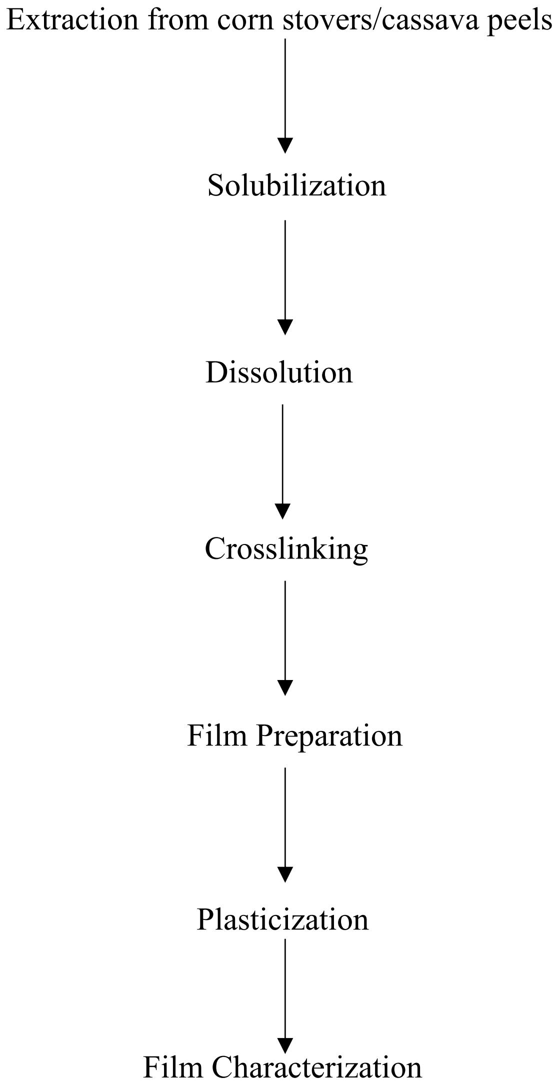
About 68% (w/w) of $ZnCl_2$ solutions and corn stover cellulose extract (1-3% w/w) were used. Initially cellulose paste was prepared by adding 0.4 g (w/w) of corn stover cellulose extract to 1.6 mL of distilled water. In a separate beaker, predetermined weights of $ZnCl_2$ were dissolved in 6.0 mL of distilled water to make solutions with weight percentage of 50–78 and equilibrated at 65(±1) ˚C in a water bath for about 10 min. Later, $ZnCl_2$ solution was added to the cellulose paste and mixed thoroughly for 30 mins. 20 μL of HNO_3 was added to the solution for further dissolution and were thoroughly mixed overnight in a water bath at 85 ℃.

3.4 Crosslinking

Variable amounts of $CaC1_2$ (0-40 μg) were added to Zn-Cellulose extract solutions at room temperature to crosslink the cellulose chains.

3.5 Film preparation

The films were hand-casted on a glass plate (21 x 30 cm) using a thin-layer chromatographic plate applicator. The glass plate along with the film were immersed in 500 mL ethanol. The film was coagulated for 30 mins and immersed in fresh ethanol bath (500 mL) for another 30 mins. The film was then fixed on a frame and air dried at the room temperature, then it was placed in a water bath for 30 mins to remove any excess salt and subsequently soaked in glycerol (5% v/v) for another 30 mins. Finally, the film was air-dried for further characterization.



3.6 Film Characterization

3.6.1 Films color

A Konica Minolta colorimeter was used to evaluate the color profile using Hunter L*a* b* scale to understand the effect of cellulose, starch and $CaCl_2$ on the quality of the films. The films were placed on a white standard plate and the L, a, and b values were measured. L values range from O (black) to 100 (white), a value ranges from -80 (greenness) to 100 (redness), and b values ranges from -80 (blueness) to 70 (yellowness). All measurements will be performed in triplicate. Total color difference (Δ E), yellowness index (YI), and whiteness index (WI) were calculated using the following equations (Ghanbarzadeh et al., 2010).

$$\Delta E = [(L_{standard} - L_{sample})^2 + (a_{standard} - a_{sample})^2 + (b_{standard} - b_{sample})^2]^{0.5} \ldots\ldots(1)$$

$$YI = 142.86\ b/L \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

W1=

Figure 4: The preparation and characterization of films

3.6.2 Film thickness

Film was cut into 4 equal halves and film thickness was measured at five different positions with hand- held digital micrometer with a precision of 0.01 mm. Average readings from duplicate measurements are reported.

3.6.3 Water solubility

The water solubility of films is defined as the percentage of the dry matter solubilized in water after 24 hrs. immersion . The water solubility of the films was determined according to Singh, Chatli and Sahoo, 2014 but with some modification. The 3 cm x 3 cm cut films are dried at 105 ℃ overnight and weighed. Then they are immersed in 50 mL water container with mild agitation (175 rpm) at 25 ℃ for 24 hrs. The final insolubilized dry matter of film was determined gravimetrically in the vacuum oven (105 ℃/24 hrs). The percentage of total soluble matter in the film was calculated as a function of the initial dry matter.

$$\% \text{ TSM} = \frac{\text{W1}-\text{w2}}{\text{W1}} \quad \text{X } 100$$

where W is the water solubility (%), W1 is the initial dry weight of films (g) Films weight after immersion and W2 is the films weight after drying. Average value from duplicate measurements are reported.

3.6.4 Moisture absorption

The moisture absorption of the films is the amount of water it can uptake or hold and was determined at room temperature using the procedure outlined by Ghanbarzadeh et al., (2010) but with a slight modification. The films were cut into patches of 3 x 3 cm and dried at 105 ℃ overnight. Initial mass (W1) of the dried films was quantified and immersed in a beaker containing 100 mL of distilled water for different time intervals, 5, 10, 15, 20, 30, 60, 90 and 120 mins. The wet samples were carefully blotted using a paper towel to remove excess water from surface and reweighed (W2). The water uptake of each sample was calculated as follows:

$$\text{Water uptake } \% = \frac{\text{W1}-\text{w2}}{\text{W1}} \quad \text{X } 100$$

Where W1 and W2 are the weights of the sample after desired interval time and the initial weight of the dried sample, respectively. All measurements were performed in duplicates and average values reported.

3.6.5 Moisture content

The films are cut into 3 x 3 cm and placed in a forced air convection oven for 2 hrs.at 135 ^{o}C. The loss of water was used to calculate the moisture content (AOAC, 2005). The analysis was carried out in duplicate for an average reading.

3.6.6 Water vapor permeability

Water vapor permeability (WVP) was measured using method by Ghanbarzadeh et al., (2010) but with some modification. Special glass cups with an average diameter of 1.8 cm were used. Films were cut into discs with a diameter slightly larger than the diameter of the cup. Four grams of anhydrous $CaSO_4$ was placed at the bottom of the cup to maintain relative humidity (RH) of 0 and then films were glues at the top. The cups were placed in a desiccator containing saturated K_2SO_4 solution on the bottom desiccator that provides a RH of 97% at room temperature. Cups were weighed at 1 hr intervals for 8 hrs and water vapor transport was determined by the weight gain.

The changes in the weight of the cups was recorded as a function of time and slopes were determined by linear regression (weight change vs. time). The water vapor transmission rate (WVTR) was calculated as the slope (g/h) divided by the transfer area (m^2). WVP (g $m^{-l}s^{-1}$ Pa^{-1}) was calculated using the following equation:

$$\text{WVP} = \frac{\text{WVTR}}{\text{P(R1}-\text{R2)}}\,\text{X}$$

where P is the saturation vapor pressure of water (Pa) at the test temperature (25 °C), R1 is the RH in the desiccator, R2, the RH in the cup and X is the film thickness (m). Under these conditions, the driving force [P (R1 - R2)] is 3073.93 Pa. All measurements were performed in triplicate and average values reported.

3.6.7 Tensile strength of films

The tensile strength of the films was determined using the established protocol (Xu, Chen, Rosswurm, Yao, and Janaswamy, 2016) but with some modification. Briefly, films were cut into rectangular strips of 8 cm long and 1 cm wide, and the tensile strength was measured using the MTS EM Tensile with mechanical grip at room temperature. The experimental parameters included an initial grip spacing of 60 mm with extension rate l5 mm/s, data collection frequency of 50 Hz and a trigger force of 50 N. The initial grip spacing was set at 60 mm. Average values from triplicate measurements were used to calculate the films strength as follows:

$$TS = \frac{F}{S}$$

where TS is the tensile strength (Pa), F is the maximum force when the film breaks (N) and S is the cross-sectional area of the films (width x thickness as m^2).

3.6.8 Film Transparency

A smooth and undamaged films were selected and cut it into ten strips of 30 x 10 mm. Each strip was adhered on one side of a dry glass cuvette. Transparency of the films was calculated from the percent transmittance of light by exposing the films in the optical pathway at a wavelength of 600 nm on a spectrophotometer (Genesys 20, ThermoSpectronic) (Lan, He, & Liu, 2018; Czon et al., 2018). Dry, clean, and clear glass cuvette was used as the control and the transmittance was set to be 100% (Abs = 0) and then relative transmittance of the films was measured. Transparency was calculated using following equation.

$$\text{Transparency} = \frac{(\log(\%T_{600})}{X}$$

Wherein, $\%T_{600}$ is the transmittance at 600 nm and X is the film thickness (mm).

3.6.9 Fourier-transform infrared spectroscopy (FTIR)

FTIR spectroscopy was performed to establish the presence or absence of the various vibrational modes of the cellulose and starch in the films. Spectra was recorded using the Thermo Scientific Nicolet 380 FT-IR Spectrometer equipped with ZnS ATR Crystal (Thermo Fisher Scientific Inc., USA) in mono-reflection at an angle of incidence of 45^0. Powdered film was placed on the ATR crystal, pressed collected data using the established procedure (Rao and Rao, 2015) with some modification. Each spectrum of the sample was recorded at 8 cm^{-1} resolution and 256 scans in the wavenumber range 650 - 4000 cm^{-1} against an empty cell as a background. Data was be analyzed using the OMNIC software.

3.6.10 Biodegradability of films

Films were cut into 8 x 8 cm strips and initial weight was measured. They were then buried in soil and weights were determined at 1st, 3rd, 5th, 7th, 15th, and 30th day to assess left over film.

3.7 Statistical analysis

The results were analyzed by R program and Microsoft Excel (version 2016) software. Least Significant Difference (LSD) was determined through ANOVA and further Post Hoc comparison by using Tukey HSD test to find out difference between means. P value of 0.05 was utilized for defining the implication of the results.

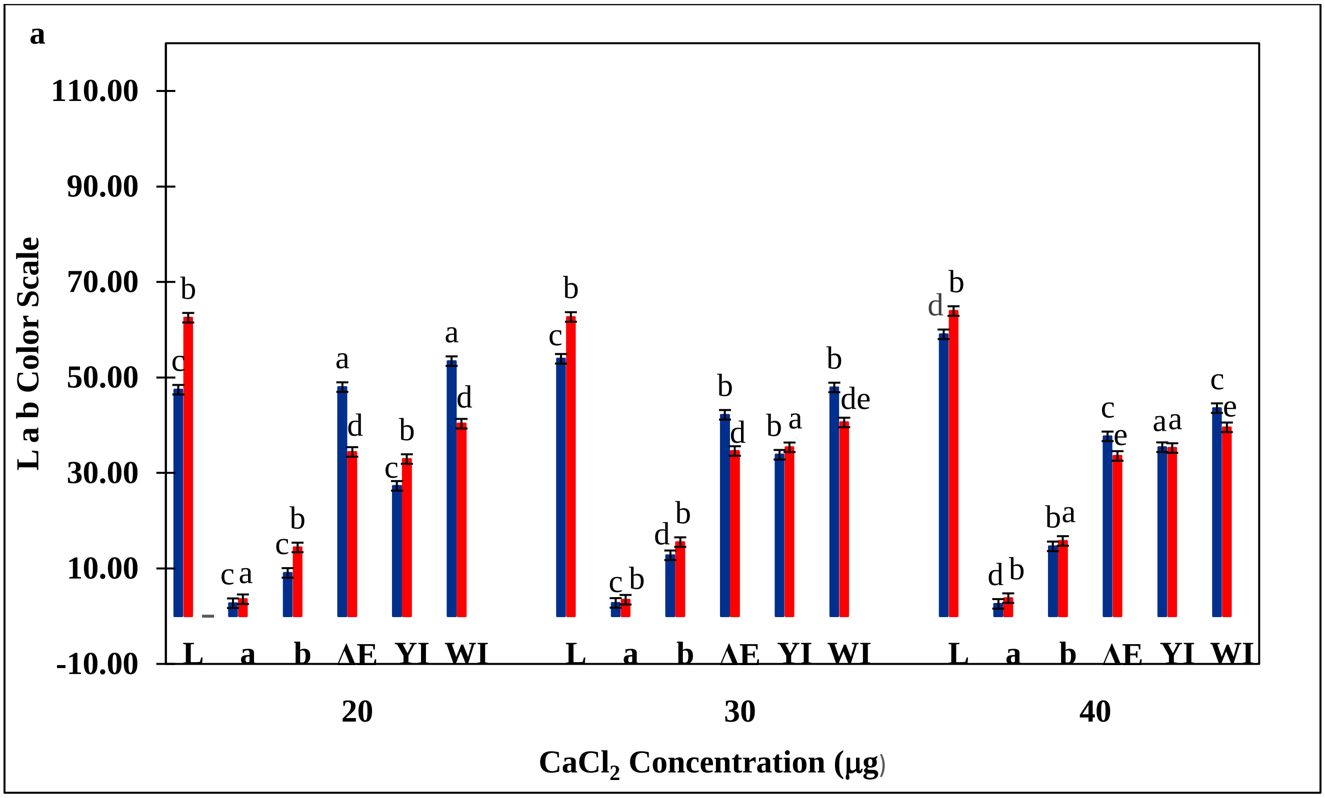
CHAPTER 4: RESULTS AND DISCUSSION

4.1 Agricultural -based cellulose (Corn Stovers and Cassava Peels)

4.1.1 Film color

The color of films affects their acceptability to a great extent. It is important that the transparency is preserved or at least their color is as close as possible to the natural pigment of the food it is intended to be used on. The Hunter lab color scale gave the L*a*b* parameters , total color difference (ΔE), whiteness index (W1), and yellowness index (YI) of the agricultural-based cellulose compared to pure cellulose and petroleum-based films are presented in Figure 5. The films are brownish in color and there are significant differences ($p < 0.05$) between corn-stover and cassava cellulose prepared with different concentrations of $CaCl_2$. The L values of corn stover cellulose are in between 47.43 and 59.03 while those for cassava peel range between 62.67 and 63.91 implying films of light brown nature. The values of a (<0) and b (<0) indicate that cellulose-based films to be more of red and yellow too.

The color of the films can further be described using the color function ΔE, which is the degree of total color difference against the standard white plate. Films with higher L* values and lower b* values have a relatively lower color function. Herein, it has been observed that increase in a and b, total color difference (ΔE), whiteness index (W1), and yellowness index (YI) with increase in the calcium chloride concentration. The Least Significant Difference (LSD) test shows a significant difference between the agricultural-based cellulose films (corn stover and cassava peel) and the microcrystalline and petroleum-based films. Both the MCC films and plastic films are whiter (L > 99.00), green (a < 0) and yellow (b > 0). The agricultural-cellulose based films could be conveniently used to package food products that are light, while the MCC films for products requiring a clear or transparent packaging.



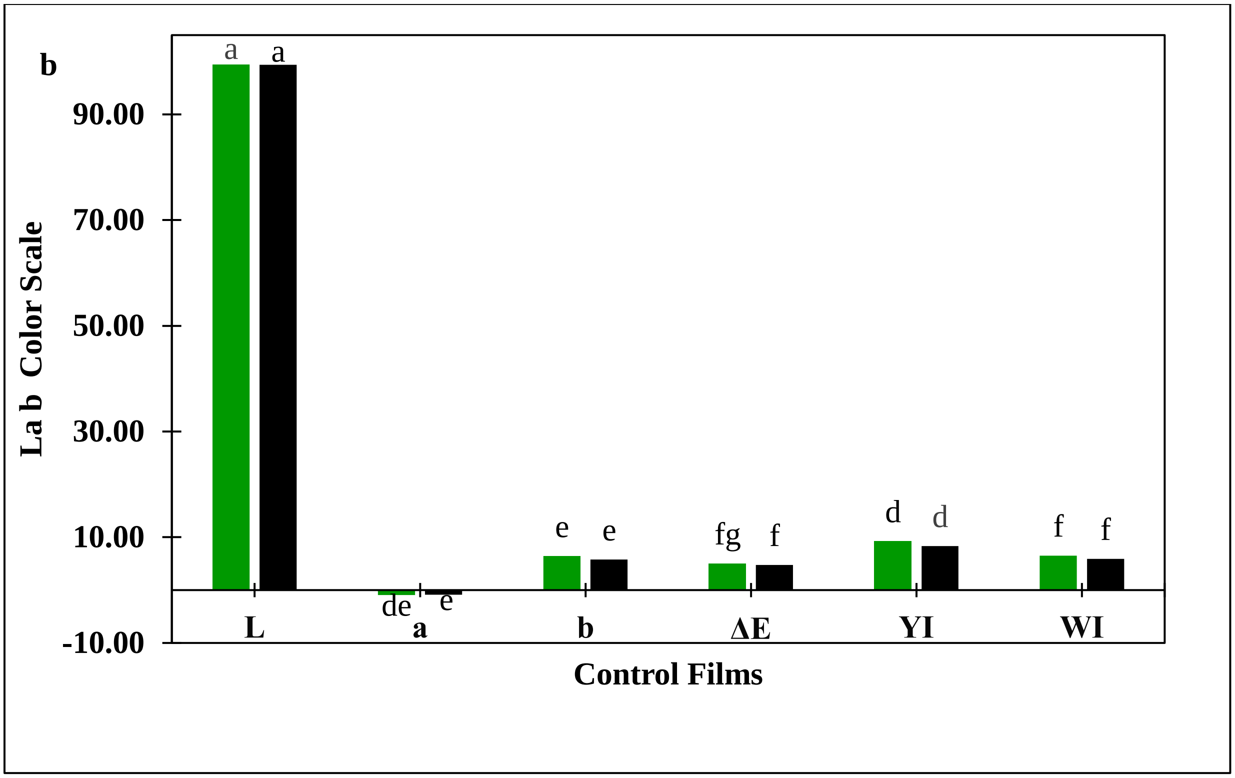


Figure 5: L a b color scale for a) Corn stover and Cassava peel cellulose films b) Avicel and plastic films.

4.1.2 Film thickness

The physio-mechanical properties of biofilms are influenced by their thickness. The thickness of the corn-stover cellulose films range between 0.11 and 0.15 mm ± 0.01, while that of cassava cellulose films ranges between 0.11 and 0.13 mm ± 0.01. There is a significant difference in the thickness in the agricultural-based cellulose films and those from Avicel (microcrystalline cellulose). However, there were differences between the cellulose-based films and petroleum-based film (0.08 mm ±0.01), hence the cellulose-based films are thicker (Figure 6). The increase in thickness could be due to the morphology and high molecular weight of the cellulose extract from corn stover and cassava. However, there is a need for more research to ascertain how these factors influence film thickness and other physical and mechanical properties.

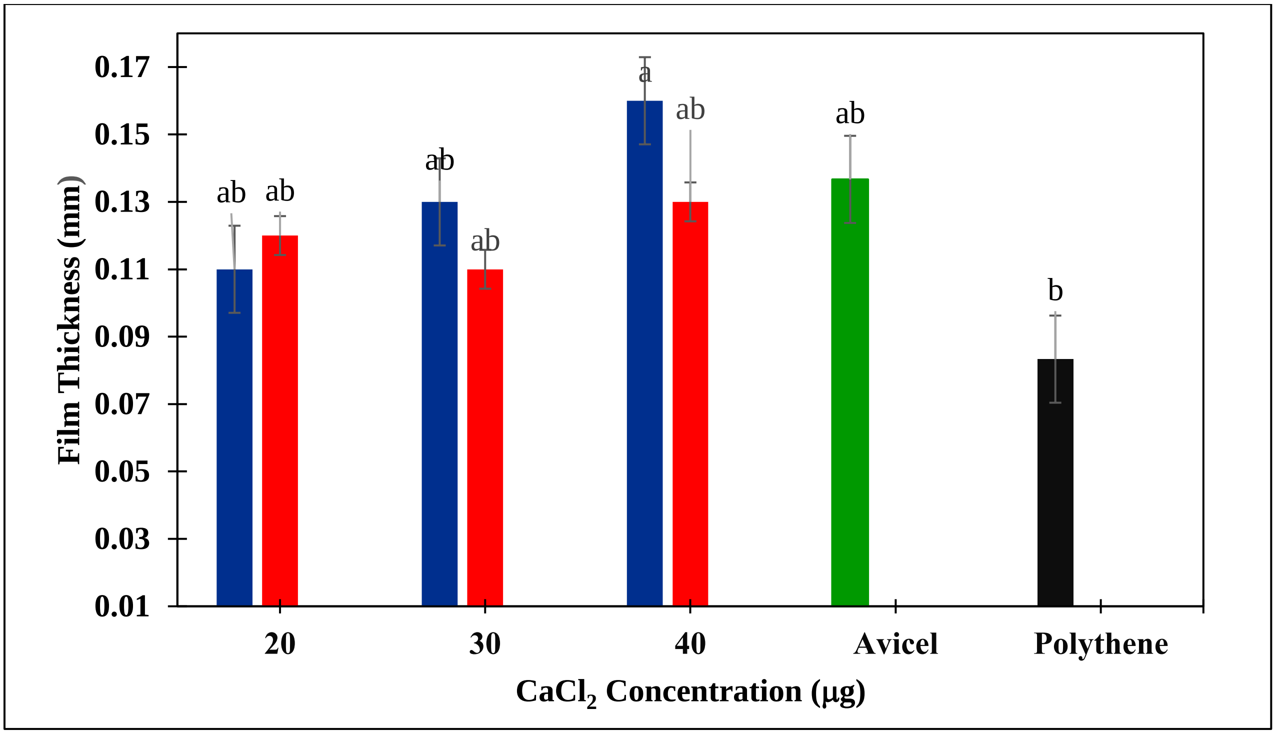


Figure 6: Film thickness for corn stover (red), cassava peel (blue), Avicel and plastic films.

4.1.3 Water solubility

Water resistance is an important parameter for biodegradable films suited for food packaging applications since film would be in contact with the food. Biofilms meant for food packaging applications are required to be insoluble in water so as to enhance water resistance and product integrity and shelf life. The water solubility is also related to biodegradability. The percentage water solubility of corn-stover and cassava cellulose-based films is shown in Figure 7. The results demonstrate that the higher the CaCl$_2$ concentration, the lower the water solubility of the films. There is no significant difference between the corn stover and cassava cellulose-based films ($p > 0.05$). However, there is a slight increase of solubility observed in the cassava-peel cellulose films. The films water solubility ranges between 45.8 and 58.65%. There is a significant difference between the pure Avicel films and agricultural-based films ($p < 0.05$). The MCC films have a water solubility of 78.86%. This means that the pure cellulose films swell more when immersed in water compared to the corn-stover and cassava peel cellulose films. The petroleum-based films solubility was 11.01% which is significantly different from the pure cellulose and agricultural-based films. Films with high solubility are best suited for consumption while those with low solubility are good as food packages (Domene-López, García-Quesada, Martin-Gullon & Montalbán, 2019, and Garcia, Pinotti & Zaritzky, 2006). The high solubility of the agricultural-based films also suggests that they could degrade at a higher rate than the petroleum-based films (Domene-López, García-Quesada, Martin-Gullon & Montalbán, 2019)**.**

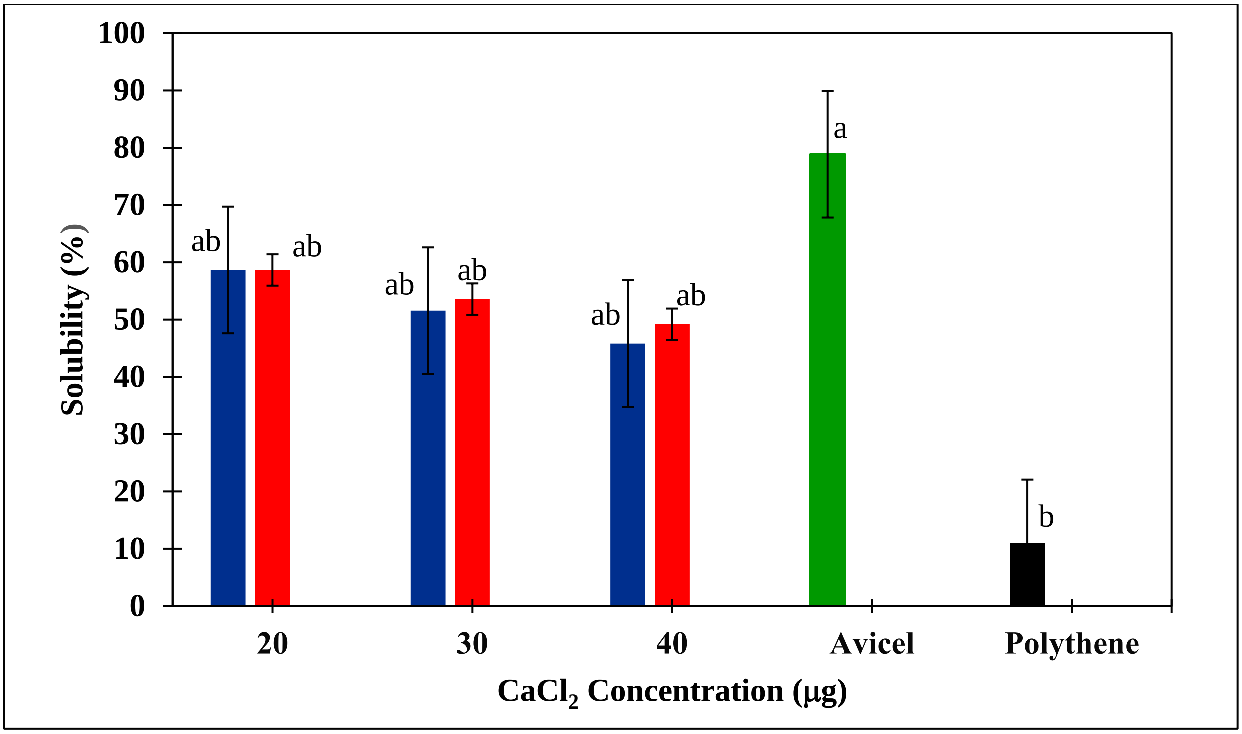


Figure 7: Percentage of water solubility for corn stover, cassava peel, Avicel and plastic films.

4.1.4 Moisture absorption

Moisture absorption is an important parameter for bio-based polymers with regard to their degradation. Cellulosic fibers are naturally hygroscopic in nature hence absorb moisture resulting in their swelling, microcracking and hence degradation of films (Laxmeshwar, Madhu Kumar, Viveka & Nagaraja, 2012). Figure 8 portrays the percentage water solubility of the agricultural-based cellulose compared to those of pure cellulose and petroleum-based films. There was a significant difference ($p < 0.05$) between the corn-stover, cassava-peel, pure cellulose, and petroleum-based films. The films have a high rate of moisture absorption ranging between 79-83% for the corn-stover films and 89-90% for cassava-peel cellulose films. The films developed from MCC have moisture absorption rate of 78%. In contrast, petroleum-based films had a moisture absorption rate of 19.14%.

The cellulose-based films have a relatively high absorption rate that can be attributed to the hygroscopic and swelling characteristic of cellulose fibers (Célino, Fréour, Jacquemin & Casari, 2014; Laxmeshwar, Madhu Kumar, Viveka & Nagaraja, 2012: Kalia et al., 2011. This means that the films would disintegrate completely due to the high absorptivity rate, hence degrade at a high rate. Swelling occurs because water penetrates into the film matrix (Cornejo-Ramírez et al., 2018). Further studies are warranted on the films to determine how the addition of fillers such as nanofillers can lower the sensitivity of films to moisture absorption and hygroscopy.

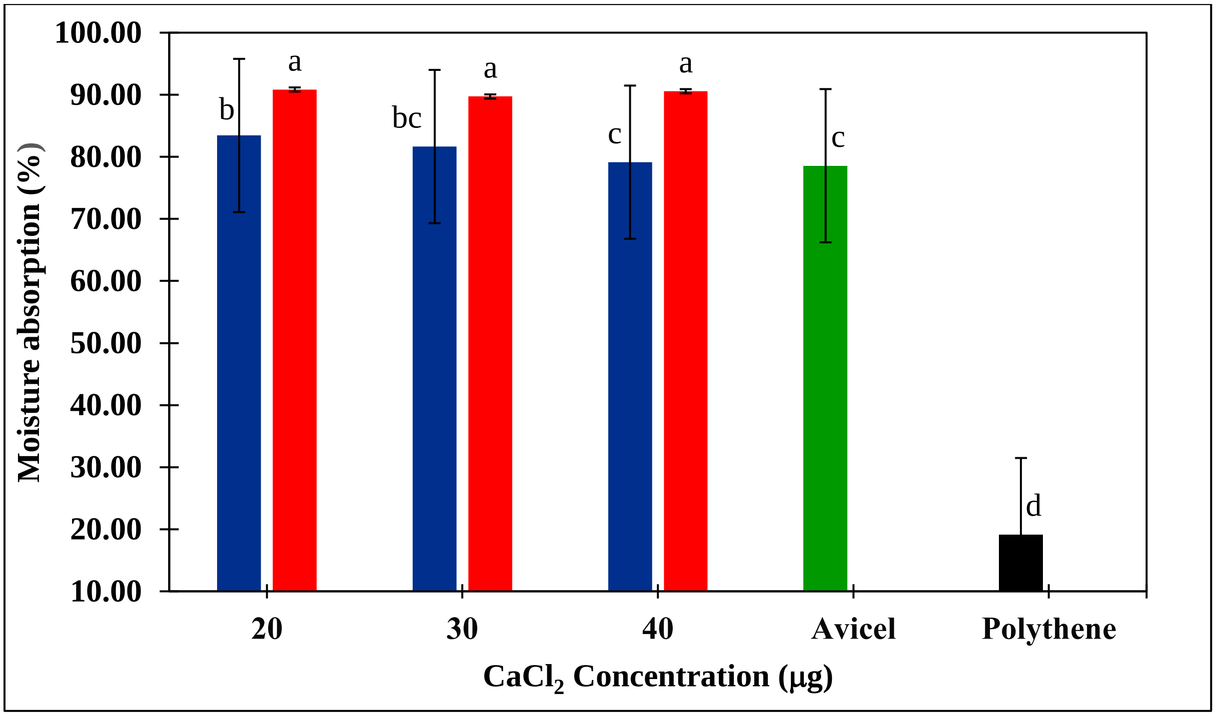


Figure 8: Moisture absorption for corn stover, cassava peel, Avicel and plastic films.

4.1.5 Moisture content

The loss or gain of moisture in a food package significantly influences the product integrity. The packages should prevent oxygen and moisture transmission between products and the environment, consequently, prevent food deterioration. Figure 9 highlights the percentage moisture content of agricultural-based cellulose compared to those of pure cellulose and petroleum-based films. There is no significant difference ($p < 0.05$) in the cellulose-based films (corn stover, cassava peels and pure cellulose). The moisture content of the films ranges between 54.5 to 59.9 % for the cellulose-based films. However, there is a significant difference between the petroleum-based films and the cellulose based films. Plasticizer such as glycerol influences the attractive forces between cellulose chains and increases the free volume so that the resulting will films have higher moisture content (Arık Kibar & Us, 2013). Similar research is warranted on the agricultural-based cellulose films.

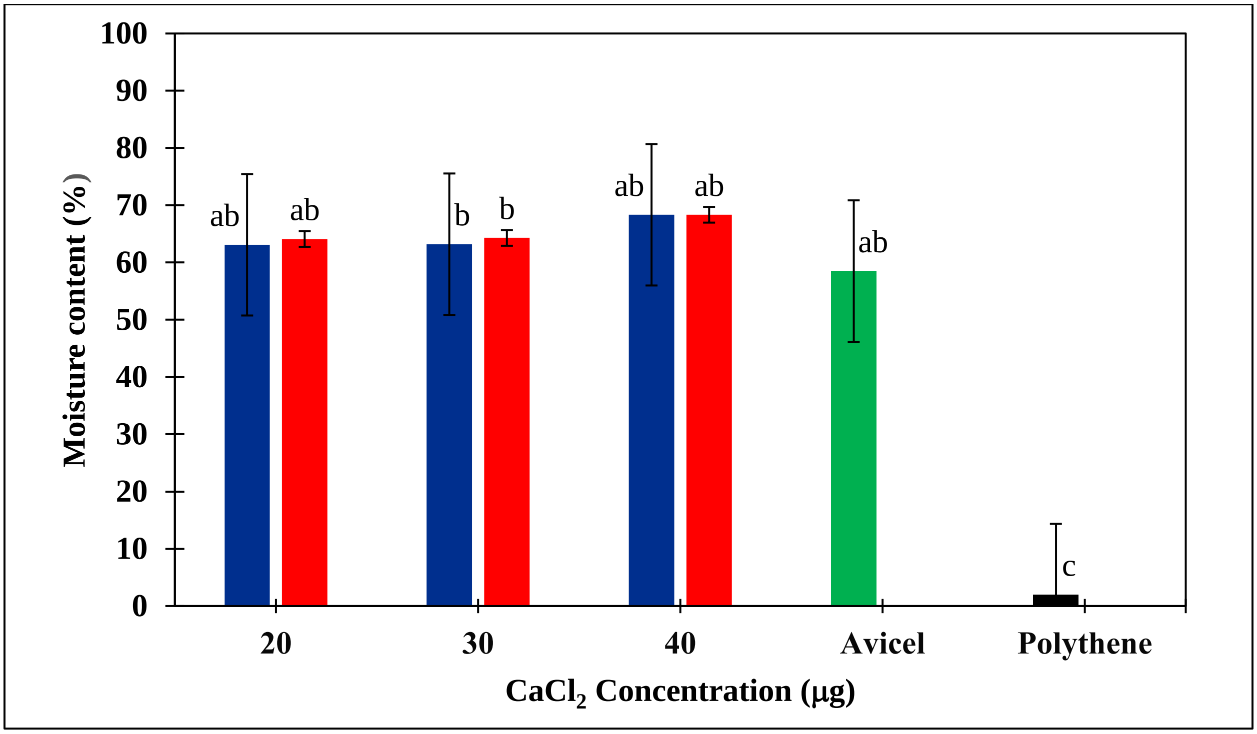


Figure 9: Moisture content for corn stover, cassava peel, Avicel and plastic films.

4.1.6 Film transparency

One major factor for the deterioration of foods such as nuts, dairy products, wine, and meat products is photo-oxidation. It results in both sensorial quality and nutritional value of these products and could even lead to the formation of toxins (Kwon et al., 2018). Therefore, there is need to determine the embedding light absorption or blocking properties for active packages compared to the petroleum-based plastics. Figure 10 highlights the rate of transparency of agricultural-based cellulose compared to those of pure cellulose and petroleum-based films. There is no significant difference ($p < 0.05$) in the cellulose-based films (corn stover, cassava peels and pure cellulose). Film transparency decreased significantly ($p < 0.05$) with an increase in the $CaCl_2$ concentration. The decrease in the light transmittance of films could be attributed to lower light passage when more of the crosslinking agents were added. (Khoirunnisa, Joni, Panatarani, Rochima & Praseptiangga, 2018) made similar results in their study to determine how metallic nanoparticles influence the water barrier properties, UV-screening, and transparency of gelatin films. An increase in total solids results in lower amount of light is being transmitted through the films leading to lower transparency. However, there is a significant difference between the transparency rate in petroleum -based films and the cellulose based films. The difference would be due to the variations in color and thickness.

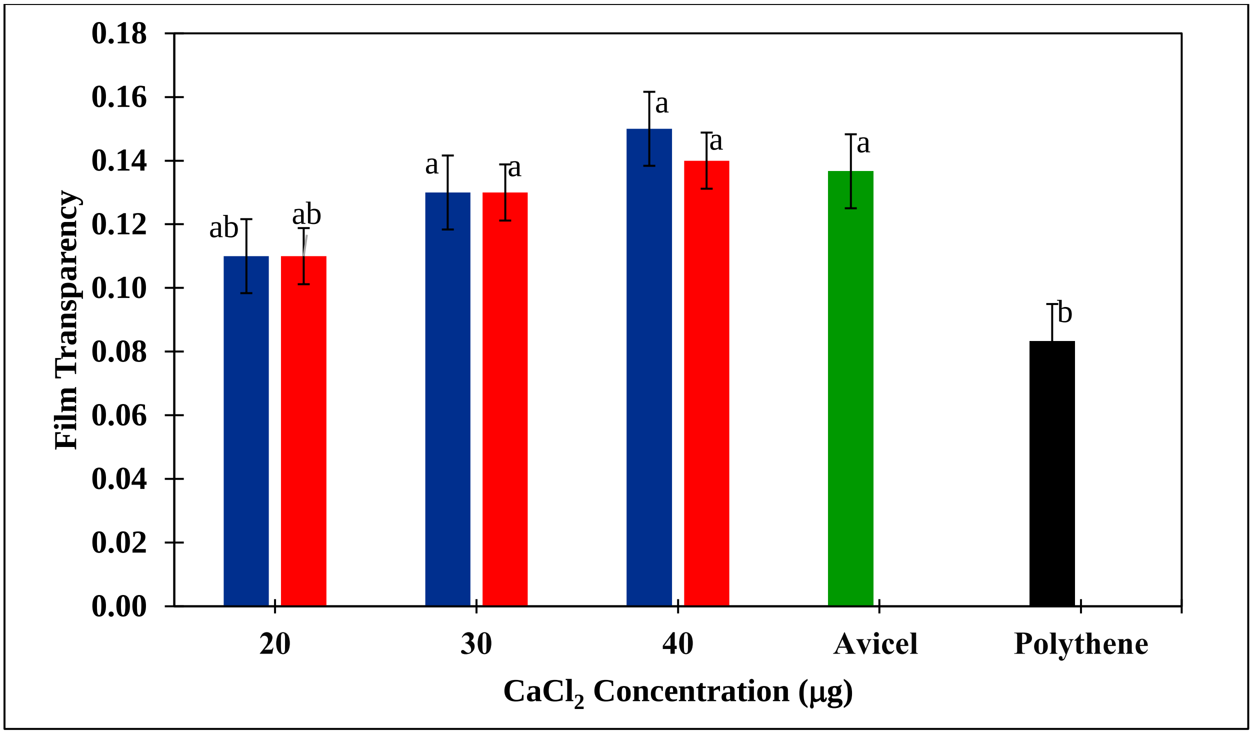


Figure 10:Transparency in corn stover, cassava peel, Avicel and plastic films.

4.1.7 Biodegradability

Biodegradable polymers are capable of decomposing into a biomass that is predominantly broken down by enzymatic action or broken down into inorganic compounds, methane, carbon dioxide, or water over a specified period of time (Basiak, Lenart & Debeaufort, 2018). The Figure 11 shows the percentage weight left for the agricultural-based corn stover and cassava peel cellulose-based films compared to those of pure cellulose and petroleum-based films after being buried in the soil for 30 days. The cellulose-extract films lost 90% of the total weight over the thirty-day period. The films gradually decomposed, hence a reduction in weight. There is a significant difference observed ($p < 0.05$) between decrease in the biodegradable films and the petroleum-based film. The weight of the plastic film is fairly constant over the period and only 20% is lost. Similar findings were noticed for cellulose fibre-reinforced with poly(vinyl alcohol) films (Laxmeshwar, Madhu Kumar, Viveka & Nagaraja, 2012). The films developed in this research have good biodegradation behavior that should help to combat non-degradation and accumulation of petroleum-based plastics.

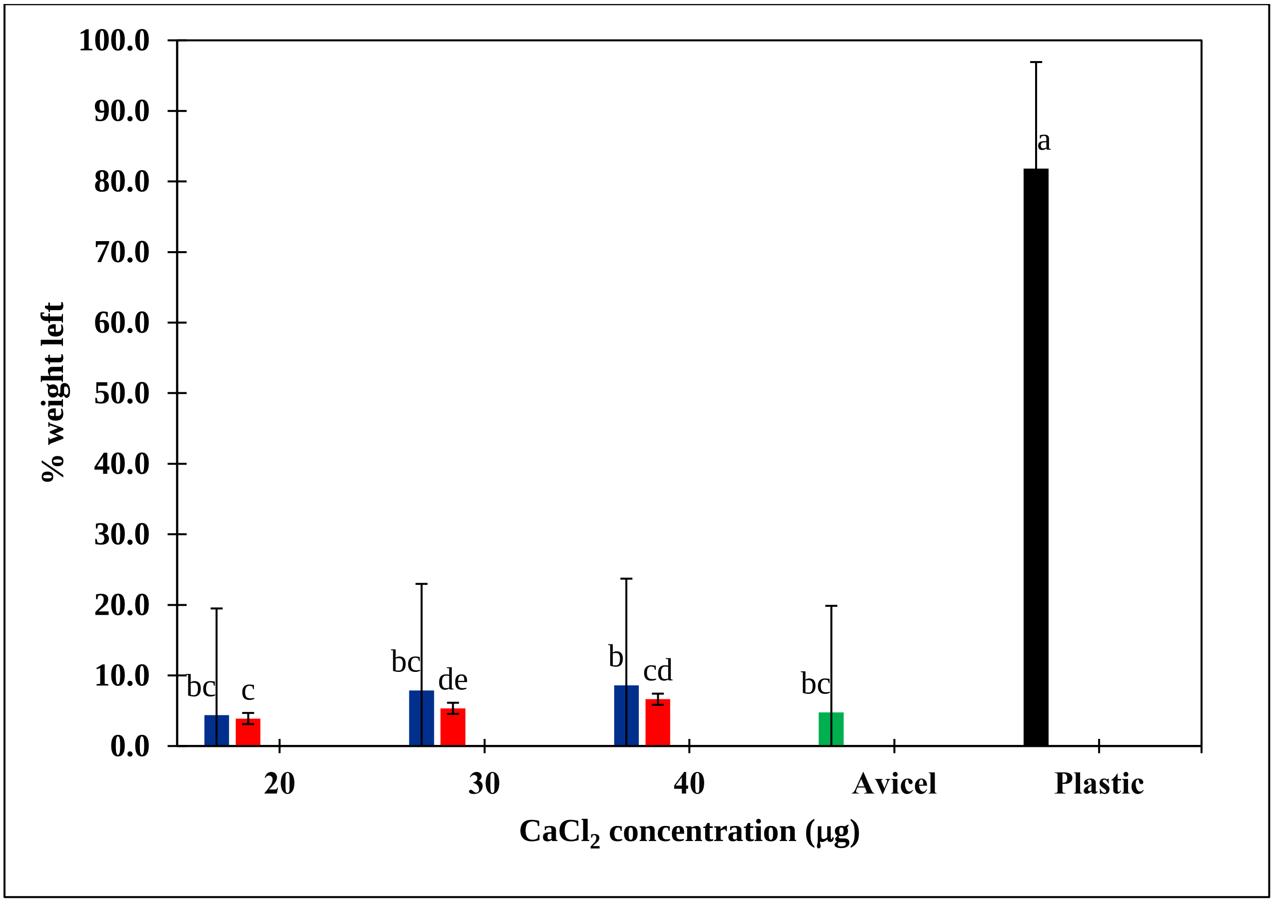


Figure 11: Biodegradability for corn stover, cassava peel, Avicel and plastic films.

4.1.8 Tensile strength

Tensile tests determine the force required to break the biodegradable film and the extent to which it elongates or stretches before its breaking point. Tensile strength is a useful mechanical property that specifies the film strength. Films with higher tensile strength are stronger and vice versa. The effect of $CaCl_2$ on the tensile strength of cellulose-based films is shown in Figure 12. An increase in $CaCl_2$ concentration results in an increase in the tensile strength. There is a significant difference between the films prepared with different proportions of the crosslinking agent. For instance, at a concentration of 40 µg $CaCl_2$, the corn-stover films have a higher tensile strength of 2.61 Mpa compared to films prepared with 20 µg $CaCl_2$ tensile strength is 1.16 Mpa. Films developed from MCC have a much lower tensile strength at 1.45 Mpa. This shows that the agricultural-based cellulose films are stronger and can resist mechanical damage during handling, processing, and storage more than pure microcrystalline cellulose films.

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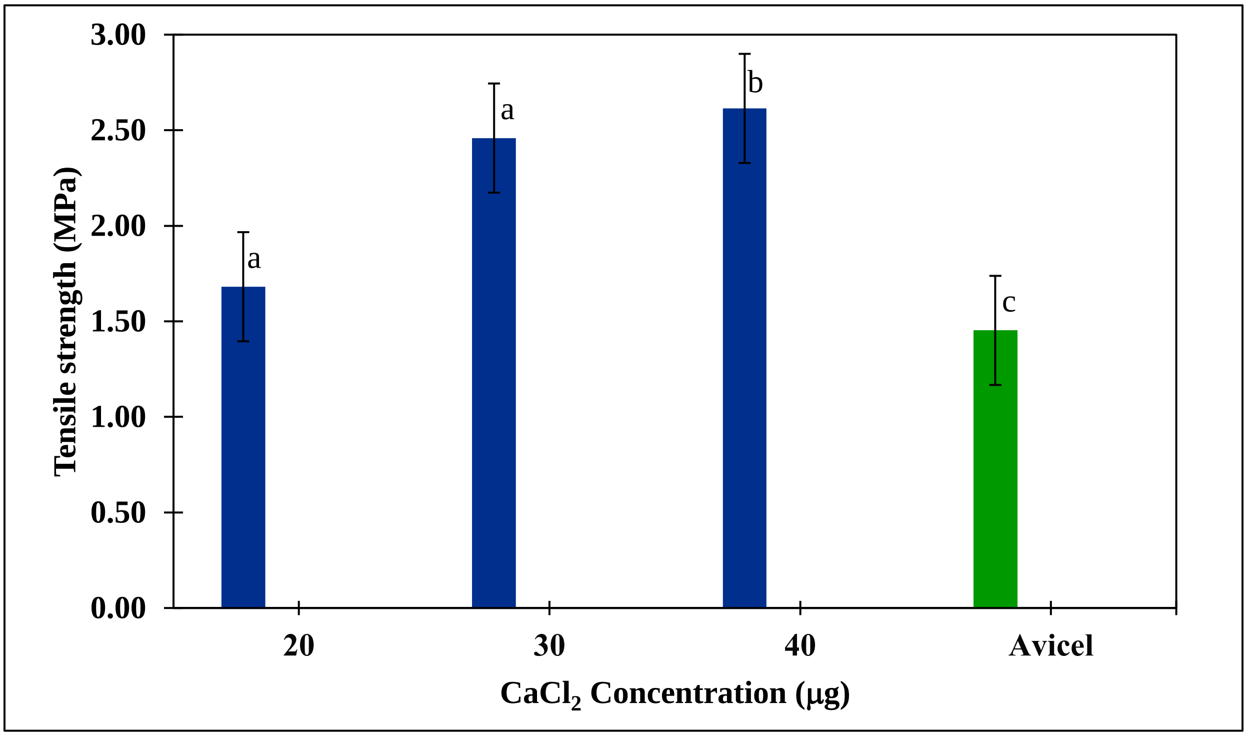


Figure 12:Tensile Strength for corn stover (blue), and Avicel (green).

4.1.9 Water vapor permeability

The rate of moisture transfer between a food product and its surrounding environment depends on the nature of packaging material. The determination of vapor permeability is a key functional property of the films and consequently a significant determinant of product stability. Figure 13 highlights the rate of WVP agricultural-based cellulose films compared to petroleum-based films. There is no significant difference between the rate of WVP for the cellulose-based films. Generally, an increase in the rate of WVP is observed with the increase in addition of $CaCl_2$ used for crosslinking the cellulose chains. The observed increase in the WVP values would have been due to the to an increase in chain immobility in the films and crosslinking. There is significant difference between films developed from cellulose and the petroleum-based films ($p < 0.05$). This can be attributed to the differences in film thickness, which influences the rate of moisture permeability and transfer (Phan et al., 2005).

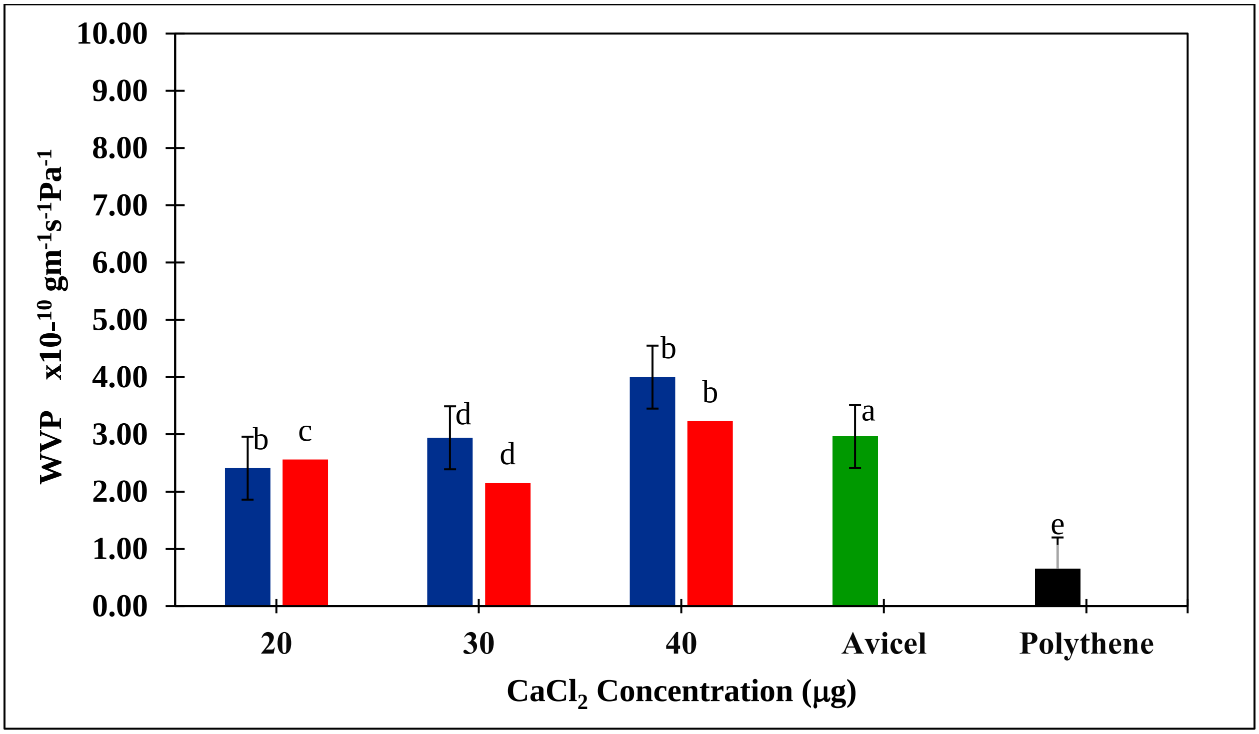


Figure 13: WVP of corn stover, cassava peel, Avicel and plastic films.

4.1.10 FTIR Characterization

FTIR spectroscopy is a significant analysis because it provides information about the presence or absence of molecular fragments and the specific functional groups. It helps to determine the structure of the cellulose fibers (Hospodarova, Singovszka & Stevulova, 2018). Figure 14 shows the percentage transmittance and wavenumber for the agricultural-based cellulose films compared to Avicel and petroleum-based films. There is no significant difference the films containing cellulose (corn-stover, cassava peel and MCC) despite the addition of $CaCl_2$. Peaks in the range 3400 - 3000 cm^{-1} are characteristic of stretching vibration of C-H and O-H bonds. A broad smooth peak at 3334 cm^{-1} is characteristic of the hydroxyl groups vibration. The peak also includes the vibrations due to inter- and intra-molecular hydrogen bonds in cellulose (Rosa et al., 2010). The bands in the region of 1000 - 900 cm^{-1} correspond to vibration of water molecules that are absorbed during cellulose dissolution (Poletto, Pistor, Zeni & Zattera, 2011). The bands at around 1320 - 1400 cm^{-1} are linked to crystalline structure of cellulose, while these at 800-900 cm^{-1} is associated with amorphous regions. There is a significant difference between the petroleum-based and cellulose-based films.

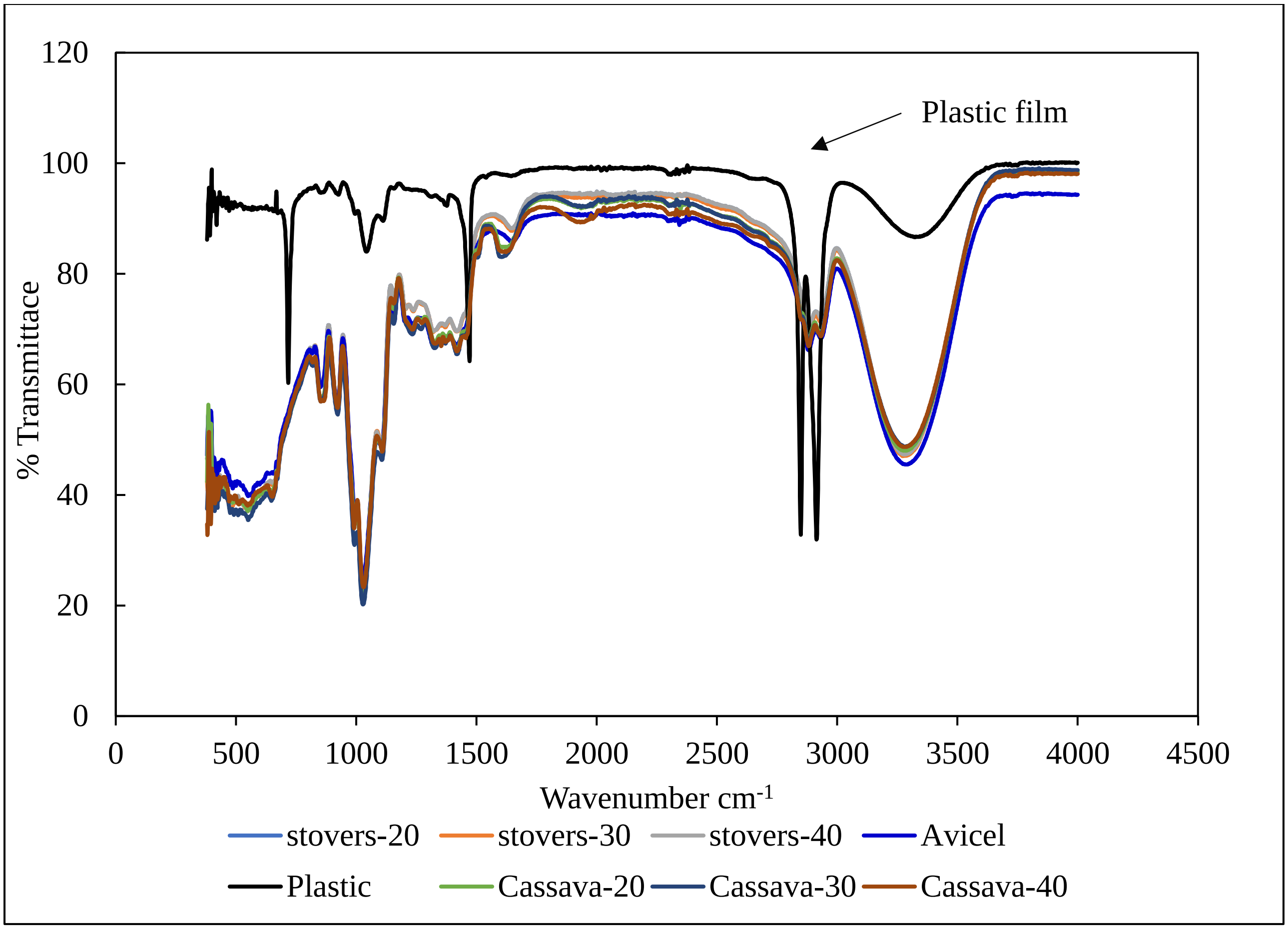


Figure 14: FTIR characterization of corn stover, cassava peel, Avicel and plastic films.

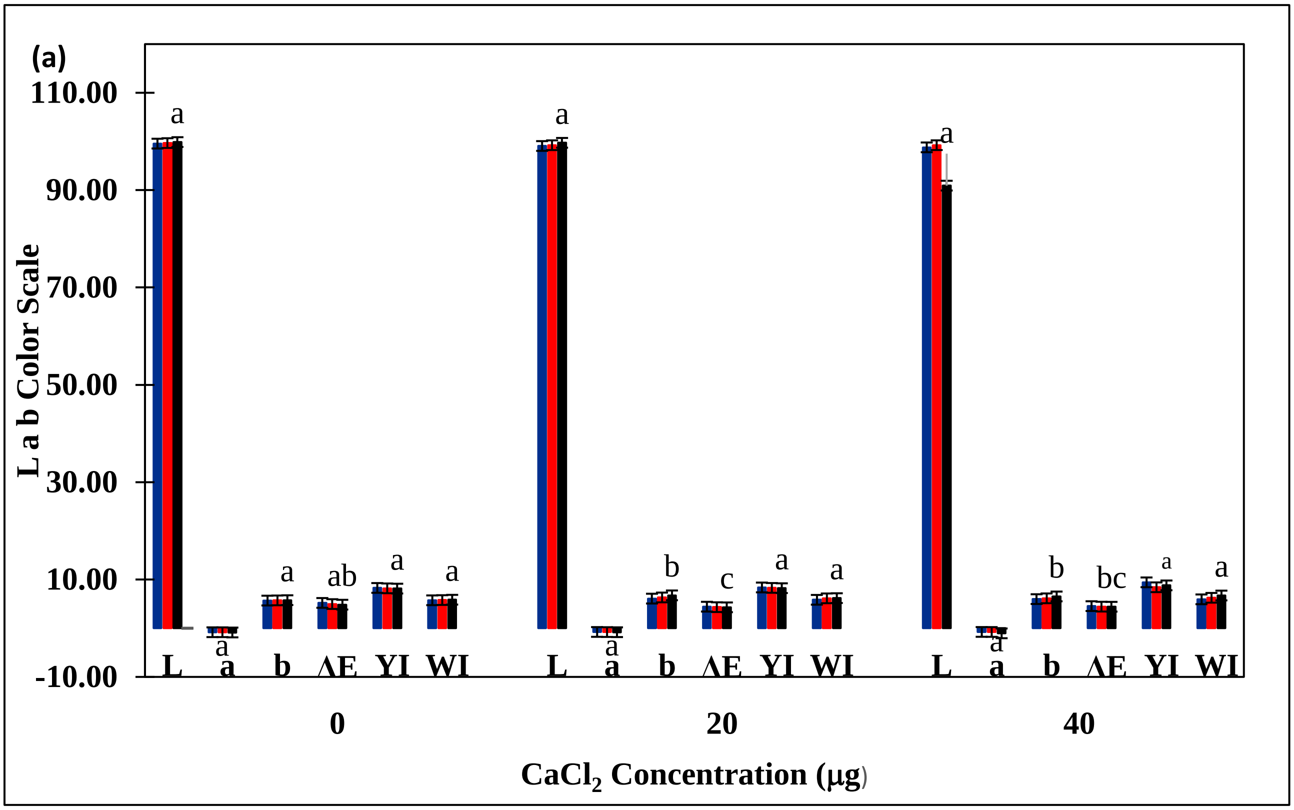
4.2 Starch-cellulose blended Films

4.2.1 Film color

The color of the films may influence their acceptability. Generally, the desirable characteristics in edible film packaging and coating are high transparency and lightness. The Hunter lab color scale gave the L*, a* and b* parameters, total color difference (ΔE), whiteness index (WI), and yellowness index (YI) of corn and potato starch-Avicel, Avicel and plastics films are presented in Figure 15.

The potato starch and corn starch films are white. There were no significant differences ($p < 0.05$) in color in films developed from different concentrations of $CaCl_2$ used for crosslinking or the potato and corn starch. The high L values (< 99.00) observed in both the potato and corn starch-Avicel films imply that they are white. The impact of different L* value readily reflects on the whiteness index (WI) of the films. The values of a (<0) and b (>0) indicated that potato and corn starch films tended to be green and yellow.

Generally, the a and b total color difference (ΔE), whiteness index (WI), and yellowness index (YI) increased with concentration of starch and calcium chloride. The color of the films can further be described using the color function ΔE, which is the degree of total color difference against the standard white plate. Films with higher L* values and lower b* values have a relatively lower. However, the Least Significant Difference (LSD) does not show significant difference between the films. This is because the microcrystalline cellulose, potato and corn starch are predominantly white therefore have less effect on the color of the films. The Least Significant Difference (LSD) test shows that there is no significant difference between the starch-cellulose blend films and the microcrystalline as well as the petroleum-based films. Therefore, the films can be conveniently used for products requiring a clear to white packaging. The films could be further described using another color function namely ΔE, which indicates the degree of total color difference against the standard white plate. Films with lower b* and higher L* values show relatively lower ΔE than those with higher b* and lower L*.



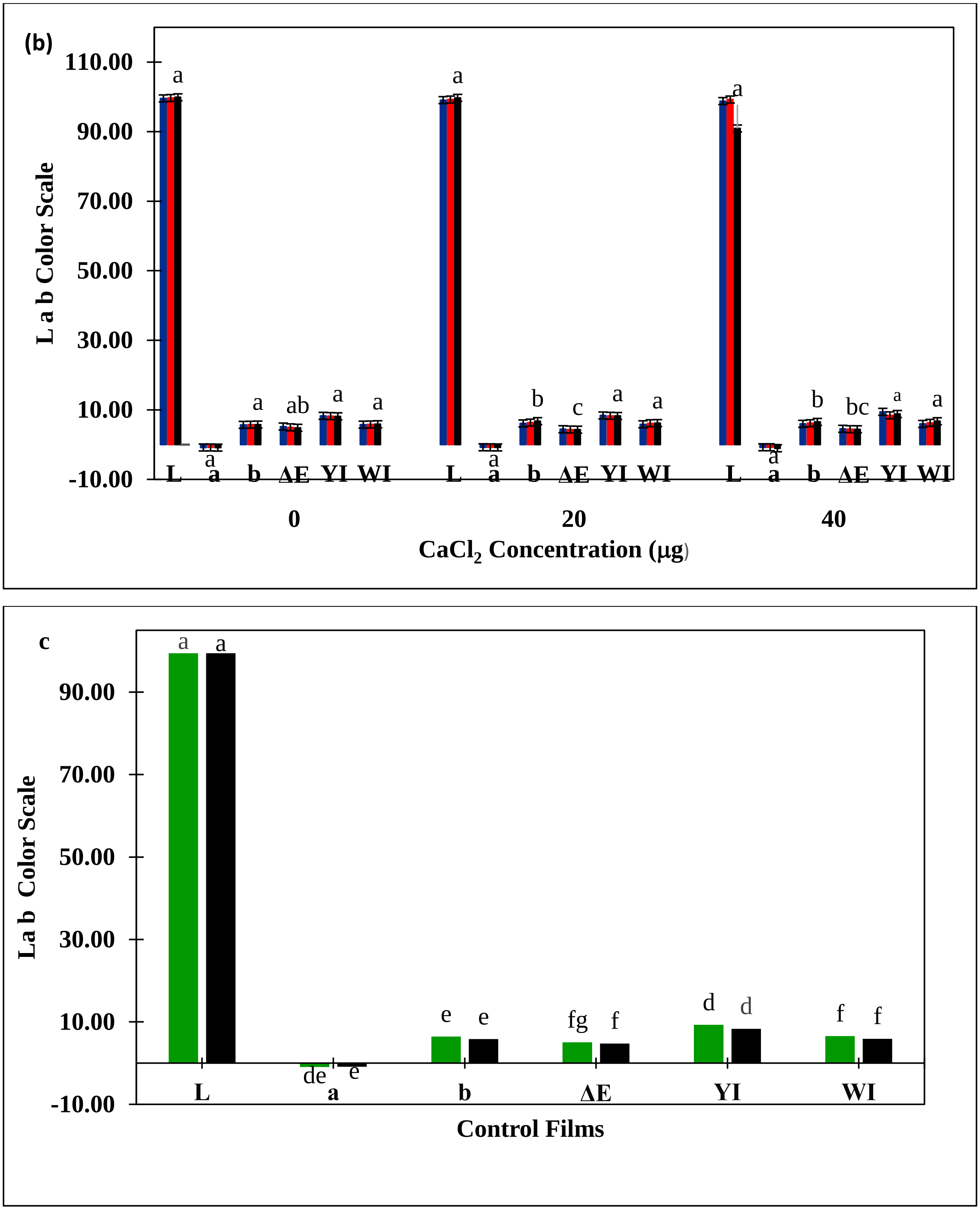


Figure 15: The Hunter color values (L, a and b), total color difference (ΔE), yellowness index (YI) and whiteness index (WI) of films of (a) corn starch-Avicel and (b) potato starch-Avicel films (c) control films (Avicel and plastic films).

4.2.2 Film thickness

Thickness is one of the important parameters that affects the mechanical and physical properties of films. The thickness of the films ranges between 0.12 and 0.16 mm ± 0.01. The film thickness depends on the levels of starch and $CaCl_2$. An increase in concentration of starch and $CaCl_2$ results to an increase in thickness as shown in Figure 16. Indrianti, Pranoto & Abbas, (2018) made similar observations in edible films from modified potato starch. The increase in thickness is due to an increase in the total solids in the solution. For instance, 50% increase in starch concentration results in an increase in thickness from 0.13 to 0.15 mm. There is no significant difference ($p < 0.05$) between the films prepared from potato and corn starch, though the potato starch films were slightly thicker. However, there are significant differences ($p > 0.05$) between the cellulose-based films and petroleum-based film (0.08 mm ±0.01), hence cellulose-based films are thicker; difference in the amylopectin amount in the corn and potato starches might be the reason. There is a need for more research to ascertain how the starch components influence the film thickness.

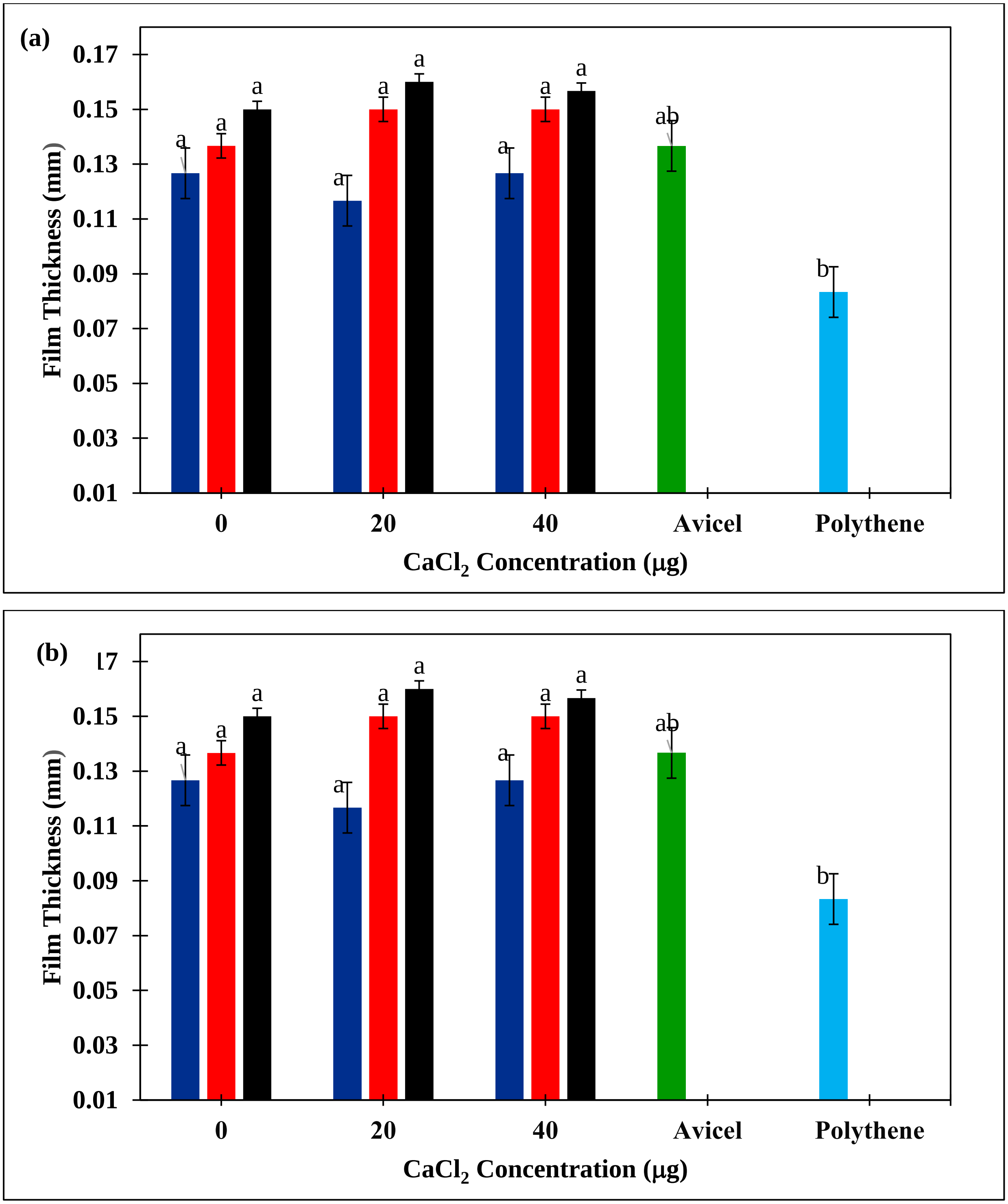


Figure 16: The thickness of (a) corn starch-Avicel and (b) potato starch-Avicel, Avicel, and plastic films.

4.2.3 Water solubility

Films are expected to be water resistant so as to enhance product integrity and shelf life. Water solubility is an important indicator of water resistance of the biodegradable films. The degree of water solubility of biodegradable films made from water-sensitive biopolymers such as starch is a key parameter, and water solubility is closely related to biodegradability. The percentage water solubility of all films is illustrated in Figure 17. The results demonstrate that the higher the starch and $CaCl_2$ concentration, the lower the water solubility of films. There are significant differences between the corn starch and potato starch-Avicel films ($p < 0.05$). Corn starch-Avicel films have a lower water solubility of 33.20-38.99% than the potato starch-Avicel films (50.73-54.95%). These values are higher than those reported by Domene-López, García-Quesada, Martin-Gullon & Montalbán,(2019) and Garcia, Pinotti & Zaritzky, (2006) who studied on the influence of starch composition and molecular weight on physicochemical properties of biodegradable films. Due to higher solubility, the films are better suited as edible films. The solubility could be due to a disruption on the starch network, reduced cohesiveness of the starch matrix leading to increase in water solubility. There is a significant difference ($p < 0.05$) between the starch-Avicel, blended films and the pure MCC films. The MCC films have a water solubility of 78.86%, but with addition of starch and crosslinking agents, the water solubility decreases. The pure cellulose films possibly swell more when immersed in water but the starch and $CaCl_2$ reduce the rate of solubility. The petroleum-based films solubility was 11.01% which is significantly different from the pure cellulose and agricultural-based films. Based on these findings it can be inferred that water solubility, as in the case of moisture content is greatly influenced by the starch-cellulose composition or molecular weight of the blended polymers starch (Domene-López, García-Quesada, Martin-Gullon & Montalbán, 2019).

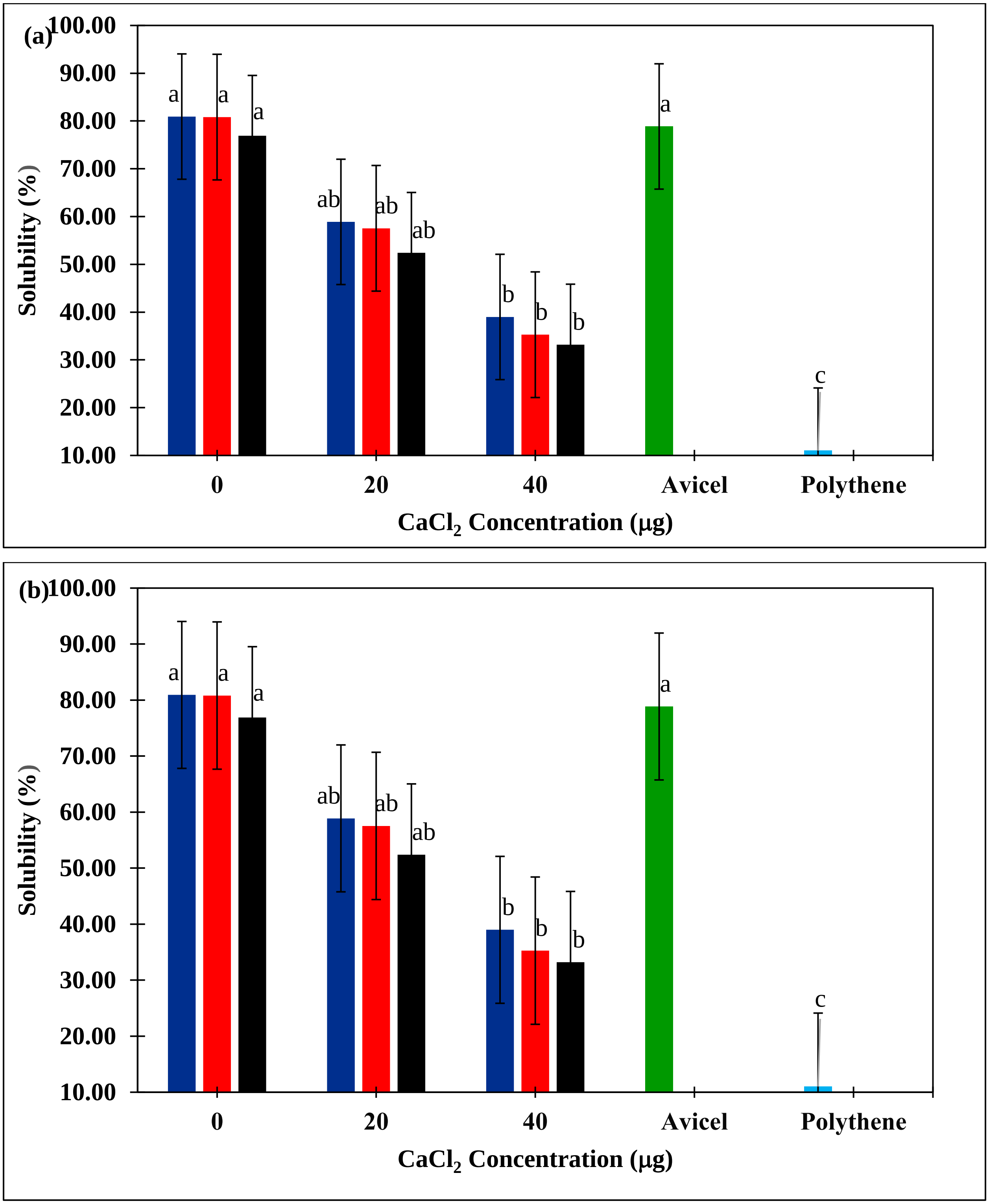
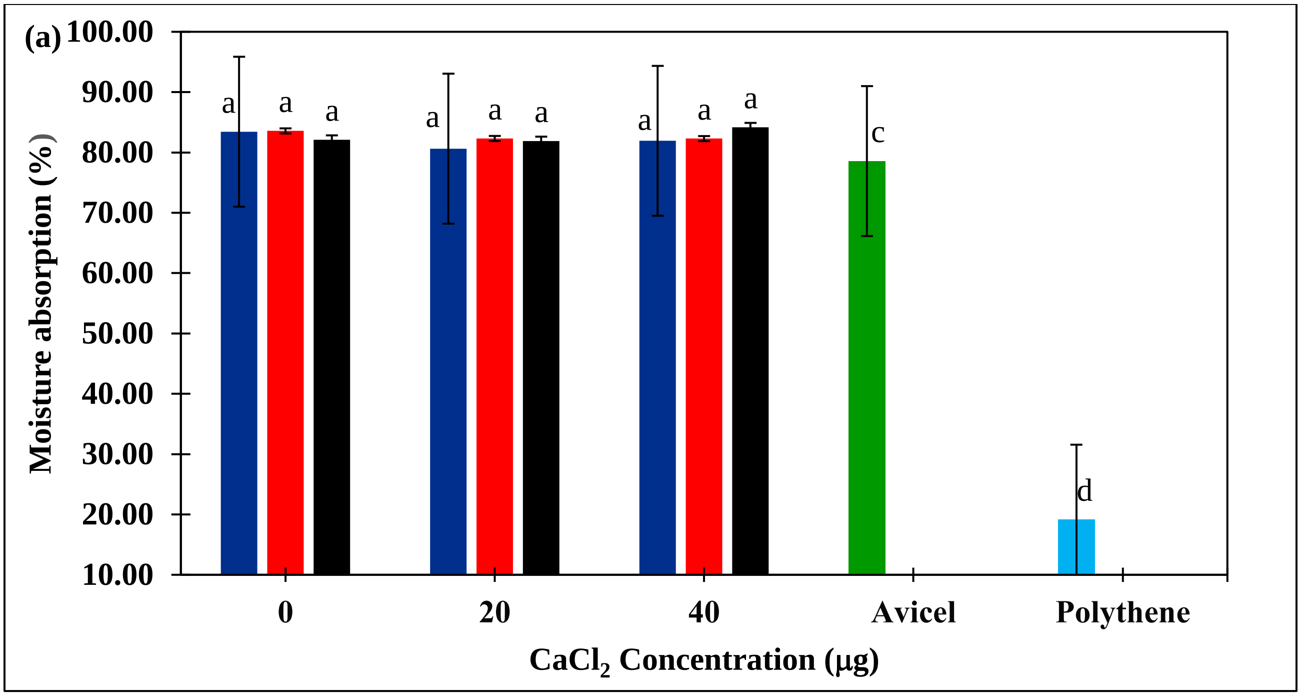


Figure 17: The water solubility of (a) corn starch-Avicel and (b) potato starch-Avicel, Avicel, and plastic films.

4.2.4 Moisture absorption

The moisture absorption characteristic of the films is important for predicting the stability of the films during storage since the shelf life of the biodegradable packages at different storage conditions is dependent on the moisture uptake. The percentage water solubility of films is illustrated in figure 18. There was significant difference ($p < 0.05$) between corn starch-Avicel and potato starch-Avicel films. The moisture absorption rate ranges between 79-84%. These are relatively high absorption rates presumably due to strong tendency of intermolecular associations between starch and cellulose chains and their hygroscopic and swelling characteristic (Othman, Kechik, Shapi'i, Talib & Tawakkal, 2019). This means that the films would disintegrate completely. There was a significant difference ($p < 0.05$) between the starch-Avicel blended films and films developed from MCC. As is the case with water solubility, the starch and $CaCl_2$ influence the rate of moisture absorption. The, petroleum-based films were significantly different from the cellulose-based films with a moisture absorption rate of 19.14%. The cellulose-based films have a relatively high absorption rate that can be attributed to the hygroscopic and swelling characteristic of cellulose fibers (Célino, Fréour, Jacquemin & Casari, 2014; Laxmeshwar, Madhu Kumar, Viveka & Nagaraja, 2012: Kalia et al., 2011). Swelling occurs because water penetrates into the film matrix (Cornejo-Ramírez et al., 2018). The presence of hydrophilic groups in starch dictate the swelling nature, hence moisture absorption rate of the films.



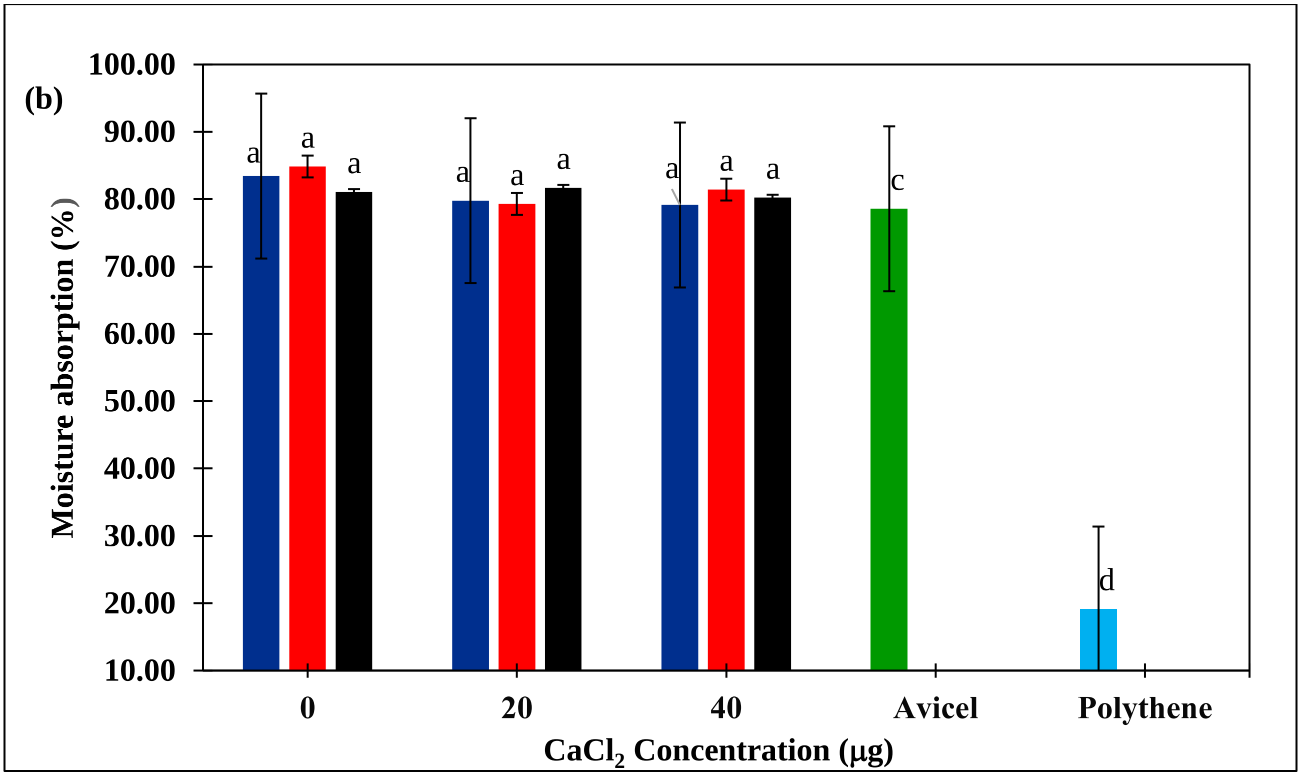


Figure 18:The water absorption of (a) corn starch-Avicel and (b) potato starch-Avicel, Avicel, and plastic films.

4.2.5 Moisture content

The moisture content of the films is important because moisture is transferable from the package into food product and in-turn influences the shelf-stability of products (Othman, Kechik, Shapi'i, Talib & Tawakkal, 2019). The amount of moisture present in a film is the indication of the hydrophilicity and indeed is influenced by the nature of the biopolymer(s), humidity, presence or absence of hydrophilic and hydrophilic polymers and other additives. Figure 19 highlights the effect of starch and calcium chloride on the moisture content of cellulose films. There is a significant difference ($p < 0.05$) in the films with higher concentration of total solids. As in thickness, higher the amount of total solids (starch and calcium chloride), lower the moisture content. There is a significant difference ($p < 0.05$) in the starch-cellulose blended films and those developed from pure cellulose. The degree of crosslinking also reduces the moisture (Alcázar-Alay & Meireles, 2015). The starch-mineral complex forms films that are hydrophobic in nature hence reduction in the moisture. The moisture content of the films is a reflection of their water solubility and water sorption properties. Also, there is a significant difference between the petroleum-based films and the cellulose based films due to the minimal weight loss observed on the plastic film.

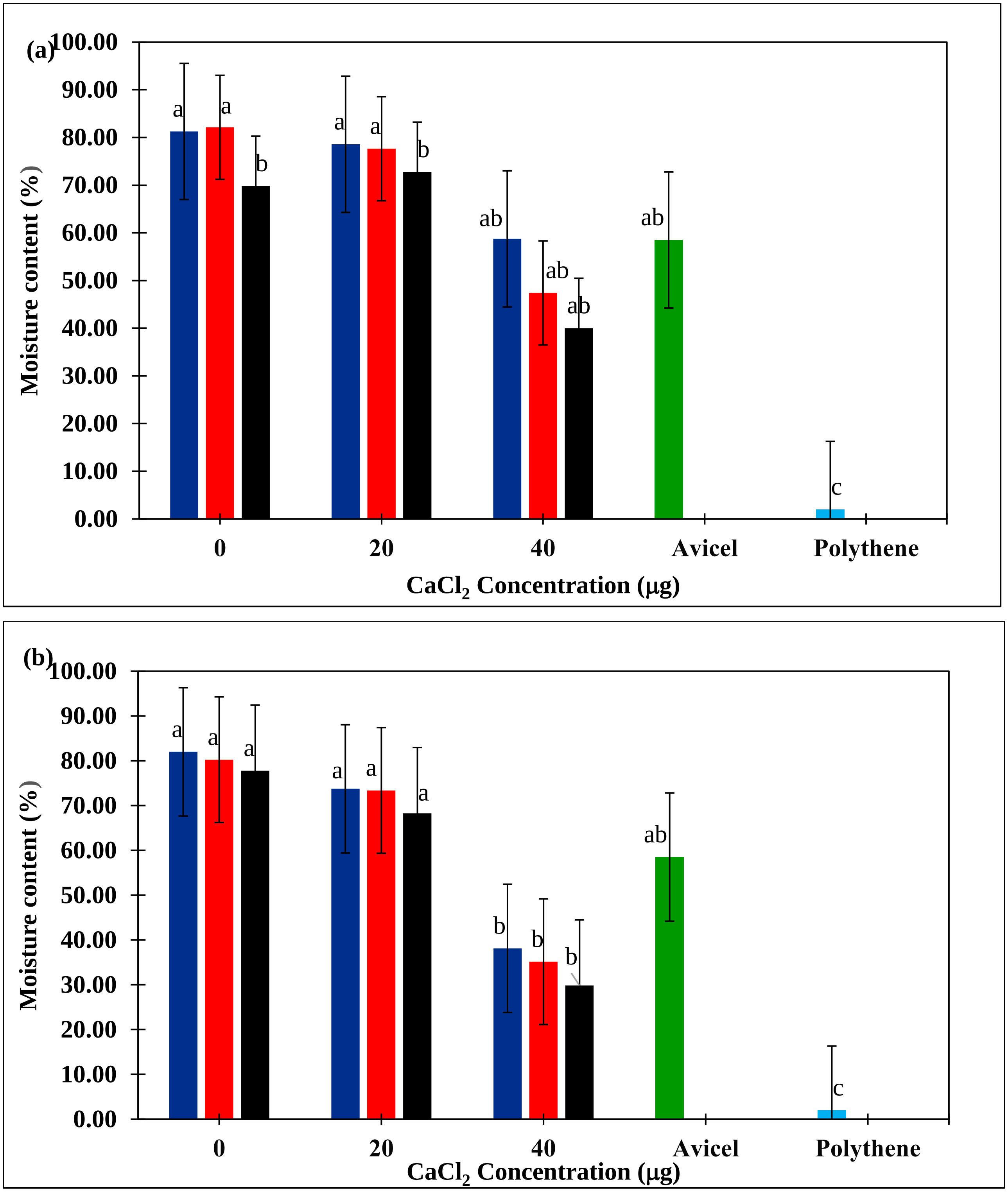


Figure 19: The moisture content of (a) potato starch-Avicel films and (b) corn starch-Avicel, Avicel, and plastic films.

4.2.6 Water vapor permeability

The nature of packaging material determines the rate of moisture transfer between the food and its surrounding atmosphere. This is why the determination of permeability is a key functional property of the films. The developed films should completely avoid or retard the moisture transfer. Figure 20 highlights the WVP of corn starch-Avicel and potato starch-Avicel films. As was with thickness, water solubility, moisture content, WVP decreased with increase in starch and $CaCl_2$ amounts. A reduction in the WVP would have been due to the to the reduced chain mobility in the films due to crosslinking (Shah, Naqash, Gani & Masoodi, 2016). There are significant difference between corn starch-Avicel films and potato starch-Avicel films ($p < 0.5$). An increase in starch and $CaCl_2$ levels led to a significant decrease in the rate of water vapor permeability. For instance, without $CaCl_2$ and starch at 50 μg, the WVP of corn-Avicel films is 9.48 $gm^{-l}s^{-1}Pa^{-1}$, while that of potato starch-Avicel starch was 9.28 $gm^{-l}s^{-1}Pa^{-1}$. When the starch concentration was increased to 200 μg and $CaCl_2$ at 40 μg, the WVP of corn starch-Avicel was 3.72 $gm^{-l}s^{-1}Pa^{-1}$ while that of potato starch-Avicel was 3.95 $gm^{-l}s^{-1}Pa^{-1}$. There is a significant difference between films developed from cellulose and the petroleum-based films ($p < 0.05$). This can be attributed to differences in film thickness, the nature and molecular weight of the cellulose based films which allows them to swell and influence the rate of moisture permeability and transfer (Phan et al., 2005).

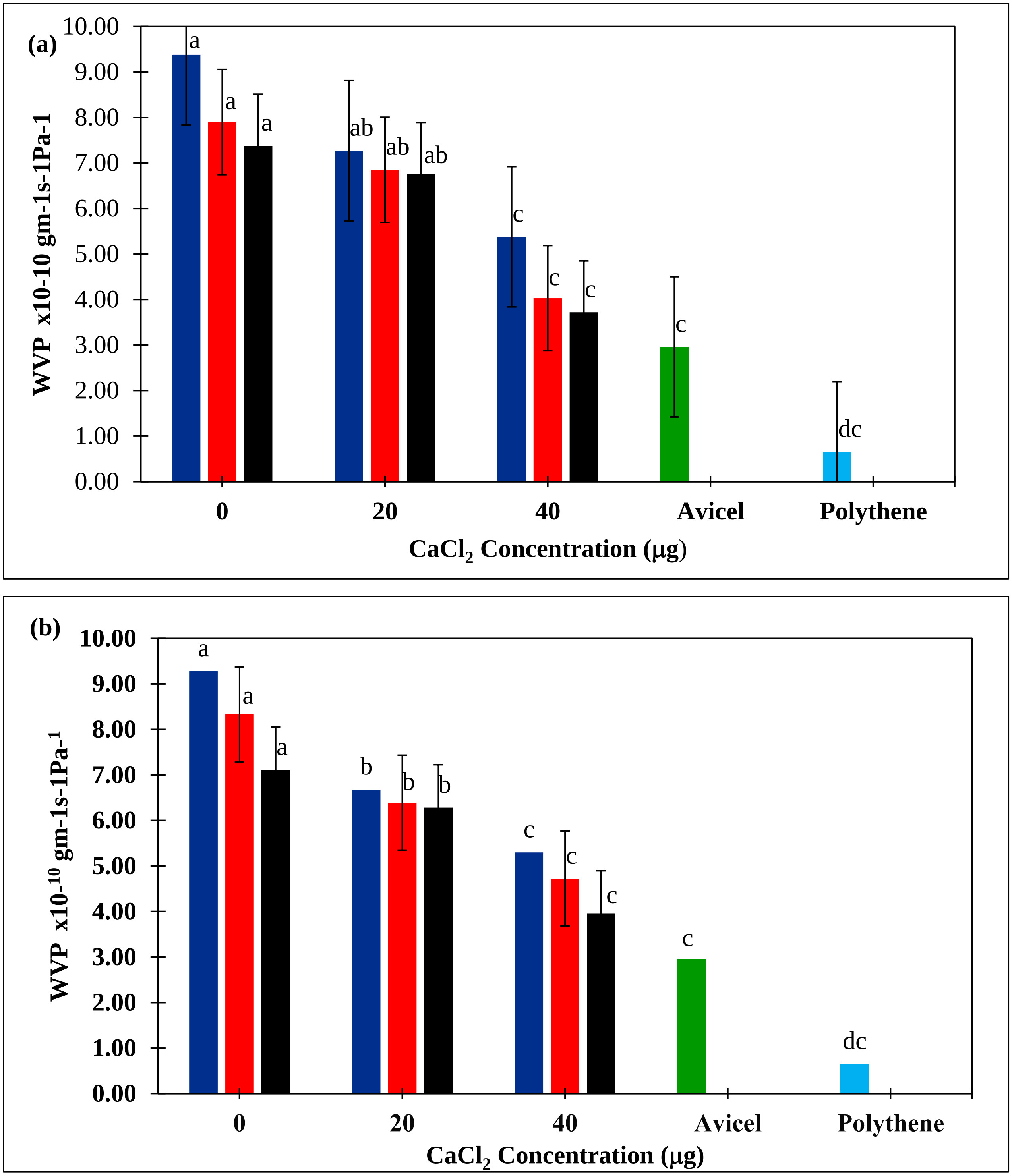
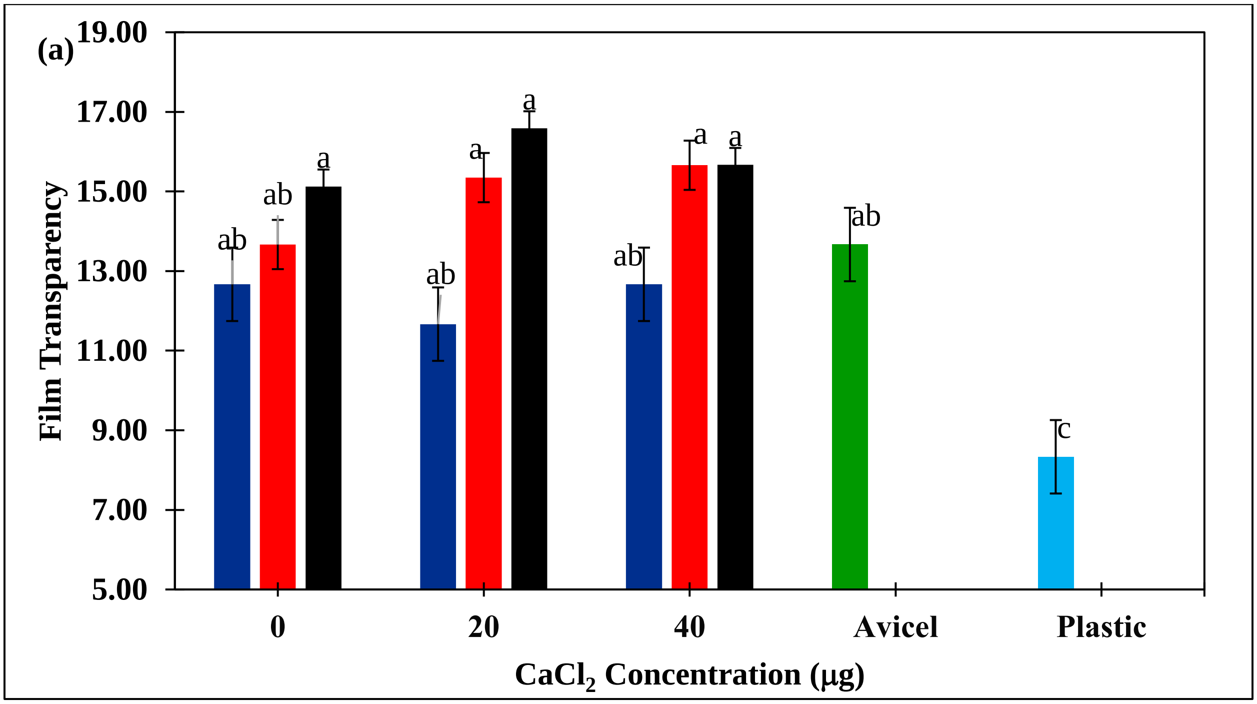


Figure 20: The water vapor permeability of (a) corn starch-Avicel and (b) potato starch-Avicel, Avicel, and plastic films.

4.2.7 Film transparency

High light absorbance of films due to high opacity is a desirable property of food packaging films since it is an excellent barrier to light-induced lipid oxidation. On the other hand, consumers may prefer packages with higher transparency so that they can see the food that is being packaged. Film transparency decreased significantly ($p < 0.05$) with an increase in starch and the crosslinking calcium ions. An increase in concentration of starch and $CaCl_2$ decreases the transparency (Figure 21). Lower amount of light is being transmitted through the films leading to lower transparency. Corn starch films reinforced with $CaCO_3$ nanoparticles showed similar trend (Sun, Xi, Li & Xiong, 2014). There is a significant difference between the transparency rate in petroleum-based films and the starch-Avicel films. The difference in opacity is in line with increase in film thickness.



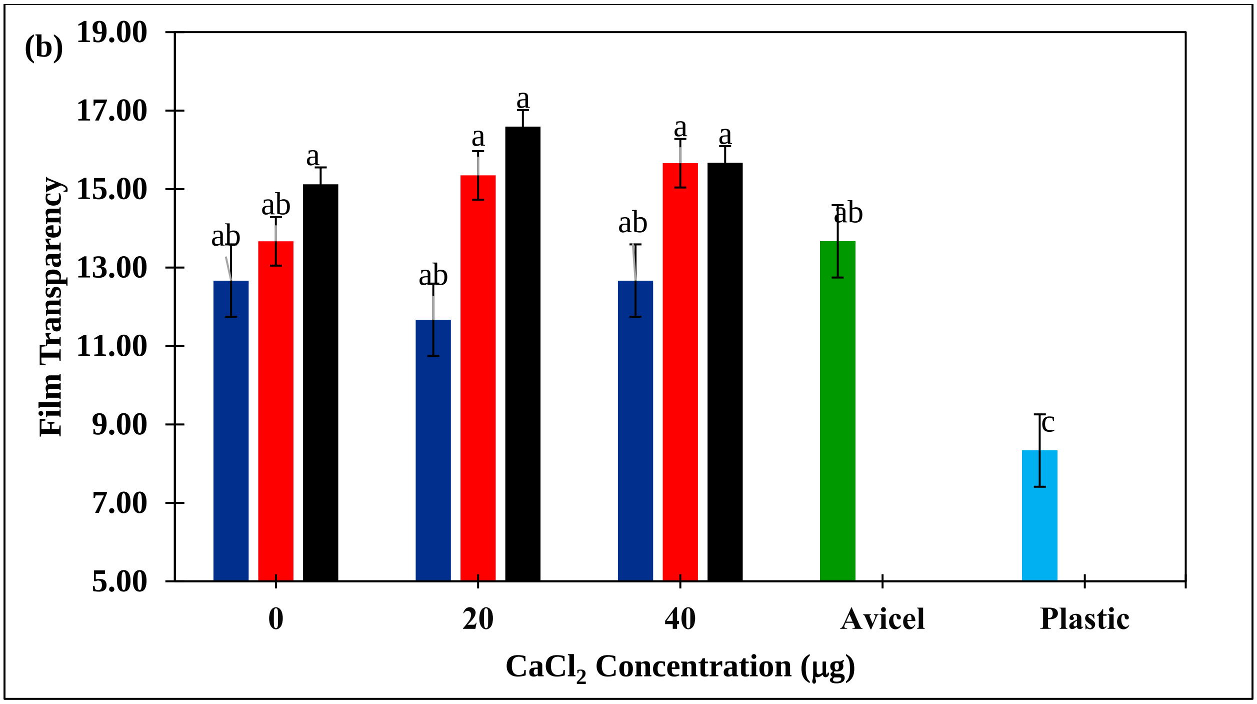


Figure 21: The transparency of (a) corn starch-Avicel and (b) potato starch-Avicel, Avicel, and plastic films.

4.2.8 Tensile strength

Tensile strength is a useful mechanical property that indicates the film strength. Films with higher tensile strength are stronger. Tensile strength of a film is the maximum stress that it could withstand while it is being stretched before it cracks or breaks. The effect of starch and $CaCl_2$ on the tensile strength of films are shown in Figure 22. An increase in starch and $CaCl_2$ concentration resulted in an increase in tensile strength of the films. There was a significant difference ($p < 0.05$) between the potato starch-Avicel and corn starch-Avicel films. For instance, at a concentration of 40 µg $CaCl_2$. The potato starch films had a higher tensile strength of 4.07 Mpa compared to corn starch films whose tensile strength is 3.22 Mpa. This shows that the potato starch-Avicel films can resist mechanical damage during handling, processing, and storage more than corn starch-cellulose films. The high levels of amylose in the potato starch compared to relatively low levels of corn starch could significantly influence to the lower tensile strength of the films. Also, there is a significant difference ($p < 0.05$) between the starch-Avicel blended films and the Avicel-only film. This could be due to the increase in starch and $CaCl_2$ concentration that increases films tensile strength.

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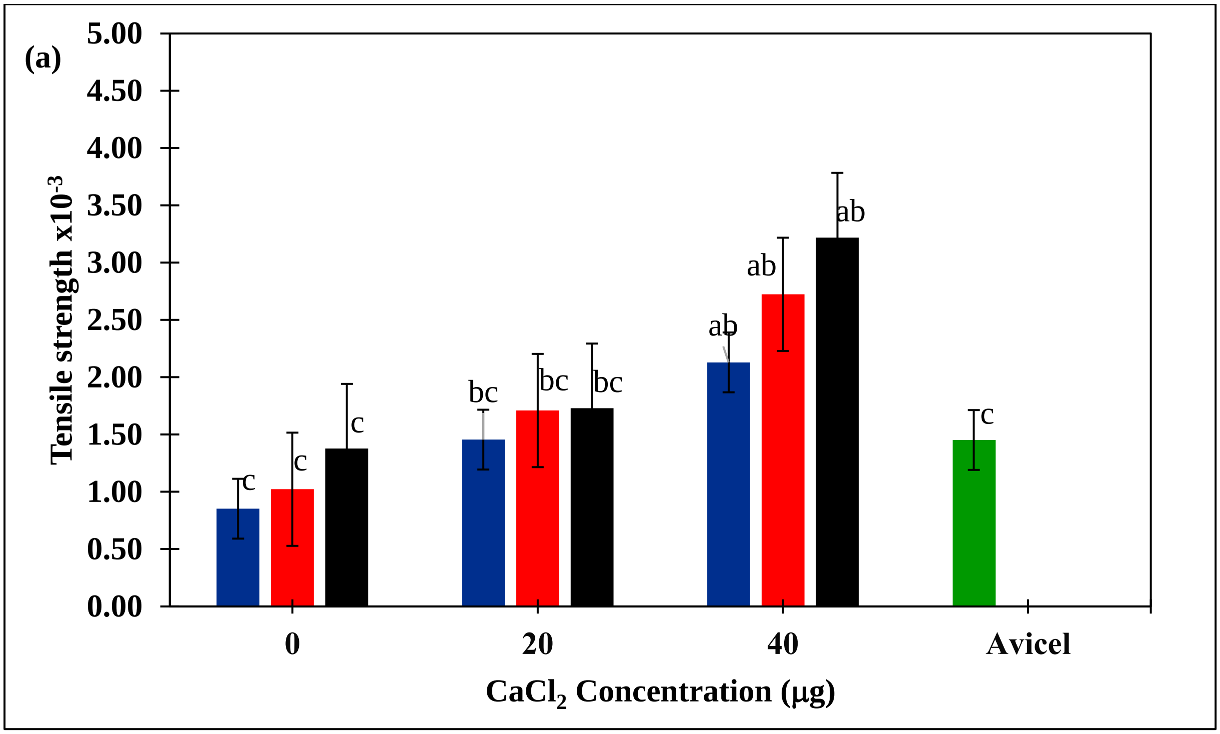


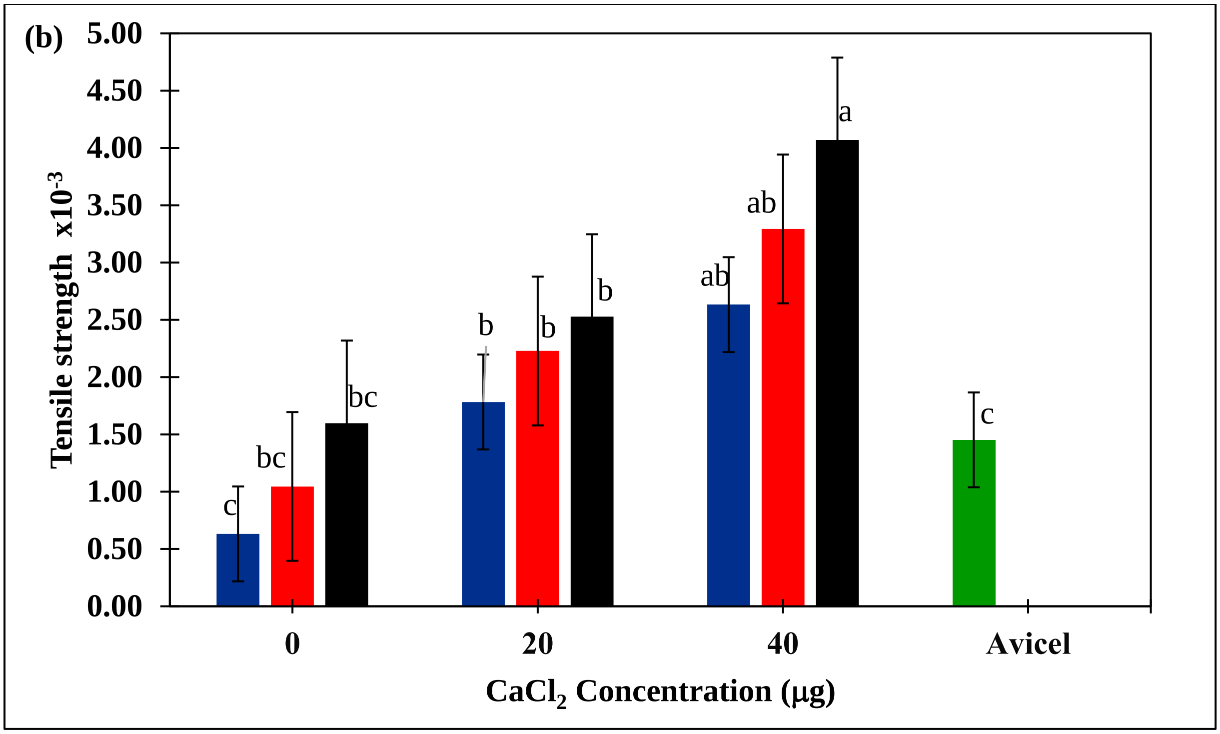


Figure 22: Tensile strength comparison of (a) corn starch-Avicel and (b) potato starch-Avicel, Avicel and plastic films.

4.2.9 Biodegradability

Starch-cellulose based biodegradable films are economical, abundant, and renewable. Their degradation behavior is important to obtain controlled-release or to reduce the time required for the plastic to disappear from the environment; studies on the influence of specific starch structures on the films degradation can help to design starch-cellulose blended materials for different purposes with desirable degradation rates. The Figure 23 highlights the percentage weight left for the corn and potato starch-cellulose films after being buried in the soil for 30 days. The total weight loss for corn starch films was between 94.87 to 96.84%, while that for potato starch-Avicel films ranges between 95.01-95.94%. The films gradually decomposed, hence a reduction in weight. There is no significant differences observed ($p > 0.05$) between decrease in weight for the corn starch-

Avicel and potato starch-Avicel films. These results agree with the findings of starch films with a total weight loss of more than 90% after 31 days (Torres, Troncoso, Torres, Díaz & Amaya, 2011). There is a significant difference observed ($p < 0.05$) between decrease in the starch-cellulose based films and the petroleum-based film. The weight of the plastic film is fairly constant over the period and only 20% is lost. Similar findings were observed on cellulose fiber-reinforced with poly(vinyl alcohol) films (Laxmeshwar, Madhu Kumar, Viveka & Nagaraja, 2012). Overall, the prepared films have the desirable biodegradability rate that could help to combat problems associated with degradation of petroleum-based plastics.

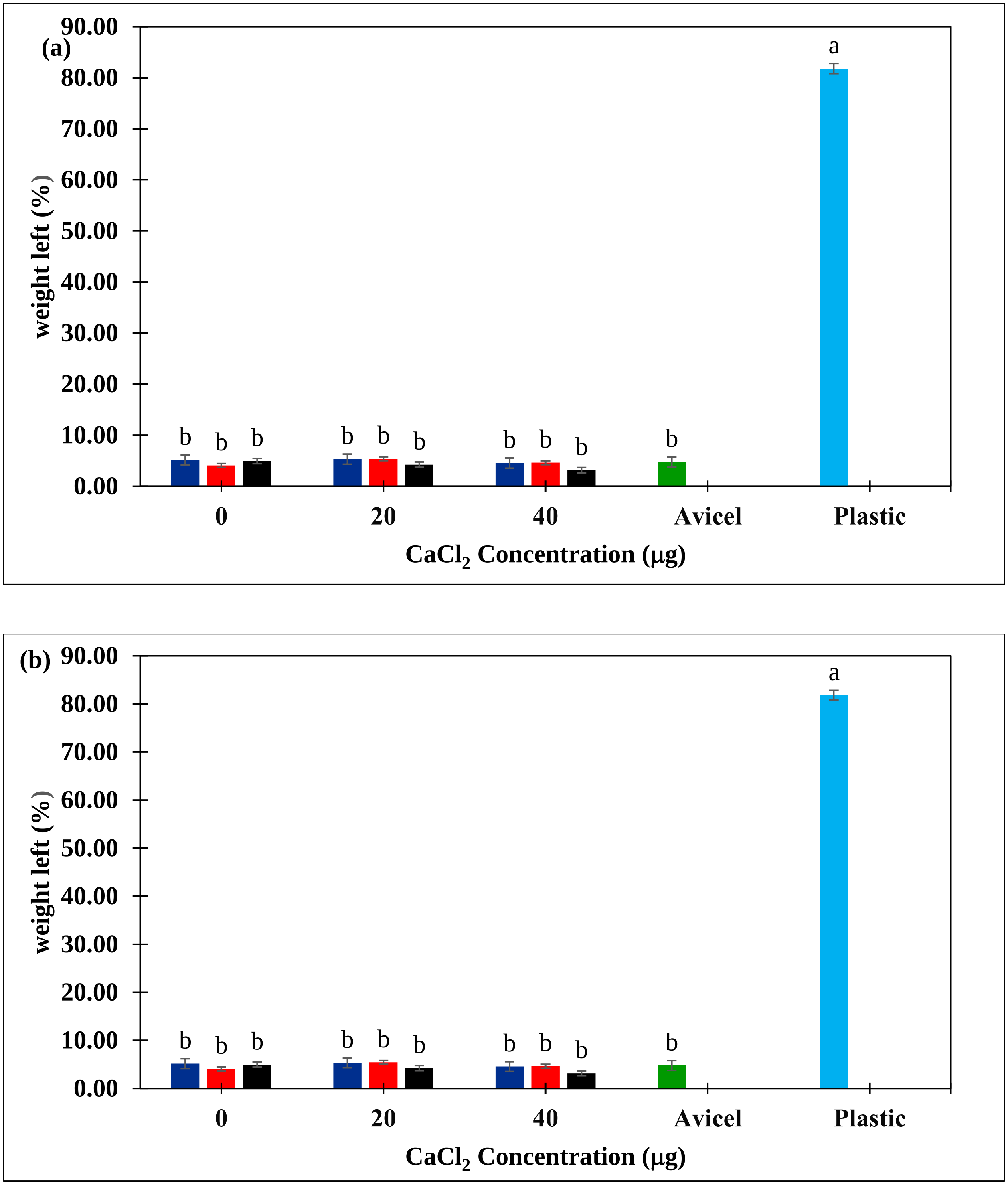
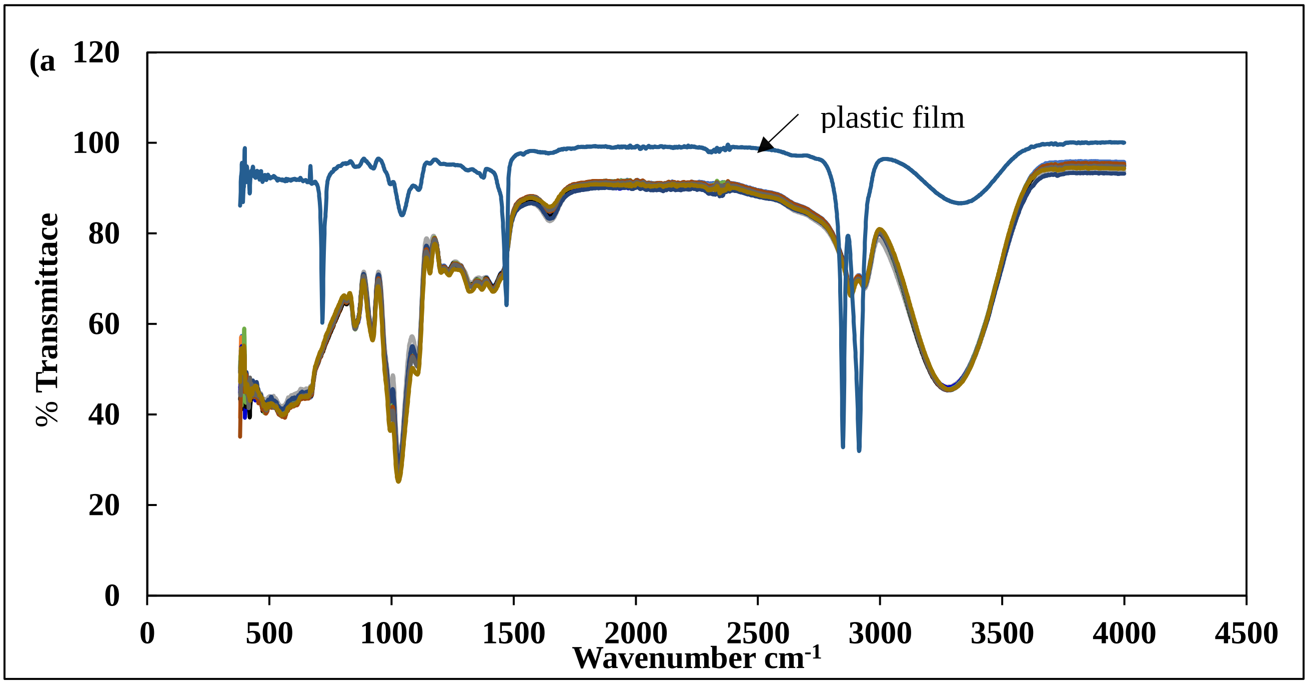


Figure 23: The biodegradability comparison of (a) corn starch-Avicel and (b) potato starch-Avicel,

Avicel, and plastic films.

4.2.10 FTIR Characterization

Fourier-Transform Infrared Spectroscopy (FTIR) spectroscopic analysis gives useful information about chemical structure and changes that occur in a polymer system due to blending and casting process. Figure 24 shows the FTIR spectra of MCC-corn starch-Avicel and potato starch-Avicel cellulose films. There is no significance difference between the corn starch-cellulose and potato starch cellulose blended films. The biopolymer films show FTIR bands similar to those reported by Harunsyah, Sariadi & Raudah, (2018). The polymers starch and cellulose are chemically similar, with the same glycosidic units so that the absorptions peaks are same. The observed peaks in the wave number range of 3300 - 3200 cm^{-1} that are characteristic for stretching vibration of C-H and O-H bonds. A broad smooth peak at 3334 cm^{-1} is due to the vibrations of the inter- and intra-molecular hydrogen bonds between starch and cellulose chains and characteristics of stretching vibration of the hydroxyl groups (Rosa et al., 2010). The peak at 1650 - 1660 cm^{-1} represents the C=O vibration. The bands at 1150 - 1200 cm^{-1} represent the C–O–C asymmetrical stretching. Interestingly, no new bonds are noticed due to complex formation of cellulose and starch chains. There is a significant difference between the starch-Avicel blended films, and the petroleum-based films as shown in the figures below. The plastic films generate peaks at different wavelengths than the starch-cellulose films due to presence of different compounds present in the petroleum-based films. This could help explain differences in biodegradation rates in the cellulose-based films and plastic films.



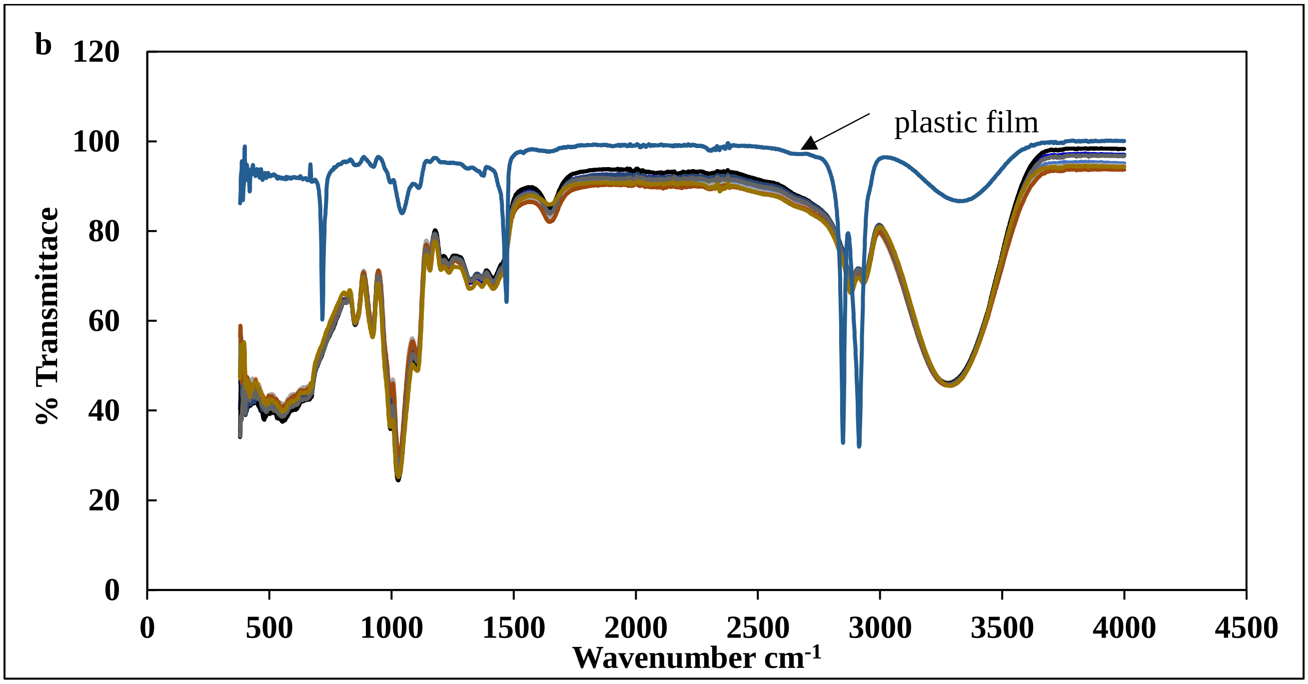


Figure 24: FTIR spectra of (a) corn starch-Avicel and (b) potato starch-Avicel, Avicel, and plastic films.

CHAPTER 5: CONCLUSIONS

Cellulose and starch are naturally found in abundance and are inexpensive biopolymers and can be easily processed to develop biodegradable films that are viable alternatives to petroleum-based plastics. The films prepared in this research have an array of favorable characteristics with unique physicochemical properties with myriad food applications. The potato starch films display higher tensile strengths compared to corn starch films due to the presence of higher amount of amylose. The cellulose-potato starch and corn starch blended films are white and can be conveniently used for products requiring a clear to white packaging. The films have a degree of water solubility, moisture absorption, and water vapor permeability that are closely related to biodegradability which means that the films would disintegrate completely due to the high absorptivity rate. The presence of hydrophilic groups in starch determine the swelling nature, hence moisture absorption rate of the films. Their degradation behavior is important to obtain controlled-release or to reduce the time required for the plastic to disappear from the environment; studies on the influence of specific starch structures on the films degradation can help to design starch materials for different purposes with desirable degradation rates. The FTIR spectra reveal the presence of organic matter in the starch-Avicel blend films which translates to high degradability. The agricultural-cellulose based films can be conveniently used to package foods products that are light and oxygen sensitive, while the MCC films can be used on products requiring a clear or transparent packaging.

The films have the functional properties of packaging material and could have potential to preserve food and extend storability, which needs to be proved. The films are eco-friendly and fit-for-purpose substitute to petroleum-based packages. The bio-based films can be a sustainable replacement for the single-use plastics because the polymers are abundantly available in nature. Since the films are biodegradable, they will help to alleviate the pollution menace that has resulted from petroleum-based packages. These bio-based films will also improve human health along with guaranteed food safety and security, efficient utilization of resources, reduced cost of production of packaging materials and finally, an equivalent of non-plastic alternative.

CHAPTER 6: FUTURE WORKS/ RECOMMENDATIONS

1. Further studies on the addition of substituents such as nanofillers and their ability to lower the sensitivity of films to moisture absorption and hygroscopy have to be established.
2. There is a need for more research to ascertain how the morphology and high molecular weight factors influence film thickness and other physical and mechanical properties.
3. The polymers can be used to develop edible films, and further establishment of their nutritional benefits, sensory evaluation, and their safety through microbiological analysis is in need.
4. The rate of atmospheric transfers due to the nature of the packaging material and its effectiveness in storing food need to be established too.
5. More importantly, large scale production of agriculture-based films needs to be established.

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