UNIVERSITAT ROVIRA I VIRGILI

ALTERNATIVE WATER SOLUBLE POLYMERIC FILMS TO POLY(VINYL ALCOHOL) FOR SINGLE UNIT DOSE PRODUCTS

Jie Ma

ADVERTIMENT. L'accés als continguts d'aquesta tesi doctoral i la seva utilització ha de respectar els drets de la persona autora. Pot ser utilitzada per a consulta o estudi personal, així com en activitats o materials d'investigació i docència en els termes establerts a l'art. 32 del Text Refós de la Llei de Propietat Intel·lectual (RDL 1/1996). Per altres utilitzacions es requereix l'autorització prèvia i expressa de la persona autora. En qualsevol cas, en la utilització dels seus continguts caldrà indicar de forma clara el nom i cognoms de la persona autora i el títol de la tesi doctoral. No s'autoritza la seva reproducció o altres formes d'explotació efectuades amb finalitats de lucre ni la seva comunicació pública des d'un lloc aliè al servei TDX. Tampoc s'autoritza la presentació del seu contingut en una finestra o marc aliè a TDX (framing). Aquesta reserva de drets afecta tant als continguts de la tesi com als seus resums i índexs.

ADVERTENCIA. El acceso a los contenidos de esta tesis doctoral y su utilización debe respetar los derechos de la persona autora. Puede ser utilizada para consulta o estudio personal, así como en actividades o materiales de investigación y docencia en los términos establecidos en el art. 32 del Texto Refundido de la Ley de Propiedad Intelectual (RDL 1/1996). Para otros usos se requiere la autorización previa y expresa de la persona autora. En cualquier caso, en la utilización de sus contenidos se deberá indicar de forma clara el nombre y apellidos de la persona autora y el título de la tesis doctoral. No se autoriza su reproducción u otras formas de explotación efectuadas con fines lucrativos ni su comunicación pública desde un sitio ajeno al servicio TDR. Tampoco se autoriza la presentación de su contenido en una ventana o marco ajeno a TDR (framing). Esta reserva de derechos afecta tanto al contenido de la tesis como a sus resúmenes e índices.

WARNING. Access to the contents of this doctoral thesis and its use must respect the rights of the author. It can be used for reference or private study, as well as research and learning activities or materials in the terms established by the 32nd article of the Spanish Consolidated Copyright Act (RDL 1/1996). Express and previous authorization of the author is required for any other uses. In any case, when using its content, full name of the author and title of the thesis must be clearly indicated. Reproduction or other forms of for profit use or public communication from outside TDX service is not allowed. Presentation of its content in a window or frame external to TDX (framing) is not authorized either. These rights affect both the content of the thesis and its abstracts and indexes.

Alternative Water Soluble Polymeric Films to Poly(vinyl alcohol) for Single Unit Dose Products

by

Jie Ma

Doctoral Thesis

Supervisors:

Dr. José Antonio Reina Lozano
Dr. Florence Courchay

UNIVERSITAT ROVIRA i VIRGILI

Tarragona

2020

UNIVERSITAT
ROVIRA I VIRGILI

Department of Analytical Chemistry and Organic Chemistry

C/ Marcel·lí Domingo, 1
Campus Sescelades
43007, Tarragona
Tel: 977 559 769
Fax: 977 558 446

Florence Courchay, Principle Scientist at the Procter & Gamble Services Company NV, R&D Process Converting and Film development, Soluble Unit Dose Department; and José Antonio Reina Lozano, Associate Professor at the University Rovira i Virgili, Department of Analytical Chemistry and Organic Chemistry.

We state that the present study, entitled "Alternative Water Soluble Polymeric Films to Poly(vinyl alcohol) for Single Unit Dose Products", presented by Jie Ma for the award of the degree of Doctor, has been carried out under our supervision at the Department of Chemical Engineering at the University Rovira i Virgili, and that it fulfils all the requirements to be eligible for the Doctor International Mention.

Tarragona, 09 January 2020

Supervisor of the doctoral thesis:

Dr. Florence Courchay

Supervisor of the doctoral thesis:

Dr. José Antonio Reina Lozano

Acknowledgments

First of all, I would like to express my sincere gratitude to my supervisors, Dr. José Antonio Reina Lozano and Dr. Florence Courchay for their supervision, for providing continuous guidance and generous support on my PhD study, for always encouraging me to be confident, and for their patience, motivation and immense knowledge. They have always been tremendous mentors for me, both in research field and in my career development. I am also grateful to have Dr. Tània Gumí as my supervisor in the initial part of my PhD study, and I would like to thank her for all the kind help.

Besides, I would like to thank the SMARTMEM committee for enrolling me to carry on my research in both Universitat Rovira i Virgili (URV) and Procter & Gamble Brussels Innovation Center (P&G BIC), for giving me access to laboratory and research facilities in both sectors, and for the excellent administrations. SMARTMEM has provided me such a great opportunity to experience both academic and industrial world during my 3-year PhD study, has offered plenty of useful trainings and workshops on techniques and on my personal/career grow, and has given me chances to go to different part of the world to disseminate and communicate my research work.

I sincerely thank all the supervisors and staffs in the frame of SMARTMEM program. My special appreciation goes to Dr. Regine Labeque for her kindness, her caring, her constant guidance and brilliant advises on my PhD work. I also would like to give special thanks to Professor Marta Giamberini for all her generous help and support. I would like to thank Professor Ricard Garcia-Valls from URV, and Dr. Alberto Martinez, Mr. Miguel Brandt, Dr. Raul Rodrigo Gomez, Dr. Emily Boswell and Ms. Susana Fernandez Prieto, from P&G, for their trainings and invaluable professional suggestions on my research work. What’s more, I would like to thank Ms. Fabienne De Decker and Ms. Gabriela Espinosa for helping me in Belgian and Spanish visa

paper work, relocation, and all the administrations. My sincere thanks also go to my SMARTMEM colleagues, Gianmarco, Mario, Rita and Domenico, during these 3 years we supported each other, helped each other, shared best moments and went through difficulties all together; we shared cultures and created a lot of beautiful memories.

My thanks go to Memtec group in URV. Other than the professors mentioned, I would like to specially thank Pepa for all the management in lab and warm help in daily life. I thank Nuria for kindly providing administration information in the department of chemical engineering in URV. Moreover, I would like to give thanks to Bartosz, Ada, Anna, Kamila and Ruben for all the help, for teaching me tricks in chemistry in lab 212/312, also for sharing lovely moments with me in our group events.

I also would like to give my thanks to all the colleagues in SUD department in P&G BIC, which is full of incredible, extraordinary and smart people that inspire me at work every day. I enjoyed a lot both the physical and social environment there: open space, nice and energetic people, coffee area, interesting conversations and funny department activities. I learned a lot from technical trainings and people. I would like to thank Duong, Stefan, Els, Johan, Cindhuja, and Ann for generously giving me trainings on different perspectives of research in SUD. My special thanks go to the film team, especially Varlik and Luca for their trainings to me on film property tests and daily support in the film lab. I also would like to thank Inge and Eva for their kind help in administrative issues in the department.

I would like to thank all technicians of Servei de Recursos Científics i Tècnics in URV and Analytical department in P&G BIC for kindly helping me in my sample characterization and analysis, especially Koen, Jurgen, Mariana and Francesc.

My stay in Tarragona and Brussels were fantastic because of special friends I met on my way. I could never imagine that I would find such a special group of friends. I would like to thank a lot of people: Zhonghao, Kamila, Meri, Andrea, Xavier, Keo, Joel, Miguel, Nais, Yvonne, Davide, Begoña, Adri, Silvia, Marta, Carlos, Ines, Maria, Xuzhao, Zhiwu, Xiaozhen, Kevin, Yiou, Constantina, Aleksandra, Carolina, David, Lucia, Giuseppe, Alessandro, Gianmarco, Fabiana, Sylvia, Erick… with whom I shared good time in playing pingpong, after work events, and weekend activities. I would like to thank all the fellows who participated Ekiden run with me and recognized me as captain: Joel, Leone, Mario, Jean and Nelly: we did a good job all together!

A special appreciation to my boyfriend, my best friend, and the man of my life: Pau. I feel so lucky that I got to meet you, know you and fall in love with you during this PhD journey. Thanks for always supporting me and tolerating me during all the time, and for helping me at any time I need. Thank you for being so understanding, and for being such a great friend. I look forward to a life with you. I love you!

A great gratitude to my family: my grandfather, my parents, and my brother, for their endless love and support throughout my life. They always encouraged me to be myself, to be brave, to work hard, and to follow my dream, and they always believe in my ability to achieve my goals. I can always feel your love, as I can always feel grandma’s guidance from long distance. Your belief in me has made this journey possible. 我爱你们!

Thank you all for your advices, guidance and support!

Jie Ma

To people I love

LIST OF ABBREVIATIONS

DH	Degree of hydrolysis
DMA	Dynamic mechanical analysis
DP	Degree of polymerization
DPG	Dipropylene glycol
DSC	Differential scanning calorimetry
DVS	Dynamic vapor sorption
ESEM	Environmental scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
GA	Glutaraldehyde
HSP	Hansen solubility parameters
HSPip	Hansen solubility parameters in practice
IEP	Isoelectric point
M_W	Molecular weight
NaCAS	Sodium caseinate
PA	Polyamides
PBAT	Poly(butylene adipate-*co*-terephthalate)
Pdiol	Propylene glycol
PE	Polyethylene
PEG	Polyethylene glycol
PEO	Polyethylene oxide
PP	Polypropylene

PS	Polystyrene
PU	Polyurethanes
PVA, PVOH	Poly(vinyl alcohol)
PVAc	Poly(vinyl acetate)
PVC	Poly(vinyl chloride)
PVP	Polyvinylpyrrolidone
P&G	Procter & Gamble
RH	Relative humidity
SA	Sodium alginate
SRI	Stain removal index
SUD	Single unit dose
Tc	Crystallization temperature
Tg	Glass transition temperature
TGA	Thermo gravimetric analysis
Tm	Melting temperature
WVP	Water vapor permeability

Table of Contents

Chapter 1. General Introduction and Objectives

1.1 Background

The single unit dose (SUD) product – laundry detergent pod (pouch) (**Figure 1-1**) is a new form of detergent emerged in the consumer market in 2012 by Procter & Gamble as Tide pods. Laundry detergent pod is a water-soluble pouch that contains highly concentrated laundry detergent, softener and other laundry products wrapped by a water-soluble film. The pack makes proper dosage for a normal-size laundry load, which is easy to dose, handle, transport and store, and effective, convenient and simple for consumers to use.

Figure 1-1 Laundry detergent pod.

The functions of the water-soluble film are: 1) it is used to pack detergent; 2) it separates closed compartments in a multi-compartment pod; 3) it limits migration of detergent ingredient; 4) in a laundry appliance, the film dissolves in water and release all the ingredients.

Currently, the most used water-soluble material for the laundry detergent pod is poly(vinyl alcohol) (PVA). As a film-forming polymer, PVA has advantages over many other water-soluble polymers, such as its high water solubility, excellent mechanical properties, and good water vapor barrier properties. However, as SUD business continues to grow, we would like to look for alternative polymers showing similar solubility, permeability and mechanical properties of PVA, and to discover if they would bring more benefits.

Knowing that the films for SUD products must be dissolved to release the detergent during laundry appliance, the key and starting point would be looking for water soluble polymers, and then test the compatibility with current detergent. Water soluble polymers should be very polar, with functional groups such as hydroxyl group, carboxyl group, amine group, amide group, etc. However, the starting polymers might not meet all the requirements, hence chemical modification or blending may be necessary to tune the properties.

To check the potential applicability of the new materials, the performance of every new film prepared will be compared with that of conventional PVA films; the results will also provide a necessary feedback for further polymer modifications and/or blending. Thus, the choice of the starting polymers for the further modifications/blends will be made by taking into account the strong and weak points detected on the previously used materials, and the known structure-properties relationships.

This project “Alternative water-soluble polymeric films to PVA for single unit dose products” is aimed to focus on single unit dose for fabric and home care pods without changing the current structure, and the scope may include polymer blends with less than 40% PVA. Starch polymers were purposefully neglected as other groups within P&G are investigating them.

1.2 Water-soluble polymers

A polymer is a large molecule or macromolecule composed of many repeating units. Polymers have been synthesized to suit specific needs or rather solve specific problems, so there is need to understand the role of polymers. Polymers can be classified based on any of the following categories: 1) source (natural, semi synthetic, synthetic); 2) structure of polymer (linear, branched chain, crosslinked or network polymers); 3) type of polymerization (addition, condensation polymers); 4) thermal and mechanical behavior (elastomers, thermoplastic, thermosets); 5) biodegradability (biodegradable, non-biodegradable) [1].

Many polar synthetic polymers dissolve, disperse, or swell in water, resulting in modifying the physical properties of aqueous systems in the form of gelation, thickening or emulsification/stabilization. They have repeating hydrophilic units or blocks of units, the polymer chains obtain hydrophilic groups that are substituents or are incorporated into the backbone. The hydrophilic groups can be non-ionic, anionic, cationic. There are various functions of these polymers: used as dispersing and suspending agents, stabilizers, thickeners, gellants, flocculants and coagulants, film-formers, humectants, binders and lubricants [2].

There are polymers of the same function that can be obtained from natural resources, such as starch, gum, pectin, protein, cellulose, etc.

There are various industrial applications of water-soluble polymers, such as coatings, adhesives, pharmaceuticals, food, paint, water treatment, textiles, constructions and paper [1].

Here in this thesis, we focus on film-forming water-soluble polymers that have the potential to be used in single unit dose applications.

1.2.1 Poly(vinyl alcohol) (PVA)

1.2.1.1 Chemical structure and preparation of PVA

Poly(vinyl alcohol) is one of the most important water-soluble synthetic polymers. Its general formula is $[CH_2CH(OH)]_n$. PVA has a chemical structure with a pendant hydroxyl group.

PVA is not prepared by polymerization of the corresponding monomer - vinyl alcohol, since it tautomerizes to acetaldehyde under normal condition. Therefore, PVA is produced by the hydrolysis of poly(vinyl acetate) (PVAc), following the polymerization of vinyl acetate [3]. The preparation procedure of PVA from vinyl acetate can be seen from**Figure 1-2**.

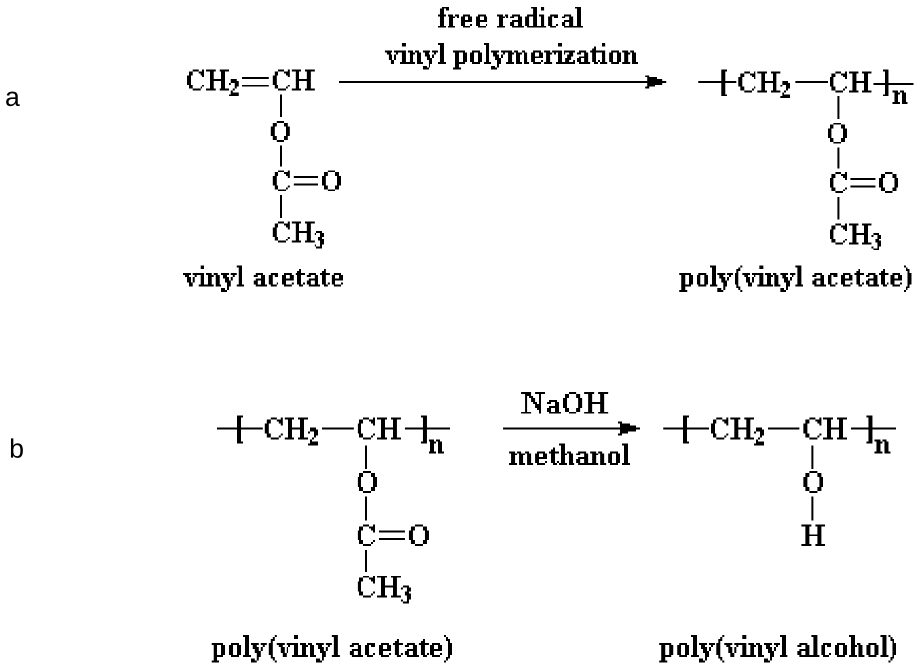


Figure 1-2 Preparation procedure of PVA: a. Free radical vinyl polymerization of vinyl acetate, b. hydrolysis of poly(vinyl acetate).

PVA was discovered by Haehnel and Hermann [4], who added alkali to a clear alcoholic solution of PVAc, and obtained ivory-colored PVA. The degree of hydrolysis in PVA is determined by the molar percentage of acetate groups in the PVAc feedstock that are replaced by hydroxyl groups. Commercial PVA grades are generally classified as fully hydrolyzed, and partially hydrolyzed (**Figure 1-3**) [5][6].

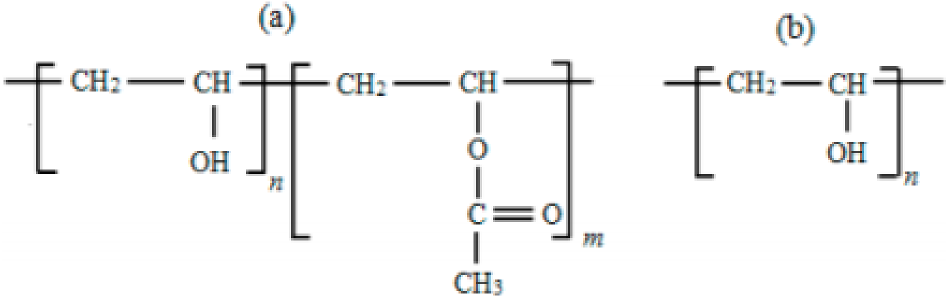


Figure 1-3 (a) Partially hydrolyzed and (b) fully hydrolyzed PVA.

1.2.1.2 Properties of PVA

PVA is soluble in polar solvents, i.e. water, dimethyl sulfoxide (DMSO), ethylene glycol (EG), and *N*-methyl pyrrolidone (NMP).[7] PVA exhibits outstanding chemical resistance and physical properties, which resulted in broad industrial use. It is an excellent adhesive, possessing oil, grease and solvent resistance.

PVA molecular weight (depending on degree of polymerization (DP)) and degree of hydrolysis (DH) greatly affect the overall behavior of PVA and sometimes determine the specific applications. At a constant degree of hydrolysis, the more the PVA molecular weight increases, the more viscous the PVA solution is in water, the higher the tensile strength and water resistance of the resulting PVA film; at a constant molecular weight, a high degree of hydrolysis decreases water solubility, and increases water resistance, crystallinity, and tensile strength of the resulting film. A summary of the general trends of the influences of molecular weight and degree of hydrolysis on the properties of PVA can be seen in **Figure 1-4** [8].

The solubility, viscosity, and surface tension of PVA solutions depend on temperature, concentration, % hydrolysis and molecular weight of the material

[9].

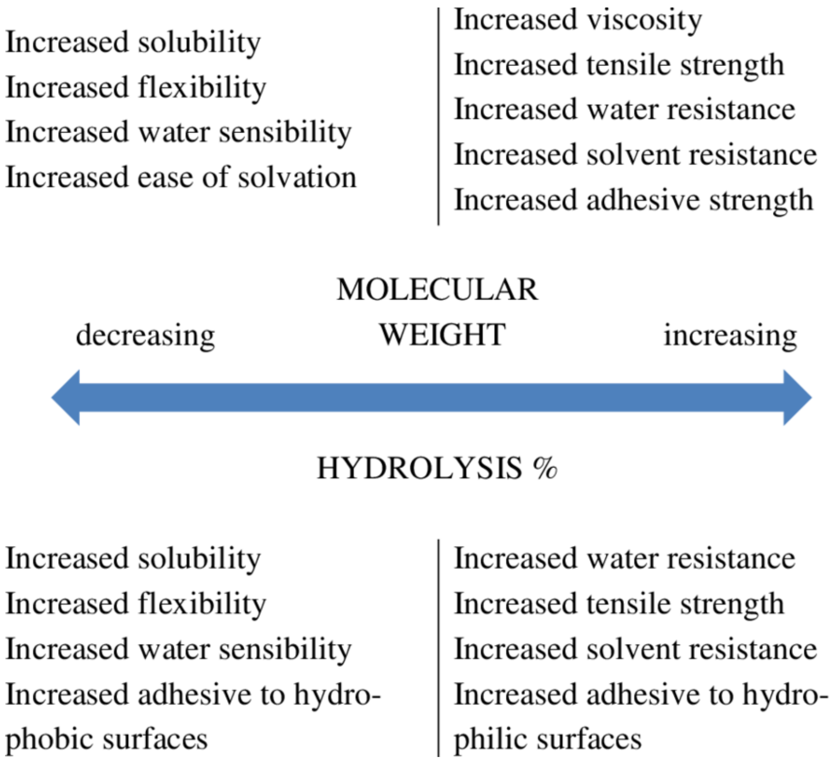
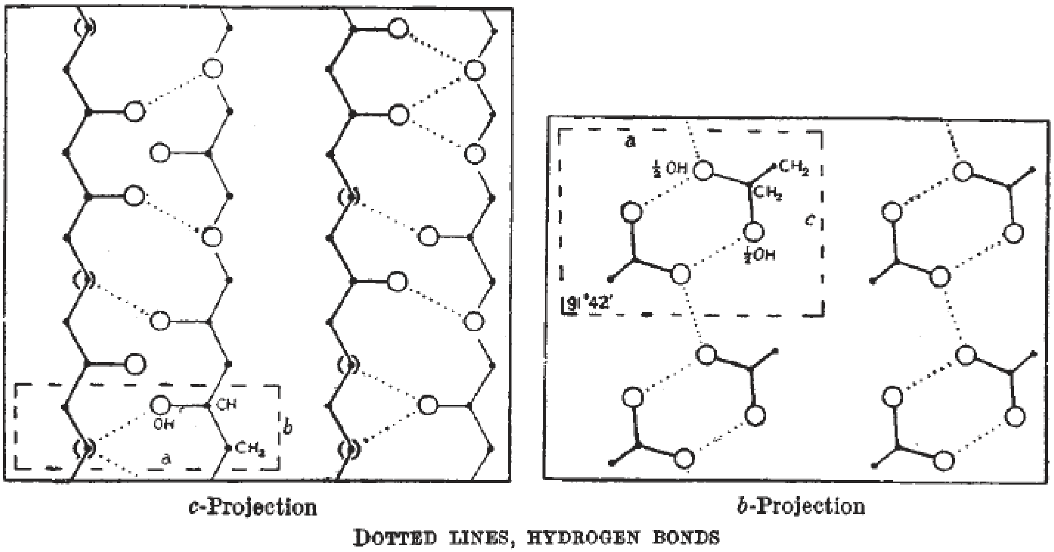


Figure 1-4 Effect of molecular weight and degree of hydrolysis on the properties of PVA [8].

1.2.1.3 Crystal structure of PVA

PVA is semi-crystalline. The highly crystalline structure of PVA has been noted when it was produced in the early years. Bunn suggested that the random steric pattern of substituents made PVAc noncrystallizable, however, when hydrolysed to PVA, with smaller hydroxyl groups, it is crystalline because of hydrogen bonding. **Figure 1-5** shows the crystal model of PVA, where hydroxyl groups are randomly arranged in left- and right-hand positions in a highly satisfactory way. The arrangement may be described as a layered structure, where a double layer of molecules is held together by hydroxyl bonds [10].



c-Projection

b-Projection

DOTTED LINES, HYDROGEN BONDS

Figure 1-5 Crystal model of PVOH [10].

Atactic PVA has a high melting point, resulting from the high level of hydrogen bonding in crystals. Also the hydrogen bonding controls the water solubility of the polymer: the polymer won't dissolve until the crystal structure is broken even though the amorphous part of the polymer may be swollen by the ingress of water [11].

1.2.1.4 Applications of PVA film for detergent

PVA has good to excellent film-forming, water-soluble, adhesion, elasticity and barrier properties, for which it has been widely used in water-soluble films packaging applications. Films made of PVA have high tensile strength, oxygen and water vapor barrier properties.

Many patents have been published disclosing the use of PVA homopolymer or copolymer and its blending, forming films for packing detergent unit dose products [12]–[21]. For example, F. De Buzzaccarini, S. Coosemans and L. Gualco invented water-soluble, liquid-containing pouches where the film is mainly made of PVA [18]; G. Delamarche, D. Ingram and G. Spieles invented water-soluble pouches wrapped by modified PVA film with powder coatings to reduce weeping [12]; V. Catalfamo invented water-soluble substrates made of modified PVA film with resistance to dissolution prior to being immersed in water [13].

1.2.2 Possible candidates among water-soluble polymers

Possible materials for the project can be water-soluble polymers containing functional groups such as hydroxyl, carboxyl, amine, amide, sulfonate, etc. We should also consider other properties such as film forming properties, tensile strength, thermoforming properties, sealing ability, and chemical resistance since the film is intended to be used in single unit dose products.

As mentioned above, we have purposefully neglected starch polymers as other groups within P&G are investigating them, so we searched for water soluble polymers (non-PVA/non-starch) that are used in the field of film packaging in patents and literature.

1.2.2.1 Patent landscaping

Prior art has been segregated into 5 categories of water soluble polymers.

1. Non-PVA/ Non-starch compositions that are used to make water soluble detergent pouches;

2. Non-PVA/ Non-starch compositions that are used to make water soluble pouches or capsules in other applications such as agriculture, medical, etc.;

3. Non-PVA/ Non-starch water soluble compositions that are applied over a substrate;

4. Water-soluble films made of starch or glucans and are used for making

detergent pouches;

5. Water-soluble films that can be made by using any of the compositions based on a list of polymers among which PVA/starch is also present.

The 1st and 2nd categories are more interesting for this PhD project, since this project is focusing on water soluble films that are used for pouches that are non-PVA/non-starch.

8 references are disclosing water soluble film compositions that are exclusively made of neither PVA nor starch under the category of non-PVA/non-starch pouches used in detergent field:

EP0556781B1 discloses a film particularly as a packaging material for powder detergents prepared from a water-soluble copolymer of *N*-vinylacetamide, and a vinyl monomer other than *N*-vinylacetamide. Film is molded with the copolymer and plasticizer, and the film is susceptible to low changes in chemical and physical properties after a long storage, hence solubility in water is maintained [22].

FR2997402A1 describes a water-soluble film for packaging solid composition such as detergents, comprising mainly guar gum and gelatin. The resulting film is biodegradable and has good mechanical properties and good stability at room temperature [23].

EP1784448 claims a water-soluble film comprising polyamid and nanoclay prepared by solvent casting for the packaging of detergents. The incorporation of nanoclay helps control the viscosity of the polyamide solution without adjusting the concentration of the solution or molecular weight of the polyamide [24].

EP0388105 invented a unit packaging detergent with water-soluble film that comprises a polyester of a polyether polyol containing polyoxyethylene groups. The advantage of this film is it can maintain a very high mechanical stregth under a high humidity thanks to its low equilibrium moisture content [25].

US2016/0244701 claims an invention of water-dispersible films comprising an ethylene acrylic acid copolymer and a crosslinking agent that are suitable for packaging high water containing formulations such as liquid detergents. The films selectively disintegrate in media with high water content, depending on the ionic strength of the media [26].

US4557852 describes a polymer sheet for delivering laundry care additive and other laundry care products such as bleach, comprising low molecular weight acrylic copolymers; this invention avoids clumping of the active ingredient and minimizes spot damage to the fabrics [27].

US7057008 discloses an invention related to packaging mainly made from water-soluble nylon compositions that is suitable for any of a number of conventional molding applications including blow molding [28].

WO9700282 describes a water-soluble film that is suitable for sachets for packaging agrochemical and laundry care compositions, comprising mainly acid-functional olefinic addition copolymer; the film is flexible and plasticizer-free [29].

16 references were found disclosing the use of water-soluble films or pouches or capsules in application areas other than detergents (**Figure 1-6**) [29]–[44]. The patents disclose the list of polymers from which film can be made and may also include PVA/starch along with other polymers. Majority of water-soluble films are made using Natural polymers and Polyethylene oxide/ polyethylene glycol. Gums, gelatin, proteins, etc., are grouped under natural polymers. Gelatin is widely used

for food packaging and gums are used in edible film packaging. Agricultural chemicals, Medical, Food packaging and Edible films are the areas where the water-soluble films are made with polymers other than PVA or starch.

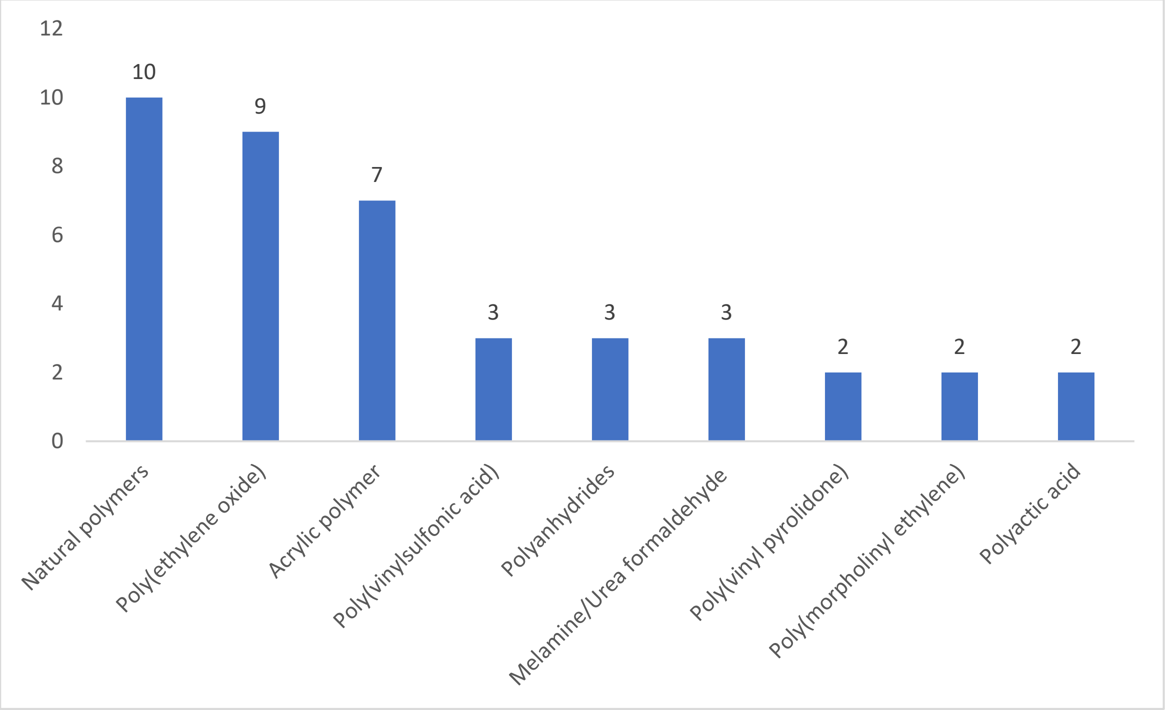


Figure 1-6 Patents under the category of Non-PVA/Non-Starch + Other applications.

Based on the patent landscaping results, checked market availability and price, we chose to investigate the following polymers: polyethylene oxide (PEO), polyvinylpyrrolidone (PVP), sodium alginate (SA) and Lactips material (made of milk protein) for initial screening. These polymers were selected also considering their properties such as cold water solubility, film-forming property, mechanical properties, biodegradability, and chemical resistance. **Table 1-1** compares the properties of these polymers with PVA.

Table 1-1 Properties comparison of selected water-soluble polymers.

	PVA	PEO	PVP	Sodium Alginate	Lactips
Solubility in cold water	medium	high	medium	medium	medium
Also soluble in	none of common solvents	many organic solvents	polar solvents	none of common solvents	many organic solvents
Film forming property	high	high	high	high	high
Tensile strength	high	medium (depends on MW)	medium	medium	medium
Ductility	medium	medium	medium	low	medium
Sealing ability	water & heat sealing	water sealing	water & heat sealing	water & heat sealing	water & heat sealing
Chemical resistance	poor alkaline and acidic resistance	reactive with oxidizing agents, acids, alkalis.	low reactivity	reacts with phenolic group, compounds of copper and zinc, and quaternary ammonium salts	low reactivity, reacts with enzyme trypsin
Biodegradability	Biodegradable	Biodegradable	Biodegradable	Biodegradable, biopolymer	Biodegradable, biopolymer

1.2.2.2 Polyethylene glycol / polyethylene oxide

Polyethylene glycol (PEG) and polyethylene oxide (PEO) are synonymous. PEG usually refers to polymers with molecular weight less than 20,000 g/mol, and PEO usually refers to larger polymers. In this thesis the term PEG will be taken to include polymers of all molecular weights.

In general, PEG's general formula $H-(O-CH_2-CH_2)_n-OH$, in which n is the average number of repeating oxyethylene groups. It is a linear chain polymer with enteric linkages. PEGs exist in a wide range of molecular weights: PEG 200-600 are liquids at room temperature, PEG 1500 are semisolids, PEG 3000-20,000 and above are semi-crystalline solids, and higher molecular weights (>100,000) are resinous solids [46].

PEG is prepared by the polymerization of ethylene oxide by both acids and bases. PEG is soluble in water and a number of common organic solvents such as acetonitrile, anisol, chloroform, 1,2-dichloroethane, and dimethylformamide. It is insoluble in aliphatic hydrocarbons, diethylene glycol, ethylene glycol and glycerin [47].

The structure of PEG was studied in both the individual molecule conformation in crystalline state, and those molecules arrangement into micro- and macroscopic structures. X-ray diffraction [48] studies suggested that PEG has a helical conformation consisting of seven chemical units and two turns in a fiber identity period of 19.3 Å, which was confirmed by IR [47], Raman [49], and NMR [50] studies, and scanning tunneling microscopy studies have imaged the helical structure [51]. When solid PEG is melted, it loses its helical structure and obtains a liquid containing random coils forms; when PEG is dissolved in chloroform and methylene chloride, it also obtains random coils, while when dissolved in water, it retains the helical conformation, though less ordered [52]. PEGs are arranged as lamellae in the crystal lattice, with chains extended or folded. In both cases, the hydroxyl end groups are rejected onto the outside of the lamellae [53].

PEG is semicrystalline and could contain a significant proportion of amorphous material, which depends on the conditions of sample preparation and molecular weight of PEG. Therefore, PEG exhibits a glass transition temperature that depends on the molecular weight of the material.

PEG is a low-toxic, film-forming material; it is hydrophilic since it has ability to form hydrogen bonds [54] [55]. Because of its relatively low price, favorable low toxicity, biocompatibility, hydrophilicity and water solubility, PEG is widely used in medical/pharmaceutical use, cosmetic use, chemical use, and biological use. PEG can be applied in adhesives, thickeners, contact lens fluids, stabilizers, friction reduction agents, plasticizers and solubilizing agents for drugs [56].

1.2.2.3 Polyvinylpyrrolidone

Polyvinylpyrrolidone (PVP), commonly called polyvidone or povidone, is a water-soluble polymer produced from the polymerization of the monomer *N*-vinylpyrolidone [57]. Its chemical structure is shown in **Figure 1-7**. PVP was firstly developed in Germany by I. G. Farben during the 1930s, to be as a blood plasma expander for trauma victims [58].

PVP is soluble in water and other polar solvents, such as alcohols, acids, ethyl lactate, glycols, lactams and nitroparaffins. PVP is widely used in personal-care, pharmaceutical, agricultural, and industrial products, because of desirable performance attributes: biological compatibility, low toxicity, film-forming and adhesive characteristics, complexing ability, relatively inert behavior toward salts and acids, and thermal and hydrolytic stability [59].

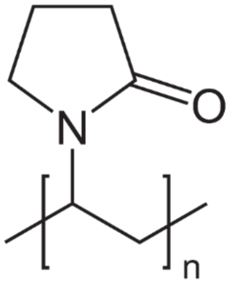


Figure 1-7 Chemical structure of PVP.

1.2.2.4 Sodium Alginate

Sodium alginate is a biopolymer with a large availability in nature. Sodium alginate is the salt of alginic acid, which is a polysaccharide obtained from brown seaweeds. Alginate is a linear copolymer with homopolymeric blocks of (1-4)-linked β-D-mannuronate and its C-5 epimer α-L-guluronate residues, respectively, covalently linked together in different sequences or blocks. The chemical structure of sodium alginate can be seen in **Figure 1-8**.

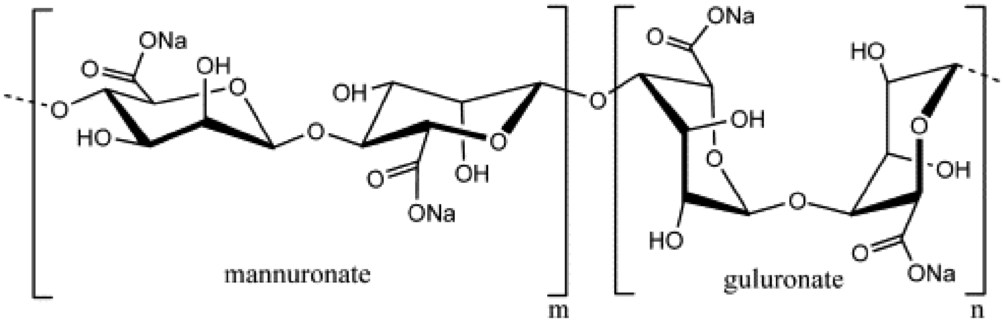


Figure 1-8 Sodium alginate chemical structure.

Alginate can be extracted from raw seaweeds by a treatment with aqueous alkali solutions, typically NaOH, in which the natural alginate in various salt forms is converted into water-soluble sodium alginate [60]. After filtration, by adding calcium chloride, the alginate can be precipitated from the solution.

Alginate has particular colloidal properties such as thickening, suspending, film forming, gel producing, and emulsion stabilizing, which makes it a potential biopolymer film or coating component. It is very consumer-friendly because it is renewable, biodegradable, and vegetable. It has been widely used in food, fabric and medical fields [61] [62].

More recently, alginate has been investigated extensively because of its tissue compatibility and use in tissue engineering, including the regeneration of skin tissue, cartilage, bone, pancreas, liver, muscles and nerves, in addition to being used in the encapsulation of cells for the controlled release of drugs [63].

1.2.2.5 Lactips material

Lactips is a thermoplastic material, made from the main protein of milk - casein. Lactips material is composed of a) 65%-75% casein and/or caseinate (3 embodiments: only casein, only caseinate, casein/caseinate blends); b)15%-25% plasticizer (preferably water and/or glycerol); c) 15%-20% biodegradable polymer (preferably PBAT: Poly(butylene adipate-*co*-terephthalate)) [64]. Lactips material is an amorphous material that appeared as pale yellow pellets without odour. It is water-soluble, biodegradable, bio-compatible and even edible.

- Caseins and caseinates

Caseins represent about 80% of proteins in milk. Casein is a type of phosphoprotein containing about 0.85% phosphorus. The phosphate groups are responsible for many of the important characteristics of casein, especially its ability to bind relatively large amounts of calcium, transporting calcium to the young generation. Calcium binding by the individual caseins is proportional to the phosphate content. Casein consists of α(s1)-, (s2)-, β- and κ- casein, with molecular weight 23614, 25230, 23983 and 19023, respectively. [65]

The large number of proline residues in caseins leads the protein chain to bend particularly, which inhibits the formation of closely packed secondary structures. Because of this the hydrophobic residues result in strong association reactions of the casein monomers and render them insoluble in water [66].

Casein is precipitated from skim milk by acidifying it to produce acid casein, or the milk is treated with rennet to produce rennet casein. The precipitated casein curd is separated from the whey, washed, and dried. The water-soluble derivatives of acid caseins, produced by reaction with alkalis, are called caseinates [67].

All the major caseins associate with themselves and with each other. At low temperature (4°C), casein exists in solution as monomers (**Figure 1-9** shows the β-casein monomer), and the monomers polymerize as the temperature increases. The degree of polymerization increases with increasing protein concentration and increasing temperature. The major caseins interact with each other and in the presence of Ca^{2+}, these associations lead to the formation of casein micelles [65].

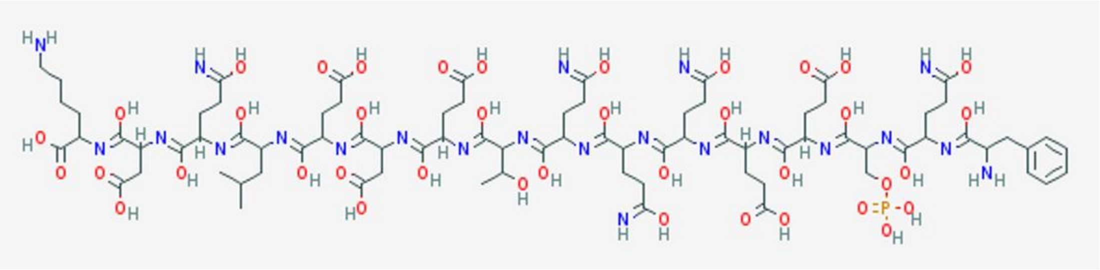


Figure 1-9 Chemical structure of β-casein monomer.

In terms of physical chemistry, the casein micelles exist in milk as a very stable colloidal dispersion. As a protein, casein is made up of hundreds of individual amino acids, each of which may have a positive or a negative charge, depending on the pH of the milk system. At isoelectric point (IEP), all the positive charges and all the negative charges on the casein remain in balance (i.e., the net charge on the protein is zero); this pH value is 4.6 for casein. The IEP is the pH at which the protein is least soluble [67].

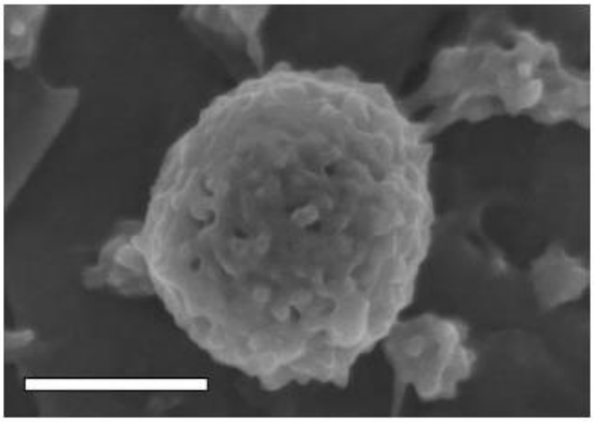


Figure 1-10 Electron micrograph of an individual casein micelle. Scale bar=200nm [68].

About 85% to 90% of casein in bovine milk exists in a colloidal form, known as micelles, which are porous, spherical aggregates with diameters ranging from 50 to 600 nm. Figure 1-10 shows the micellar structure of casein [68]. Various models of have been suggested for the casein micelle structure. It has been suggested that the integrity of the micelle is attributed to the hydrophobic interactions between casein molecules, between caseins and calcium phosphate nano-clusters, or between casein aggregates and casein-calcium phosphate aggregates. The structure of the casein micelle is still elusive, but the “hairy” layers of κ-casein on the surface of the micellar structure are generally accepted [69].

The main casein components have several genetic variants and contain variable numbers of phosphoryl residues, especially α(s_2)-casein exhibiting a large variability in phosphorylation. κ-Casein contains only one phosphoryl residue, and it is also glycosylated. Another unique feature of caseins is the large amount of proline residues, especially in β-casein, which greatly affects the structure of caseins, because the proline residues disrupt the formation of α-helix and β-sheet.

In addition, all casein proteins have different hydrophobic and hydrophilic regions along the protein chain. α(s)-caseins contain 8-10 seryl phosphate groups, while β casein contains about 5 of these residues, and it is more hydrophobic than α(s) -caseins and κ-casein. Because α(s)-caseins and β-caseins are highly phosphorylated, they are very sensitive to the concentration of calcium salts, that is, they will precipitate with excess Ca^{2+} ions. Unlike other caseins, κ-caseins are glycoproteins, and they have only one seryl phosphate group. Hence, they are stable in the presence of calcium ions, and they play an important role in protecting other caseins from precipitation and make casein micelles stable.

Casein is not heat sensitive; only temperatures up to or above 120^{o}C causes the casein to gradually become insoluble, whereas they are sensitive to pH and will precipitate at its isoelectric pH [70].

Caseinate is produced from freshly precipitated acid casein curd or from dry acid casein by reaction with dilute alkali solutions. Sodium caseinate and calcium caseinate are the two commonly widely used forms of casein, which are used as a source of nutrition, for pharmaceutical preparation and in food ingredients. Casein is insoluble in water; therefore, it is necessary to dissolve it into an alkali solution making the pH at 6.5 or higher, to produce a caseinate solution [67].

Caseinates present thermoplastic and film-forming properties due to their random coil nature and their ability to form weak intermolecular interactions – hydrogen bonding, electrostatic bonding and hydrophobic interactions.

- Poly(butylene adipate-*co*-terephthalate)

Poly(butylene adipate-*co*-terephthalate) (PBAT) is an aliphatic-aromatic copolyester that is biodegradable and compostable. It can be degraded within a few weeks with naturally occurring enzymes [71]. The chemical structure of PBAT can be seen in **Figure 1-11**. It consists of butylene adipate unit and butylene terephthalate unit, whose ratio affects the biodegradability and material properties of PBAT; i.e., the rate of biodegradation, thermal and mechanical properties all depend on this ratio. It has reported that the optimal compromise between biodegradability and physical properties of PBAT can be obtained by 35-55 mol% of terephthalic acid with regard to the total amounts of acid components [72].

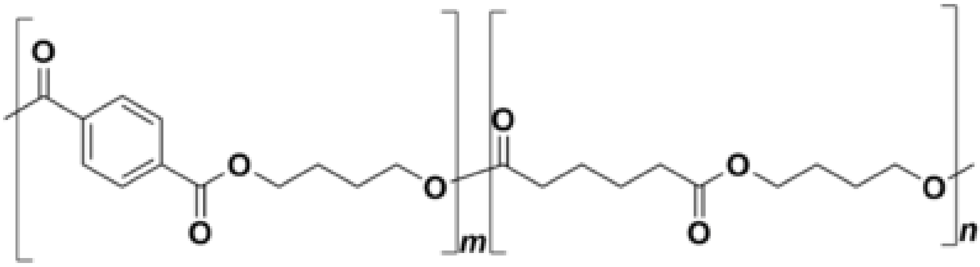


Figure 1-11 Chemical structure of PBAT.

PBAT is a random copolymer known for being flexible and tough. PBAT is not water soluble, it is designed mainly for film extrusion and extrusion coating. The flexibility and toughness of PBAT makes it ideal for blending with other biodegradable polymers that have high elastic modulus and stiffness, but are brittle [73].

The advantage for using PBAT as the flexible complement to other biodegradable polymers is that it preserves biodegradability, which allows for replacing industry-standard plastics with environmentally friendly plastics that will disappear in a short period of time without harm.

1.2.2.6 Material screening

The materials selected were immersed in the detergent for 3 days at room temperature. After immersion, PVP absorbed ingredients from the detergent, swelled significantly, became green and sticky; PEG and sodium alginate swelled and behaved similar as PVA; Lactips material lost 30% weight. Based on the results, PEG, sodium alginate and Lactips material were chosen for further investigation.

1.3 Polymeric film preparation

Films of different arrangements are formed in order to meet different industrial and domestic demands. There are mainly 3 types of film preparation methods in the current industry:

- Blown film extrusion
- Cast film extrusion
- Solution casting and solvent evaporation

1.3.1 Blown film extrusion

Blown film extrusion is widely used to manufacture packaging film. This technique is a major processing technique used in a biaxial melt draw film. In a blown film extrusion process, the polymer is melted in an extruder, and the hot melt is pumped through a die. The molten polymer flows around the mandrel and emerges through a round opening to form a thin-walled tube which is simultaneously axially drawn and rapidly expanded. Air is then blown in through the die head into the ring, thereby inflating the tube into a thin tubular bubble. This tube is then flattened at the nip rolls and then taken to the winder. The hot melt is cooled by annular streams of high-speed air from air rings externally and sometimes internally. In most installations, the extruders are horizontal and the blown film bubble is formed vertically upward, as can be seen in **Figure 1-12** [74].

The blow-up-ratio (BUR) is defined by:

$$BUR = \frac{Bubble\ diameter}{Die\ diameter}$$

The bubble diameter at the freeze line is usually 1.2 to 4 times larger than the die diameter. By varying the BUR, screw speed, air pressure, and winder speed, films of different thicknesses (10-150µm) and a degree of orientation can be achieved [75].

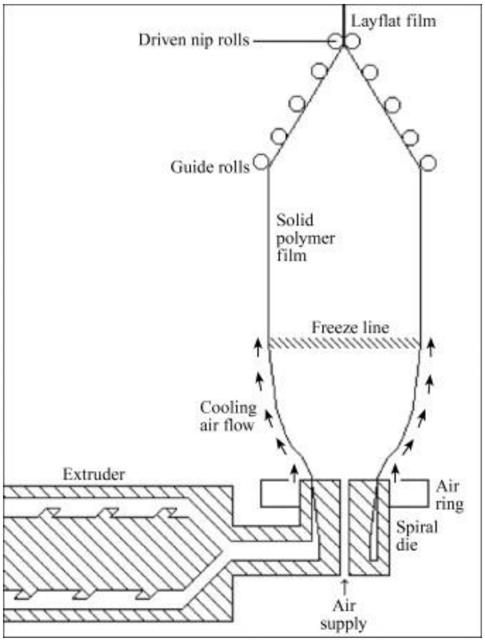


Figure 1-12 Scheme of the blown film extrusion [74].

This technique is used to process a variety of polymers, such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), polyamides (PA), and polyurethane (PU). The markets served by blown film extrusion process include industrial films and bags, agricultural and construction films, barrier films, stretch films, PVC cling films, laminating films, can liners, and high barrier small tube systems [76].

Figure 1-13 shows a production facility with a large tower and windup from Macchi for blown film extrusion, and **Figure 1-14** shows a small blown film line showing the extruder, die, and blown film from Rulli Standard [77].

Figure 1-13 Macchi blown film tower [77].

The advantages of blown film extrusion are[78]:

- In a single operation, flat and gusseted tubing is formed;
- Film thickness and width can be regulated by controlling air volume in the bubble;
- Elimination of the end effects like edge bead trim along with non-uniform temperature which occur in flat die film extrusion;
- Capability of biaxial orientation, which allows uniformity in all mechanical properties;
- High productivity;
- Allowing combination of different materials and properties.

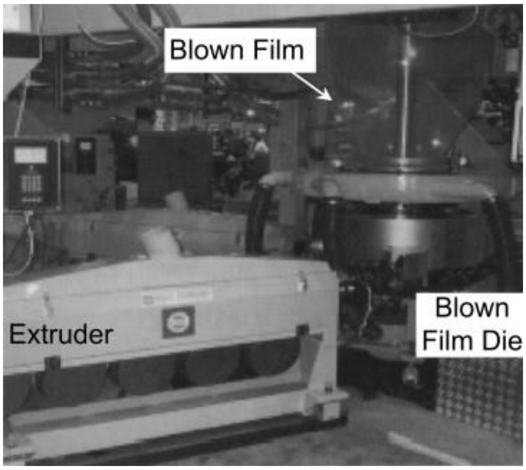


Figure 1-14 Rulli standard blown film line [77].

1.3.2 Cast film extrusion

Cast film extrusion is another common plastic manufacturing process widely used in the industry. In this process, plastic resins or pellets are melted under high temperature and/or pressure, and pushed through a slit die into films; then the product is cooled down, and wounded up to a roll. By cast extrusion, film is with rectangular shape, and its width is significantly larger than its thickness. For cast films, the molten resin is discharged from the die, and stretched in the machine direction before solidification, therefore, the film has orientation in the machine direction.

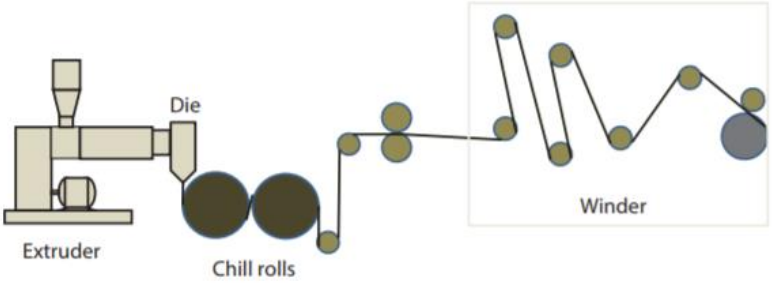


Figure 1-15 Scheme of a cast extrusion process [79].

There are three main unit operations in a cast extrusion process: plasticating extrusion, shaping and cooling, and the downstream winding operation. As shown in **Figure 1-15**, a single-screw extruder is used to convey resins, plasticate (melt), and then pump the molten polymer at the desired rate and discharge with an acceptable temperature and pressure. Molten plastics are extruded through a die and shaped into film. Then the extruded film is cooled down on a chill roll (or other cooling instruments), and the solidified films are wound up into a roll as the final products [79].

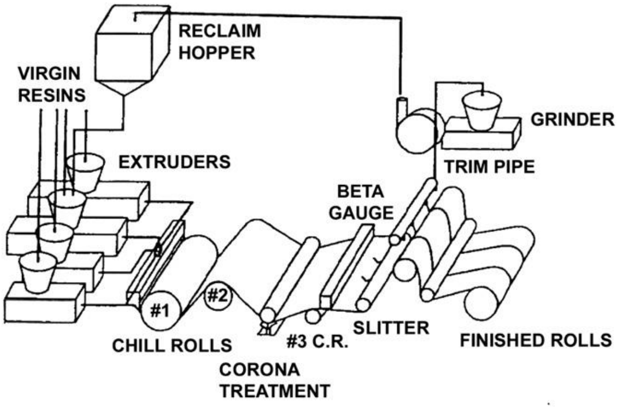


Figure 1-16 Multi-resin cast film extrusion [76].

Several different compatible resins can be mixed with feedblock technology and/or in a multilayer die and extruded onto a chill roll to form film. A schematic illustration can be seen in **Figure 1-16**, and **Figure 1-17** shows the melt pipes that feed a multilayer die [76].

Similar as blown film extrusion, cast film extrusion can also be applied to process many types of polymers into films for packages, bags and barrier films.

Compared to blown film extrusion, cast extrusion operates at a higher rate, resulting from the higher capacity for cooling. Cast extrusion can prepare film profiles with better gauge uniformity. Moreover, cast extruded films are generally more optically transparent than blown films, since the casted films are solidified at higher rate where crystalline structures are smaller. However, casted films have less balance in tensile properties as significant film stretching is applied only in the machine direction and only minimal orientation can sometimes be achieved in the transvers direction. The cost of cast film extrusion is higher than blown film extrusion due to the cooling system, and also the need for auxiliary equipment to deal with edge trim requirement [79].

Figure 1-17 Four melt pipes feeding a multilayer die [76].

1.3.3 Solution casting and solvent evaporation

Solution casting method is applied in the industry of medicals, battery separations and packaging. The basic principle is similar to cast film extrusion, but the flow of the polymer is obtained by dissolving it in a solvent instead of heating it during mechanical shearing in an extruder [80]. As shown in **Figure 1-18** [81], a solution is cast onto the surface of a rotating drum, or a continuous polished stainless steel belt, and then it is dried by solvent evaporation.

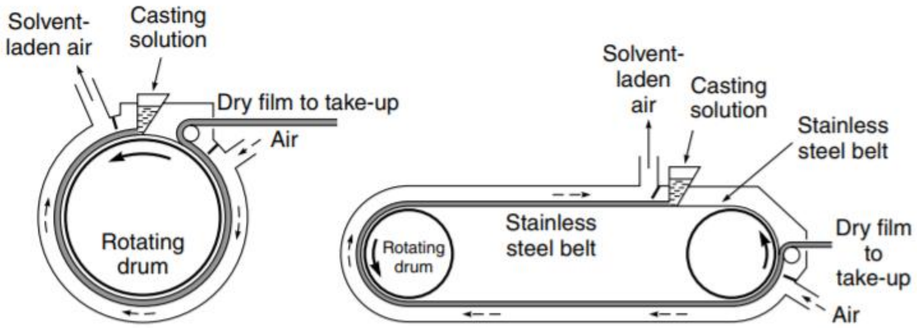


Figure 1-18 Machinery used to make solution-cast film on an industrial scale.

The advantages of solution casting over traditional extrusion methods include [82]:

- Processing at low temperatures which is good for thermally activated films or temperature sensitive active ingredients;
- Ability to produce non-thermoplastic film;
- Simplified procedure for adding additives and fillers;
- Wide range of material choices with casting from either aqueous or solvent-based solutions;
- Better film thickness uniformity and wider range of film thickness (12µm-150µm);
- Excellent film flatness and dimensional stability;

- Isotropic orientation as film is not stretched during manufacture.

Moreover, solution casting is also commonly used in laboratory-scale preparation of small samples of films. In this case, to prepare the film, the polymer is dissolved in a solvent, and forms a solution with a certain concentration and viscosity to prevent it from running over or aggregate. The solution spreads onto the substrate, and as the solvent evaporates, polymer chains interpenetrate, going through a gel state, and eventually forming a film with further drying. Solvent evaporation depends on temperature, atmospheric pressure, and relative humidity (RH %) if the solvent is water. These variables can be adjusted by controlling the process conditions.

Generally, there are two ways to cast films by the method of solution casting:

One is to pour a certain amount of polymeric solution in a petri-dish and let it fully cover the area of the petri-dish naturally, then wait for the solvent evaporation and eventually solidify the film. The film thickness can be controlled by the amount of solution.

Another way is to spread a polymeric solution across a flat plate with a casting knife that has a certain gap, then the solution is left to stand, and the solvent evaporates to leave a film. Specially, the film thickness can be controlled by changing the gap of casting knife. **Figure 1-19** shows a typical hand-casting knife [83].

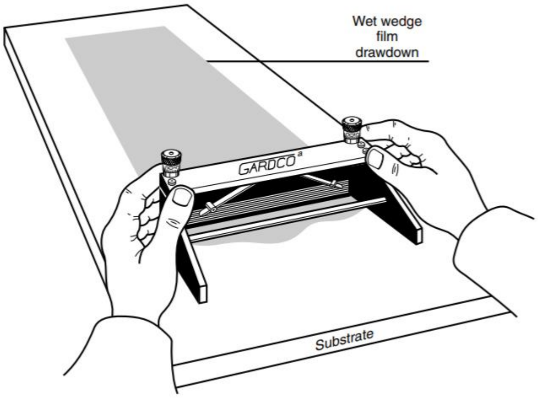


Figure 1-19 A typical hand-casting knife.

In this PhD project, we focus on solution casting as extrusion methods are more for industrial-scale and require complex equipment that are not available in current labs.

1.4 Objectives of the thesis

As described in the preceding sections, as SUD business continues to grow P&G would like to find some other materials able to replace PVA film. The objective of this PhD project is to look for alternative materials for SUD film, which would have similar detergent compatibility, water solubility, permeability and mechanical properties as PVA film. Additionally, we would like to discover whether the new material would bring new benefits.

In this thesis, films made of PEG, sodium alginate, Lactips material, were prepared, properties of those films were tested, and pouching prototypes of some of the films were prepared. Solution casting was selected as the method for preparing the films.

This thesis is composed of 8 chapters. Apart from **Chapter 1** (General introduction and objectives), **Chapter 2** (Materials and test methods), and **Chapter 8** (General conclusions and future work),

Chapter 3 describes PEG-based films and their properties;

Chapter 4 describes sodium alginate-based films and their properties;

Chapter 5 describes Lactips material-based films, as well as their properties;

Chapter 6 describes pouch prototyping with Lactips film and discusses pouch stability;

Chapter 7 describes sodium caseinate-based films and their properties.

References

[1] V. G. Kadajji and G. V. Betageri, “Water Soluble Polymers for Pharmaceutical Applications,” *J. Polym.*, vol. 3, pp. 1972–2009, 2011.

[2] “Water-Soluble Polymers, Synthetic - Chemical Economics Handbook (CEH) | IHS Markit.” [Online]. Available: https://ihsmarkit.com/products/synthetic-water-soluble-chemical-economics-handbook.html. [Accessed: 15-Mar-2019].

[3] P. J. Hendra and E. J. Loader, “Vinyl Alcohol : a Stable Gas Phase Species ? Charge Transfer in Mono-hydroxo and Mono-fluoro Complexes of Tripositive Cations in the First Transition Series,” *Nature*, vol. 216, pp. 790–791, 1967.

[4] W. Haehnel and W. O. Hermann, “Verfahren zur Herstellung von Polymerem Vinylalkohol,” DE450286, 1924.

[5] R. K. Tubbs, “Sequence Distribution of Partially Hydrolyzed Poly(vinyl acetate),” *J. Polym. Sci. Part A-1 Polym. Chem.*, vol. 4, pp. 623–629, 2003.

[6] O. Olabisi and K. Adewale, *Handbook of Thermoplastics, Second Edition*. Boca Raton: CRC Press, 2016.

[7] J. C. J. F. Tacx, H. M. Schoffeleers, A. G. M. Brands, and L. Teuwen, “Dissolution behavior and solution properties of polyvinylalcohol as determined by viscometry and light scattering in DMSO , ethyleneglycol and water,” *Polym. J.*, vol. 41, pp. 947–957, 2000.

[8] K. Khana, M. Nthoiwa, C. Diaz, and Y. Chaudhari, “Vinyl Alcohol Polymers,” in *Handbook of Thermoplastics, Second Edition*, vol. 8, Boca Raton, London, New york: CRC Press, 2015, pp. 53–88.

[9] S. Monnerie, W. Suter, E. L. Thomas, and W. R. J. Young, “Structure and Applications of Poly(vinyl alcohol) Hydrogels Produced by Conventional Crosslinking or By Freezing/Thawing Methods,” in *Advances in Polymer Science*, Berlin: Springer, 2007, pp. 37–65.

[10] Bunn.C.W., “Crystal structure of polyvinyl alcohol,” *Nature*, vol. 161, pp. 929–930, 1948.

[11] H. E. Assender and A. H. Windle, “Crystallinity in Poly(vinyl alcohol). 1. An X-ray diffraction study of atactic PVOH,” *Polym. J.*, vol. 39, pp. 4295–4302, 1998.

[12] G. Delamarche, D. Ingram, and G. Spieles, “Water Soluble Pouches,” WO200345813, 2003.

[13] V. Catalfamo, “Water Soluble Substrate with Resistance to Dissolution Prior to Being Immersed in Water,” WO200853381, 2008.

[14] F. W. Denome, S. G. Friedrich, and R. Labeque, “Water Soluble Film Having Improved Dissolution and Stress Properties, and Packets Made Therefrom,” WO201194472, 2011.

[15] S. Fernandez-pri-eto, I. Guimet, R. Labeque, A. M. Broeckx, Walter, and J. Smets, “Stable Water Soluble Unit Dose Articles,” WO201339964, 2013.

[16] R. Labeque, F. C. Courchay, R. R. F. Keuleers, S. G. Friedrich, D. M. Lee, and T. J. Yogan, “Articles Comprising Water Soluble Polyvinyl Alcohol Blend Film and Related Methods,” WO201661053, 2016.

[17] R. Labeque, F. C. Courchay, S. G. Friedrich, and D. M. Lee, “Articles Comprising Water Soluble Polyvinyl Alcohol Film with Plasticizer Blend and Related Methods,” WO201661054, 2016.

[18] F. De Buzzac-carini, S. J. L. Coosemans, and L. M. P. Gualco, “Water Soluble, Liquid Containing Pouch,” WO2006130647, 2006.

[19] R. R. F. Keuleers, S. G. Friedrich, L. K. Yeung, and S. NII, “Water Soluble Packets, Cross Reference to Related Application,” WO2017218404, 2017.

[20] F. C. Courchay, R. Labeque, S. G. Friedrich, and D. M. Lee, “Water Soluble Unit Dose Articles Made from a Combination of Different Films and Containing Household Care Compositions,” WO2017218441, 2017.

[21] S. G. Friedrich, D. M. Lee, T. J. Yogan, and R. Labeque, “Water Soluble Polyvinyl Alcohol Blend Film, Related Methods, and Related Articles,” WO2016061069, 2016.

[22] H. Kamata, T. Yamaguchi, and Y. Hosoda, “Water-soluble Thermoplastic Film and Use Thereof,” EP0556781B1, 1999.

[23] L. Marion, L. B. Laurent, and F. H. Guillaume, “Water-Soluble Film, Useful for Packaging Solid Composition e.g. Food Product Including e.g. Salt, Pharmaceutical and/or Cosmetic Composition or Detergent, Comprises Thickener, Plasticizer, Gelling Agent, and Texturizing Agent,” FR2997402 (A1), 2013.

[24] R. Pagilagan and U. Parkersburg, “Water Soluble Polyamide Compositions, Solutions Thereof, Films and Sheets Therefrom and Process of Making Films and Sheets Therefrom,” EP1784448, 2010.

[25] T. Fujita, C. Isoda, and K. Aketa, “Unit Packaging Detergent,” EP0388105, 1994.

[26] S. Backe, A. S. Karikari, and P. Mercando, “Water Dispersible Films for Packaging High Water Containing Formulations,” US 2016/0244701, 2013.

[27] G. O. Schulz and T. D. Gueldenzopf, “Polymer Sheet for Delivering Laundry Care Additive and Laundry Care Product Formed from Same,” US4557852, 1985.

[28] R. U. Pagilagan, “Packaging and Containers Made of Water-soluble Polyamides and Processes for Their Manufacture,” US7057008, 2006.

[29] M. Heuts, “Water Soluble Films,” WO9700282, 1997.

[30] T. Cheng, G. J. Griscik, and D. L. Gee, “Oral Pouch Products with Immobilized Flavorant Particles,” US8124147, 2006.

[31] S. T. Gouge, L. E. Hodakowski, P. J. Weber, and C. R. Chen, “Gel Formulations for Hazardous Products,” US20020077371, 2002.

[32] Z. Shuxi and Y. Ping, “Water-soluble Eatable Material for Packing Flavouring of Instant Noodles,” CN1125681, 1996.

[33] Z. Wanli, “Edible Instant Film and its Production Method,” CN1165766, 1997.

[34] C. Qingxiong, “Package of Soluble Seasoning of Instant Noodle,” CN201264757, 2009.

[35] Y. Yan, P. Yonghong, L. Guilin, and Z. Pingsheng, “Food Packaging Material Convenient to Use and Application Thereof,” CN106275828, 2016.

[36] L. S. Moo, “Method for Forming Insulating Film Between Metal Wirings of Semiconductor Device.,” CN1056468, 2000.

[37] D. B. Edwards, W. J. Mccarthy, L. E. Hodakowski, C. R. Chen, S. T. G. Raleigh, and P. J. Weber, “Laminated Bags for Containerization of Toxic or Hazardous Materials,” US5429242, 1995.

[38] D. M. Lee and J. L. Childers, “Edible Water-soluble Film,” US2014/0199460, 2014.

[39] A. J. Desmarais, H. E. Knoop, L. C. Dull, and J. A. Raymond, “Water Soluble Packaging System, Film and Method,” US2001/0054567, 2001.

[40] E. Croze and M. Gautier, “Agrochemical Compositions in the Form of Dispersible Granulates,” EP661000, 1995.

[41] I. Bernhard and M. Reginald, “Water Dispersible or Water Soluble Polymer Film as Carrier of Dermatological and Cosmetic Agents,” EP2090293, 2009.

[42] Y. Tokita and T. Takagi, “Laminated Film, Method for Production Thereof, and Bag and Package Using the Laminated Film,” EP867276, 1998.

[43] G. C. Knudsen, “Hazardous Chemical Shipping Container,” EP631947, 1994.

[44] A. Desmarais, H. Knoop, and J. Raymond, “Water Soluble Bag Packaging System and Method for Packaging,” WO9737903, 1997.

[45] B. R. Alan, “Cellular-air Water-soluble Film Packaging.,” WO9402377, 1994.

[46] Q. M. Craig, “A review of thermal methods used for the analysis of the crystal form , solution thermodynamics and glass transition behaviour of polyethylene glycols,” *Thermochim. Acta*, vol. 248, pp. 189–203, 1995.

[47] F. E. Bailey and J. V. Koleske, *Poly (ethylene oxide)*. New York: Academic press, 1976.

[48] H. Tadokoro, Y. Chatani, T. Yoshihara, S. Tahara, and S. Murahashi, “Structural Studies on Polyethers, [-(CH2)M-O-]n.II1. Molecular Structure of Polyethylene Oxide,” *Macromol. Chem. Phys.*, vol. 73, pp. 109–127, 1964.

[49] Y. Matsui, T. Kubota, H. Tadokoro, and T. Yoshihara, “Raman Spectra of Polyethers,” *J. Polym. Sci. Part A Polym. Chem.*, vol. 3, pp. 2275–2288, 1965.

[50] T. M. Connor and K. A. Mclauchlan, “High Resolution Nuclear Resonance Studies of the Chain Conformation of Polyethylene Oxide,” *J. Phys. Chem.*, vol. 69, pp. 1888–1893, 1965.

[51] G. Caple, B. L. Wheeler, R. Swift, T.L.Porter, and S. Jeffers, “Scanning Tunneling Microscopy of Polythiophene , Poly(3-methylthiophene), and Poly(3-bromothlophene),” *J. Phys. Chem.*, vol. 94, pp. 5639–5641, 1990.

[52] L. Koenig and A. C. Angood, “Raman Spectra of Poly(ethylene glycols) in Solution,” *J. Polym. Sci. Part A-2*, vol. 8, pp. 1787–1796, 1970.

[53] P. J. P. Arlie, P. A. Spegt, and A. E. Skoulios, “Etude de la Cristallisation des Polymeres I. Structure Lamellaire de polyoxyethylenes de Faible Masse Moleculaire,” *Macromol. Chem. Phys.*, vol. 99, pp. 160–174, 1966.

[54] S. Zivanovic, J. Li, P. M. Davidson, and K. Kit, “Physical, Mechanical, and Antibacterial Properties of Chitosan/PEO Blend Films,” *Biomacromolecules*, vol. 8, pp. 1505–1510, 2007.

[55] W. C. Lai, W. Bin Liau, and T. T. Lin, “The Effect of End Groups of PEG on the Crystallization Behaviors of Binary Crystalline Polymer Blends PEG/PLLA,” *Polym. J.*, vol. 45, pp. 3073–3080, 2004.

[56] B. Chen, Z. Yang, Y. Zhu, and Y. Xia, “Zeolitic imidazolate framework materials: recent progress in synthesis and applications,” *J. Mater. Chem. A*, vol. 2, pp. 16811–16831, 2014.

[57] F Haaf, A. Sanner, and F. Straub, “Polymers of NVP: Synthesis, Characterization

and Uses," *Polym. J.*, vol. 17, pp. 143–152, 1985.

[58] V. Buhler, *Polyvinylpyrrolidone Excipients for Pharmaceuticals, Povidone, Crospovidone and Copovidone*. Berlin: Springer, 2005.

[59] L. Robert, "N -Vinylamide Polymers," in *Encyclopedia of Polymer Science and Technology*, New York: Wiley, 2005.

[60] D. E. Clark, H. C. Green, and C. Kelco, "Alginic Acid and Process of Making Same," US2036922, 1936.

[61] J. W. Rhim, "Physical and Mechanical Properties of Water Resistant Sodium Alginate Films," *LWT - Food Sci. Technol.*, vol. 37, pp. 323–330, 2004.

[62] F. Debeaufort, J. A. Quezada-Gallo, and A. Voilley, "Edible films and coatings: Tomorrow's packagings: A review," *Crit. Rev. Food Sci. Nutr.*, vol. 38, pp. 299–313, 1998.

[63] S. Winkler and D. L. Kaplan, "Biosynthesized Materials: Properties and Processing," in *Encyclopedia of Materials: Science and Technology*, 2001, pp. 609–615.

[64] P. Frederic and A. Gilles, "Thermoplastic Granule Made of Casein and/or Caseinate, Composition and Manufacturing Method.," FR2963013, 2012.

[65] P. F. Fox and D. J. Mcclements, *Dairy Chemistry and Biochemistry: Edition 2*. New York: Wiley, 1998.

[66] W. Doster, R. Gebhardt, R. Gehrke, P. Müller-Buschbaum, E. Maurer, and E. Bauer, "Thin Casein Films as Prepared by Spin-Coating: Influence of Film Thickness and of pH," *Biomacromolecules*, vol. 7, no. 6, pp. 1773–1780, 2006.

[67] A. R. Sarode, P. D. Sawale, C. D. Khedkar, S. D. Kalyankar, and R. D. Pawshe, “Casein and Caseinate: Methods of Manufacture,” in *Encyclopedia of Food and Health*, Oxford: Academic press, 2015, pp. 676–682.

[68] D. G. Dalgleish, P. A. Spagnuolo, and H. Douglas Goff, “A Possible Structure of the Casein Micelle Based on High-resolution Field-emission Scanning Electron Microscopy,” *Int. Dairy J.*, vol. 14, pp. 1025–1031, 2004.

[69] M. Guo and G. Wang, “Whey Protein Polymerisation and its Applications in Environmentally Safe Adhesives,” *Int. J. Dairy Technol.*, vol. 69, pp. 481–488, 2016.

[70] C. Phadungath, “Casein Micelle Structure: A Concise Review Internal Structure Model of Casein,” *Sci. Technol.*, vol. 27, pp. 201–212, 2005.

[71] M. Yamamoto and B. Se, “Biodegradation of Aliphatic – Aromatic Copolyesters : Evaluation of the Final Biodegradability and Ecotoxicological Impact of Degradation Intermediates,” *Chemosphere*, vol. 44, pp. 289–299, 2016.

[72] U. Witt, R. J. Müller, and W. D. Deckwer, “Biodegradation Behavior and Material Properties of Aliphatic/Aromatic Polyesters of Commercial Importance,” *J. Environ. Polym. Degrad.*, vol. 5, pp. 81–89, 1997.

[73] L. Jiang, M. P. Wolcott, and J. Zhang, “Study of Biodegradable Polylactide/Poly(butylene adipate-co-terephthalate) Blends,” *Biomacromolecules*, vol. 7, pp. 199–207, 2006.

[74] J. Vlachopoulos and V. Sidiropoulos, “Polymer Film Blowing : Modeling,” in *Reference Module in Materials Science and Materials Engineering*, Amsterdam:

Elsevier, 2015.

[75] S. A. Ashter, “Processing Biodegradable Polymers,” in *Introduction to Bioplastics Engineering*, Oxford: William Andrew, 2016, pp. 179–209.

[76] R. John and J. Wagner, “Blown Film, Cast Film and Lamination Processes,” in *Multilayer Flexible Packaging, Second Edition*, Amsterdam: Elsevier Inc., 2016, pp. 107–112.

[77] R. John, J. Wagner, M. Eldridge, F. Harold, and J. Giles, “Troubleshooting Blown Film,” in *Extrusion, Second edition*, Amsterdam: Elsevier, 2014, pp. 365–370.

[78] “Blown Film Extrusion (Film blowing).” [Online]. Available: http://www.industrialextrusionmachinery.com/plastic_extrusion_blown_film_extrusion.html.

[79] H. Kim, M. A. Spalding, K. A. Koppi, W. Hobson, and J. Dooley, “Cast Film Extrusion of Polyethylene,” in *Handbook of Industrial Polyethylene and Technology: Definitive Guide to Manufacturing, Properties, Processing, Applications and Markets*, Beverly: Scrivener Publishing, 2018, pp. 411–427.

[80] M. Biron, “Thermoplastic Processing,” in *Thermoplastics and Thermoplastic Composites, Second Edition*, Amsterdam: Elsevier, 2013, pp. 767–820.

[81] K. J. Mackenzie, “Film and Sheeting Materials,” in *Encyclopedia of Chemical Technology*, New York: Wiley, 2015, pp. 1–27.

[82] “Using Polymer Solution Casting to Deliver High-Quality Films.” [Online]. Available: https://www.tollcoating.com/using-polymer-solution-casting-to-deliver-high-quality-films/.

[83] R. W. Baker, *Membrane Technology and Applications*. New York: Wiley, 2004.

Chapter 2. Materials and Test Methods

2.1 Materials

PVA Mowiol® 18-88 resin in pellets form was supplied by Sigma Aldrich and used as received. It has a molecular weight of about 130,000 and residual acetate content 10.0%-11.6%.

M8630 film supplied by Monosol with a thickness of 76μm (±10%) was also used as a reference film, it is a mixture of PVA (87%-89% hydrolyzed)/monocarboxylate copolymer, chitosan and other components.

PEGs of different molecular weights were studied in this PhD project. PEG400, PEG 4000, PEG10,000 and PEG 20,000 were supplied by Alfa Aesar and used as received. PEG 100,000, and PEG 400,000 were supplied by Sigma Aldrich and used as received.

Sodium alginate was supplied by Sigma Aldrich and used as received.

Lactips Caretips L0003 pellets as well as films were supplied by Lactips company and used as received. The materials used are referred as Lactips.

PVA Mowiol® 18-88 resin was used as reference material to cast film.

Current detergent Ambrosia 3.0 from P&G was used for pouch prototyping and compatibility tests.

2.2 Methods

2.2.1 Film preparation

Solution casting and solvent evaporation method are employed to prepare films in this project. As the materials are water soluble, water is chosen to be the solvent, which is environmentally friendly as no organic solvent is used in the experiment.

Film formation from polymeric solutions is relatively straight forward a process, as the polymer is in the dissolved state. The solution spreads onto the substrate surface, and as the solvent evaporates, the polymer chains interpenetrate, going through a gel state then forming the film with further drying [1].

In laboratory scale, there are generally 2 ways to prepare polymeric film by solution casting and solvent evaporation method:

- Petri-dish
- Casting knife

In the method of petri-dish, a certain amount of polymeric solution is poured into the dish and gently swirled to cover the bottom of the dish, and dish is placed on a leveled surface. A homogeneous film can be obtained after solvent evaporation [2]. The thickness of the film could be regulated according to the amount of solution dosed into the petri-dish.

Figure 2-1 shows the scheme of film formation process using petri-dish.

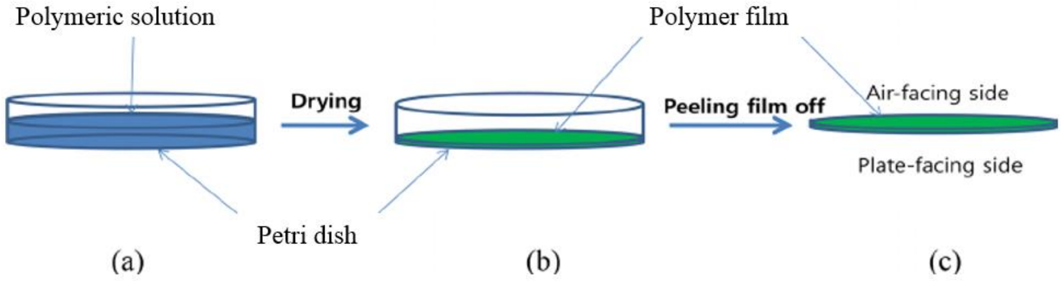


Figure 2-1 Scheme of film formation process using petri-dish.

Simple film preparation experiments were conducted using petri-dish: 10g and 15g of different polymeric solution were poured into a 15cm diameter petri-dish, and the thickness of the prepared films can be seen in **Figure 2-2**. It can be seen that the more the solution is poured, the higher the film thickness. What's more, the film thickness deviation is relatively high, especially when the solution is very concentrated which means that the solution itself is hard to spread, leading to film inhomogeneity. Additionally, another drawback of the petri-dish process is that the film area prepared by petri-dish is not big enough for further characterizations and prototyping.

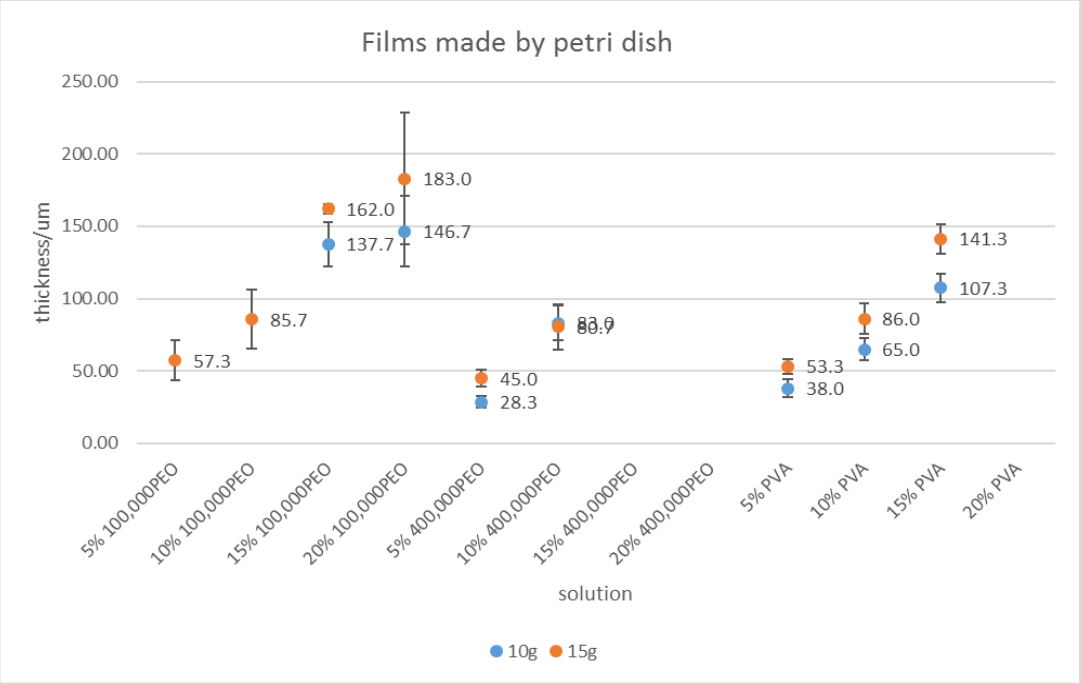


Figure 2-2 Thickness of films made by petrei-dish.

In the method of casting knife, polymeric solution is poured onto a support, and then a casting knife is used to spread the solution on the support. After solvent evaporation, a homogeneous film is obtained. The thickness of the film can be regulated according to the gap of casting knife. There are 3 types of casting knife in laboratory scale:

- Manual k-hand coater
- Automatic casting knife

- Manual film applicator

k-hand coater / k-bar is a simple but effective instrument for spreading a solution onto a substrate, which can be glass, Teflon, silicon or others. It is composed of a stainless-steel rod with a stainless-steel wire wounding onto it, as can be seen in **Figure 2-3**. This k-bar is supplied by RK Print Coat Instrument Ltd.

Figure 2-3 Picture of k-hand coater / k-bar.

The thickness of the film prepared by k-bar depends on the diameter of the wire and the distance between each section of the wire. **Figure 2-4** shows a detailed scheme of how the wire is wounding on the rod.

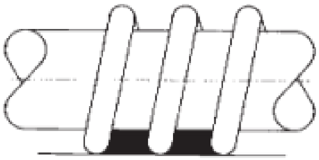


Figure 2-4 Open wound of wire in a k-bar.

Another way of casting in the lab is to use an automatic casting machine which is able to push a casting knife with a certain gap and spread the polymeric solution onto a support, instead of spreading the solution manually. This casting system k paint applicator is supplied by RK print. **Figure 2-5** shows the automatic casting knife.

The casting knife used here is a square frame which has different gaps in each side (150 µm, 200 µm, 250 µm, 300 µm).

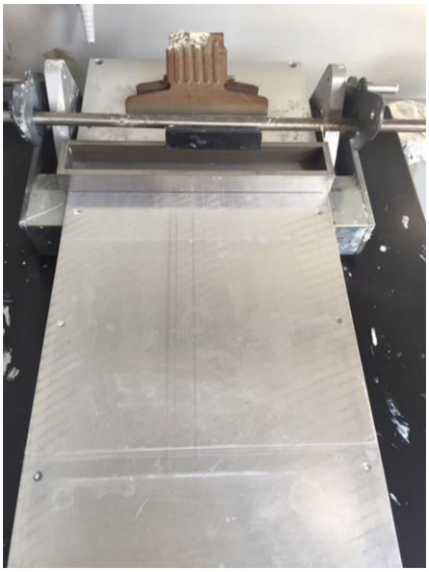


Figure 2-5 Picture of automatic casting knife.

All the wet gaps of casting knife and k-bar were used to prepare films, and it was found by experiments that films prepared with a wet gap of between 300 µm to 500 µm could achieve the objective film thickness of 76 µm ± 4 µm, using 10%-15% polymeric solutions, as can be seen from **Figure 2-6**.

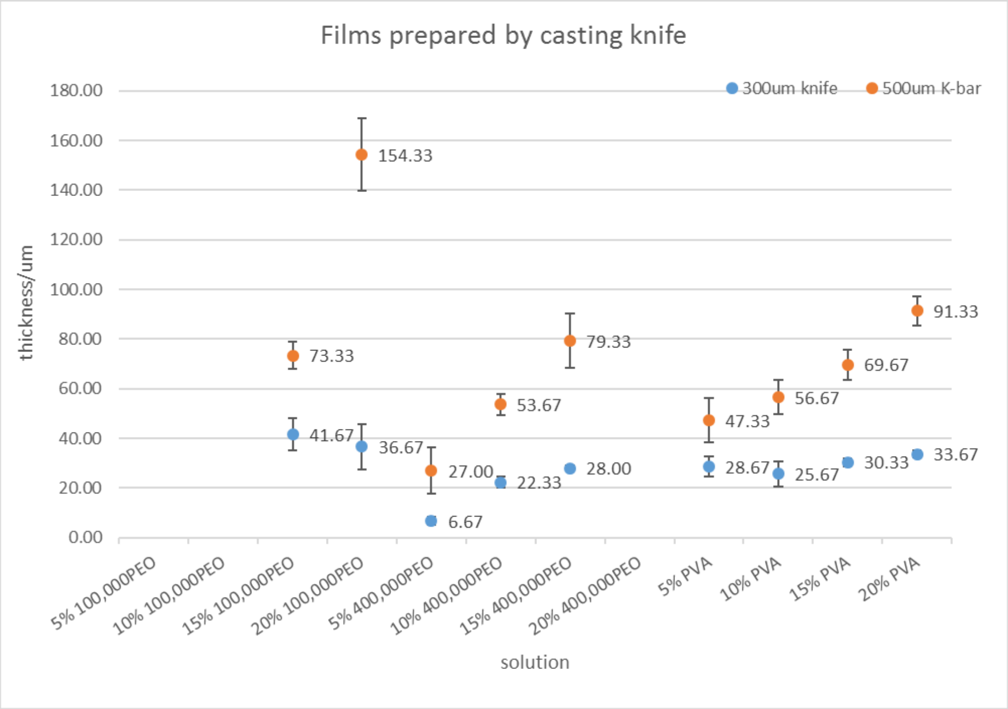


Figure 2-6 Thickness of films prepared by casting knife.

A casting knife that could modify its level of wet gap is necessary in this work. Therefore, a film applicator supplied by Elcometer was employed to prepare films during the PhD work. As shown in **Figure 2-7**, this film applicator has two screws on top of the casting knife which could regulate the gap between the knife and support, which is the wet gap, in this way it can regulate film thickness.

Figure 2-7 Picture of film applicator which could regulate wet gap.

The film preparation procedure in this PhD work is showed in **Error! Reference source not found.**:

- Polymer resins/powders are dosed in demineralized water to prepare a 15% solution. The mixture is stirred in a 50mL glass bottle either at room temperature (most polymers) or with heat at 80°C in a propylene glycol bath with reflux (PVA) until the polymer is fully-dissolved in water making a homogeneous solution, air bubbles were driven by ultra-sonication and vacuum;
- The homogeneous solution is poured onto a treated glass support ($ClSi(CH_3)_3$ in $CHCl_3$);
- The solution is spread into a thin layer using a film applicator with wet gap in the range of 350 μm to 450 μm;
- The resulted film is left standing there at ambient condition (22°C, 35%RH) for 20h;
- The dried film is peeled off from the support.

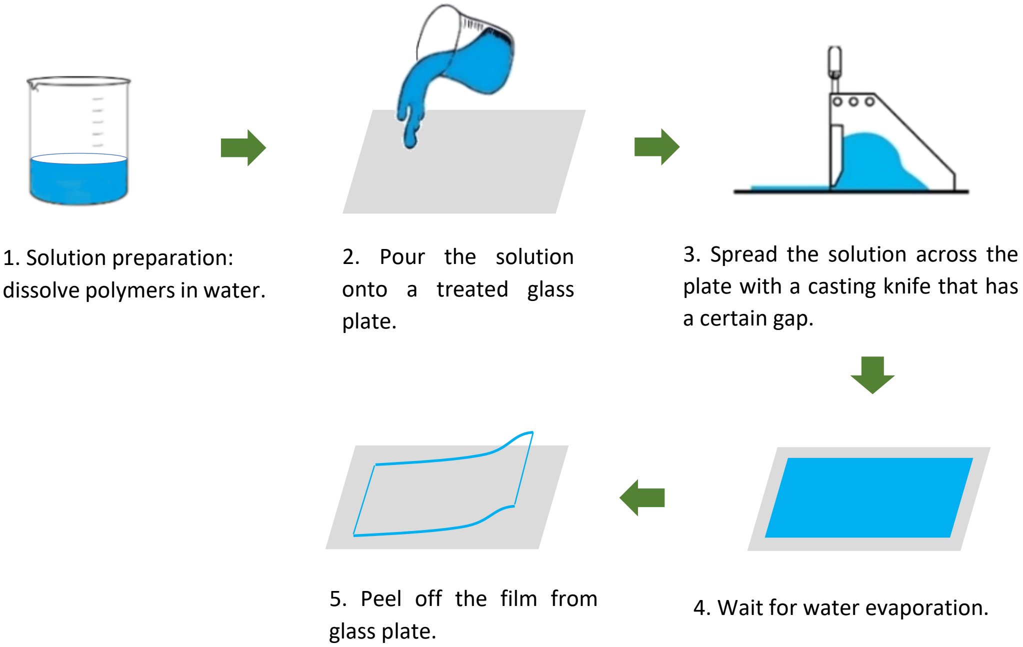


Figure 2-8 Film preparation procedure.

2.2.2 Environmental Scanning Electron Microscopy (ESEM)

Environmental scanning electron microscopy (ESEM) technique is a scanning electron microscope that allows for the option of collecting electron micrographs of specimens that are “wet”, uncoated, or both by allowing for a gaseous environment in the specimen chamber. This technique has been developed and commercially exploited for more than a decade. This electron microscopic device enables specimens to be observed in their natural, moist state, without being dried, vacuumed or sputtered with metals such as gold or platinum.

Basically, ESEM differs from its conventional counterpart SEM in as much as the specimen need not be observed in vacuum. In ESEM the high vacuum electron column is separated from a low vacuum environment of the sample chamber. This is being done by means of two closely spaced pressure limiting apertures (PLA) at the bottom of the final lens of the high-voltage vacuumed column. The spatium below, between and above these narrow apertures is vigorously and continuously pumped, and that creates practically separated vacuum systems in the column (high vacuum) and in the sample chamber. Therefore, the atmosphere of particular gas concentrations and pressures up to 20 Torr may be maintained in the chamber. Water vapour proved the most advantageous gas for ESEM operation because it is convenient, cheap, non-toxic and it ionizes easily to provide excellent imaging results. “Environmental” doesn’t mean ambient pressure, but rather values close to the triple point of water, thus the specimens need not be absolutely dry and vacuumed as in conventional SEM. The relative humidity within the chamber may be increased by lowering temperature [3].

In this PhD project, ESEM analysis is performed using a low-vacuum **ESEM FEI Quanta 600** apparatus, without sputter coating. Film samples are prepared to see its surface and cross section. To make a cross sectional cut on polymeric thin film sample without destroying the sample structure, the sample is immersed in liquid nitrogen to be frozen, and then it is broken by cutting or direct bending, to have a natural fracture.

2.2.3 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is one of the thermo-analytical techniques. The term thermo analysis incorporates those techniques where some physical parameter of a system is determined and/or recorded as a function of temperature [4]. In the case of DSC, , it looks at how a material’s heat capacity (Cp) is changed with temperature: there is a differential scanning calorimeter measuring the heat absorbed or released by the sample relative to a reference, and it heats the sample with a linear temperature ramp [5]. DSC is the most applied technique for studying the thermal events on polymers like melting temperature, heat of fusion, latent heat of melting, reaction energy and temperature, glass transition temperature, crystalline phase transition temperature and energy, and some other specific heat or heat capacity. it is one of the most often used thermal analysis methods due to its high speed, simplicity and availability [6].

DSC measures the energy needed between a substance and an inert reference material at a nearly zero temperature difference, as the two specimens are subjected to the same temperature program.

There are two types of DSC systems in common use:

- Power compensation DSC

The temperatures of the sample and reference are controlled independently in a power compensation DSC system. There are two separate furnaces for sample and reference, the temperatures of each are kept identical by varying the power input to the two furnaces; the energy required to do this is a measure of the enthalpy or heat capacity changes in the sample relative to the reference.

- Heat flux DSC

In this system (**Figure 2-9**), the sample and reference are connected by a low resistance heat flow path symmetrically. The assembly is enclosed in a single furnace. Enthalpy or heat capacity changes in the sample cause a difference in its temperature relative to the reference. The primary signal measured is the temperature difference between the sample and the reference. For example, if a heat-consuming process takes place in the sample, its temperature is lower than the reference temperature. The heat flow is then calculated according to the temperature difference [7].

In this PhD project we use heat flux DSC. A **Mettler-Toledo Differential Scanning Calorimeter mod. 822e** in dynamic mode is employed.

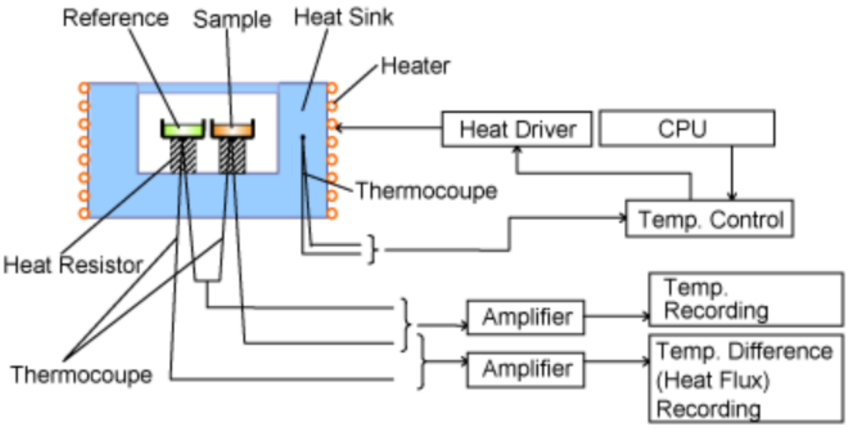


Figure 2-9 Schematic representative of heat flux DSC instrument [7].

Figure 2-9 shows the schematic representative of heat flux DSC instrument. Heat Flux DSC is composed of the holders of the sample and reference, the heat resistor, the heat sink, and the heater. Heat of heater is delivered into the sample and the reference through heat sink and heat resistor. Heat flow is proportional to the heat difference of heat sink and holders. In case the sample occurs endothermic or exothermic phenomena such as transition and reaction, this endothermic or exothermic phenomena is compensated by heat sink as the heat sink has the enough heat capacity compared to the sample. Therefore, the temperature difference between the sample and the reference is kept constant. The difference the amount of heat supplied to the sample and the reference is proportional to the temperature difference of both holders. By calibrating the standard material, the unknown sample quantitative measurement is achievable [8].

The typical polymer DSC plot can be seen in **Figure 2-10** [9]. Generally there are curves of heat flux versus temperature or versus time. As is shown, when the polymer is heated at a certain temperature, the plot shifts upward suddenly, which means that there is more heat flow and an increased heat capacity of the polymer. This happens because the polymer has just gone through glass transition temperature. Usually we take the middle of the incline to be the glass transition temperature (Tg).

Above the glass transition, the polymer attains more mobility: the molecules wiggle and squirm and never stays in one position for very long. When it reaches the right temperature, the molecules gain enough energy to move into very ordered arrangements, which is crystals, and this process is called crystallization. During this process, the polymer gives off heat, which means that it doesn't need too much heat to keep the temperature of the sample rising, therefore, there is a drop in the heat flow, and normally we take the lowest point of the dip to be the polymer's crystallization temperature (Tc). Since the polymer releases heat when crystallizes, it is an exothermic transition. The area of the dip is the latent energy of crystallization of the polymer.

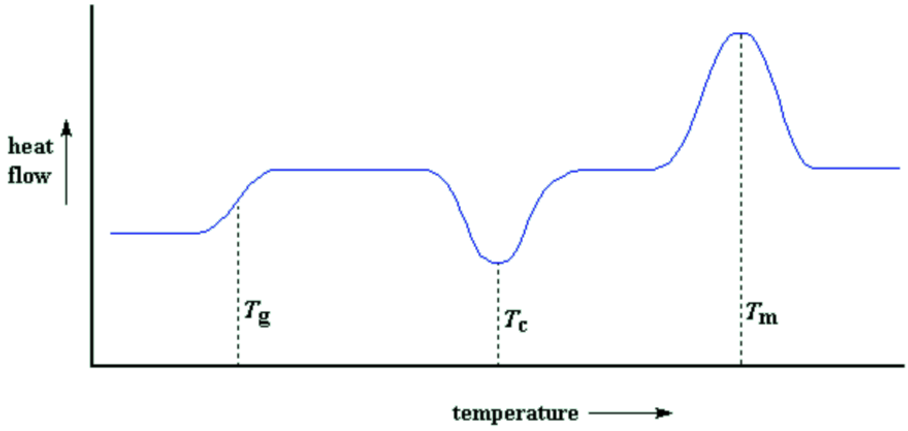


Figure 2-10 Typical DSC plot of heat flux versus temperature.

If keep heating, the polymer will reach another thermal transition, which is melting. When it reaches a certain temperature, the polymer crystals begin to fall apart, the chains come out of their ordered arrangements and start to move freely. In this transition it requires heat which means that the heater needs to supply more heat and give a higher heat flow where we see a peak. The highest point of the peak is the polymer's melting temperature (T_m). Since the polymer absorbs energy when melts, it is an endothermic transition. The area of the peak is the latent energy of melting for the polymer.

2.2.4 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) is another thermal-analytical technique, which applies a stress or strain to a sample at controlled frequencies, temperature and/or humidity, and analyzes the response to obtain phase angle and deformation data. Two approaches are used: (i) forced frequency, where the signal is applied at a set frequency and (ii) free resonance, where the material is perturbed and allowed to exhibit free resonance decay. Most DMAs are of the former type, while the torsional braid analyzer (TBA) is of the latter type. In both the approaches, the instrument is very sensitive to the motions of the polymer chains, and it is a powerful tool for measuring transitions in polymers. It is estimated to be 100 times more sensitive to the glass transition than differential scanning calorimetry (DSC), and it resolves other more localized transitions such as side chain movements that are not detected in the DSC. In addition, the technique allows the rapid scanning of a material's modulus and viscosity as a function of temperature, strain, or frequency. DMA may also be referred to as dynamic mechanical thermal analysis (DMTA), dynamic mechanical spectroscopy (DMS), or dynamic thermomechanical analysis (DTMA) [10].

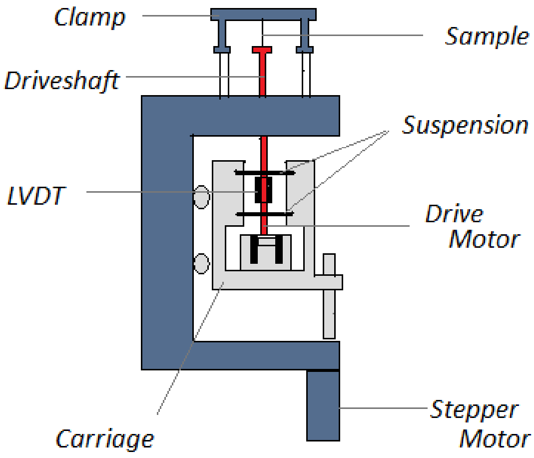


Figure 2-11 Schematic of DMA instrument.

Figure 2-11 shows the schematic of a DMA instrument [11] which composes of a displacement sensor, which measures a change in voltage as a result of the instrument probe moving through a magnetic core, a temperature control system or furnace, a drive motor, and a drive shaft support.

In this PhD project, we employ **TA Instruments DMA 800** to apply a sinusoidal stress on the sample and measure the strain, to calculate its E modulus to see the stiffness of films.

2.2.5 Karl-fischer titration

Karl-fischer titration is a classic titration method to determine water amount in a sample. There are two methods: coulometric or volumetric titration. The difference of these two methods is that, in coulometric method the titrant is generated electrochemically in the titration cell instead of added directly to the sample. This Karl-fischer method was invented by a German chemist Karl Fischer [12].

Karl Fischer presented the following equation for water determination with his reagent:

$$2H_2O + SO_2 \cdot (C_5H_5N)_2 + I_2 + 2C_5H_5N \rightarrow (C_5H_5N)_2 \cdot H_2SO_4 + 2C_5H_5N \cdot \mathrm{HI}$$

In this PhD project we use coulometric method, employing the instrument **Metrohm Titrino 751**, a 730 sample changer and a double Pt electrode (60340000). The Pt anode generates I_2 when current is provided through the electric circuit. As can be seen in **Figure 2-12**. Hydranal titrant 5 is used as titrant, and Hydranal is used as solvent.

Figure 2-12 Coulometric Karl Fischer titration.

The detailed operating procedure is as follows:

- Weigh about 0.5-1g film, immerse it in 30mL hydranal solvent in a 50mL beaker, and seal it with aluminum foil;
- Stir the system for 15min to let the solvent extract water from the film;
- Remove the film from solvent as fast as possible to avoid water vapor from the environment being absorbed by the solvent;

- Place the beaker on the sample holder, and start the titration;
- Read water content.

2.2.6 Infrared spectroscopy

Infrared spectroscopy is the analysis of infrared light interacting with a molecule. This technique is widely used in organic chemistry, polymer science, petrochemical engineering, pharmaceutical industry and food analysis [13]. IR spectroscopy provides a sensitive probe for specific functional groups in polymers [14][15]. Therefore, we can use group frequencies for structural analysis. Group frequencies are vibrations that are associated with certain functional groups. It is possible to identify a functional group of a molecule by comparing its vibrational frequency on an IR spectrum to an IR stored data bank.

Absorbing groups in the infrared region absorb within a certain wavelength region. The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. In this way, IR spectroscopy can be very sensitive to determination of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation. Also, each molecule has a characteristic spectrum often referred to as the fingerprint. A molecule can be identified by comparing its absorption peak to a data bank of spectra. IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds. **Figure 2-13** shows the diagram of a classic dispersive IR spectrometer [16].

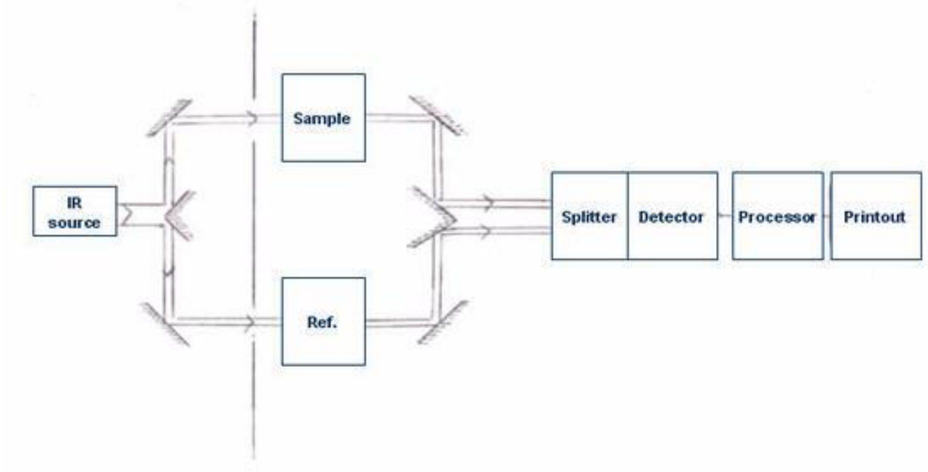


Figure 2-13 Diagram of a classic dispersive IR spectrometer.

In this PhD project, **Fourier Transform Infrared Spectrometer 680 Plus from Jasco** is employed for determining functional groups in polymers.

2.2.7 Slide frame dissolution test

Slide frame dissolution test is a method to evaluate the disintegration time of water-soluble film in water, as well as its subsequent relative dissolution time when held stationary in a plastic fixture. This test is a standard method **MSTM-205** used by Monosol [17].

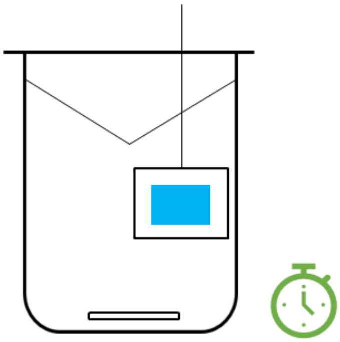


Figure 2-14 Diagram of slide frame dissolution test set-up.

The set-up of the test is shown in **Figure 2-14**, and the detailed procedure is as follow:

- Measure the thickness of the film using a digital micrometer Thwing – Albert Model 89-100 thickness tester. In this PhD project we make sure that all the film thickness is about 76 ± 4µm;
- Fix the film sample in a slide frame, and make sure there are no wrinkles;
- Fill a 600mL beaker with 500mL of distilled water, place a rod and adjust the stirring speed to control the vortex height to 400mL level;
- Control and maintain water temperature at 10˚C (± 1 ˚C);
- Immerse the slide frame into water and start the stopwatch at the same time;
- Record the time that film breaks (rupture time) and the time that there is no more film water (dissolution time);
- Stop the stirring, clean equipment, and repeat the experiment.

Standard test method for residue with dissolution chamber by **MonoSol MSTM-119** was employed to test film dissolution property. A cut and weighed circular disc of water-soluble film is trapped in a dissolution chamber (**Figure 2-15**) (i.e. between two stainless steel mesh screens clamped together) and placed horizontally in a beaker of stagnant water at a specified temperature. After the specified time period, the dissolution chamber is removed and partially dismantled, dried and weighed to calculate the amount of residue.

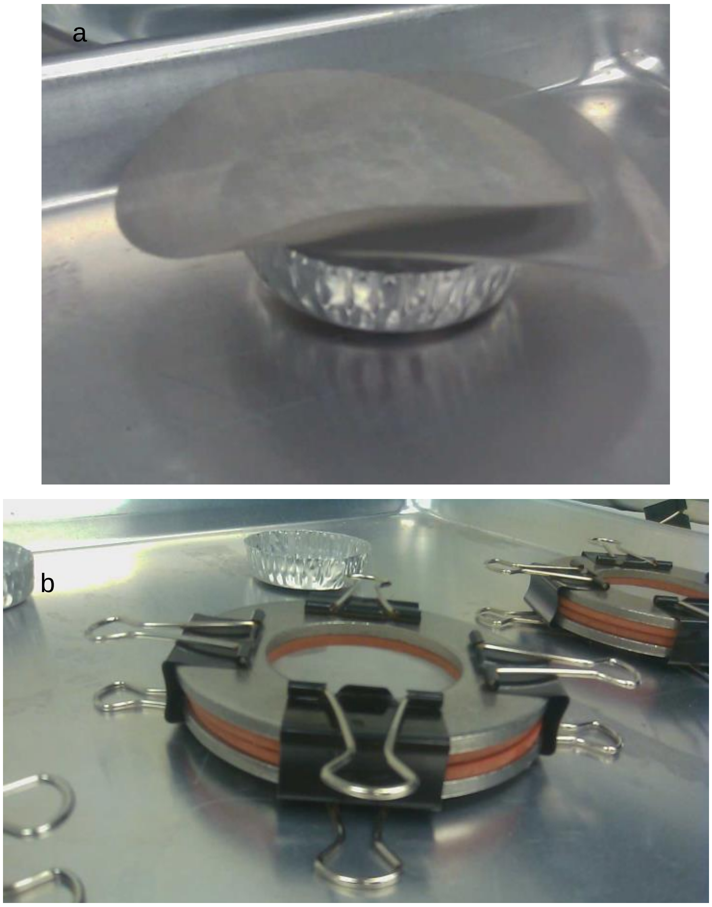


Figure 2-15 a. Weighing set-up and b. dissolution chamber set-up.

The detailed procedure is:

- Use the template to cut a 1.5” diameter specimen;
- Weigh each specimen and track each specimen through the test;
- Weigh each set of two clean dry screens and track them through the test;
- Assemble each dissolution chamber by flatly sandwiching the film specimen between the center of tow screens followed by the two rubber gaskets (one on each side) and then the two washers. Secure the assembly with four binder clips evenly spaced around the washers and the clips folded back;

- Fill the beaker with 1,500 ml of reverse osmosis water at laboratory room temperature. Record the temperature;
- Set the timer to prescribed time of immersion (ex. 10 min.);
- Move the assembly at a 45-degree angle into the water surface and immediately start the timer. The chamber should rest on the bottom and only on the four binder clips folded back;
- The film's elevation is ~10 mm off the bottom. This entry angle helps remove air bubbles from the chamber;
- At the prescribed elapsed time (ex. 10 min.), slowly remove at an angle the chamber;
- Hold the chamber horizontally over an aluminum pan to catch any drips from the screens and carefully remove the binder clips, washers and gaskets. Do not break open the sandwich screens;
- Place the sandwich screens (screen/film/screen) over the pan and into an oven at 100 ^{o}C for 30 minutes to dry;
- Weigh each dry set of sandwiched screens including dried drippings in pan;
- Calculate % residue left for each specimen;
- % Residue = 100*{(final dry screen sandwich wt. – initial screens wt. [no film]) / film wt.};
- Repeat steps 1-8 for each specimen.

2.2.8 Tensile property test

Tensile properties consist of the reaction of the materials to resist when there are forces applied in tension. Tensile properties include information about the modulus of elasticity, elastic limit, elongation, proportional limit, reduction in area, tensile strength, yield point, yield strength, and other tensile properties [18]. To determine the tensile properties of one material, a standard test method **ASTM D 882** -

Standard Test Method for Tensile Properties of Thin Plastic Sheeting is employed, using a **Model 5567 Instron® Tensile Tester** with a rubber coated 25mm wide grips (Instron® No. 2702-032). This produces a load versus elongation curve which is then converted into a stress versus strain curve (**Figure 2-16**).

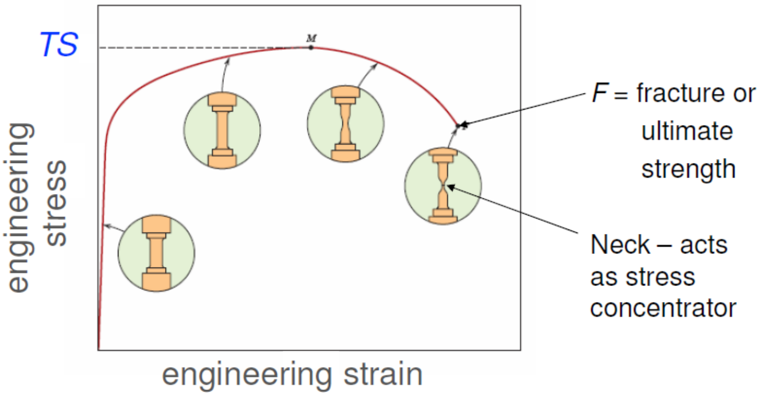


Figure 2-16 Engineering stress and strain curve.

$$Engineering\ stress = \sigma = \frac{F}{A_0}$$

$$Engineering\ strain = \varepsilon = \frac{l_i - l_0}{l_0}$$

$$Where\ F = force\ applied\ to\ the\ specimen,$$

$$A_0 = original\ cross\ sectional\ area$$

$$l_i = instantaneous\ length,\ l_0 = orinigal\ length$$

2.2.9 Immersion test

As the film is to be used in a soluble unit dose product, there is an internal test method in P&G - **TMD 00543**, to measure the tensile properties of the film after immersion in the detergent, which is called immersion test.

In the detergent, there are 4 main solvents: water, propylene glycol (Pdiol), dipropylene glycol (DPG), and glycerol. When the film gets contact with detergent, there is complex interactions: solvents can migrate into and out of the film which causes film swelling or de-plasticizing, which would finally affect film tensile properties.

The detailed procedure of immersion test is as follow:

- Prepare a film sample of 12cm by 17cm;
- A certain amount of detergent is poured into a glass tray, covering the bottom;
- Place the film gently onto the detergent, avoid bubbles and wrinkles;
- Pour the remaining of the 150mL in the glass tray, covering the film;
- Place the glass tray in a controlled stability room (35˚C, 40%RH) for 5 days, and then remove the tray from the storage condition and leave it for 1 night at 21 ˚C;
- Remove film from the tray and remove the excess of juice from the film;
- Wipe the film thoroughly with a dry paper;
- Cut 5 stripes of 25mm in machine direction with sample cutter, and test the tensile properties with Model 5567 Instron® Tensile Tester.

2.2.10 Water vapor permeability (WVP) test

Water vapor permeability (WVP) is one of the main performance indexes of package materials. For soluble unit dose product, water could influence pouch strength, leakage, sticking, and weeping, therefore, it is interesting to study the thermodynamics of water in contact with film, and the sorption-desorption kinetics and permeability.

The **ASTM E96-95** standard method was employed to test the WVP of the film, using a SPSx-1µ high load vapor sorption analyzer supplied by ProUmid, the set-up of the equipment can be seen in **Figure 2-17 a** & **b**.

In this method, the film specimen is sealed to the open mouth of a test dish containing molecular sieve (**Figure 2-17 c**), and the assembly placed in a controlled atmosphere where there is certain pressure difference maintained on two sides of the specimen. Periodic weighings determine the rate of water vapor movement through the specimen into the molecular sieve.

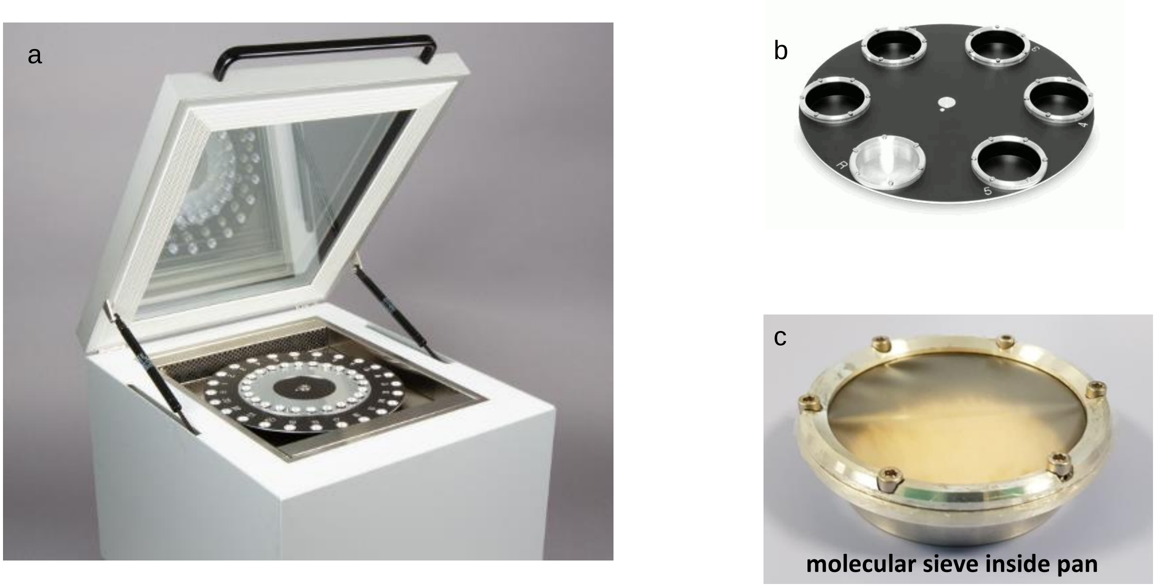


Figure 2-17 SPS equipment, Carousel, and molecular sieve inside the dish.

After a certain time of test, a chart (**Figure 2-18**) is obtained: the X-axis represents the experiment time (hours), the Y-axis stands for the sample weight on the, and the secondary vertical axis is shared by temperature (°C) and relative humidity (%). The first 6 hours is for film conditioning, where the humidity of the environment outside film is at 35%RH. Afterwards the humidity of the environment increases to 50%RH, and the dish start to gain weight. After 2 hours the system reaches equilibrium and there is an linear slope from 8 hours to 19 hours, where the slope is representing the steady state amount of water vapor diffusing through the film per unit time (g/h).

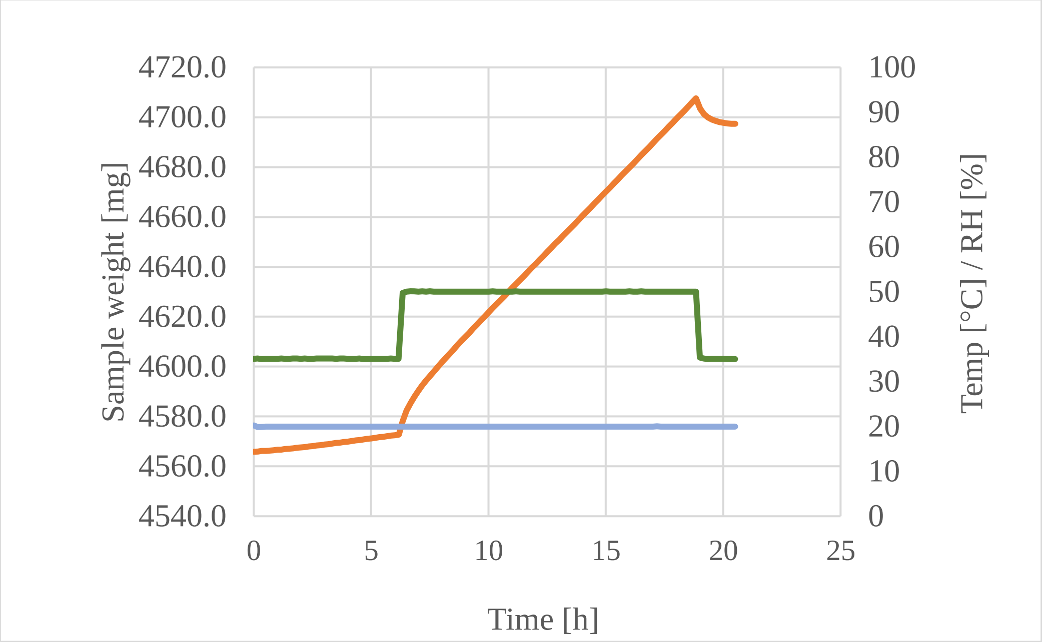


Figure 2-18 Typical chart for WVP test: temperature in light blue, relative humidity in green and the sample kinetics in orange.

The water vapor permeability can be calculated using the equation:

$$WVP = \frac{Mass\ * Thickness}{Time * Area\ * \ \Delta Vapor\ Pressure} = \frac{m * T}{t * A * \Delta P_y}$$
$$= [\mathrm{g}\, Pa^{-1} h^{-1} m^{-1}] = \frac{m * T * 24}{t * A * \ S(R1 - R2)} = [\mathrm{g}\, Pa^{-1} day^{-1} m^{-1}]$$

Where ΔVapor Pressure is equivalent to the saturation vapor pressure at test temperature S (e.g. S at 20°C=2338.8Pa) multiplied by the difference of the relative humidity at the source expressed as a fraction R1 (e.g. R1=0.5) and R2, the relative humidity inside the cup expressed as a fraction (R2=0 for the method).

2.2.11 Film-detergent compatibility test

As the interaction between film and detergent is very important for pouch stability, a compatibility study of the film with detergent, as well as main solvents is fundamental to understand the behavior of the system.

The detailed procedure is as follow:

- Weigh the prepared film specimen (W_i);
- Place the film onto 20mL detergent/solvent in a butcher cup, avoid air bubbles in the film-detergent/solvent interface;
- Pour another 20mL detergent/solvent into the system;
- Cover the cup with a lid, and place the cup in a controlled temperature room for 3 days;
- Take out the film from the cup and gently clean it with paper;
- Weigh the film again (W_f) and calculate the weight difference.

A gravimetric method is used for the calculation:

$$\%SW = \frac{W_f - W_i}{W_i} \times 100$$

2.2.12 Hansen Solubility Parameters in Practice (HSPip)

Hansen solubility parameters were developed by Charles M. Hansen in his PhD thesis in 1967 [19] to predict if one material will dissolve in another and form a solution.

In his theory [20], each molecule is given three Hansen parameters, each generally measured in MPa$^{0.5}$:

- dD: the energy from dispersion forces between molecules
- dP: the energy from dipolar intermolecular force between molecules

- dH: the energy from hydrogen bonds between molecules

In Hansen space (**Figure 2-19**), these 3 parameters can be treated as coordinates for a point in three dimensions. Based on “like dissolves like”, the nearer the two molecules are in Hansen space, the more likes that they can dissolve each other. How can we decide the range? A value called interaction radius (R_0) is given to the substance being dissolved. This value determines the radius of the sphere in Hansen space and its center coordinates the three Hansen parameters.

The distance (Ra) between two molecules in Hansen space can be calculated using the formula:

$$(Ra)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{p2} - \delta_{p1})^2$$

Combining this with the interaction radius gives the relative energy difference (RED) of the system:

$$RED=Ra/R_0$$

- If RED<1, the molecules are likely to dissolve each other
- If RED=1, the system will partially dissolve
- If RED>1, the system will not dissolve

To study the compatibility of film with the detergent, we would like to study the position interaction radius of the film in Hansen space, and to see if the main solvents are within the sphere or not. If the solvents are not inside the sphere, it means that the solvents wouldn’t dissolve the film, which in turn means that they are compatible.

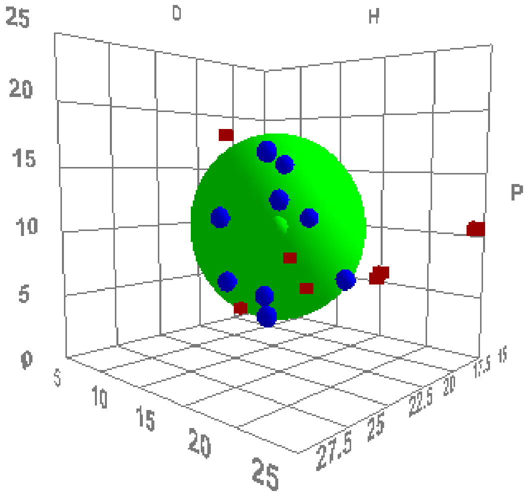


Figure 2-19 Hansen space.

Experiments are conducted to determine the Hansen sphere of the film”

- Grind film pieces into fine powder with liquid nitrogen;
- Dose 10mg powder in test tubes and add 2mL of 58 screening solvents;
- Place the tubes on a roller mixer for 24h and visually check whether dissolved.

HSPip Software was employed to calculate the HSP.

Distinction a: If dissolve, score 1 in the software, if not, score 0.

Distinction b: If the film doesn’t dissolve in any solvents, the solvents in which the polymer gives a light suspension and the solvents in which the polymer is swollen, get score 1, and the solvents in which there is no interaction with the polymer (sediment at the bottom or floating at the top) get score 0.

In this way, the Hansen sphere is calculated in the software, and RED of solvents and the film will be known.

2.2.13 Tackiness test

Tack or tackiness in the context of material behavior is associated with stickiness and may result from adhesive forces between two materials in contact or cohesive forces in a material bridging two substrates. For the laundry pouch, it is very important to know the stickiness of the film sealing with solvent, since sealing is key to pouch quality: if the pouch is not sealed well, it would lead to leakage.

To study sealing quality, we use a **texture analyzer (XT-Plus)** to measure the tackiness (adhesiveness) of the film (**Figure 2-20**): where two films are sealed and then mechanically pulled apart, in the process measuring the forces and energy required for separating the sealed films, to better understand the adhesion forces and kinetics of film sealing. **Stable Micro Systems software** (Macro Tackiness) was employed to process data. To form a good seal, it requires the formation of strong bonds through polymer interdiffusion in presence of a plasticizer, which in this case is water, therefore, a spray gun is employed to spread a certain amount of water onto the bottom film, and then seal two films with pressure.

In this test (**TMD01860**), two pieces of film are maintained to their respective probe with double-sided tape, and the film below is sprayed with water, and are combined with the film above by the applied force of 50kg. After the desired curing and sealing time, the films are then pulled apart. The peak positive force, area under the curve and gradient to positive peak are recorded to describe the maximum force, work of adhesion and stiffness of the bond, respectively.

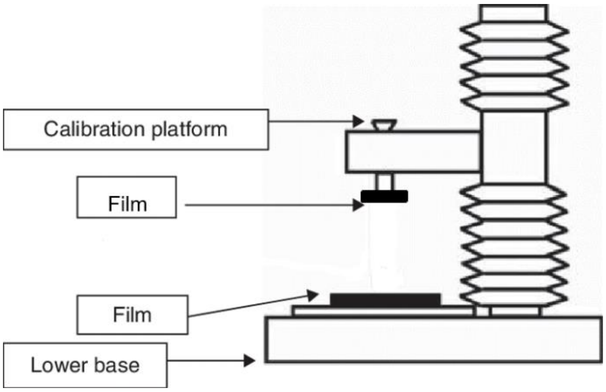


Figure 2-20 Schematic representative of texture analyzer.

2.2.14 Pouch making

The typical SUD product for laundry has 3 compartments, 2 top and 1 bottom, wrapped by top film, bottom film and middle film separating top and bottom detergents. **Figure 2-21** shows the pouch in a lateral view.

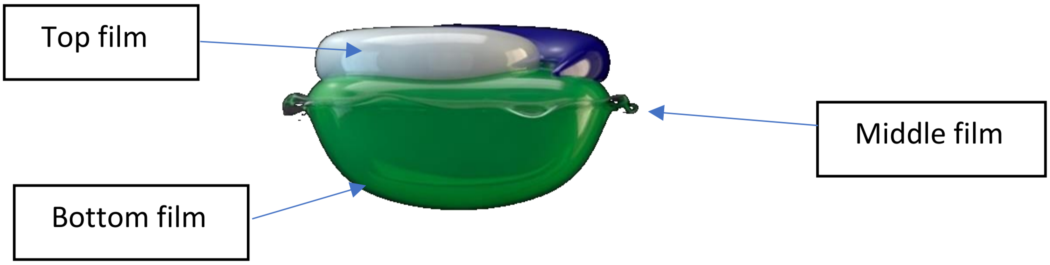


Figure 2-21 Lateral view of a typical multi-compartment pouch.

Figure 2-22 shows how films and detergents are converted to pouches in industry in a continuous process:

- Bottom film is un-winded from the film roll and delivered to the conveyor, where the rectangular cavities are situated;
- Bottom film was heated with IR lamp for softening the film, followed by vacuum deformation of the film into the cavities;

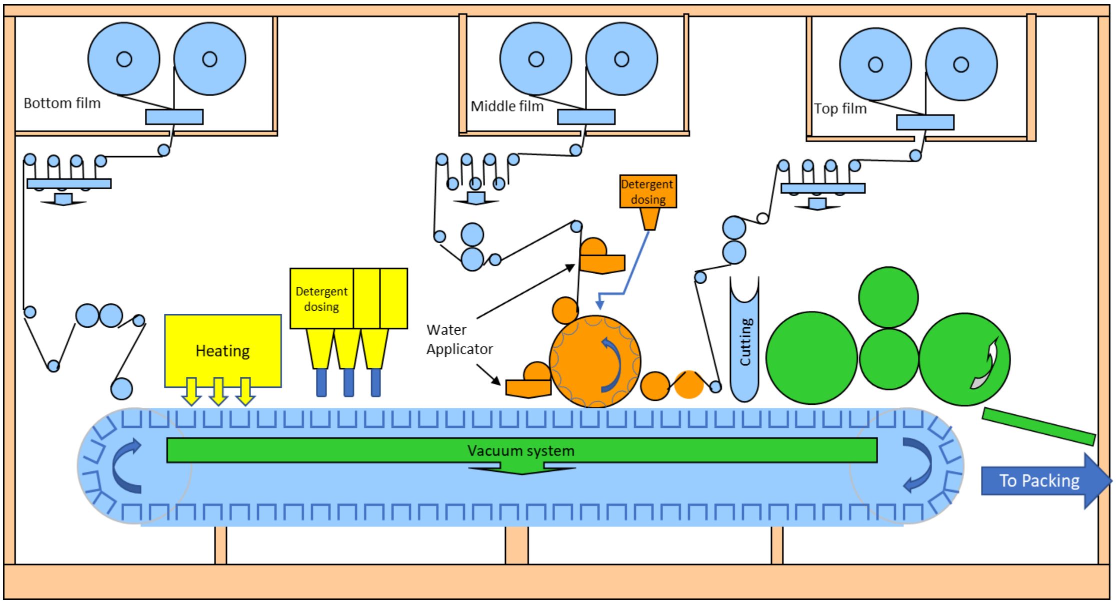


Figure 2-22 Schematic representative of pouch converting.

- Exact amount of detergent is dosed into the bottom part;
- In the mean time, the 2 top part is processed with same principles, and sealed with middle and top film by water;
- Top compartments and bottom compartment are sealed together, forming the pouch.

In lab scale, pouches could be prepared with a **1-up instrument** – a former sealer machine (**Figure 2-23**). For this PhD project, we would like to study film thermoforming and sealing capabilities, where mono pouch making already meets the requirement. A mono pouch is composed of only the bottom part, wrapped by bottom film and top film, without top compartments.

Figure 2-24 is a schematic representative of pouch making by 1-up method (**SOP013092**):

Figure 2-23 Former sealer machine for 1-up.

- Take a sample of film (approx. 15cm square) and place it onto the single cavity mould, and anchor this in place using a rubber ring;
- Heat the film over the cavity using a hand held hair-dryer. The hair-dryer is typically held about 6cm from the film and heated for about 10 seconds. This will aid vacuum deformation and prevent the film turning opaque when deforming;
- Switch the vacuum on and observe the film being drawn into the cavity;
- Fill the cavities with the desired detergent using a micropipette for liquids. Carefully avoid contamination of the seal area which could lead to poor seal quality. Any granules or liquid in the seal area must be removed.
- Place another piece of film (top) on a rubber support, and pour sealing solution onto the film with a pipette, and spread all over the film with a metallic bar;

- Place the top film on the mould as fast as possible, covering the detergent. The two films are heated and combined together with a certain pressure;
- Once the sealing is completed, the mono pouch is prepared and ready for test.

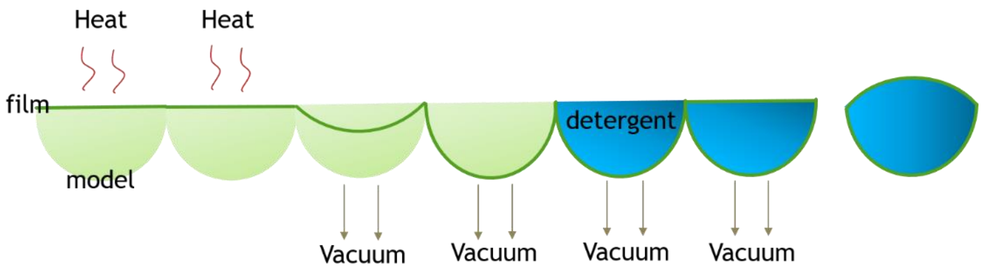


Figure 2-24 Schematic representative of pouch making by 1-up method.

2.2.15 Pouch stability test

The purpose of pouch stability test is to study the stability of pouch at certain temperatures and humidity. Pouches are exposed to a controlled temperature and humidity in different stability rooms for 3 months, and the behavior of the pouch is recorded.

2.2.16 Global stain removal test

Stain-removal test is designed to measure stain removal performance of laundry detergents via use of technical stains in washing machines. In this PhD project, the purpose of doing stain removal test is to study the impact of film on the performance of stain-removal of the pouch. 54 different stains are on a 10X10 inch fabric swatch and are either hand-applied or sewn on. The fabric is washed with certain detergent and dried, and Image analysis is used to measure stain removal performance.

References

[1] L. A. Felton, “Mechanisms of Polymeric Film Formation,” *Int. J. Pharm.*, vol. 457, pp. 423–427, 2013.

[2] J. Taylor and J. R. N. Taylor, “Identification of Kafirin Film Casting Solvents,” *Food Chem.*, vol. 90, pp. 401–408, 2005.

[3] H. Turkulin, “Investigations into the Photodegradation of Wood Using Microtensile Testing,” *Holz als Roh-und Werkst.*, vol. 54, pp. 1–6, 1996.

[4] G. Chatwal and S. Anand, “Thermal Methods,” in *Instrumental Methods of Chemical Analysis*, Mumbai: Himalaya Publishing House, 2002, pp. 2749–2751.

[5] B. A. Shirley, “Differential Scanning Calorimetry,” in *Methods in Molecular Biology*, New Jersy: Humana Press, 1995, pp. 191–218.

[6] K. Kodre and S. Attarde, “Differential Scanning Calorimetry: a Review,” *J. Pharm. Anal.*, vol. 3, pp. 11–22, 2014.

[7] “Polymerization Technology – Laboratory Course Differential Scanning Calorimetry. Polyethylene Terephthalate Synthesis. Catalyst Screening.” [Online]. Available: https://www.semanticscholar.org/paper/Polymerization-Technology-—-Laboratory-Course-.-./99119eb35c672bc7074ede41a67d513f0606acc0.

[8] “Principle of Differential Scanning Calorimetry (DSC).” [Online]. Available: https://www.hitachi-hightech.com/global/products/science/tech/ana/thermal/descriptions/dsc.html.

[9] “Differential Scanning Calorimetry.” [Online]. Available: https://pslc.ws/macrog/dsc.htm.

[10] K. P. Kevin and N. Menard, “Dynamic Mechanical Analysis,” in *Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation*, New York: John Wiley & Sons Ltd, 2017.

[11] J. D. Ferry, “Some Reflections on the Early Development of Polymer Dynamics: Viscoelasticity, Dielectric Dispersion, and Self-diffusion,” in *Macromolecules*, vol. 24, 1991, pp. 5237–5245.

[12] K. Fischer, “Neues Verfahren Zur Maßanalytischen Bestimmung des Wassergehaltes von Flüssigkeiten und Festen Körpern,” *Angew. Chem*, vol. 48, pp. 394–396, 1996.

[13] R. P. Quirk, “Anionic Synthesis of Polymers with Functional Groups,” in *Comprehensive Polymer Science and Supplements*, Amsterdam: Elsevier Ltd, 1989, pp. 83–106.

[14] J. L. Koenig, *Chemical Microstructure of Polymer Chains*. New York: Wiley-Interscience, 1980.

[15] R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds (Fifth Edition)*. New Jersy: Wiley, 1991.

[16] “Infrared: Theory.” [Online]. Available: https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Vibrational_Spectroscopy/Infrared_Spectroscopy/Infrared%3A_Theory.

[17] Monosol, “Standard Test Method for Solubility of MonoSol ® Water Soluble Film when contained within a Plastic Holder Standard Test Method for Solubility of MonoSol ® Water Soluble Film when contained within a Plastic Holder,” 2003.

[18] R. Rahman, S. Zhafer, and F. Syed, “Tensile Properties of Natural and Synthetic Fiber-reinforced Polymer Composites,” in *Mechanical and Physical Testing of Biocomposites, Fibre-Reinforced Composites and Hybrid Composites*, Amsterdam: Elsevier Ltd, 2019, pp. 81–102.

[19] C. M. Hansen, *The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient and Their Importance in Surface Coating Formulation.* Copenhagen: Copenhagen Danish Technical Press, 1967.

[20] S. Abbott, C. M. Hansen, and H. Yamamoto, *Hansen Solubility Parameters in Practice*. Hansen-Solubility.com, 2015.

Chapter 3. PEG Film, its Blending with PVA and Modifications

3.1 Introduction

Following the purpose of the PhD project, the first water-soluble material studied was PEG. PEG is a synthetic polymer with a general molecular formula ($-CH_2CH_2O-)_n$. It is non-toxic, water-soluble, semi-crystalline and biocompatible with high viscosity [1]. Since PEG is a high flexible-chain polymer, pure PEG films have relatively low mechanical and physical properties. Therefore, PEG is often blended with other polymers to be used in the field of water-soluble films, especially in the area of drug-controlled release [2]–[4].

Polymer blends are physical mixtures of two or more polymers (homopolymers or copolymers) and are of great technological significance [5]. Chemically complementary structures among polymers formed through secondary forces, such as Coulomb forces, hydrogen-bonding and van der Waals forces are important in blending systems [6]–[9]. The films formed by blending two or more polymers usually lead to modified physical and mechanical properties compared to films made of the individual components. For example, the blending of chitosan with PEG altered properties from either polymer alone: chitosan contributes to antimicrobial effect of the films, decreases tendency to spherulitic crystallization of PEG, and enhances puncture and tensile strength of the films, and PEG contributes to thinner films with lower water vapor permeability [3]; the blending of PEG and PVAc with poly(vinyl chloride) (PVC) decreased high Young's modulus of PVC film and increased its elongation at break [10]; the blending of PEG with Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV)/ Poly(butylene succinate) (PBS) increased the tensile elongation of the blend without PEG, etc [11]–[13]. Polymer blending is a simple method compared to other modification techniques, and it has advantages like reproducibility and commercial feasibility.

PVA is a water-soluble polymer that is hydrophilic, semi-crystalline and non-toxic. PVA is known to have excellent mechanical strength but relatively low ductility, which would complement with PEG regarding tensile properties. Therefore, the blending of PEG with PVA as a film-forming material is very interesting for the objective of this PhD project.

As a packaging film, flexibility is of importance during handling and storage. Therefore, plasticizers are needed to increase film flexibility due to their ability to reduce internal hydrogen bonding between polymer chains while increasing molecular space. Plasticization refers to a change in the thermal and mechanical properties of a given polymer, involving: 1) lowering the rigidity of the polymer at room temperature; and 2) increase of the elongation at break at room temperature [14]. Water can act as plasticizer, and glycerol, a non-toxic, sweet-tasting viscous liquid, also referred to as glycerin or glycerine, is also one of the most commonly used plasticizers in the field of film preparation [15]–[18].

This work is focused on the PEG properties such as tensile strength and strain and dissolution taking into account that the final application as soluble unit dose for laundry. The study of PEG/PVA blending was conducted for increasing PEG film mechanical properties. Further modifications such as the incorporating of glycerol, crosslinking and the blending of PEG with a PEG-PVA copolymer were conducted and the results are also shown in the end of the chapter.

3.2 Experimental

3.2.1 Materials

PEGs of different molecular weights were studied in this PhD project. PEG400, PEG4000, PEG10,000 and PEG20,000 were supplied by Alfa Aesar and used as received. PEG100,000, PEG400,000 and PEG800,000 were supplied by Sigma Aldrich and used as received. PVA Mowiol® 18-88 resin supplied by Kuraray was used as reference material to cast film. Glycerol was used as received from Oleon. Kollicoat IR®, and glutaraldehyde solution were purchased from Sigma Aldrich and used as received.

3.2.2 Characterizations

3.2.2.1 Environmental scanning electron microscope (ESEM)

Film surface and cross-sectional morphologies were observed at 15kV with low-vacuum ESEM FEI 600 apparatus, without sputter coating. Film cross-sections were prepared by fracturing in liquid nitrogen.

3.2.2.2 Differential scanning calorimetry (DSC)

Calorimetric studies were performed with a Mettler DSC822e thermal analyzer, using about 5 mg of sample, nitrogen as a purge gas (100ml/min) and liquid nitrogen for system cooling. The DSC procedure was consisting of 3 steps: heating – cooling-heating. At the first step, the films were heated from -80^{o}C to 230^{o}C at the heating rate of 10^{o}C/min, and then the sample was cooled down with the cooling rate of 10^{o}C/min till -80^{o}C, followed by a 2nd heating at the rate of 10^{o}C/min till 230^{o}C.

3.2.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded at room temperature using Fourier Transform Infrared Spectrometer 680 Plus from Jasco. with a resolution of 4 cm^{-1} and scanning speed of 2 mm/s^{-1}, in transmittance mode. An attenuated total reflection (ATR) accessory with thermal control and a diamond crystal (a Golden Gate heated single reflection diamond ATR from Specac-Teknokroma) was used to obtain FTIR spectra.

3.2.2.4 Film property tests

Dissolution test, compatibility test with detergent, tensile stress-strain test and mono-pouch prototyping were conducted to study film properties. The detailed theories, procedures, and instruments are referred in **Chapter 2**.

3.3 Results and discussion

3.3.1 Sample preparation

Different molecular weight of PEGs: PEG400, PEG 4000, PEG10,000, PEG 20,000, PEG 100,000, PEG 400,000 and PEG 800,000 were dissolved in water individually and formed a homogeneous solution; then the solution was treated by sonication to remove air bubbles. The solution was poured onto a glass plate and spread into a thin layer using a film applicator. The wet film was left standing at ambient condition overnight, and the resulted dry film was peeled off from the glass plate.

The solutions of PEGs with MW<100,000 didn't form proper films; solution of PEG100,000 tended to aggregate on the glass plate, and the films formed were very thick and brittle; solutions of PEG800,000 was too thick that it didn't allow a continuous flow when pouring onto the glass, therefore PEG 400,000 was selected for further investigation.

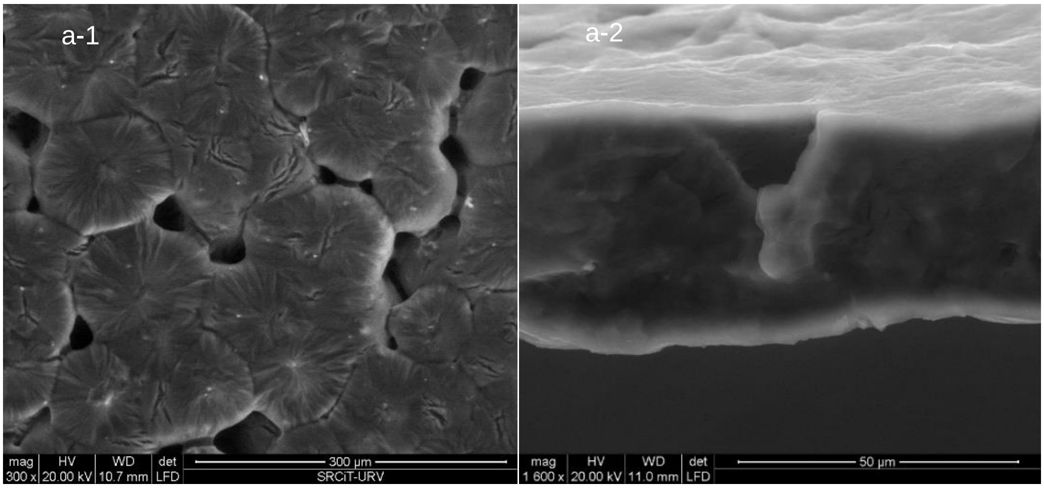
PVA film was prepared as reference: Mowiol® 18-88 resin was dissolved in water with stirring at 85°C, followed by a sonication step to remove air bubbles. Commercial film M8630 from MonoSol was also selected as reference film.

Moreover, PVA was blended with PEG at different ratios and the blends were casted into a film with the same procedure. PEG and PVA blended films with ratio of 90%:10%, 80%:20%, 70%:30%, 60%:40% were prepared, respectively, and the film with ratio 60%:40% was selected for further study since this combination had the best mechanical strength under the scope of incorporating no more than 40% PVA.

3.3.2 Film morphologies

ESEM micrographs show the morphology of the surface and cross-section of PEG, PVA, and PEG/PVA blended films, as seen in **Figure 3-1**. It is shown that all films are homogeneous. Small voids are found on the surface of PEG film, however, the film is not porous as can be confirmed by the cross-section. The voids and some lines on the film surface indicate high crystallinity of the PEG film.

PEG/PVA blended film is as flat and dense as PVA film, and no phase separation is seen on the blended film surface nor cross-section, meaning that PEG and PVA form a compatible polymer blend at microscopic scale.



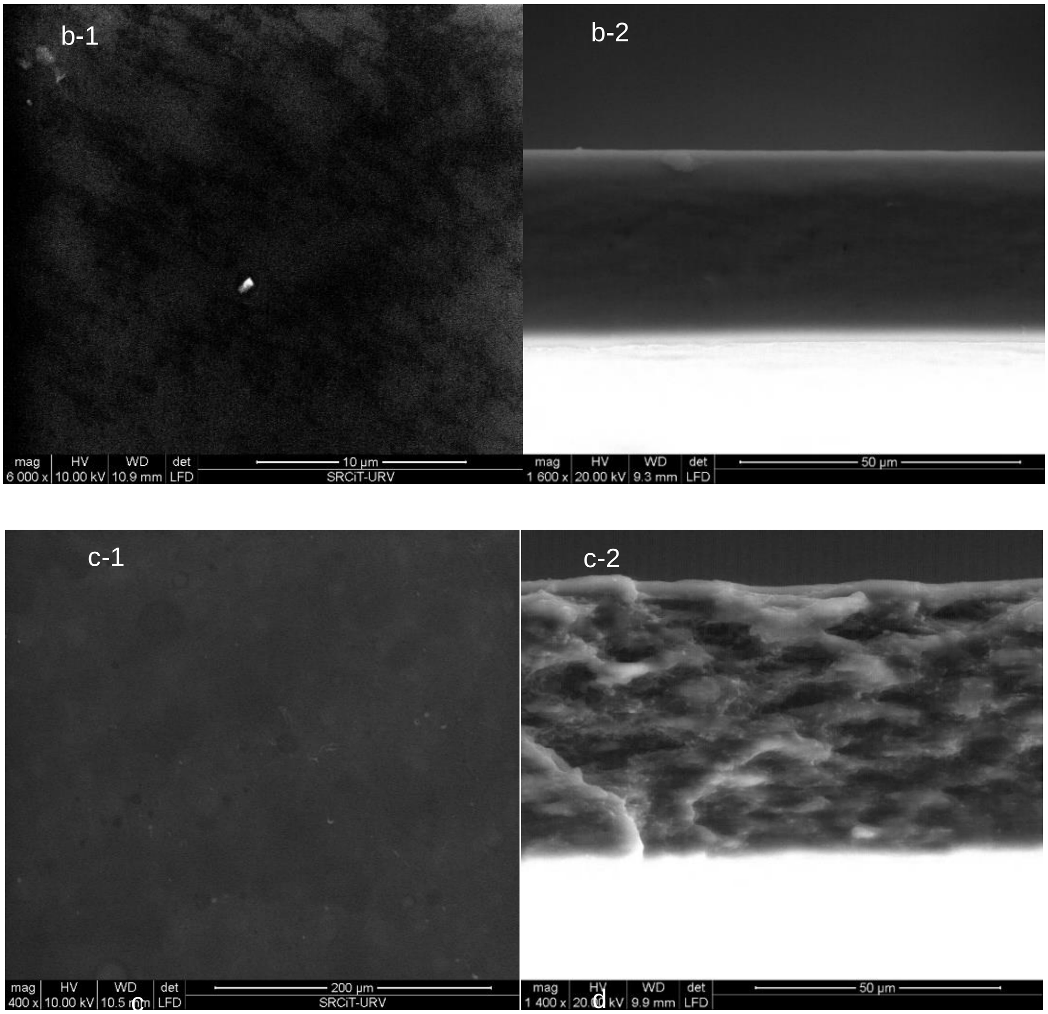


Figure 3-1 ESEM images of a. PEG film, b.PVA film, c. PEG/PVA blended film with 40%PVA. -1 surface and -2 cross-section.

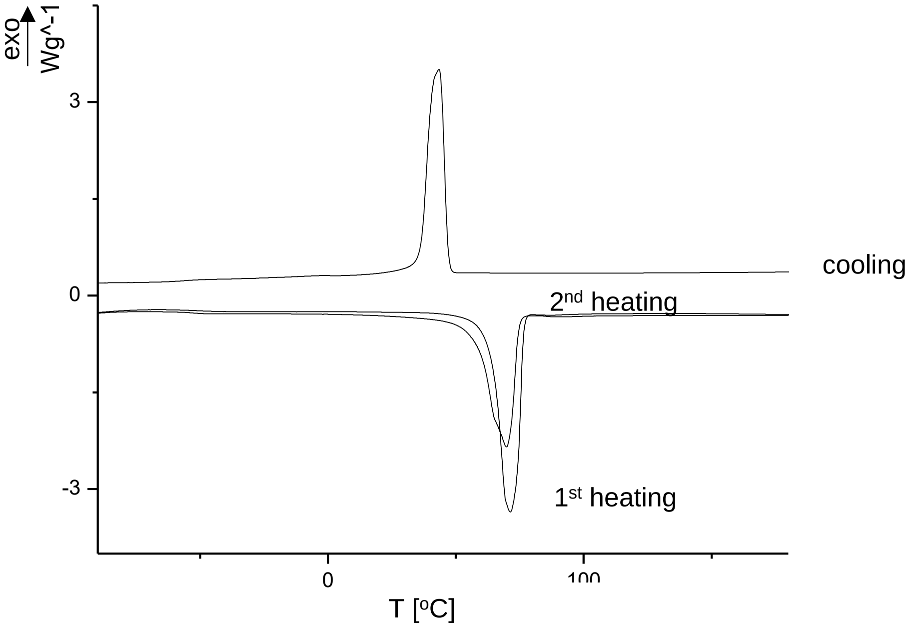
3.3.3 Thermal behavior

DSC was conducted to study the thermal behavior of films, a cycle of heating-cooling-heating from -80 °C to 200 °C with 10 °C/min rate was applied. As shown in **Figure 3-2**, PEG film in the first heating cycle shows a strong endothermic peak at 69°C, that corresponds to the melting process of the PEG crystalline part. Exothermal PEG crystallization peak occurs in the subsequent cooling cycle that compared with the melting peak is shifted to the lower temperature range. In the second heating cycle melting is repeated in similar range as the first heating with the endothermic peak 64°C.

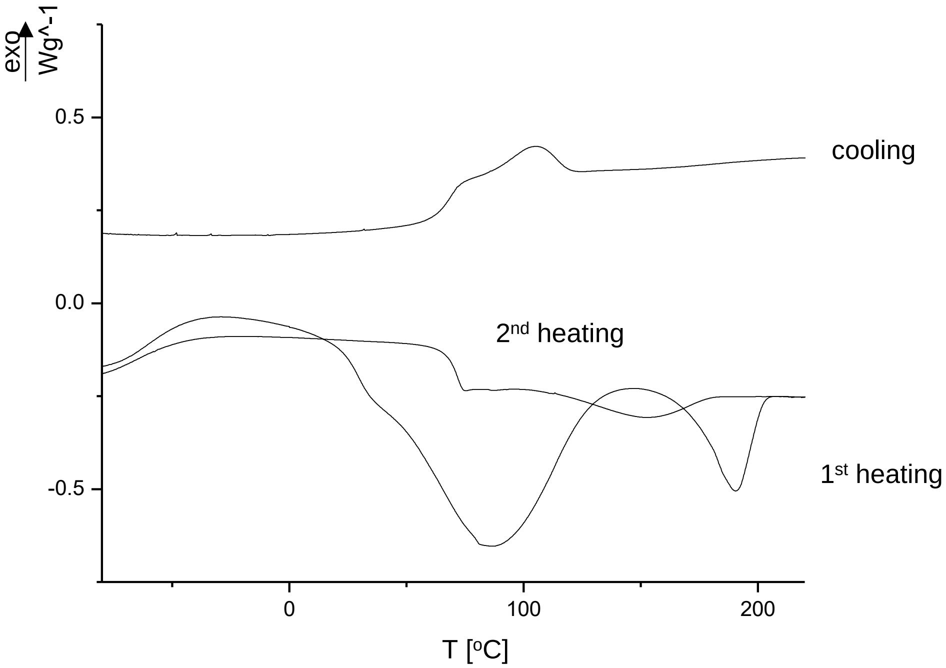
PVA film is also semi-crystalline. The first heating cycle shows a broad endothermic peak due to solvent evaporation and the melting of PVA in water phase, and another endothermic peak at 187 °C indicating the melting of PVA crystalline part. Exothermal PVA crystallization peak occurs in the subsequent cooling cycle that compared with the melting peak is shifted to the lower temperature range. In the second heating cycle, it shows the thermal behavior of pure PVA with glass transition temperature at 72 °C, and melting endotherm at 155 °C.

PEG/PVA blended film (with 40% PVA) is semi-crystalline with a single melting point at 62°C, showing no significant difference compared with virgin PEG film; no melting endotherm of PVA is seen on the DSC curve, therefore, it is believed that the PEG chains prevent almost any PVA crystallization process from taking place, leaving the PVA component in an essentially amorphous state, dispersed mainly in the amorphous phase of the PEG component.

a


exo
Wg^-1
3
0
-3
0
100
T [ºC]
cooling
2nd heating
1st heating

b


exo
Wg^-1
0.5
0.0
-0.5
0
100
200
T [ºC]
cooling
2nd heating
1st heating

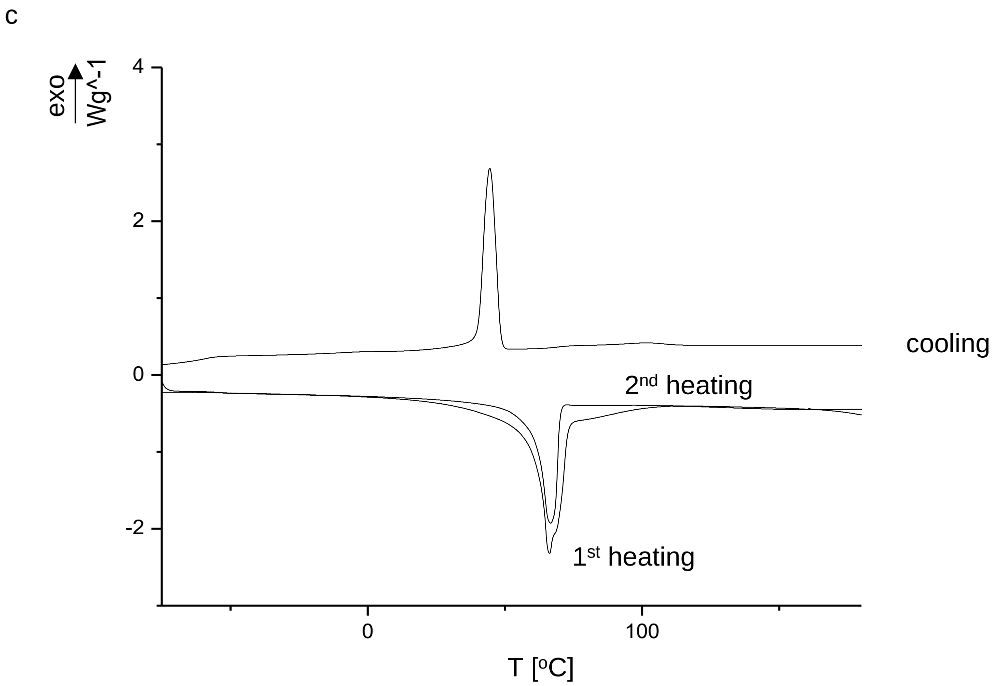


Figure 3-2 DSC curves of a. PEG film, b. PVA film and c. PEG/PVA blended film with 40% PVA.

3.3.4 Interactions between PEG and PVA

Figure 3-3 shows FTIR spectra of PEG film, PVA film and PEG/PVA blended film. In the spectrum of PEG film, there is a characteristic peak at 2902cm^{-1} which corresponds to the C-H stretch, and the peak at 1022 cm^{-1} indicating the stretching of C-O functional group.

In the PVA film spectrum, a broad O-H stretching band was seen at 3300cm^{-1}. Two peaks at 2946 and 2919cm^{-1} are related to C-H stretching. The spectrum of PVA film exhibited bands at 1732cm^{-1} for carbonyl group (C=O). The band at 1092 cm^{-1} indicates C-O stretch.

In the spectrum of the PEG/PVA blended film, it shows the characteristic peaks of both PEG and PVA. There are no important shifts of OH bands, a feature which would encourage phase mixing due to intercomponent hydrogen bond formation between PEG and PVA.

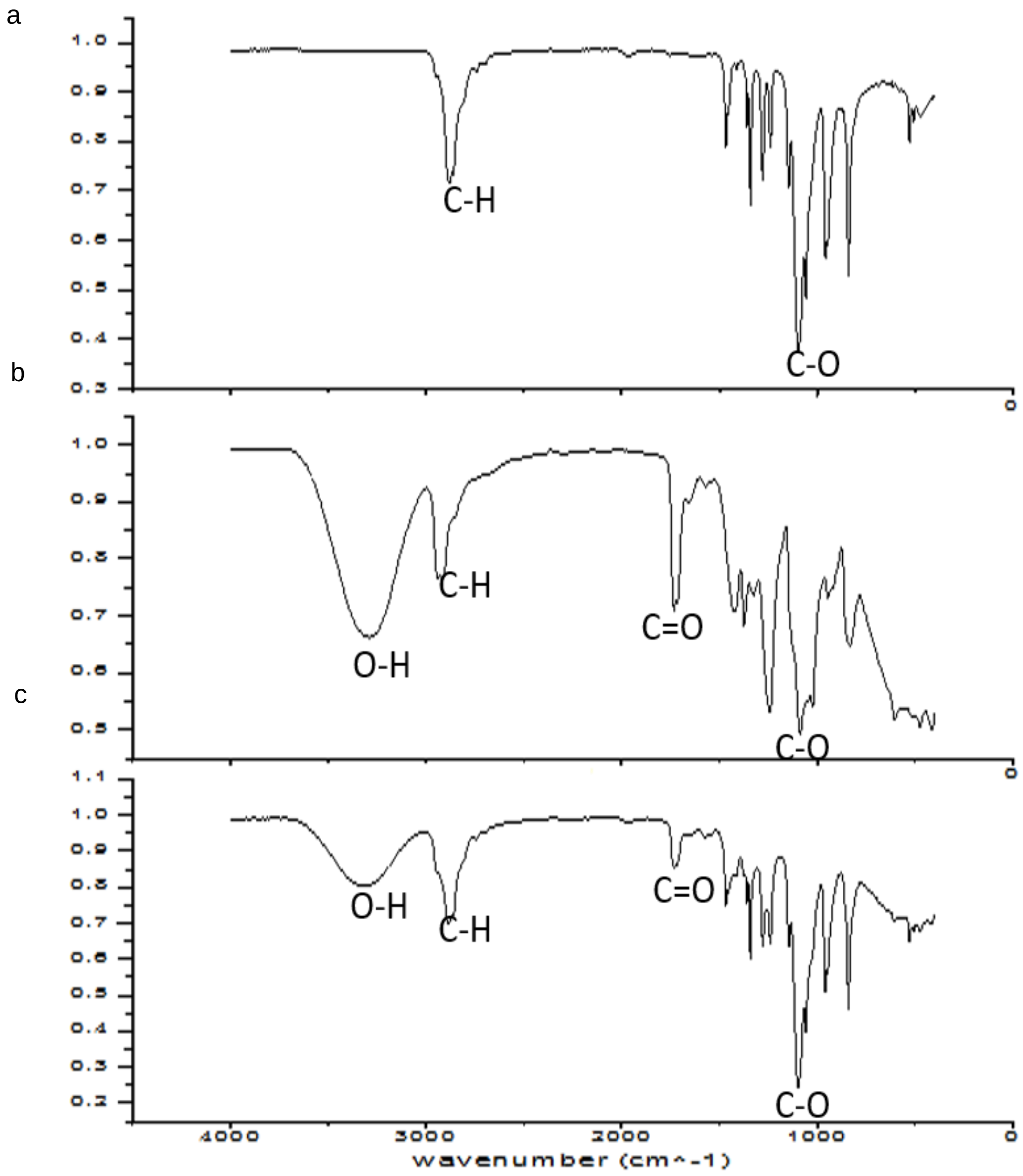


Figure 3-3 FTIR spectra of a. PEG film; b. PVA film and c. PEG/PVA blended film.

3.3.5 Dissolution properties

Slide frame test method **TMD_00719** was used to study the dissolution property of PEG, PVA and PEG/PVA blended films. The time that a film totally disappeared in the frame was recorded. **Figure 3-4** shows that at room temperature, PEG film and PEG/PVA blended film dissolve as fast as PVA film at about 50s, which is slightly slower than commercial M8630 film at about 40s.

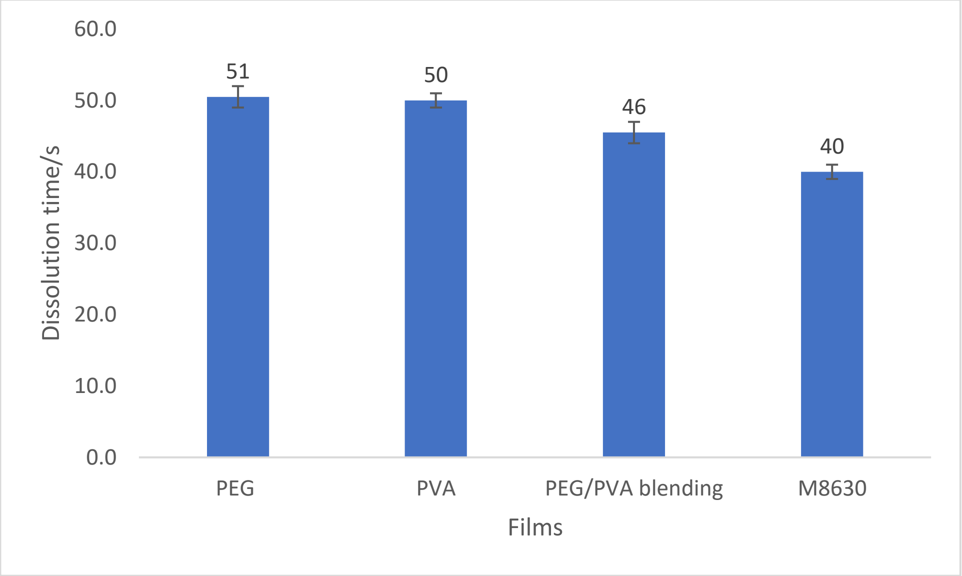


Figure 3-4 Slide frame test results of films at room temperature.

3.3.6 Mechanical properties

Mechanical properties were tested using INSTRON procedure **TMD_00543** to generate stress-strain profile at 21°C and 35% RH.

Figure 3-5 shows that the tensile strength of PVA film is 52 MPa, and it elongates to 226%. In comparison, M8630 film has excellent tensile strain at 479% and tensile stress at 48MPa, due to the addition of plasticizers. PEG film has poor tensile properties compared to PVA, with low tensile strength of 7MPa, and a tensile strain of 210%. PEG film starts to have visible pores as soon as the stretch starts until the film breaks. This is slightly improved with the blended film with 40% PVA where the tensile strength reaches 10MPa. In other words, by blending PEG with PVA, the PEG material improved its tensile strength, although the improvement is not significant. Therefore, related with M8630 film result, further film modification through plasticizer & additives addition is necessary to be investigated to increase the resistance and maximum elongation of PEG films.

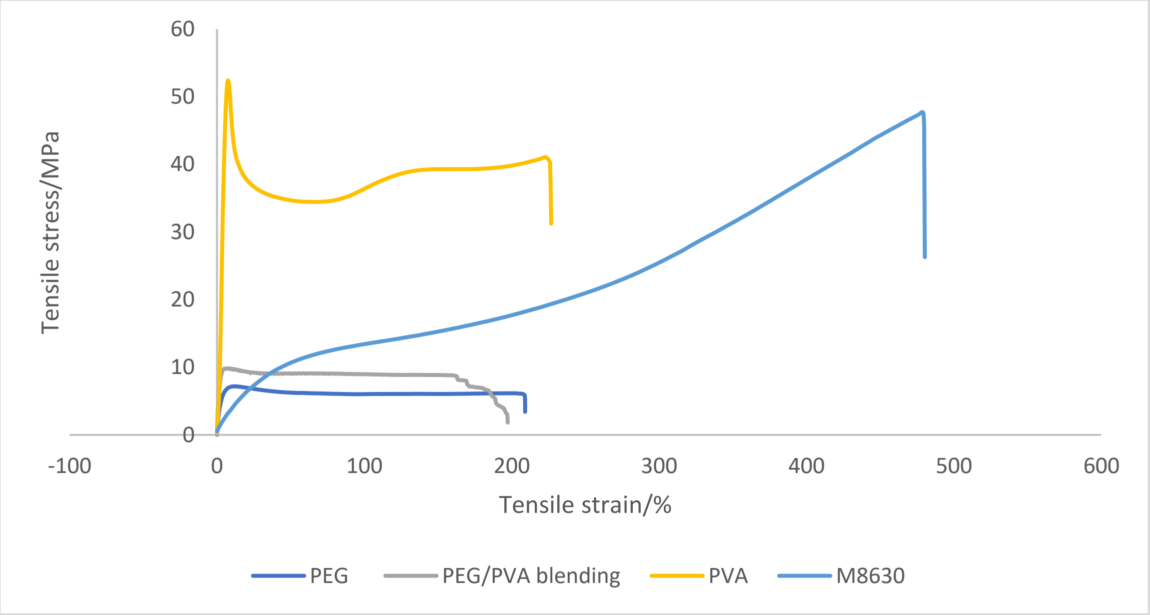


Figure 3-5 Mechanical stress-strain profiles of films.

3.3.7 Pouch prototyping

Pouch prototyping was tested for PEG and PEG/PVA blended film on the 1-up equipment. It was hard to deform the films to fit onto the cavity: the pure PEG film broke, and the PEG/PVA blended film either broke or only deformed partially, and it held very low amount of juice (**Figure 3-6 a**). Heat sealing failed with both PEG and blended films, likely due to their low melting points. Water sealing was complicated by large edge holes & cuts due to fast dissolution of PEG in water (**Figure 3-6 b**).

However, pouches with minor defects were successfully prepared and placed on storage. The pouch became sticky after 1 day at 30^{o}C, and leaked after 3h at 50^{o}C (**Figure 3-7**) due to low melting point.

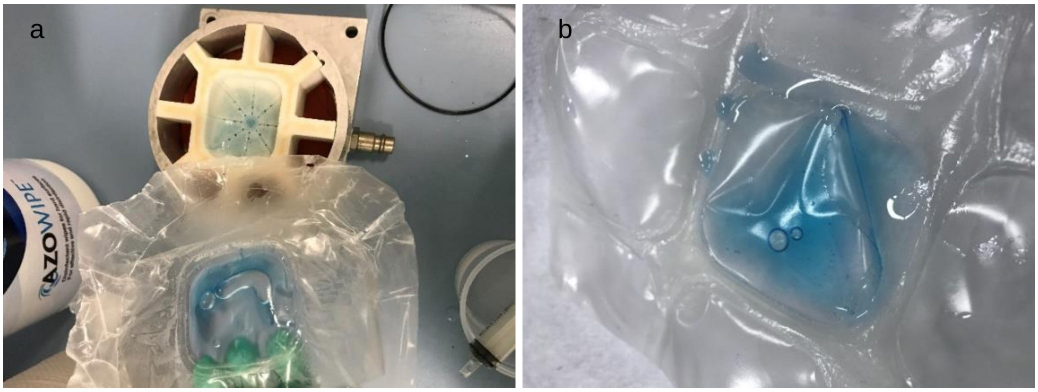


Figure 3-6 Pouch prototyping of PEG/PVA blended film a. bottom film broke; b. water sealing edge cut.

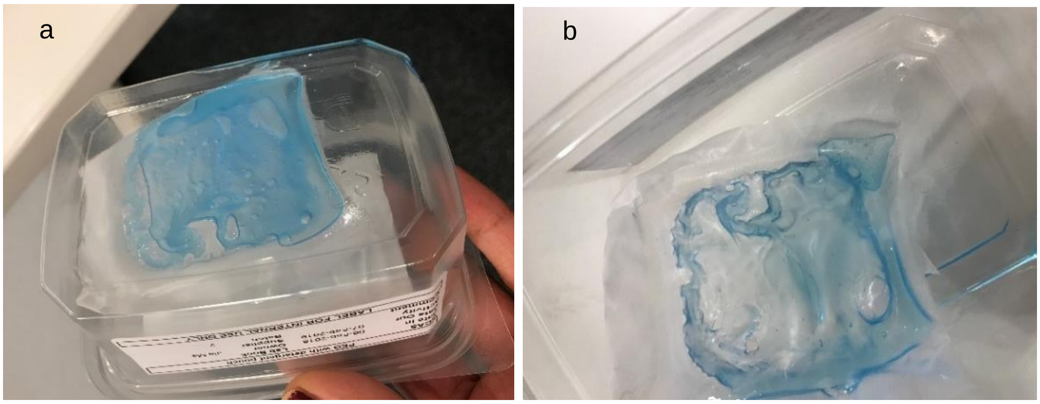


Figure 3-7 a. Pouch became sticky after 1 day at 30^{o}C; b. Pouch leaked after 3h at 50^{o}C.

3.3.8 Modifications

3.3.8.1 Plasticizer

To improve film tensile properties, plasticizer (glycerol) was added to PEG and PEG/PVA blended films, which successfully increased the film elongation, however, the tensile strength decreased at the same time.

3.3.8.2 PEG-PVA graft copolymer blending

To increase PEG film stability at high temperature, we tried blending PEG with a compatible polymer of high melting temperature range. A poly(vinyl alcohol)–polyethylene glycol graft copolymer "Kollicoat IR®" was selected for its melting point of 200°C. Because it contains 25% of PEG moieties and 75% of PVA moieties (**Figure 3-8**), this polymer was thought to have better compatibility with PEG due to the common units.

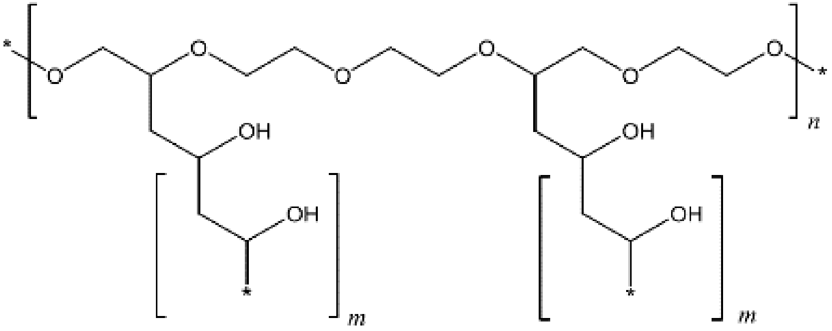


Figure 3-8 Chemical structure of Kollicoat IR®.

We blended PEG with Kollicoat IR® to keep the total PVA amount less than 40%. However, the ESEM images (**Figure 3-9**) indicate phase separation of PEG and Kollicoat IR® in the blended film.

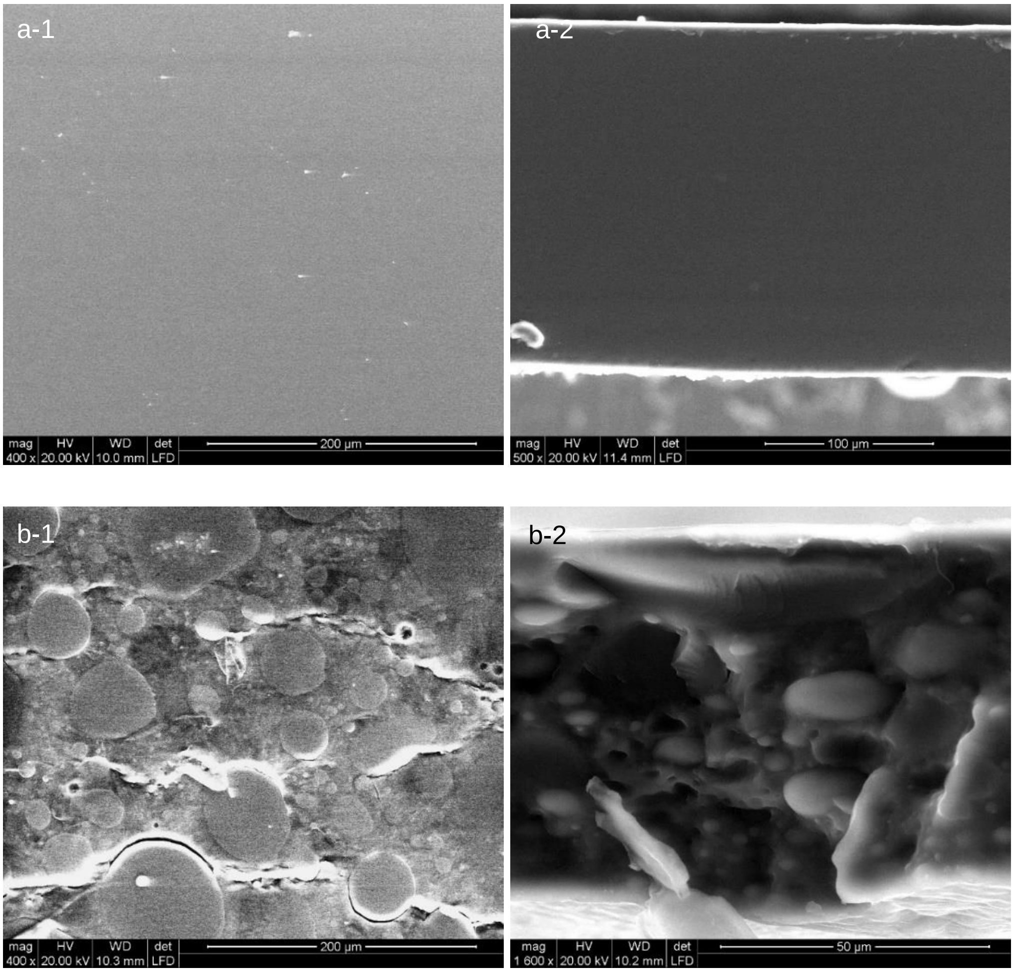


Figure 3-9 ESEM images of a. virgin Kollicoat IR® film surface (a-1) and cross-section (a-2), b. PEG/Kollicoat IR® blended film surface (a) and cross-section (b).

DSC analysis showed that the blended film exhibited two melting endotherms which confirmed incompatibility (**Figure 3-10**); what's more, Kollicoat IR® didn't help to improve film mechanical properties: the blended film appears to be easy to be torn when peeling off from glass, which showed extreme brittleness.

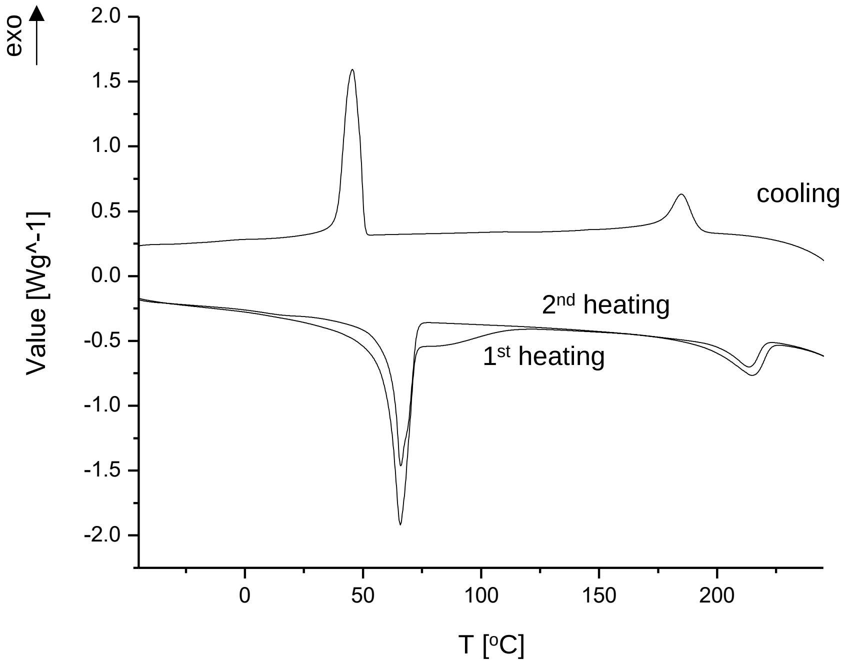


Figure 3-10 DSC curve of PEG/ Kollicoat IR® blended film.

3.3.8.3 Reaction of PEG with glutaraldehyde

We also attempted to react PEG with glutaraldehyde (**Figure 3-11**) to improve its thermal properties with minimal impact on dissolution. Thus, glutaraldehyde was reacted with PEG at pH =6 with the weight ratio of PEG: glutaraldehyde=40:1.

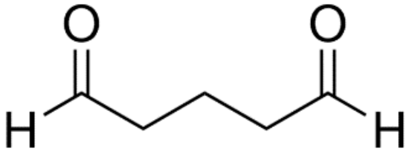


Figure 3-11 Chemical structure of glutaraldehyde.

FTIR and NMR were employed to study the reaction. However, since the PEG 400,000 chain is very long with only two active -OH groups in the end of the chains, it was hard to detect the reaction by these two tools, since the PEG is too large to see the terminal groups.

From ESEM images (**Figure 3-12**) we can see that the PEG – glutaraldehyde reacted film is homogeneous and flat, there is little voids but less than virgin PEG film.

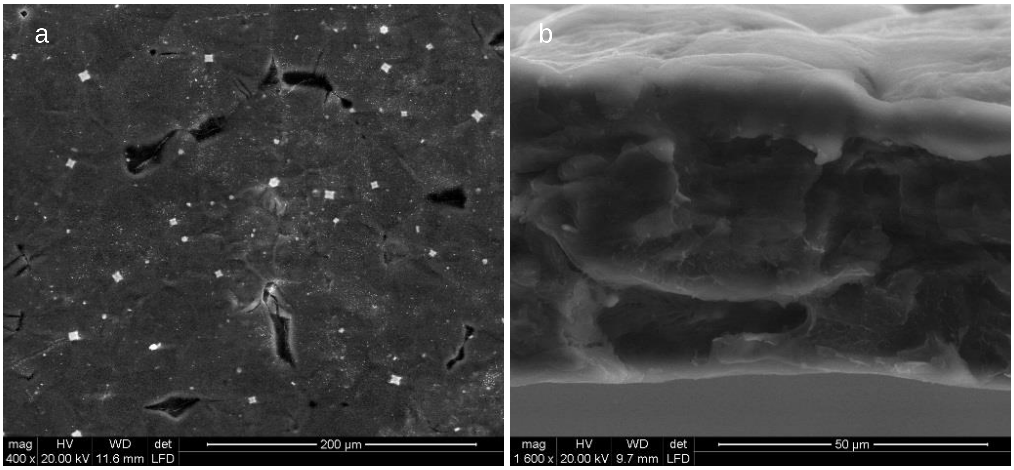


Figure 3-12 ESEM images of PEG-glutaraldehyde reacted film a. surface and b. cross-section.

According to DSC analysis, the melting endotherm insufficiently increased by only ~5°C (**Figure 3-13**) when glutaraldehyde is added to react.

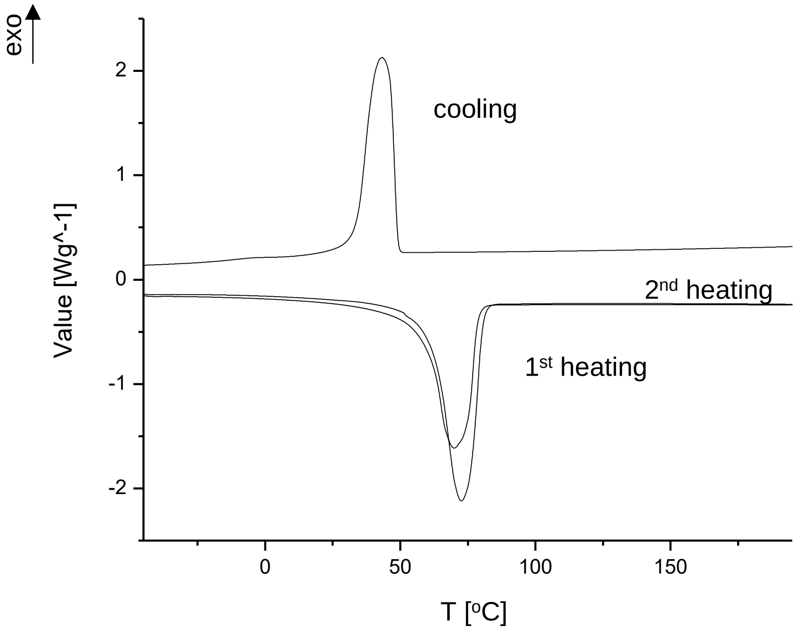


Figure 3-13 DSC curves of PEG-glutaraldehyde reacted film.

Regarding to other film properties, the dissolution time of PEG-glutaraldehyde reacted film was acceptable, although increased by 30s. The tensile strength was increased to some extent (by ~14%).

3.4 Conclusions

PEG film shows better compatibility with current detergent, and dissolves as fast as PVA film. However, this material also presents poor film mechanical resistance and low melting endotherm (~65°C), which makes it unsuitable for SUD application globally, while there is still potential to apply this film for SUD application in cold regions. Blending with PVA, addition of plasticizer and/or reaction with glutaraldehyde improved its properties, albeit not significantly enough to justify further efforts within SUD context.

References

[1] M. Zhang, X. H. Li, Y. D. Gong, N. M. Zhao, and X. F. Zhang, “Properties and Biocompatibility of Chitosan Films Modified by Blending with PEG,” *Biomaterials*, vol. 23, pp. 2641–2648, 2002.

[2] T. Chandy, D. L. Mooradian, and G. H. R. Rao, “Chitosan-PEG-alginate Microcapsules for Oral Delivery of Hirudin,” *J. Appl. Polym. Sci.*, vol. 70, pp. 2143–2153, 1998.

[3] S. Zivanovic, J. Li, P. M. Davidson, and K. Kit, “Physical, Mechanical, and Antibacterial Properties of Chitosan/PEO Blend Films,” *Biomacromolecules*, vol. 8, pp. 1505–1510, 2007.

[4] C. Won, C. Chu, and J. Doo, “Novel Biodegradable Copolymers Containing Pendant Amine Functional Groups Based on Aspartic Acid and Poly (ethylene glycol),” *Polym. J.*, vol. 39, pp. 6677–6681, 1998.

[5] L. A. Utracki, *Polymer Alloys and Blends, Thermodynamics and Rheology*. New York: Oxford University Press Hanser, 1990.

[6] N. Chen and J. Zhang, “The Role of Hydrogen-Bonding Interaction in Poly (vinyl alcohol)/ Poly (acrylic acid) Blending Solutions and Their Films,” *Chinese J. Polym. Sci.*, vol. 28, pp. 903–911, 2010.

[7] E. Tsuchida, “Formation of Polyelectrolyte Complexes and Their Structures Formation of Polyelectrolyte Complexes and Their Structures,” *Pure Appl. Chem.*, vol. A31, pp. 1–15, 1994.

[8] D. R. Paul, *Polymer Blends*. New York: Academic press, 1978.

[9] Y. Osada and M. Sato, “Thermal Equilibrium of the Intermacromolecular Complexes of Polycarboxylic Acids Realized by Cooperative Hydrogen Bonding,” *J. Polym. Sci.*, vol. 14, pp. 129–134, 1976.

[10] B. S. Mudigoudra, S. P. Masti, and R. B. Chougale, “Investigation of Mechanical Properties of Ternary Polymer PVC / PVAc / PEG Blended Films,” *Res. J. Eng. Sci.*, vol. 1, pp. 63–65, 2012.

[11] X. Hu, H. Liu, Z. Gao, T. Su, and Z. Wang, “Blending Modification of PHBV / PBS / PEG and its Biodegradation,” *Polym. Plast. Technol. Eng.*, vol. 56, pp. 1128–1135, 2017.

[12] M. R. Reddy, A. R. Subrahmanyam, M. M. Reddy, J. S. Kumar, V. Kamalaker, and M. J. Reddy, “X-RD , SEM , FT-IR , DSC Studies of Polymer Blend Films of PMMA and PEO,” *Mater. Today Proc.*, vol. 3, pp. 3713–3718, 2016.

[13] X. Gu and G. Wang, “Applied Surface Science Interfacial morphology and friction properties of thin PEO and PEO / PAA blend films,” *Appl. Surf. Sci.*, vol. 257, pp. 1952–1959, 2011.

[14] E. H. Immergut and H. F. Mark, “Principles of Plasticization,” in *Plasticization and Plasticizer Processes*, Philadephia: American Chemical Society, 1965, pp. 1–26.

[15] L. S. Sakanaka, F. Yamashita, and M. V. E. Grossmann, “Water Sorption and Mechanical Properties of Cassava Starch Films and Their Relation to Plasticizing Effect,” *Carbohydr. Polym.*, vol. 60, pp. 283–289, 2005.

[16] H. Li and M. A. Huneault, “Comparison of Sorbitol and Glycerol as Plasticizers for Thermoplastic Starch in TPS / PLA Blends,” *J. Appl. Polym. Sci.*, vol. 119, pp.

2439–2448, 2011.

[17] N. Gontard, S. Guilbert, and J. Cuq, “Water and Glycerol as Plasticizers Affect Mechanical and Water Vapor Barrier Properties of an Edible Wheat Gluten Film,” *J. Food Sci.*, vol. 58, pp. 206–211, 1993.

[18] Y. P. Chang, A. A. Karim, and C. C. Seow, “Interactive plasticizing – antiplasticizing effects of water and glycerol on the tensile properties of tapioca starch films,” *Food Hydrocoll.*, vol. 20, pp. 1–8, 2006.

Chapter 4. Sodium Alginate Film and its Blends

4.1 Introduction

In recent years, as people's awareness of environmental protection and sustainability raises, bio-sourced film forming materials (**Figure 4-1**[1]) – hydrocolloids (polysaccharides and proteins), lipids and composites thereof - are being viewed as promising alternatives to synthetic films [1]–[7]. Hydrocolloids include hydrophilic polymers of microbial, vegetable, animal, or synthetic origin which are large molecules with many hydroxyl groups [8].

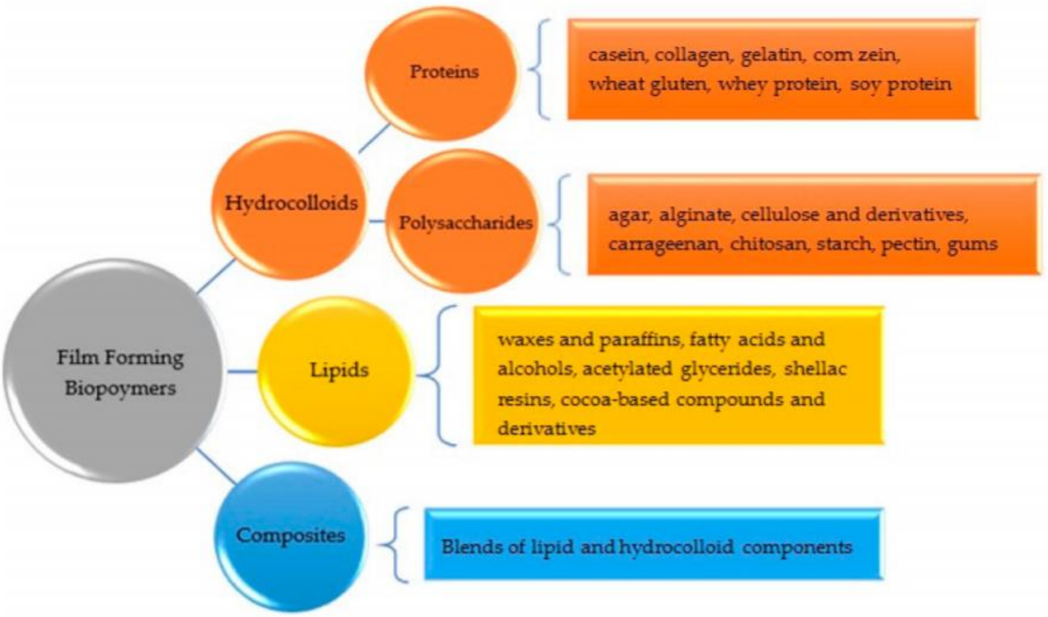


Figure 4-1 The film-forming biomaterials that have been studied extensively for film formations [1].

Polysaccharide films have advantages over protein and lipid films because of their low material cost, abundant resources, relatively stable performance, and good heat sealability and water solubility [2][9]. Sodium alginate (SA) is the salt of a natural linear binary copolymer of β-D-mannuronic acid and α-L-guluronic acid. Alginate is commonly produced by various genera of brown algae and has a high degree of safety [10]. It has good water solubility, gel ability, and film-forming properties, and is widely used in pharmaceutical and food industries [11]. However, SA has poor mechanical properties (low elasticity and high brittleness) which requires improvements as a film-forming material for packaging.

As introduced in **Chapter 3**, polymer blending is a simple method to modify physical and mechanical properties of materials, it is of great technological significance and is widely used in industry [12]–[16]. PVA is a hydrophilic water-soluble polymer which is known to have excellent mechanical strength and elasticity, which would be of help in increasing the mechanical properties of SA film. PEG is a water-soluble flexible-chain polymer that has low tensile strength but very good elongation, which could complement with SA film in mechanical properties. Moreover, in a packaging film, flexibility is of importance during handling and storage, therefore, plasticizers are usually needed to increase film flexibility.

Therefore, the blending of PVA with SA, the blending of PEG with SA, and the blending of the 3 polymers, incorporating plasticizer, are interesting for this PhD project. Thus, in this chapter, the properties of plasticized SA film and its blending with PVA, PEG and the mixture are studied and discussed; glycerol was chosen as plasticizer.

4.2 Experimental

4.2.1 Materials

Sodium alginate and PEG 400,000 were purchased from Sigma-Aldrich and used as received without further purification. PVA Mowiol® 18-88 resin (from Sigma-Aldrich) has a weight average molecular weight of 130,000. Mowiol® 18-88 resin supplied by Kuraray was used as reference material to cast film. Glycerol was used as received from Oleon.

4.2.2 Sample preparation

SA powder was dissolved in water and formed a homogeneous solution, and the solution was treated by sonication to remove bubbles. Solution casting and solvent evaporation method was utilized to prepare films. Plasticized SA films were prepared by incorporating 25% of glycerol in the SA solution.

A series of SA/PVA blended films (90%:10%, 80%:20%, 70%:30%, 60%:40%) were prepared with the mixture of aqueous solutions of individual polymers and plasticized with glycerol (25%). The blending of SA/PEG with ratio of 50%:50% was prepared and plasticized, then casted into film. Also, a study of the blending of these 3 polymers were executed with the ratio of SA:PVA:PEG=30%:40%:30%.

4.2.3 Characterizations

4.2.3.1 Environmental scanning electron microscope (ESEM)

Film surface and cross-sectional morphologies were observed at 15kV with low-vacuum ESEM FEI 600 apparatus, without sputter coating. Film cross-sections were prepared by fracturing in liquid nitrogen.

4.2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded at room temperature using Fourier Transform Infrared Spectrometer 680 Plus from Jasco. with a resolution of 4 cm^{-1} and scanning speed of 2 mm/s^{-1}, in transmittance mode. An attenuated total reflection (ATR) accessory with thermal control and a diamond crystal (a Golden Gate heated single reflection diamond ATR from Specac-Teknokroma) was used to obtain FTIR spectra.

4.2.3.3 Film property tests

Dissolution test, compatibility test with detergent, tensile stress-strain test and mono-pouch prototyping were conducted to study film properties. The detailed theories, procedures, and instruments are referred in **Chapter 2**.

4.3 Results and discussion

4.3.1 Plasticized SA film

SA film itself presents high tensile strength (59MPa) and extremely low elasticity – the elongation at break is 1.5%, as can be seen in **Figure 4-2**. When glycerol is added, the tensile strength dropped to 29MPa, and the elongation increased from 1.5% to 2.3%, but the improvement is not significant: there was almost no elasticity even for the plasticized film.

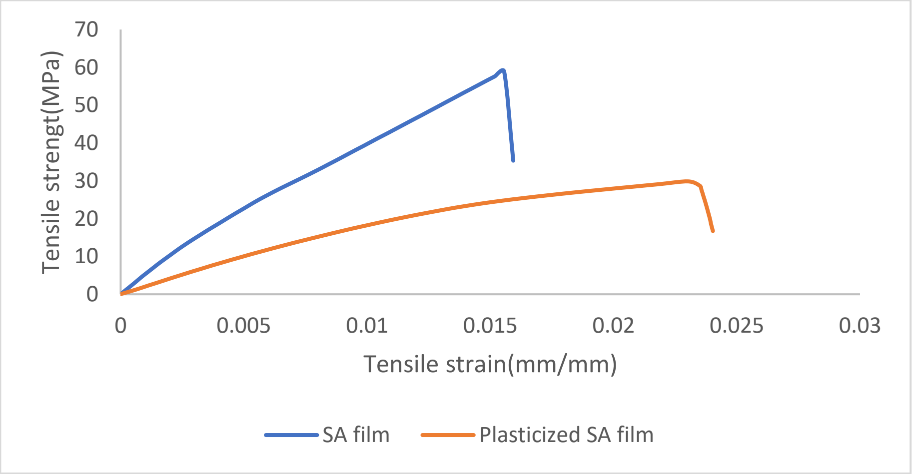


Figure 4-2 Tensile stress-strain curves of SA film and plasticized SA film.

4.3.2 SA/PVA blended films

4.3.2.1 Film morphologies

ESEM images of the surface and cross-section of SA, PVA and SA/PVA blended films are shown in **Figure 4-3**. SA and PVA films are both homogeneous, dense and flat. The blended film is homogeneous with a certain roughness. Some voids are seen on the cross-section but the film is not porous as can be confirmed on the surface.

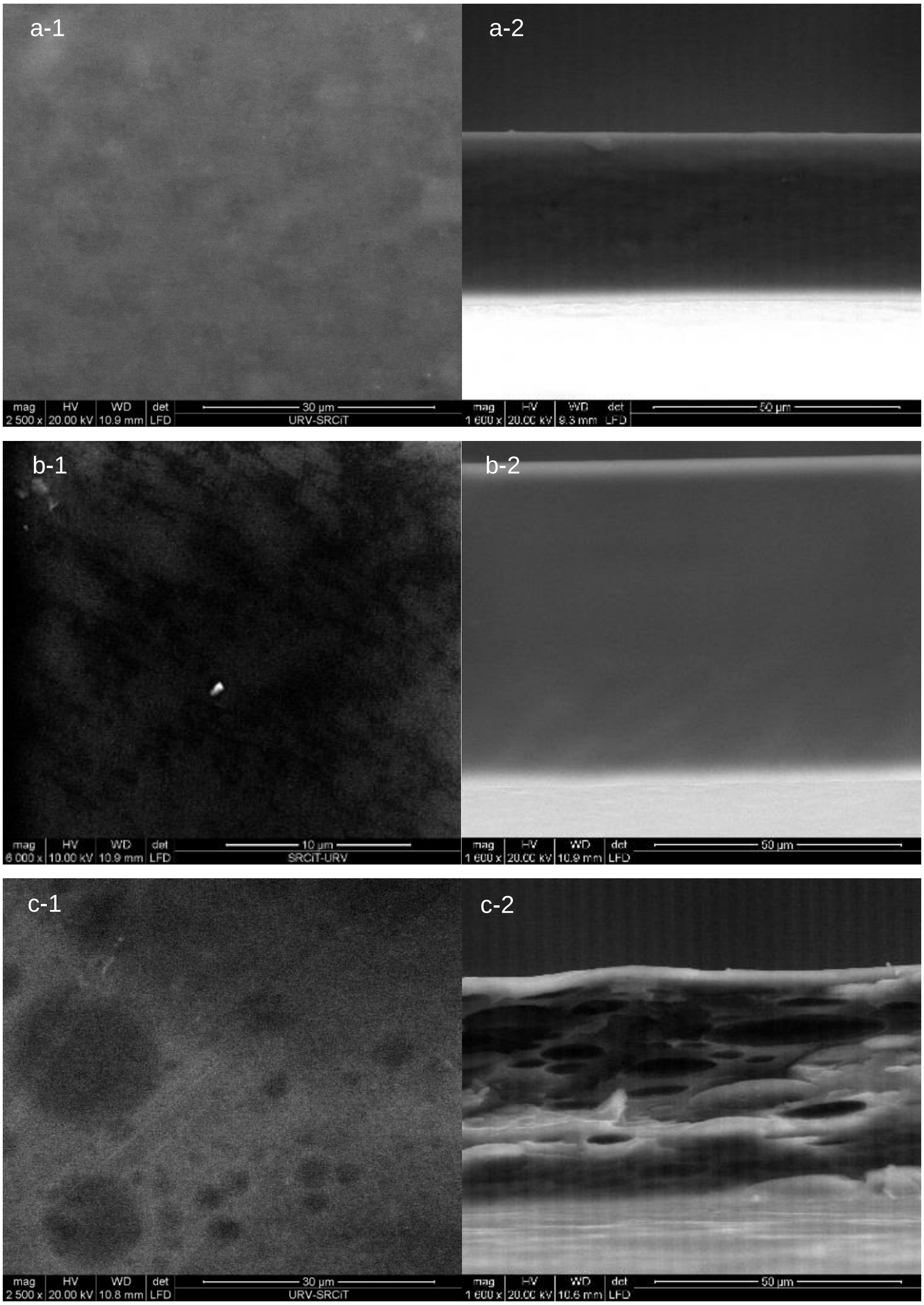


Figure 4-3 ESEM images of a. SA film, b.PVA film, c. SA/PVA blended film with 40%PVA; -1 surface and -2 cross-section.

4.3.2.2 Interactions between SA and PVA

As seen in **Figure 4-4**, spectra of SA film, PVA film and blended films of SA/PVA with different ratios are shown. In IR spectrum of SA characteristic peaks, namely asymmetric stretching of -COO^- group at 1597 cm^{-1}, the symmetric stretching of -COO^- group at 1406 cm^{-1}, the C-O stretching at 1305 cm^{-1} , and hydroxyl group stretching band at 3430 cm^{-1} have been observed.

In the PVA film spectrum, a broad O-H stretching band is seen at 3300cm^{-1}. Two peaks at 2946 and 2919cm^{-1} are related to C-H stretching. The spectrum of PVA film exhibits bands at 1724cm^{-1} for the carbonyl group (C=O), and at 1244 cm^{-1} for the stretching of C-O-C group. The band at 1085 cm^{-1} indicates C-O stretch.

The spectra of the SA/PVA blended films was characterized by the presence of the absorption bands typical of the pure components, with intensity roughly proportional the blending ratio. The characteristic band of SA appeared at 1305 cm^{-1} was observed in all the spectra of blended films and the band shifted to a lower frequency range with PVA proportions increase, indicating that there may occur a strong hydrogen bonding interaction between PVA and SA chains. In addition, it is noticed that the hydroxyl stretching bands became much broader with increasing SA content, which also confirmed the hydrogen bonding between SA and PVA chains.

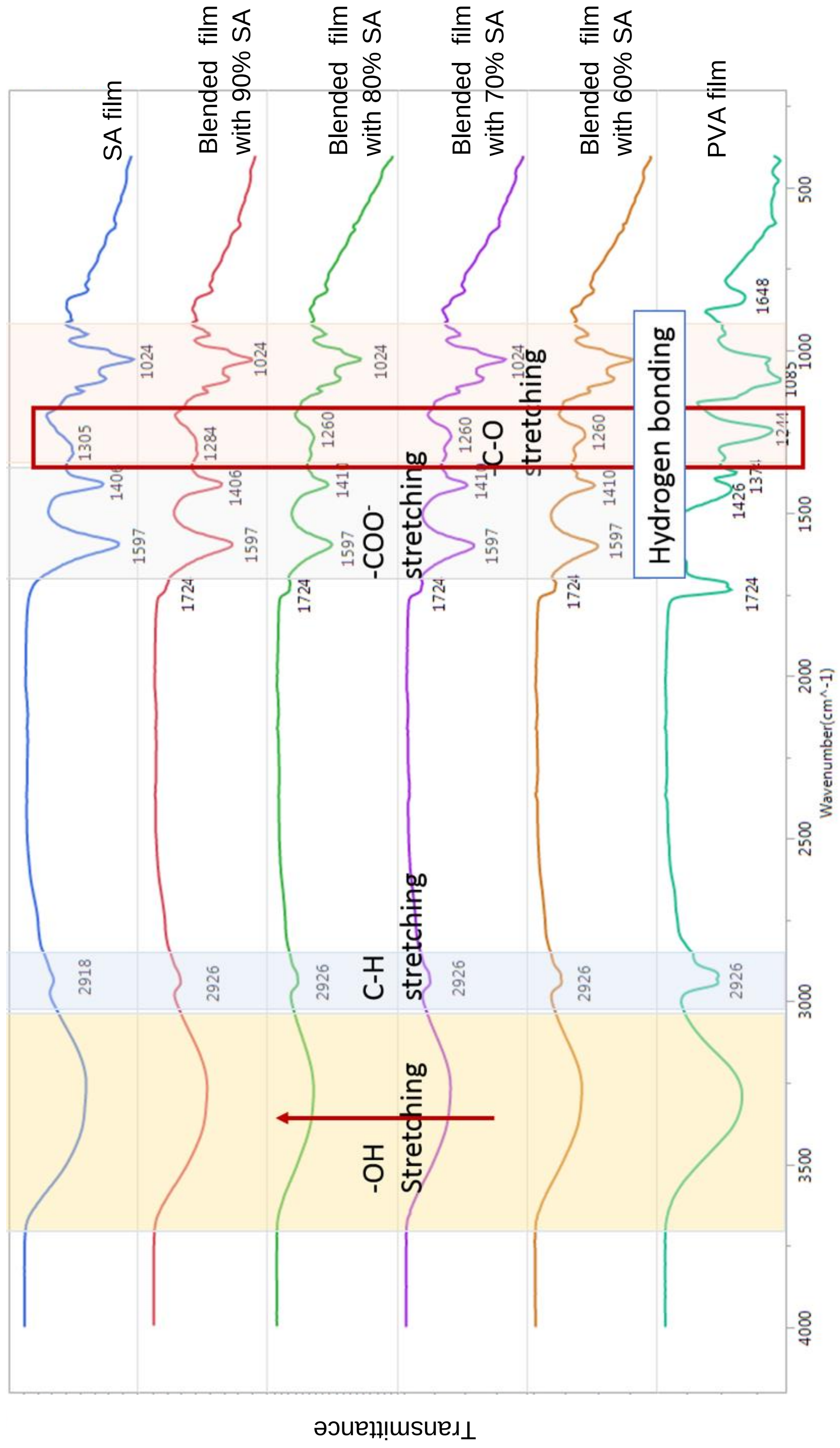


Figure 4-4 FTIR spectra of SA film and SA/PVA blending films of different ratios.

4.3.2.3 Dissolution properties

Slide frame test method **TMD_00719** was used to study the dissolution properties of SA and SA/PVA blended films. **Figure 4-5** shows that at room temperature, SA film dissolved in water within 90s, which is slower than PVA at 50s. When blended with PVA, the dissolution became faster.

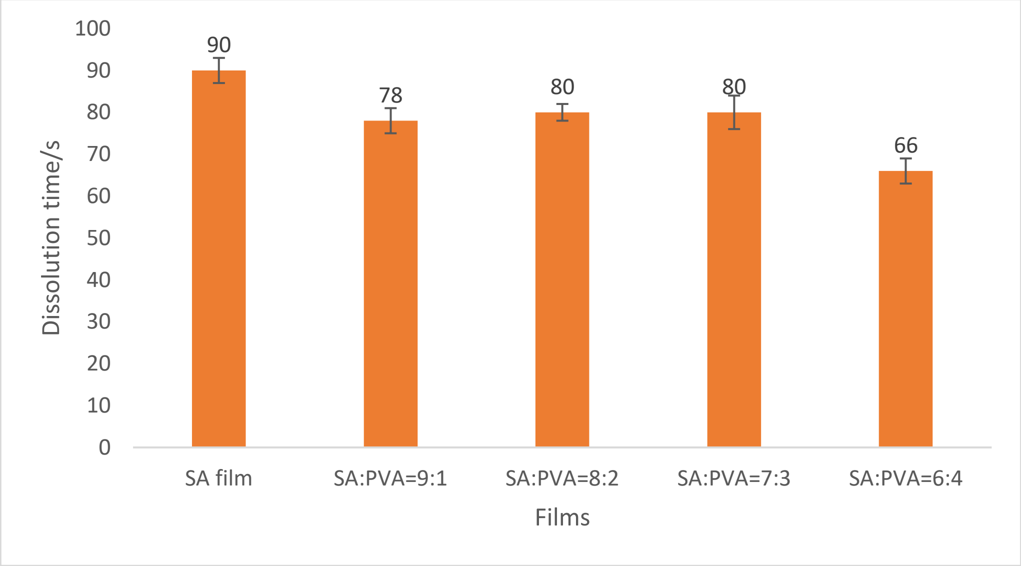


Figure 4-5 Dissolution properties of SA and SA/PVA blended films at RT.

4.3.2.4 Mechanical Properties

The mechanical properties of SA/PVA blended films didn’t improve in an important way, compared with pure SA film, as shown in **Figure 4-6**. The E-modulus of the blended films are lower than pure SA film, which means that the blended films are less stiff. When blended with 10% and 20% PVA, the elongation at break is higher than when blended with 30% and 40% PVA; it may due to the inhomogeneous thicknesses of the latter films, though the difference is not significant, as the elongation at break of all the films is less than 3% (almost no elasticity).

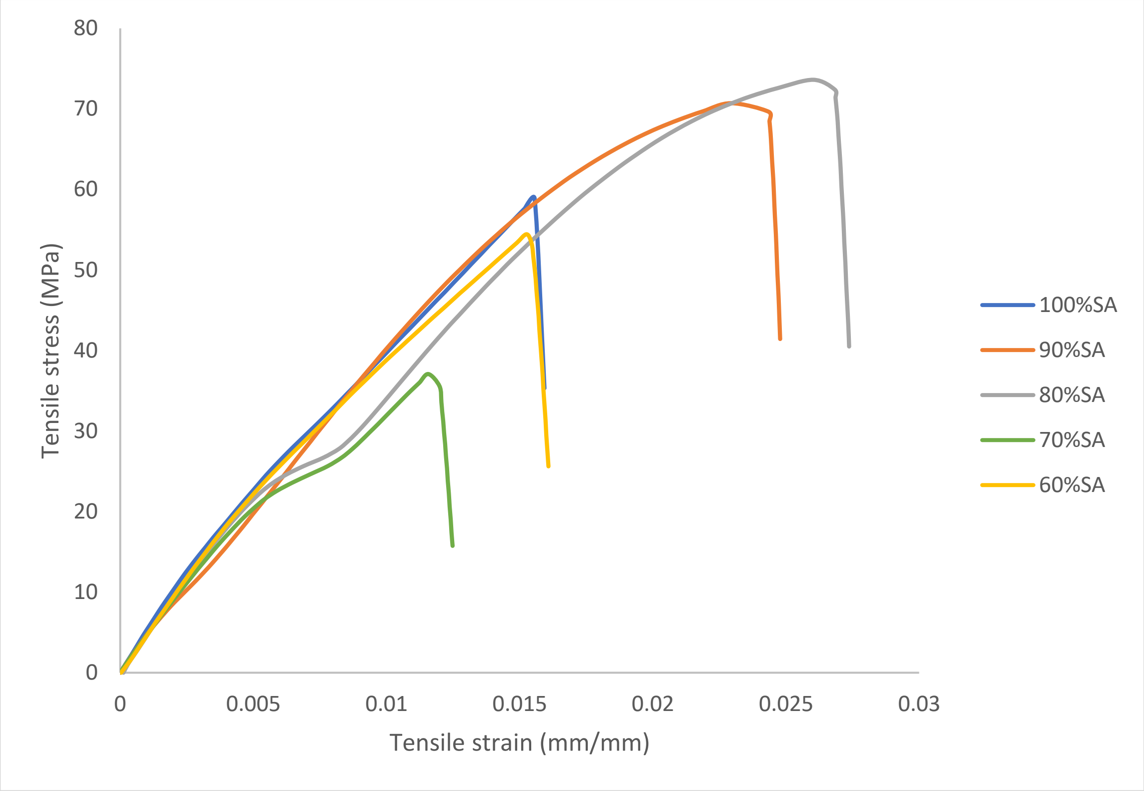


Figure 4-6 Tensile stress-strain curves of SA and SA/PVA blended films.

4.3.3 SA/PEG blended film

4.3.3.1 ESEM Images

Figure 4-7 shows the ESEM images of the surface and cross-section of SA/PEG blended film. The mixing of PEG and SA shows inhomogenity and roughness. The cross-section image shows two phase morphology, one as continuous phase and the other in the form of dispersed phase. The ESEM photomicrographs of the blending shows the phase separation and partial incompatibility between PEG and SA molecules.

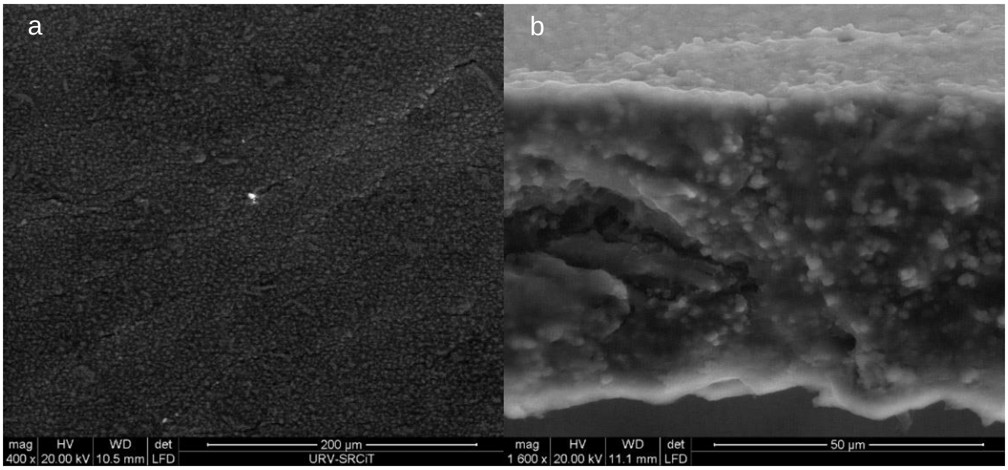


Figure 4-7 ESEM images of SA/PEG blended film a. surface and b. cross-section.

4.3.3.2 Mechanical Properties

The SA/PEG blended film showed extreme brittleness – when peeled off from glass plate, the film was easy to be broken into pieces due to low mechanical strength and elasticity; this may result from the incompatibility of the two polymers on top of brittleness of SA film.

4.3.4 SA/PVA/PEG blended film

Figure 4-8 shows the ESEM images of the surface and cross-section of SA/PVA/PEG blended film with the ratio of SA:PVA:PEG=30%:40%:30%. The images show a certain roughness and inhomogeneity. Moreover, the 3-polymer blended film showed extreme brittleness that it was sliced into pieces when peeled off from the glass plate.

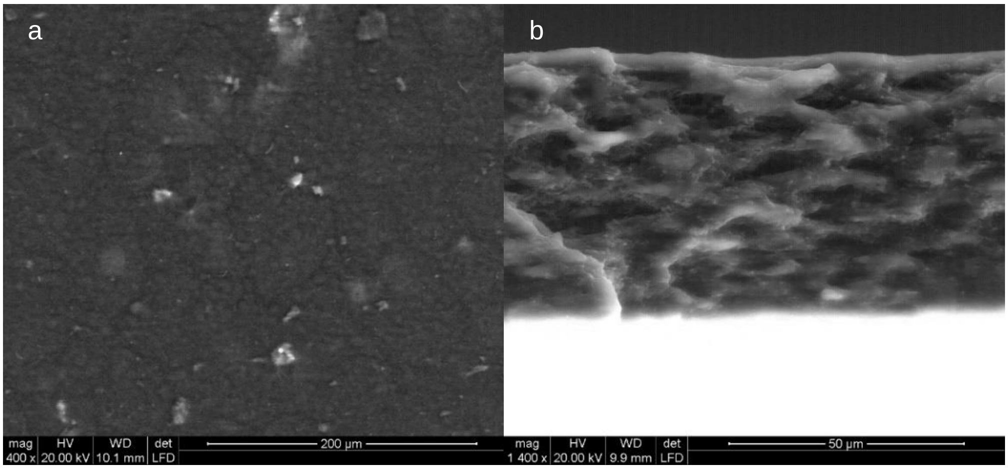


Figure 4-8 ESEM images of SA/PVA/PEG blended film. a. surface; b. cross-section.

4.4 Conclusions

Sodium alginate was blended with PVA, PEG, and the mixture of the two polymers. The blending of SA/PEG and SA/PVA/PEG showed extreme brittleness and low elasticity, probably due to incompatibility of SA and PEG. The blending with PVA slightly increased its mechanical properties and solubility in water, however the improvement didn’t meet our satisfaction for applying in SUD product.

References

[1] A. E. Films and P. Applications, “Alginate-Based Edible Films and Coatings for Food Packaging Applications,” *Foods*, vol. 7, pp. 1–38, 2018.

[2] M. Carissimi, S. H. Flôres, and R. Rech, “Effect of Microalgae Addition on Active Biodegradable Starch Film,” *Algal Res.*, vol. 32, pp. 201–209, 2018.

[3] A. Ramu, S. Munisamy, and R. Bhat, “Producing Novel Edible Films from Semi Refi ned Carrageenan (SRC) and Ulvan Polysaccharides for Potential Food Applications,” *Int. J. Biol. Macromol.*, vol. 112, pp. 1164–1170, 2018.

[4] B. Hassan, S. Ali, S. Chatha, A. I. Hussain, and K. M. Zia, “Recent Advances on Polysaccharides, Lipids and Protein Based Edible Films and Coatings: A Review,” *Int. J. Biol. Macromol.*, vol. 109, pp. 1095–1107, 2018.

[5] Y. R. Wagh and H. A. Pushpadass, “Preparation and Characterization of Milk Protein Films and Their Application for Packaging of Cheddar Cheese,” *J. Food Sci. Technol.*, vol. 51, pp. 3767–3775, 2014.

[6] S. Am, G. Gopikrishna, P. Ac, and P. Aj, “Milk Protein Based Edible Films and Coatings – Preparation , Properties and Food Applications,” *J. Nutr. Heal. Food Eng.*, vol. 8, pp. 219–226, 2018.

[7] R. Thakur, P. Pristijono, C. J. Scarlett, M. Bowyer, S. P. Singh, and Q. V Vuong, “Starch-based Films : Major Factors Affecting Their Properties,” *Int. J. Biol. Macromol.*, vol. 132, pp. 1079–1089, 2019.

[8] S. C. Shit and P. M. Shah, “Edible Polymers : Challenges and Opportunities,” *J. Polym.*, vol. 2014, pp. 1–14, 2014.

[9] K. Li, J. Zhu, G. Guan, and H. Wu, "Preparation of Chitosan-sodium Alginate Fi lms through Layer-by-layer Assembly and Ferulic Acid Crosslinking : Film Properties , Characterization , and Formation Mechanism," *Int. J. Biol. Macromol.*, vol. 122, pp. 485–492, 2019.

[10] N. Emmerichs, J. Wingender, H. Flemming, and C. Mayer, "Interaction Between Alginates and Manganese Cations : Identification of Preferred Cation Binding Sites," *Biol. Macromol.*, vol. 34, pp. 73–79, 2004.

[11] H. E. Salama, M. S. A. Aziz, and M. W. Sabaa, "Novel Biodegradable and Antibacterial Edible Films Based on Alginate and Chitosan Biguanidine Hydrochloride," *Int. J. Biol. Macromol.*, vol. 116, pp. 443–450, 2018.

[12] L. A. Utracki, *Polymer Alloys and Blends, Thermodynamics and Rheology*. New York: Oxford University Press Hanser, 1990.

[13] N. Chen and J. Zhang, "The Role of Hydrogen-Bonding Interaction in Poly (vinyl alcohol)/ Poly (acrylic acid) Blending Solutions and Their Films," *Chinese J. Polym. Sci.*, vol. 28, pp. 903–911, 2010.

[14] E. Tsuchida, "Formation of Polyelectrolyte Complexes and Their Structures Formation of Polyelectrolyte Complexes and Their Structures," *Pure Appl. Chem.*, vol. A31, pp. 1–15, 1994.

[15] D. R. Paul, *Polymer Blends*. New York: Academic press, 1978.

[16] Y. Osada and M. Sato, "Thermal Equilibrium of the Intermacromolecular Complexes of Polycarboxylic Acids Realized by Cooperative Hydrogen Bonding," *J. Polym. Sci.*, vol. 14, pp. 129–134, 1976.

Chapter 5. Lactips Film and its Blending with PVA

5.1 Introduction

Nowadays there is growing interest on bio-sourced packaging film as a replacement for synthetic polymers, leading to a sustainable, 100% bio-degradable and environmentally-friendly packaging [1]–[7]. Among the bio-sourced polymers, casein stands out for its great availability in nature constituting more than 80% of milk protein[8], as well as the water solubility of its by-product caseinates[9].

Caseins consist of a(s1)-, a(s2)-, β- and κ- casein. The caseins form complexes giving to micelles dispersed in the water phase of milk. There are diverse models describing the casein-micelle structure [10]. One of the commonly accepted models is shown in **Figure 5-1**: caseins self-associate and form sub-micelles, these sub-micelles are held together by calcium phosphate bridges, and surrounded by a layer of κ-casein to stabilize the micelle in solution, since it is the most hydrophilic and it is insensitive to calcium [11].

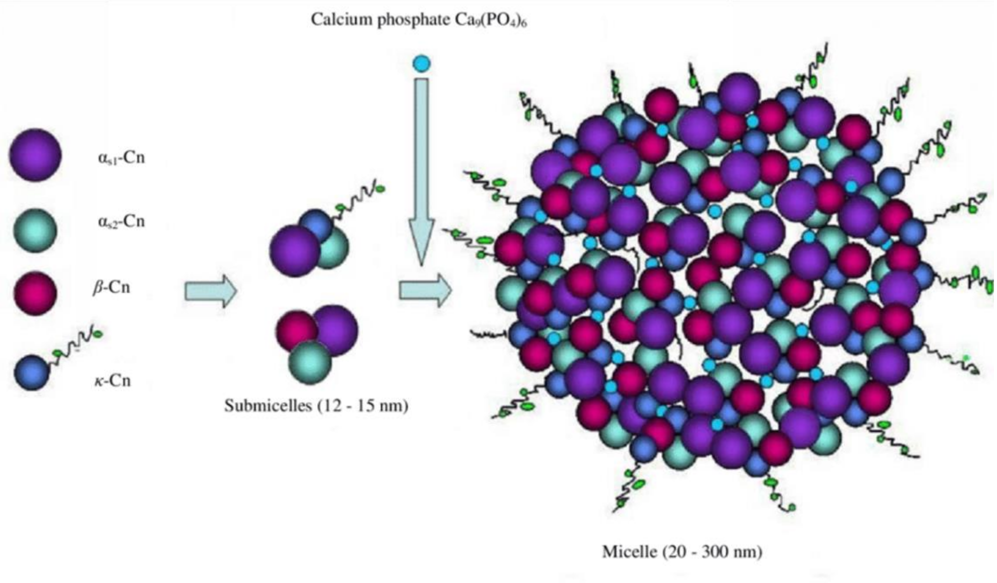


Figure 5-1 Sub-micelle model described by P. Walstra. [10] [11]

The film-forming process of casein micelles is shown in **Figure 5-2**. In general, there are 3 stages: a stable dispersion is applied to a substrate, water evaporates and bring particles into close-packing; on the 2nd stage, van der Waals and capillary forces deform the particles to render a structure without voids; finally, diffusion of casein chains across interfaces between particles imparts mechanical strength to the film and blurs the distinction between particles. If there is plasticizers added in the film, in the last stage plasticizers help the coalescence of the polymer chains by softening the casein particles [12]–[14].

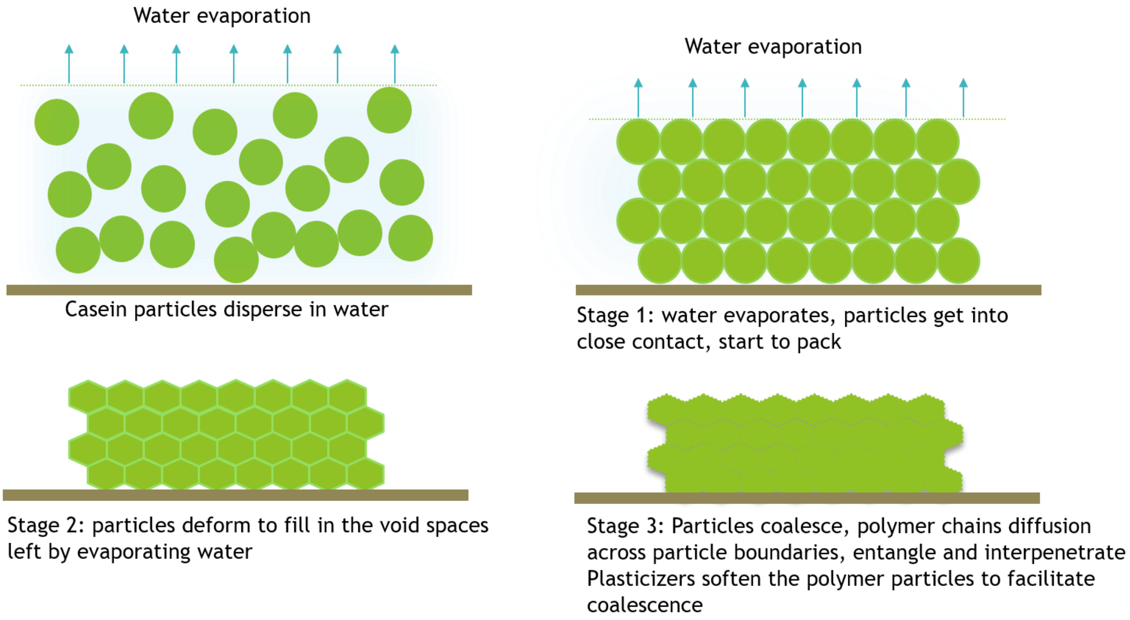


Figure 5-2 Film-forming mechanism of casein micelles.

Casein films can form a good barrier to oxygen and other nonpolar molecules, since casein provides a lot of polar functional groups such as hydroxyl and amino groups [15]. On the other hand, they possess low elasticity similar as other bio-sourced films, which could be improved using plasticizers such as glycerol and water, by increasing the free volume of the polymer network [16]–[19]. However, in SUD applications the elasticity of casein film after addition of plasticizer is not sufficient.

Lactips is a thermoplastic material, made mainly of casein. It is water soluble, biodegradable, bio-compostable, and even edible. Lactips granules are produced by extruding a mixture of casein and/or caseinate (65%-75%), plasticizer (15%-25%) and a biodegradable polymer (15%-20%) to improve the mechanical properties, preferably poly (butylene adipate terephthalate) (PBAT) [20]. PBAT is a biodegradable random copolymer, whose flexibility and toughness makes it ideal for blending with other biodegradable polymers that have high modulus and stiffness but are brittle [21][22]. Films made from Lactips materials have moderate mechanical strength and elongation.

PVA is known to have excellent mechanical strength, and with the addition of plasticizer PVA film also exhibits great elasticity. Blending of PVA with Lactips material is very interesting for SUD applications with obvious benefits in terms of natural sourcing and biodegradability.

In this chapter, the dissolution, compatibility with detergent, water vapor permeability and mechanical properties of Lactips film and its blending with PVA are studied, and the interaction between Lactips and PVA is discussed.

5.2 Experimental

5.2.1 Materials

Lactips pellets (CareTips L0003) were provided by Lactips company (France) and used as provided. PVA Mowiol® 18-88 resin supplied by Sigma Aldrich was used as reference material to cast film. Glycerol was used as received from Oleon, and sorbitol was received from Sigma Aldrich and used without further purification.

5.2.2 Sample preparation

Films were prepared by casting and vapor evaporation method, as explained in Chapter 2. Lactips (LAC)/PVA blended films were prepared by casting a water suspension of the mixture of Lactips and PVA resin, with an amount of plasticizer of 25% of PVA amount. Virgin PVA film made of Mowiol 18-88 with 25% plasticizer, and commercial M8630 film were used as reference.

5.2.3 Characterizations

5.2.3.1 Environmental scanning electron microscope (ESEM)

Film surface and cross-sectional morphologies were observed at 15kV with low-vacuum ESEM FEI 600 apparatus, without sputter coating. Film cross-sections were prepared by fracturing in liquid nitrogen.

5.2.3.2 Differential scanning calorimetry (DSC)

Calorimetric studies were performed with a Mettler DSC822e thermal analyzer, using about 5 mg of sample, nitrogen as a purge gas (100ml/min) and liquid nitrogen for system cooling. The DSC procedure was consisting of 3 steps: heating – cooling-heating. At the first step, the films were heated from -80^{o}C to 230^{o}C at the heating rate of 10^{o}C/min, and then the sample was cooled down with the cooling rate of 10^{o}C/min till -80^{o}C, followed by a 2nd heating at the rate of 10^{o}C/min till 230^{o}C.

5.2.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded at room temperature using Fourier Transform Infrared Spectrometer 680 Plus from Jasco. with a resolution of 4 cm^{-1} and scanning speed of 2 mm/s^{-1}, in transmittance mode. An attenuated total reflection (ATR) accessory with thermal control and a diamond crystal (a Golden Gate heated single reflection diamond ATR from Specac-Teknokroma) was used to obtain FTIR spectra.

5.2.3.4 Film property tests

Dissolution test, compatibility test with detergent, tensile stress-strain test and mono-pouch prototyping were conducted to study film properties. The detailed theories, procedures, and instruments are referred in **Chapter 2**.

5.3 Results and discussion

5.3.1 Optimized blending of Lactips/PVA film with plasticizer

Lactips and PVA blended films with ratio of 90%:10%, 80%:20%, 70%:30%, 60%:40% were prepared, respectively, and the film with ratio 60%:40% was selected for further study since this combination had the best mechanical strength under the scope of incorporating no more than 40% PVA. Mechanical properties were tested using INSTRON following procedure **TMD_00543** to generate stress-strain profile at 21°C, 35% RH.

A mechanical behavior comparison of Lactips film, virgin PVA film, LAC/PVA blended film with 40%PVA, and M8630 film can be seen in **Figure 5-3**. The tensile strength of PVA film is 52 MPa, and it elongated to 226%. In comparison, M8630 film had excellent tensile strain (479%) and tensile stress (48Mpa), due to the addition of plasticizers & additives. The virgin Lactips material however had poor tensile properties, with a tensile strength of 17MPa, and a tensile strain of 148%. The tensile behavior of blended film with 80% PVA was similar to PVA film, with a tensile strength of 50MPa, and a tensile strain of 270%. The blended film with 40% PVA had a lower tensile strength of 32MPa, and a tensile strain of 216%. In other words, by blending it with PVA, the Lactips material improved both tensile strength and elongation.

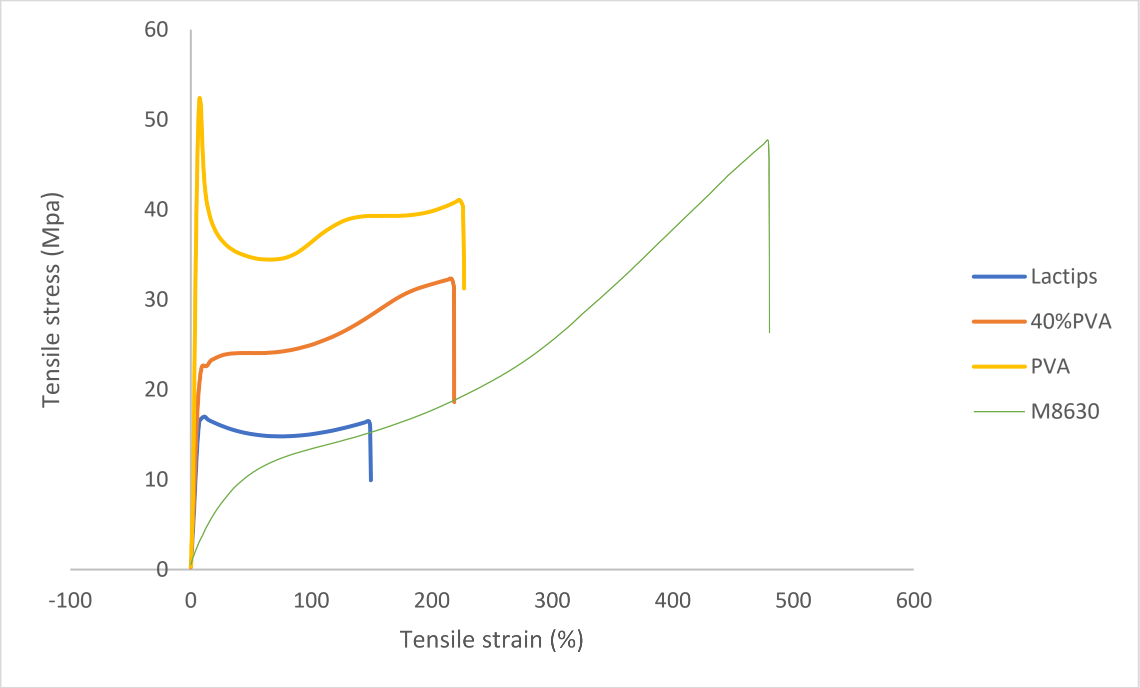


Figure 5-3 Mechanical stress-strain profiles of films (Lactips film, LAC/PVA blended film with 40% PVA film and M8630).

To decrease the stiffness of the blended films, glycerol and sorbitol were both studied as plasticizers for increasing elongation of films. Glycerol, sorbitol and the mixture of glycerol and sorbitol were added in the blend of Lactips and PVA films, respectively, at 25% with respect to PVA amount. As shown in **Figure 5-4**, the plasticized LAC/PVA blends all had better elongation, lower modulus and lower tensile strength than LAC/PVA blended film without plasticizer, where the sorbitol plasticized LAC/PVA blend exhibited lowest elongation, highest tensile strength and higher modulus, glycerol showed best elongation and lowest modulus, and the mixed plasticizer had intermediate properties. Therefore, glycerol was selected as the plasticizer for LAC/PVA blends. Water also works as a plasticizer in the film system, and as measured by Karl-Fischer instrument, the water content of Lactips film and the blended film was fixed at about 5.5%-6.5%.

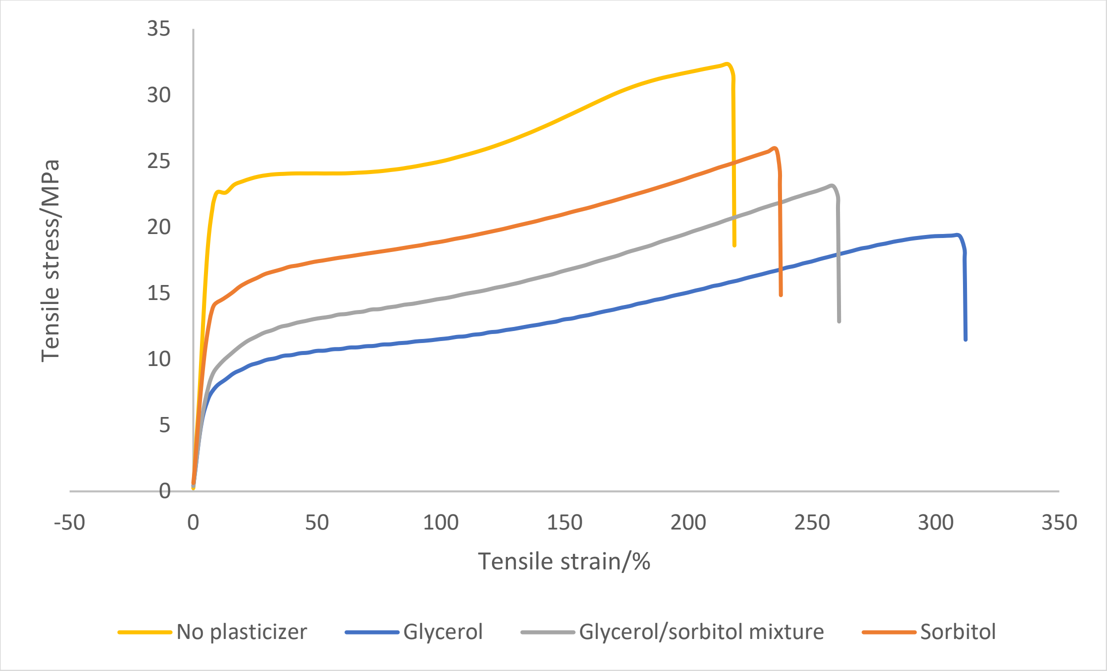


Figure 5-4 Mechanical stress-strain curves of LAC/PVA blended film with 40%PVA with plasticizers (glycerol, sorbitol, glycerol/sorbitol mixture).

5.3.2 Film morphologies

ESEM images of the surface and cross-section of Lactips, PVA, and LAC/PVA blended films are shown in **Figure 5-5**. All films appear to be homogeneous, dense and flat. No phase separation is seen on the blended film surface nor cross-section, meaning that Lactips and PVA form a compatible polymer blend at microscopic scale.

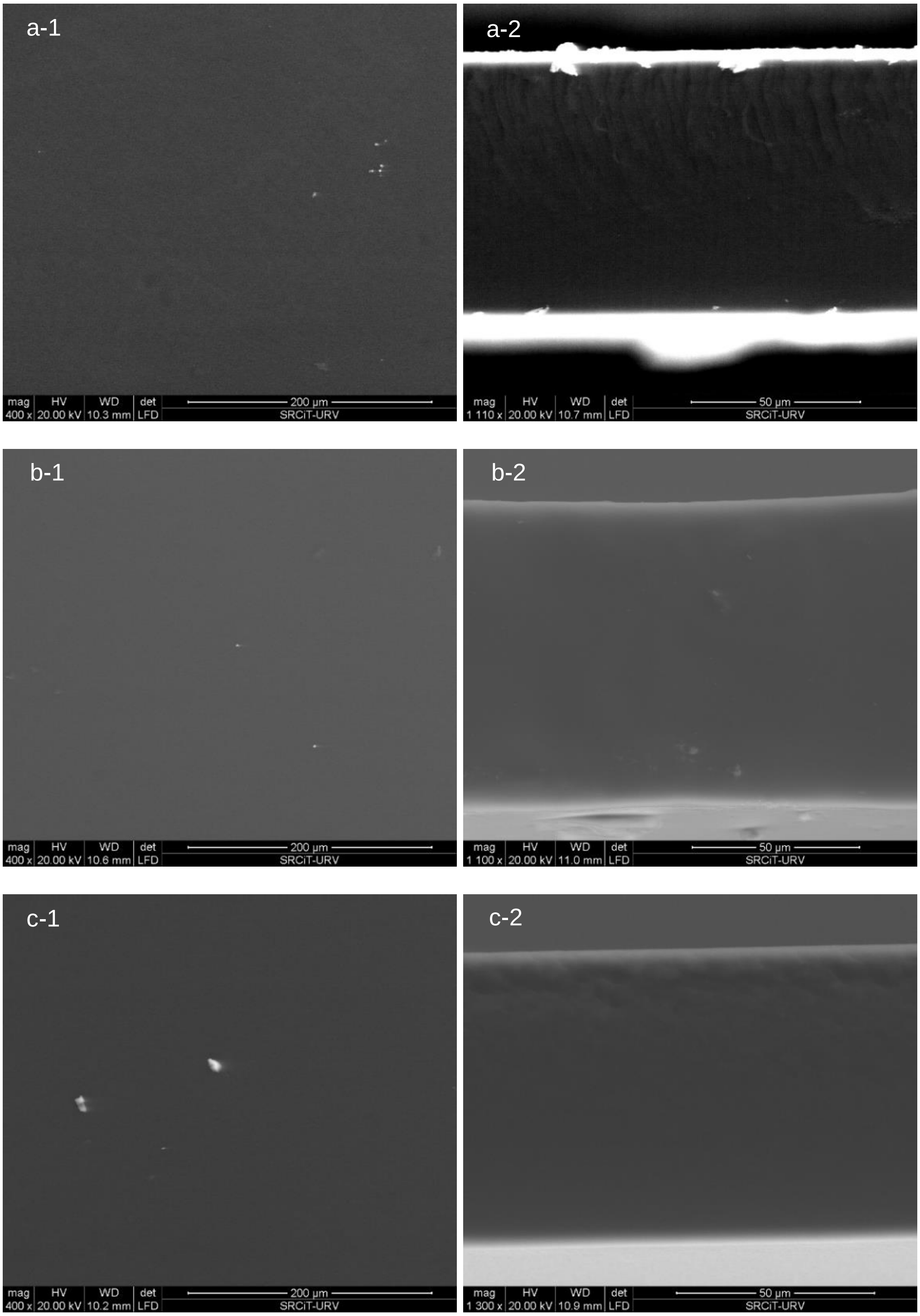
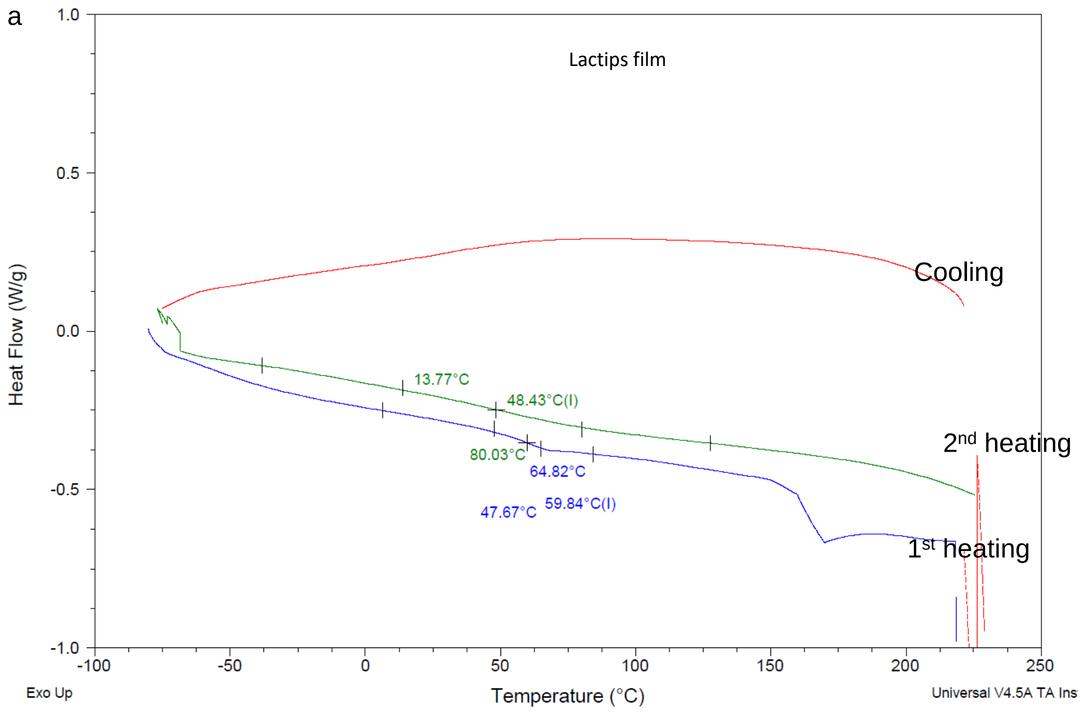


Figure 5-5 ESEM images of a. Lactips film surface and cross-section, b.PVA film surface and cross-section, c. Lactips/PVA blended film with 40%PVA; -1 surface and -2 cross-section.

5.3.3 Thermal behavior

As shown by the DSC curves in **Figure 5-6,** Lactips material is fully amorphous, with its glass transition temperature at 59ºC; PVA film is semi-crystalline with a glass transition temperature at -15 ºC and a melting endotherm at 155 ºC; LAC/PVA blended film (with 40% PVA) is semi-crystalline with a melting endotherm at 162 ºC, similar to virgin PVA film, and with only one glass transition temperature at 6 ºC, which confirms that these two polymers are miscible.



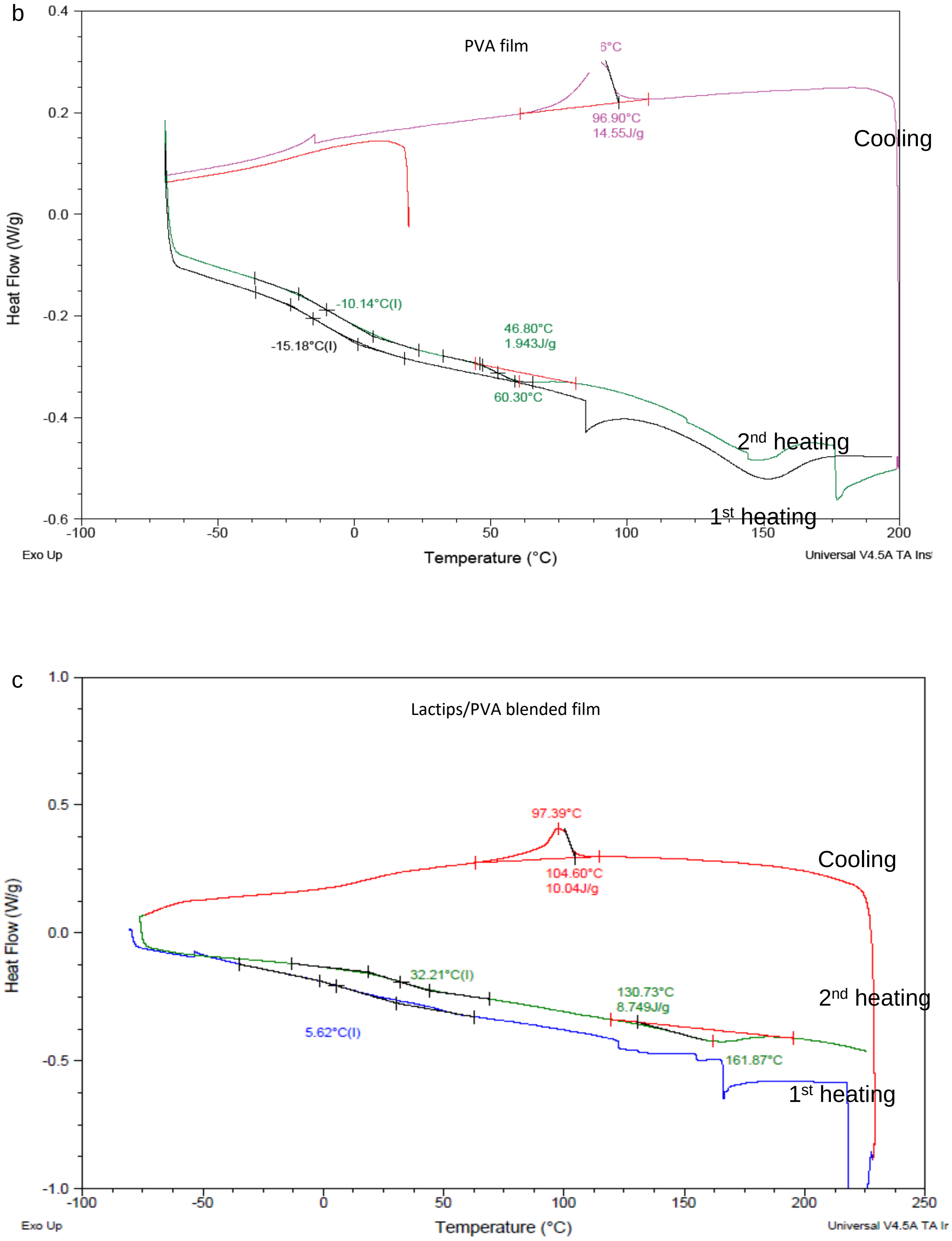


Figure 5-6 DSC curves of a. Lactips film; b. PVA film and c. LAC/PVA blended film with 40%PVA.

5.3.4 Interactions between Lactips and PVA

FTIR analysis can be seen in **Figure 5-7**. In the spectrum of Lactips film, a broad peak was seen at 3290cm^{-1}, which corresponds to the stretching of the hydroxyl groups (O-H) and amine groups (N-H). The characteristic absorption bands at 1630 and 1535 cm^{-1} indicate the bond stretching of amide (CONH) associated with the protein. The band at 1106cm^{-1} indicates C-O stretch.

In the PVA film spectrum, a broad O-H stretching band was seen at 3300cm^{-1}. Two peaks at 2946 and 2919cm^{-1} are related to C-H stretching. The spectrum also exhibited bands at 1732cm^{-1} for carbonyl group (C=O). The band at 1085 cm^{-1} indicates C-O stretch.

The spectrum of LAC/PVA blended film shows a slight band shift on the C-O band at 1100 cm^$^{-1}$ (see **Figure 5-7 b**) which seems to indicate there is hydrogen bonding between Lactips and PVA chains, further proving the interaction between Lactips and PVA.

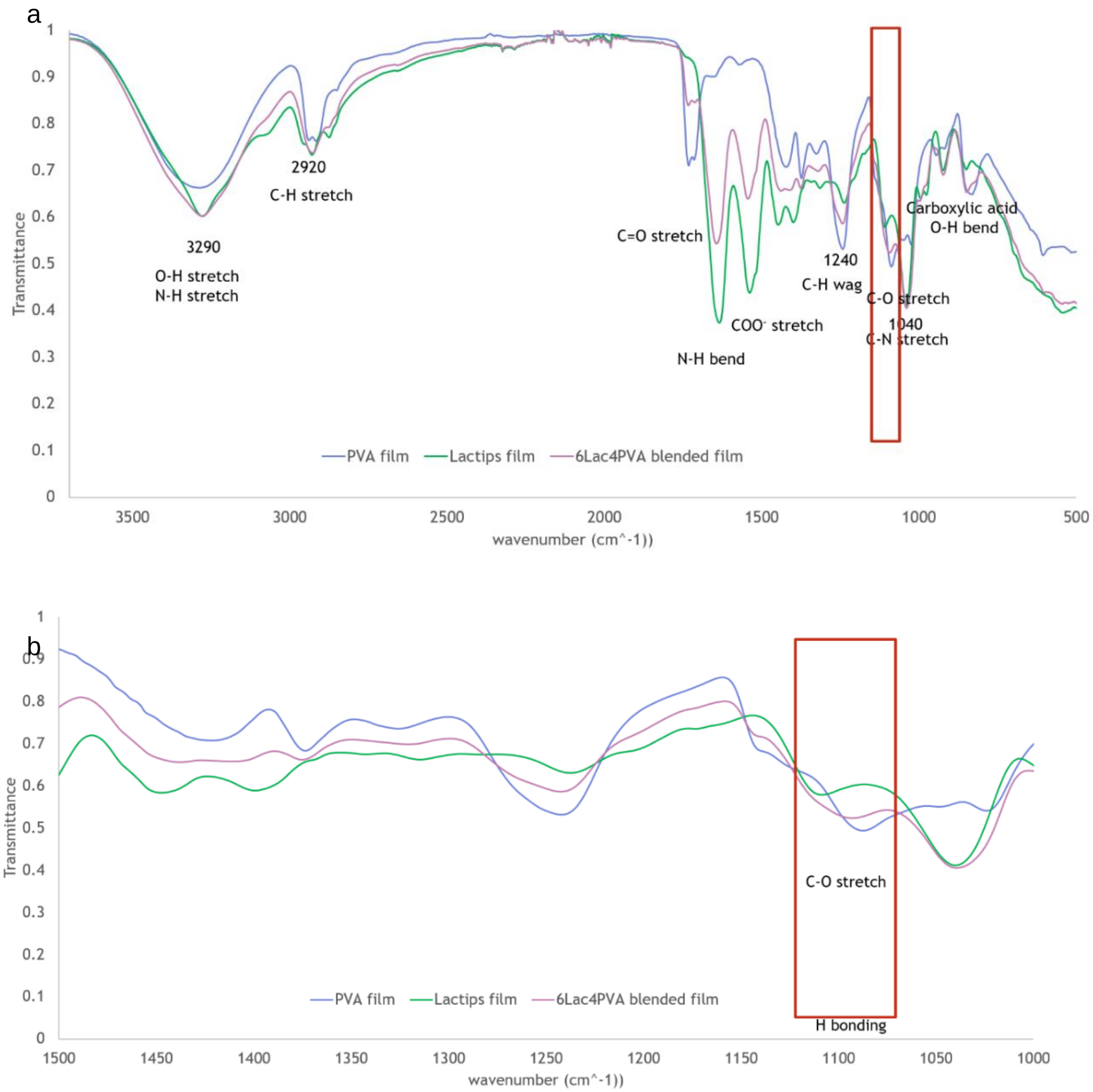


Figure 5-7 a. FTIR spectra of PVA, Lactips and LAC/PVA blended film; b. Magnified spectra at 1500-1000 cm^-1 range.

5.3.5 Compatibility with detergent

Lactips, PVA, and LAC/PVA blended films of the same size were immersed in detergent and kept in stability rooms. Weight loss/gain was calculated gravimetrically as the swell factor F= $(W_1-W_0)/W_0*100\%$, where W_1 stands for the weight of the film after immersion, and W_0 stands for the weight of the film before immersion, as explained in **Chapter 2**.

The compatibility test results are shown in **Figure 5-8**. Lactips films totally dissolved in detergent after 5 days of immersion at any temperature. However, blending Lactips material with PVA markedly improved the compatibility with detergent: after 5 days of immersion the blended films didn't lose any weight, and the swelling behavior was similar to PVA films.

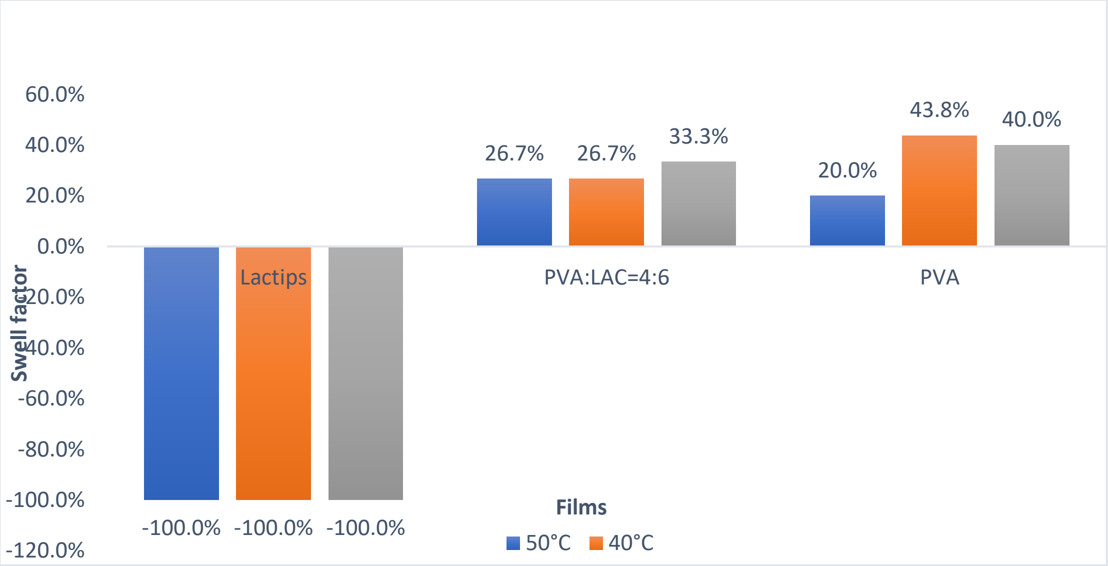


Figure 5-8 Stability test of films (LAC/PVA blended films with 40%, and PVA film) after immersion in detergent for 5 days at the indicated temperatures.

5.3.6 Dissolution properties

Slide frame test method **TMD_00719** was employed to study the dissolution properties of the films.

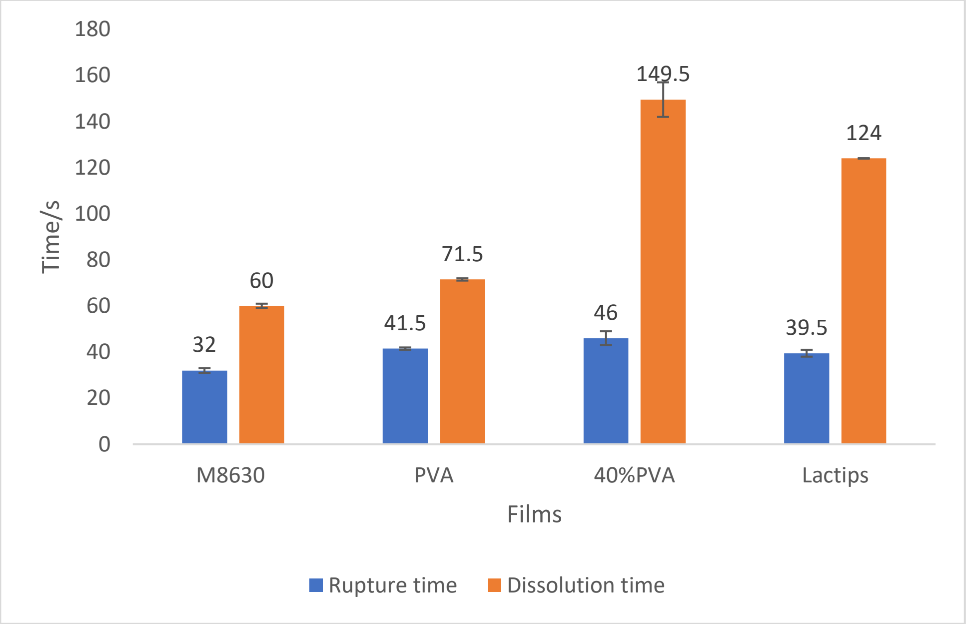


Figure 5-9 Slide frame test results of Lactips film, LAC/PVA blended films with 40% PVA, PVA film and M8630.

Figure 5-9 shows film rupture time and dissolution time. Lactips films ruptured in 40s, which is similar with the behavior of commercial M8630 film and virgin PVA film. The rupture results of blended films are higher than virgin Lactips films and virgin PVA films, probably due to the interaction between casein and PVA. The Lactips and LAC/PVA blended films totally disappeared in water in about 2-2.5 min, while the PVA films and commercial film M8630 totally disappeared in water in 1-1.5 min.

5.3.7 Dissolution properties after immersion in detergent

Since PVA is known to be sensitive to detergent interaction over time, it is interesting to study the dissolution properties of LAC/PVA blended films. A dissolution test was performed for the films that were previously immersed in detergent Ambrosia 3.0 for 5 days at different temperatures (30 ºC, 40 ºC, 50 ºC), using slide frame test method **TMD_00719**. To compare the results of the blending with different proportions of PVA, a blended LAC/PVA film with 80% PVA was prepared as well. The results of M8630, PVA film, and LAC/PVA blended films with 40% and 80% PVA are shown in **Table 5-1** and **Figure 5-10**. After being in contact with detergent, M8630 film significantly delays its solubilization (up to 10X) showing unfavorable transformation of material triggered by detergent interaction; PVA Mowiol 18-88 film also delayed solubilization (more than 2X); but the LAC/PVA blended film actually dissolved faster likely due to some dissolution of Lactips material in detergent, or the swelling of Lactips network when in contact with detergent, weakening structure and facilitating dissolution in water.

Table 5-1 Dissolution test results of M8630, PVA film and LAC/PVA blended films with 40% and 80%PVA before and after immersion in detergent Ambrosia 3.0.

Dissolution time/s	before immersion	30ºC	40ºC	50ºC
M8630	60	104	239	720
PVA	71.5	137	146	174
80%PVA	143	88	93	100
40%PVA	150	53	56	81

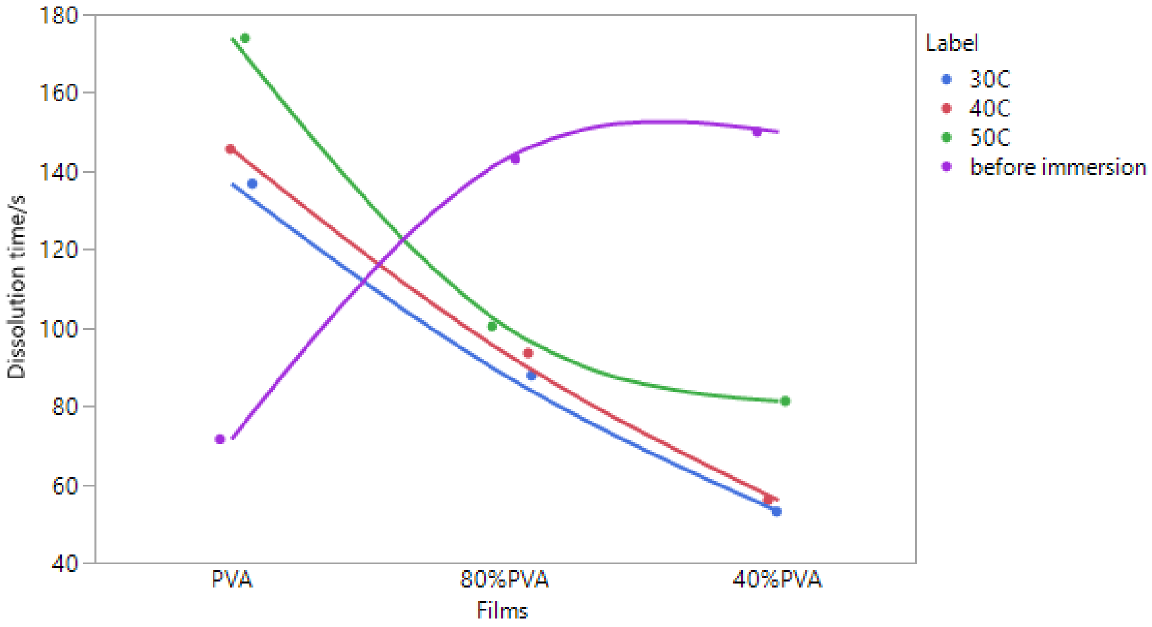


Figure 5-10 Dissolution test results of PVA film and LAC/PVA blended films with 40% and 80%PVA before and after immersion in detergent Ambrosia 3.0.

5.3.8 Immersion test

Even though the Lactips/PVA blended films showed good compatibility with the current detergent Ambrosia 3.0 when measured gravimetrically, their mechanical properties dropped significantly after immersed in the detergent Ambrosia 3.0, as can be seen in **Figure 5-11**: the tensile strength of Lactips/PVA blended film dropped by 72% down to 5MPa, with a drop in elongation as well; PVA film had a slight tensile strength drop of 11%, with an increase in elongation due to plasticizer migration into the film from the detergent, since some solvents in the detergent Ambrosia 3.0 (such as glycerol and water) also work as plasticizer.

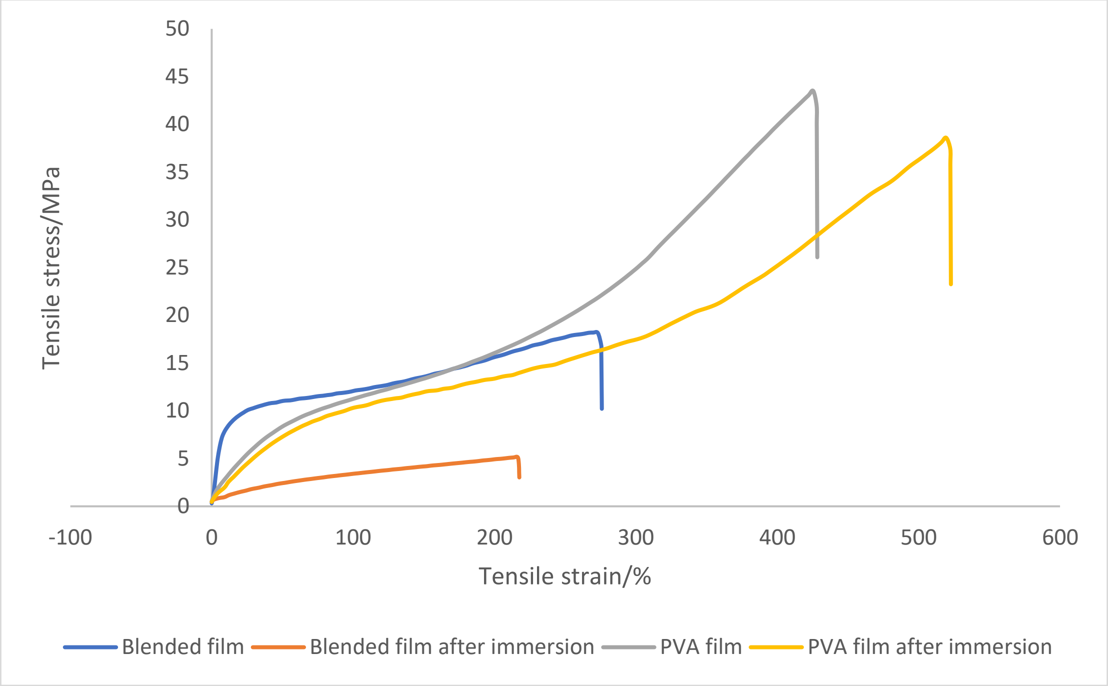


Figure 5-11 Mechanical stress-strain profiles of plasticized blended films with 40% PVA, and PVA film after 5-day immersion in Ambrosia 3.0.

5.3.9 Water Vapor Permeability

Water Vapor Permeability (WVP) of film is also an important asset of film, since water plays a role in film as plasticizer which makes film floppy. WVP was tested using a gravimetric sorption (dynamic vapor sorption) technique according to standard method **ASTM E96-95**. In **Figure 5-12** we can see that the WVP of Lactips film and LAC/PVA blended film are about 40% higher than PVA film, which may due to the extreme hydrophilic property of Lactips material where casein provides many polar functional groups such as hydroxyl and amino groups to the film matrix.

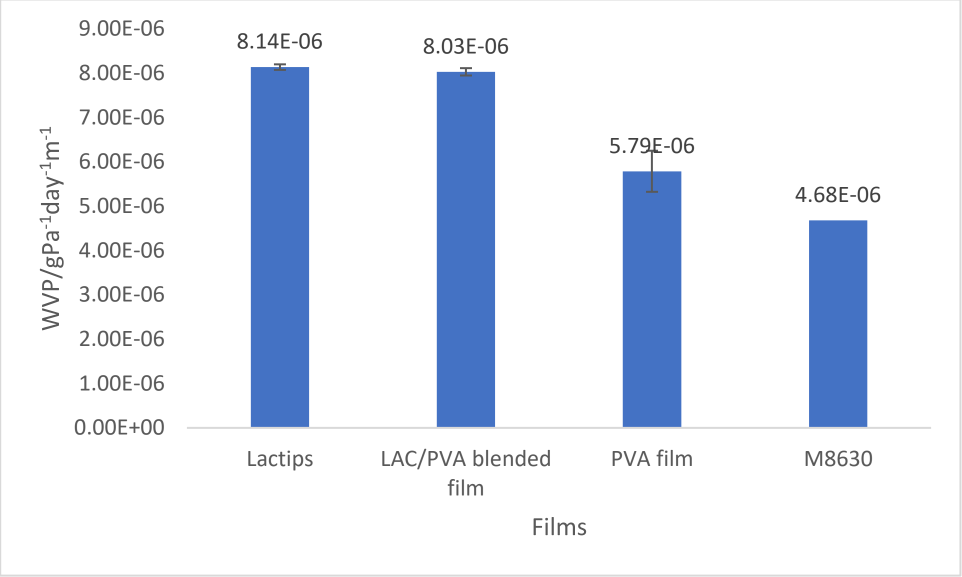


Figure 5-12 Water vapor permeability of Lactips film, LAC/PVA blended film, PVA film with 40% PVA and commercial M8630, Olympus films.

5.3.10 Hypothesis on Lactips/PVA interaction

Based on the film behavior and characterizations, we hypothesized on the nature of the polymer interactions. A simple schematic illustration is proposed in **Figure 5-13**. According to Lactips patent [20], 15-25% of biodegradable polymer preferably PBAT is introduced to bind casein micelles, which increased the flexibility and decreased the stiffness of casein films. Glycerol and water coat the system as plasticizers. Casein micelles might disintegrate from each other at the contact of detergent due to solvent migration into the gaps left between the micelles.

For the blended films, PVA acts as an additional binder to casein and PBAT. Casein micelles are “trapped” by PVA chains by hydrogen bonding, which increased the film mechanical properties, and protected the casein micelles from disintegrating into the detergent.

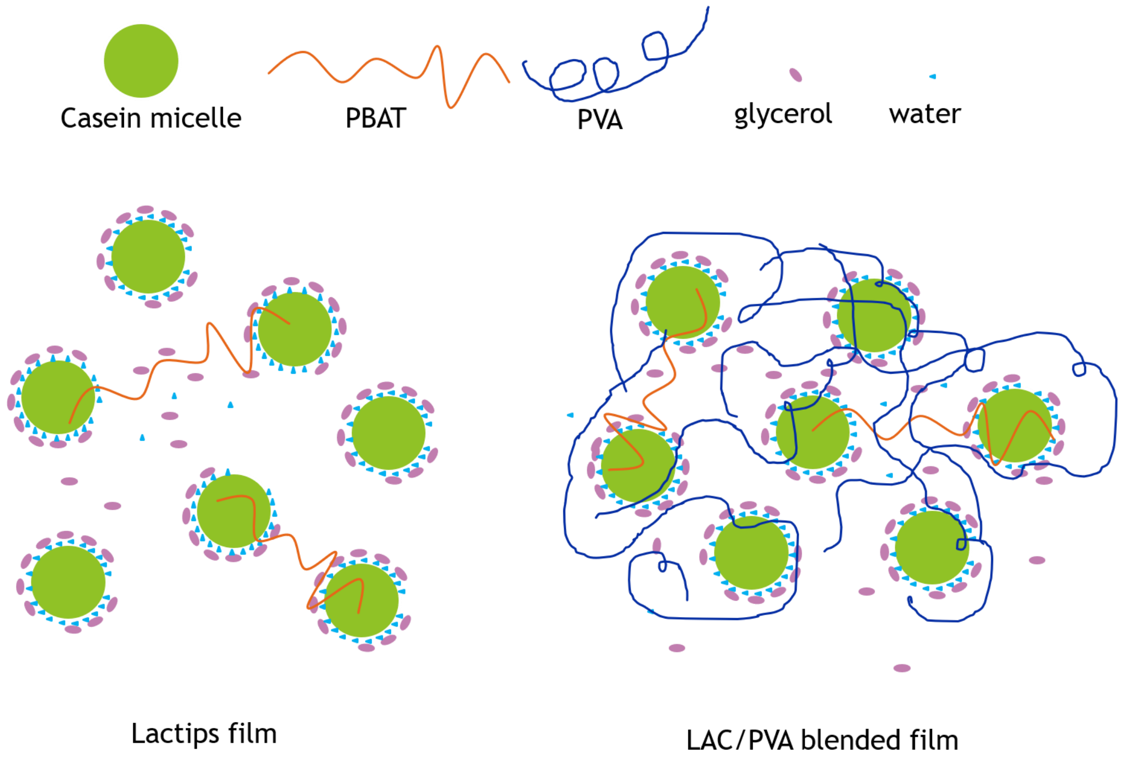


Figure 5-13 Schematic illustration of Lactips-PVA interaction.

5.4 Conclusions

Lactips material can be a good candidate to form a film for SUD applications. Lactips film is flat and dense, with excellent dissolution properties in water and acceptable mechanical and water vapor barrier properties, however, it still presents several challenges for direct SUD applications, such as detergent compatibility. The blended films at 40% PVA showed significant improvement with promising results, while providing obvious benefits in terms of biodegradability.

References

[1] L. M. Bonnaillie, H. Zhang, S. Akkurt, K. L. Yam, and P. M. Tomasula, “Casein Films: The Effects of Formulation, Environmental Conditions and the Addition of Citric Pectin on the Structure and Mechanical Properties,” *Polym. J.*, vol. 6, pp. 2018–2036, 2014.

[2] M. P. Arrieta, M. A. Peltzer, J. López, C. Garrigós, A. J. M. Valente, and A. Jiménez, “Functional Properties of Sodium and Calcium Caseinate Antimicrobial Active Films Containing Carvacrol,” *J. Food Eng.*, vol. 121, pp. 94–101, 2014.

[3] Y. R. Wagh and H. A. Pushpadass, “Preparation and Characterization of Milk Protein Films and Their Application for Packaging of Cheddar Cheese,” *J. Food Sci. Technol.*, vol. 51, pp. 3767–3775, 2014.

[4] S. Am, G. Gopikrishna, P. Ac, and P. Aj, “Milk Protein Based Edible Films and Coatings – Preparation , Properties and Food Applications,” *J. Nutr. Heal. Food Eng.*, vol. 8, pp. 219–226, 2018.

[5] R. Thakur, P. Pristijono, C. J. Scarlett, M. Bowyer, S. P. Singh, and Q. V Vuong, “Starch-based Films : Major Factors Affecting Their Properties,” *Int. J. Biol. Macromol.*, vol. 132, pp. 1079–1089, 2019.

[6] M. Carissimi, S. H. Flôres, and R. Rech, “Effect of Microalgae Addition on Active Biodegradable Starch Film,” *Algal Res.*, vol. 32, pp. 201–209, 2018.

[7] A. Ramu, S. Munisamy, and R. Bhat, “Producing Novel Edible Films from Semi Refined Carrageenan (SRC) and Ulvan Polysaccharides for Potential Food Applications,” *Int. J. Biol. Macromol.*, vol. 112, pp. 1164–1170, 2018.

[8] M. R. Ginger and M. R. Grigor, "Comparative Aspects of Milk Caseins," *Comp. Biochem. Physiol. Part B*, vol. 124, pp. 133–145, 1999.

[9] A. R. Sarode, P. D. Sawale, C. D. Khedkar, S. D. Kalyankar, and R. D. Pawshe, "Casein and Caseinate: Methods of Manufacture," in *Encyclopedia of Food and Health*, Oxford: Academic press, 2015, pp. 676–682.

[10] S. Rebouillat and S. Ortega-Requena, "Potential Applications of Milk Fractions and Valorization of Dairy By-Products : A Review of the State-of-the-Art Available Data , Outlining the Innovation Potential from a Bigger Data Standpoint," *J. Biomater. Nanobiotechnol.*, vol. 6, pp. 176–203, 2015.

[11] P. Walstra, "Casein Sub-micelles : Do They Exist ?," *Int. Dairy J.*, vol. 9, pp. 189–192, 1999.

[12] A. F. Routh and W. B. Russel, "Deformation Mechanisms during Latex Film Formation : Experimental Evidence," *Ind. Eng. Chem. Res.*, vol. 40, pp. 4302–4308, 2001.

[13] P. A. Steward, J. Hearn, and M. C. Wilkinson, "An Overview of Polymer Latex Film Formation and Properties," *Adv. Colloid Interface Sci.*, vol. 86, pp. 195–267, 2000.

[14] L. A. Felton, "Mechanisms of Polymeric Film Formation," *Int. J. Pharm.*, vol. 457, pp. 423–427, 2013.

[15] P. M. Tomasula, W. C. Yee, and N. Parris, "Oxygen Permeability of Films Made from CO 2-Precipitated Casein and Modified Casein," *J. Agric. Food Chem.*, vol. 51, pp. 634–639, 2003.

[16] L. J. Mauer, D. E. Smith, and T. P. Labuza, "Water Vapor Permeability ,

Mechanical , and Structural Properties of Edible b-casein Films," *Int. Dairy J.*, vol. 10, pp. 353–358, 2000.

[17] O. A. Diak, B. Amro, D. Jones, and G. P. Andrews, "The Manufacture and Characterization of Casein Films as Novel Tablet Coatings," *Food Bioprod. Process.*, vol. 85, pp. 284–290, 2007.

[18] A. Longares, F. J. Monahan, E. D. O. Riordan, and M. O. Ã. Sullivan, "Physical Properties of Edible Films Made from Mixtures of Sodium Caseinate and WPI," *Int. Dairy J.*, vol. 15, pp. 1255–1260, 2005.

[19] A. Ghosh, M. A. Ali, and G. J. Dias, "Effect of Cross-Linking on Microstructure and Physical Performance of Casein Protein," *Biomacromolecules*, vol. 10, pp. 1681–1688, 2009.

[20] P. Frederic and A. Gilles, "Thermoplastic Granule Made of Casein and/or Caseinate, Composition and Manufacturing Method.," FR2963013, 2012.

[21] L. Jiang, M. P. Wolcott, and J. Zhang, "Study of Biodegradable Polylactide/Poly(butylene adipate-co-terephthalate) Blends," *Biomacromolecules*, vol. 7, pp. 199–207, 2006.

[22] J. Audic and B. Chaufer, "Properties of Biodegradable Poly (butylene adipate-co -terephtalate) and Sodium Caseinate Blends," *J. Appl. Polym. Sci.*, vol. 125, pp. 459–467, 2012.

Chapter 6. Pouch Prototyping with Lactips Film and Pouch Properties

6.1 Introduction

As already mentioned, Lactips is a thermoplastic material, produced by extruding a mixture of casein and/or caseinate (65%-75%), plasticizer (15%-25%) and PBAT (15%-20%) to improve the mechanical properties [1].

In **Chapter 5** the dissolution, compatibility with detergent, water vapor permeability and mechanical properties of casted Lactips films were discussed. As a conclusion, Lactips material can be a good candidate to form a film for SUD applications. It is flat and dense, with excellent dissolution property in water and acceptable mechanical properties and water vapor barrier property, although presenting several challenges for direct SUD applications, such as detergent compatibility.

In this chapter, the study of better compatible detergents with Lactips film is presented, and a better compatible detergent was selected to convert into pouches made with Lactips film. The stability and washing performance of the Lactips pouches were also investigated.

6.2 Experimental

6.2.1 Materials

Lactips extruded film rolls (CareTips L0003) were obtained from Lactips company; the rolls are 140mm wide with 500m long film, film thickness is at 80µm.

6.2.2 Characterizations

HSPip software were used to study the interactions between the film and the detergent; compatibility test was applied to study the film behavior when in contact with the detergent; DMA was used to measure the film mechanical properties at different temperatures; tackiness test was used to assess film sealability; stability test and stain-removal test were used to study pouch properties.

The detailed theories, procedures, and instruments are referred in **Chapter 2**.

6.3 Results and Discussions

6.3.1 Detergent design

6.3.1.1 Hansen Solubility Parameters (HSP) study of Lactips film

Current SUD detergent Ambrosia 3.0 essentially dissolves Lactips film. As we know, as the majority ingredients of the detergent, solvents are most likely the contributors for the dissolution of Lactips film in the detergent. To improve the compatibility of Lactips and detergent, Hansen solubility parameters (HSP) of Lactips was studied to look for the best solvent in the detergent that would be more compatible with the Lactips film.

The polymer foil is cut into small pieces and these are grinded in liquid nitrogen into a fine powder with an IKA analytical mill. 10 mg of this powder is dosed in standard test tubes and 2 ml of each of the 58 screening solvents are added.

The test tubes are placed on a roller mixer for 24 h and visually checked whether or not they are dissolved. If the sample is dissolved, a score of 1 is given; if the sample is not dissolved, a score of 0 is given.

Lactips polymer doesn´t dissolve in any of the 58 screening solvents, every solvent gets a score of 0. So another distinction is made: the solvents in which the polymer gives a light suspension (water and water/methanol) and the solvents in which the polymer is swollen get a score of 1; the solvents in which there is no interaction with the polymer (sediment at the bottom or floating at the top) get a score of 0.

If the solubility is plotted in Hansen space using the Hansen Solubility Parameters (3-dimensional: dD = dispersive contribution / dP = polar contribution / dH = H-bonding contribution), where 1 = suspension or swelling and 0 = no suspension and no swelling, the solubility domain can be calculated.

Calculated by HSPip with genetic fitting algorithm, the solubility parameters of Lactips film is:

dD=19.61, dP=18.33, dH=20.25, R_0=10.8 with fit=0.948

The HSP information of the 58 solvents and their score is recorded in **Table 6-1**.

The calculation of relative energy difference (RED) of each solvent-Lactips system is explained in **Chapter 2**.

- If RED<1, the molecules are likely to dissolve each other
- If RED=1, the system will partially dissolve
- If RED>1, the system will not dissolve

Table 6-1 HSP info of 58 solvents, their score and calculated RED.

No.	Solvent	dD	dP	dH	Score	RED
1	Dichloromethane	17	7.3	7.1	0	1.621
2	1-Pentanol	15.9	5.9	13.9	0	1.407
3	1-Propanol	16	6.8	17.4	0	1.226
4	2-Methoxyethanol (Egmme)	16	8.2	15	0	1.201
5	Acetic Acid	14.5	8	13.5	1	1.448
6	Acetone	15.5	10.4	7	0	1.602
7	Acetonitrile	15.3	18	6.1	0	1.563
8	Benzonitrile	18.8	12	3.3	0	1.665
9	Benzylalcohol	18.4	6.3	13.7	0	1.215
10	Butan-2-ol	15.8	5.7	14.5	0	1.408

11	Chlorobenzene	19	4.3	2	0	2.086
12	Chloroform	17.8	3.1	5.7	0	1.922
13	Cyclohexane	16.8	0	0.2	0	2.517
14	Cyclohexanone	17.8	8.4	5.1	0	1.676
15	N-Methylformamide	17.4	18.8	15.9	1	0.625
16	Nitro-Ethane	16	15.5	4.5	0	1.637
17	Di-N-Butyl Ether	15.3	3.4	3.2	0	2.204
18	DMA	16.8	11.5	9.4	1	1.275
19	DMF	17.4	13.7	11.3	0	1.007
20	DMSO	18.4	16.4	10.2	1	0.982
21	Ethanol	15.8	8.8	19.4	0	1.078
22	Ethyl Acetate	15.8	5.3	7.2	0	1.804
23	Formamide	17.2	26.2	19	1	0.963
24	γ-Butyrolactone	18	16.6	7.4	0	1.249
25	Isobutanol	15.1	5.7	15.9	0	1.437
26	Degdee	15.8	5.9	5.6	0	1.876
27	Mesitylene	18	0	0.6	0	2.450
28	Methanol	14.7	12.3	22.3	0	1.060
29	Methyl Ethyl Ketone	16	9	5.1	0	1.754
30	n-Hexane	14.9	0	0	0	2.630
31	Nitrobenzene	20	10.6	3.1	0	1.715
32	Degmbe	16	7	10.6	0	1.487
33	N-Octanol	16	5	11.9	0	1.547
34	2-Phenylethanol	18.3	5.6	11.2	0	1.401
35	THF	16.8	5.7	8	0	1.662
36	Toluene	18	1.4	2	0	2.270
37	Diaceton Alcohol	15.8	8.2	10.8	0	1.426
38	1,3-Butanediol	16.5	8.1	20.9	0	1.043
39	Cyclohexanol + Methanol (9/1)	17.13	4.92	14.38	0	1.361
40	2-Ethoxyethanol (Egmee)	15.9	7.2	14	0	1.316
41	Diethyleneglycol	16.6	12	19	1	0.775

42	Ethylene Glycol	17	11	26	1	0.930
43	Propylene Glycol	16.8	10.4	21.3	1	0.845
44	Dipropylene Glycol	16.5	10.6	17.7	1	0.901
45	Acetophenone	18.8	9	4	0	1.708
46	Isophorone	17	8	5	0	1.740
47	Isobutylisobutyrat	15.1	2.8	5.8	0	2.088
48	Isoamylacetate	15.3	3.1	7	0	1.984
49	Valeronitrile	15.3	11	4.8	0	1.762
50	1-Chlorobutane	16.2	5.5	2	0	2.125
51	1.4-Dioxane	17.5	1.8	9	0	1.825
52	Butyronitrile	15.3	12.4	5.1	0	1.701
53	Methylal (Dimethoxymethane)	15	1.8	8.6	0	2.004
54	Methoxypropanol	15.6	6.3	11.6	0	1.513
55	Propylenecarbonate	20	18	4.1	0	1.510
56	N-Methyl Pyrrolidone	18	12.3	7.2	1	1.346
57	Water	18.1	17.1	16.9	1	0.452
58	Water/Meoh	16.4	14.7	19.6	1	0.674

The Lactips sphere in HSP space can be seen in **Figure 6-1** and is showing extreme hydrophilic property. The farther the solvent HSP is from the core of the sphere, the lower the possibility that the solvent would dissolve Lactips film. We know that in the current detergent solvent system (Pdiol, DPG, glycerol and water), DPG is the one that is the farthest, and water is the closest to the core.

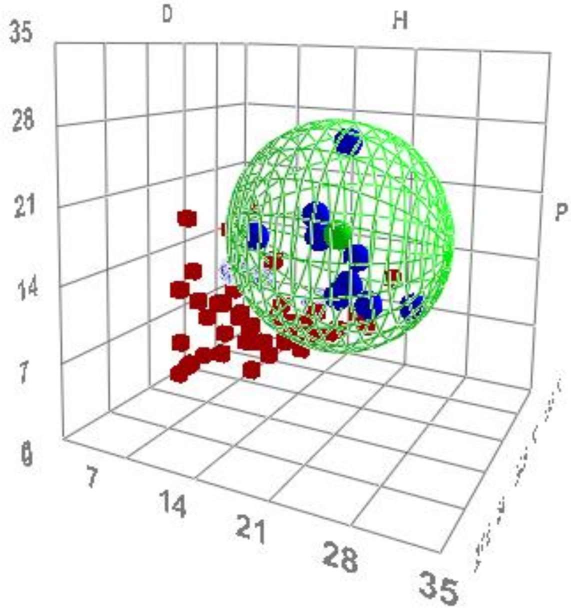


Figure 6-1 HSP study of Lactips sphere.

6.3.1.2 Compatibility test of Lactips film with different solvents and detergent

The HSP study was confirmed by immersing Lactips film in 4 main solvent of the juice and calculating the swell factor F= $(W_1-W_0)/W_0*100\%$, where W_1 stands for the weight of the film after immersion, and W_0 stands for the weight of the film before immersion, as explained in **Chapter 2**.

As a result, DPG almost didn’t change the weight of Lactips film before and after immersion, while Pdiol, glycerol (glycerine) and the detergent all totally disintegrated Lactips film (**Figure 6-2**). As a water-soluble material, the Lactips film can be dissolved in water within 1 minute.

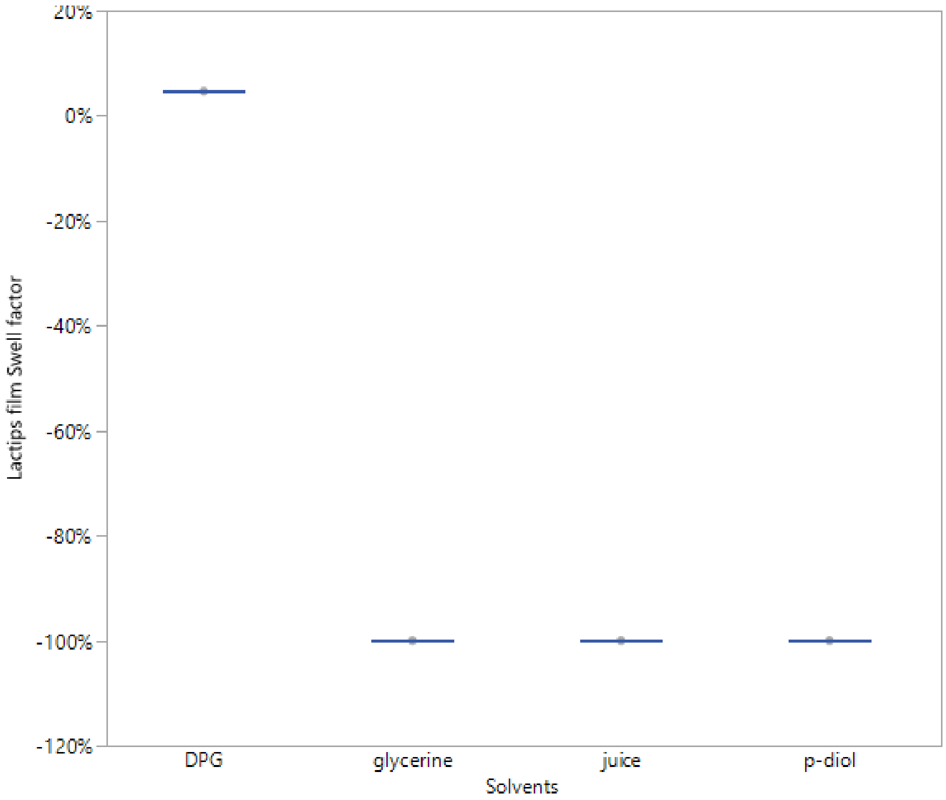


Figure 6-2 Film swell factor after immersed for 3 days at 50ºC.

6.3.1.3 Detergent design

According to the compatibility test of the Lactips film with different solvents, the idea of designing new compatible detergent leads to minimize water content and maximize DPG content. Several detergent formulations were prepared and tested with Lactips film for compatibility (**Table 6-2**). In the beginning, the water amount was maintained at 8.6%, and the DPG amount was increased gradually until 21.2%, but the film behavior in the detergent didn't change – the film disintegrated in the detergent and there was only a little piece of soft gel left on the bottom; then the amount of water was decreased until 1.4%, with 16.0% DPG (DPG LACTIPS 3.0 WB).

The film remained in the detergent but was very fragile - it could be broken easily by slightly folding the film, because the film was de-plasticized with too much DPG and little amount of glycerin. A certain amount of glycerin was added to DPG LACTIPS 3.0 WB to dilute DPG and increase glycerin amount – when glycerin amount was at 7.0% and DPG amount at 15.2%, the film was still too fragile.

We concluded that too much DPG de-plasticizes the film, and water is the key contributor to the disintegration. Another 2 versions of detergent were prepared: one with similar composition of P-diol 10.0%, DPG 5.0% and glycerin 5.0% as Ambrosia 3.0, but minimized water amount to 1.4% - the film remained in this version of the detergent, and was more flexible, though with still 16.6% weight loss. Another form changed the amount of P-diol to 5.0% and glycerin to 10.0% to minimize de-plasticization – the film remained, and behaved similarly to the former one, but this version of detergent was too thick and viscous. In the end, DPG LACTIPS 4.0 WB was chosen for the pouch converting process as the most compatible detergent with the Lactips film.

Table 6-2 Lactips compatibility with different versions of detergents.

Detergent	**Solvent composition**				**Lactips behavior**
	P-diol	DPG	Glycerin	Water	3-day immersion at 50^{o}C
Ambrosia 3.0	9.3%	4.6%	4.7%	8.6%	Soft gel
DPG LACTIPS 1.0	7.5%	9.5%	2.6%	8.6%	Soft gel
DPG LACTIPS 1.1	5.2%	12.2%	2.6%	8.6%	Soft gel
DPG LACTIPS 2.0	1.8%	21.2%	1.7%	8.6%	Soft gel

DPG LACTIPS 2.0 WB	2.1%	16.0%	2.0%	5.2%	Fragile, broke
DPG LACTIPS 3.0	9.3%	4.6%	4.7%	8.6%	Soft gel
DPG LACTIPS 3.0 WB	2.1%	16.0%	2.0%	1.4%	16.7% weight loss, very fragile
DPG LACTIPS 3.1 WB	2.1%	16.0%	3.5%	1.3%	Fragile
DPG LACTIPS 3.2 WB	2.0%	15.4%	5.5%	1.3%	Fragile
DPG LACTIPS 3.3 WB	1.9%	15.2%	7.0%	1.3%	Fragile
DPG LACTIPS 4.0 WB	10.0%	5.0%	5.0%	1.4%	16.6% weight loss, more flexible
DPG LACTIPS 4.1 WB	5.0%	5.0%	10.0%	1.4%	15.6% weight loss, more flexible

6.3.2 Pouch converting

6.3.2.1 Film deformation

It requires a certain elasticity for a film to be deformed. Heat helps soften the film to be more flexible. As already known, PVA film is deformed fully onto the cavity at 120^{o}C. If at a certain temperature the Lactips film can be less stiff than that of PVA at 120^{o}C, it means that the Lactips could be deformed fully as well at this given temperature. Therefore, we performed DMA test to study film mechanical properties at different temperatures.

The Lactips film was tested with DMA at 60, 80, 90 and 120ºC, and its stiffness was compared with the stiffness of PVA film at 120 ºC.

At 120 ºC the Lactips film was completely fluid. As can be seen in **Figure 6-3**, the Lactips film has a smaller E-modulus at 60, 80, 90ºC than PVA at 120 ºC, which means that Lactips film can be deformed fully onto the cavity at these temperatures.

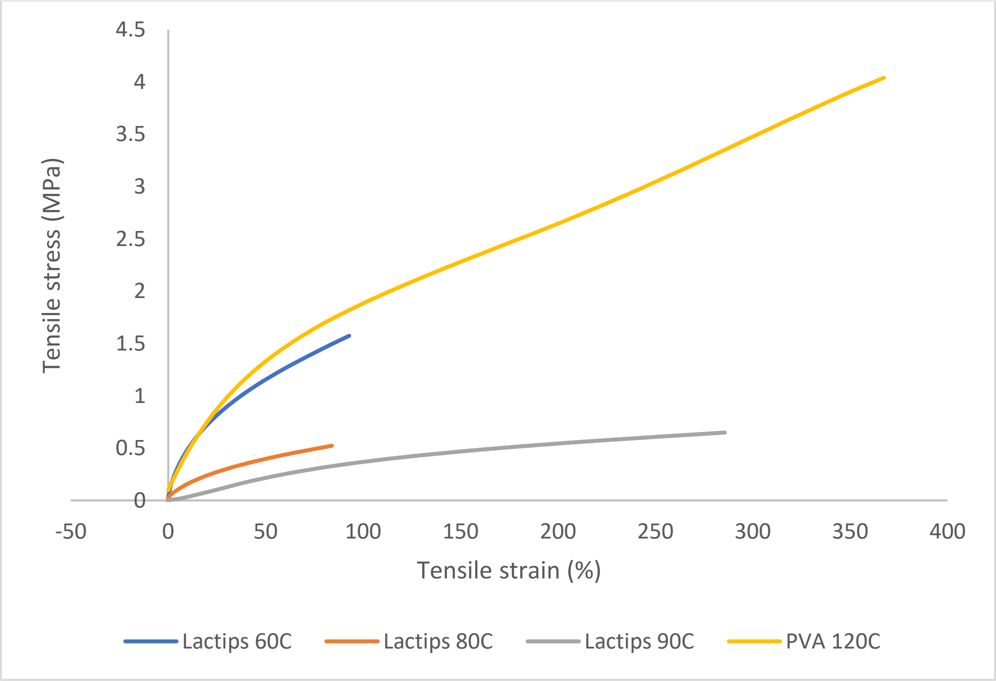


Figure 6-3 DMA results of Lactips film at 60, 80, 90ºC and PVA film at 120ºC.

Thermoforming simulation was performed with R&I software, which is a simulation software for studying the deformation property of film at different temperatures with different cavity modules designed exactly at the same parameters as the cavity modules used for film deformation in industry. With this simulation, the contact status of the film and cavity, as well as film thickness at deformation can be predicted at a certain temperature and vacuum.

As can be seen in **Figure 6-4**, the Lactips film deformation on a module cavity (41x43x14.9mm) was simulated at 60, 80 and 90°C at 200mbar (vacuum applied for PVA deformation). As shown in the legend, red (2) means best contact between the film and cavity, and blue (0) means no contact between the film and cavity, and the colors in between, which are yellow and green (1) mean contact between the film and cavity but not tight. Based on the results we can conclude that the higher the temperature, the better the contact between the film and cavity, which means better deformation of the film; only at 90 °C the film fully deformed onto the cavity.

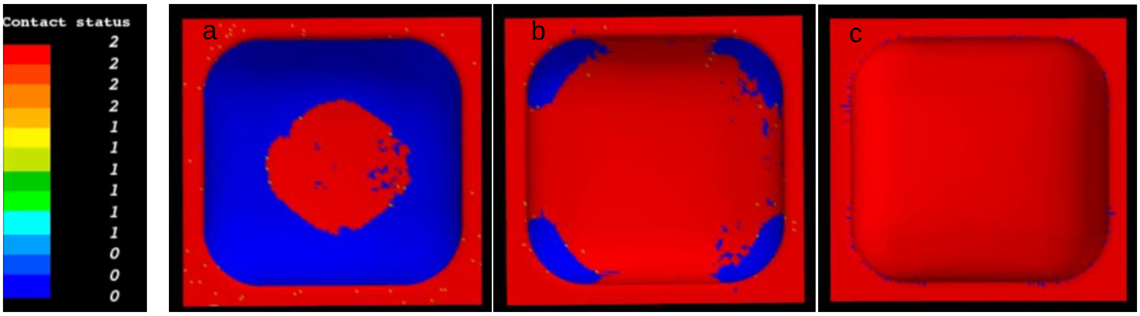


Figure 6-4 Simulated contact statuses of film with cavity at a. 60°C; b. 80°C; c. 90°C

The film thicknesses were simulated when deformed at 90 °C at different vacuum conditions – 150mbar, 200mbar, 250mbar, and 300mbar, at all conditions the film reached full deformation (contact status 2). As for the homogeneity of the deformation, as can be seen in **Figure 6-5** the thickness of the film after deformation, in general the thinnest part of the film is located in the 4 corners on the bottom. The deformations at 200mbar and 250mbar were more homogeneous compared with other conditions.

Despite the fact that the Lactips film couldn't be fully deformed at 80°C and 200mbar, the deformations at 80°C at higher vacuum conditions (250mbar, 300mbar and 350mbar) were also simulated to see if the Lactips film could be deformed with higher force. **Figure 6-6** shows that Lactips cannot be fully deformed onto the cavity at 80°C even at extremely high vacuum conditions in the industry. Therefore, the deformation condition of film at 90°C with 200mbar-250mbar vacuum was selected in pilot plant trials.

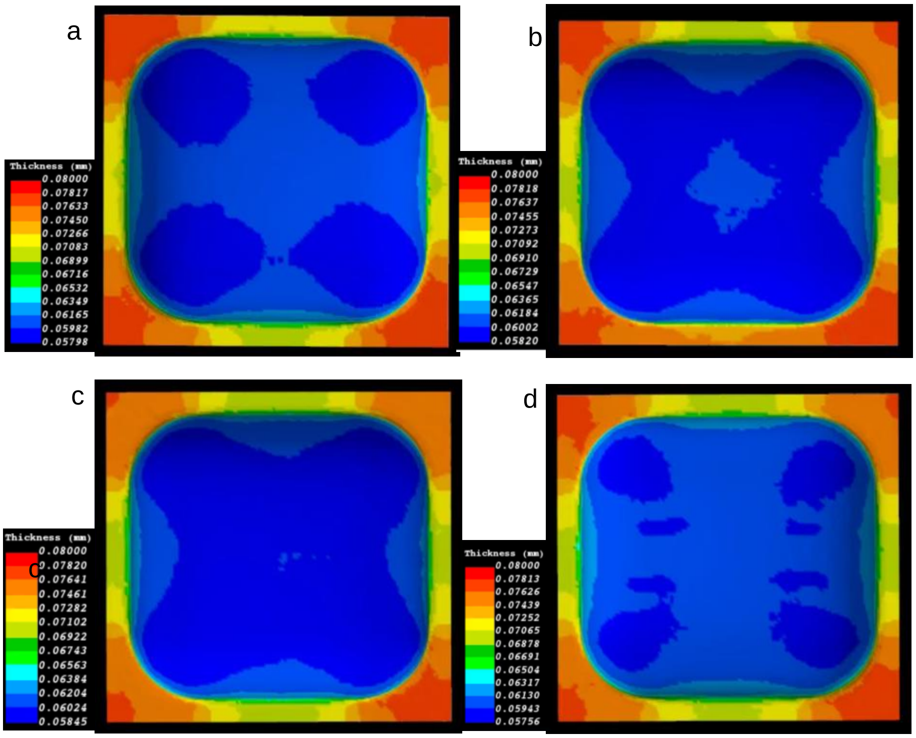


Figure 6-5 Simulated thicknesses at 90°C and a. 150mbar; b.200mbar; c. 250mbar; and d. 300mbar.

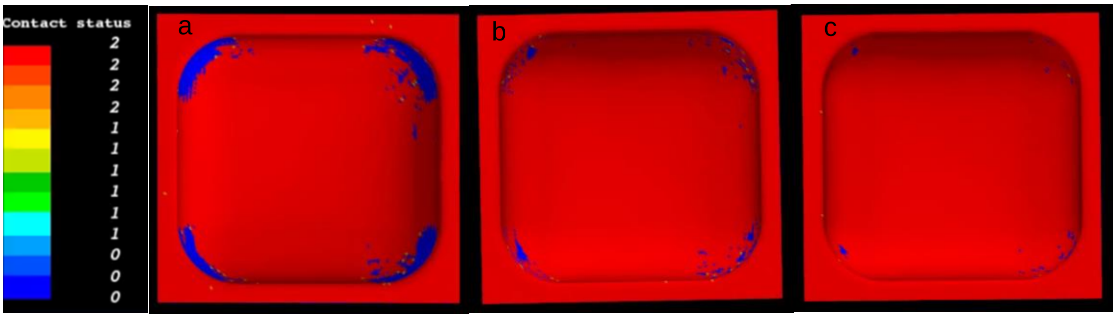


Figure 6-6 Simulated contact statuses at 80°C and a. 250mbar; b. 300mbar and c. 350mbar.

6.3.2.2 Film tackiness

SUD pouches are prepared by sealing the films together. A solvent is applied onto one film which is combined with another film; thus, polymer interdiffusion and entanglement causes long term film adhesion. Tackiness test result (**Table 6-3**) shows that Lactips film has very low cohesive strength with cold water as sealing solvent.

Table 6-3 Tackiness test of Lactips, LAC/PVA blended film with 40% PVA and PVA film.

Films	Peak positive force (tack) /g	Positive area (cohesive strength) /g.s
Lactips film	778	24
Blended film	21947	851
PVA film	40630	3738

Several seal-peel tests were conducted – seal two pieces of Lactips films or 2 pieces of blended films with cold water in a dynamic way with anilox roll and then use a pull force to separate the two films in a 90^{o} angle and record the force used. However, the films were separated very easily, which indicated low tackiness of Lactips film and blended film.

6.3.2.3 1-up and multi-up prototyping

Knowing that Lactips film doesn't seal with cold water, we applied heat to seal the film in 1-up machine at lab scale with demineralized water or a 7% Lactips aqueous dispersion as a solvent. The sealing worked when deformation temperature was set at 130^{o}C where the actual film temperature was 90^{o}C.

Multi-up prototyping was also conducted as heat transformation at deformation and sealing are more efficient. The film was fully deformed onto cavity with 1.7s IR lamp heating with 230mbar vacuum, and the sealing was successful using heat at 90°C and combination pressure (3 bar) for 10s. The pouches produced by multi-up prototyping can be seen in **Figure 6-7**.

Figure 6-7 Pouches produced by multi-up prototyping.

6.3.2.4 1-lane converting process

1-Lane converter was employed for the pouching prototype as well to see if the Lactips film can be converted in a continuous process. In this process, a heated roll was installed after the wetted wool felt, as the Lactips film needed a combination of solvent, heat and pressure to seal properly. The running speed was set at 5m/min – the minimum speed the converter could run - to increase the combining & curing time for sealing the bottom and top film. The smallest cavities were chosen due to lower elasticity of the film. The detailed procedure of 1-lane converting for Lactips film is as follows (**Figure 6-8**):

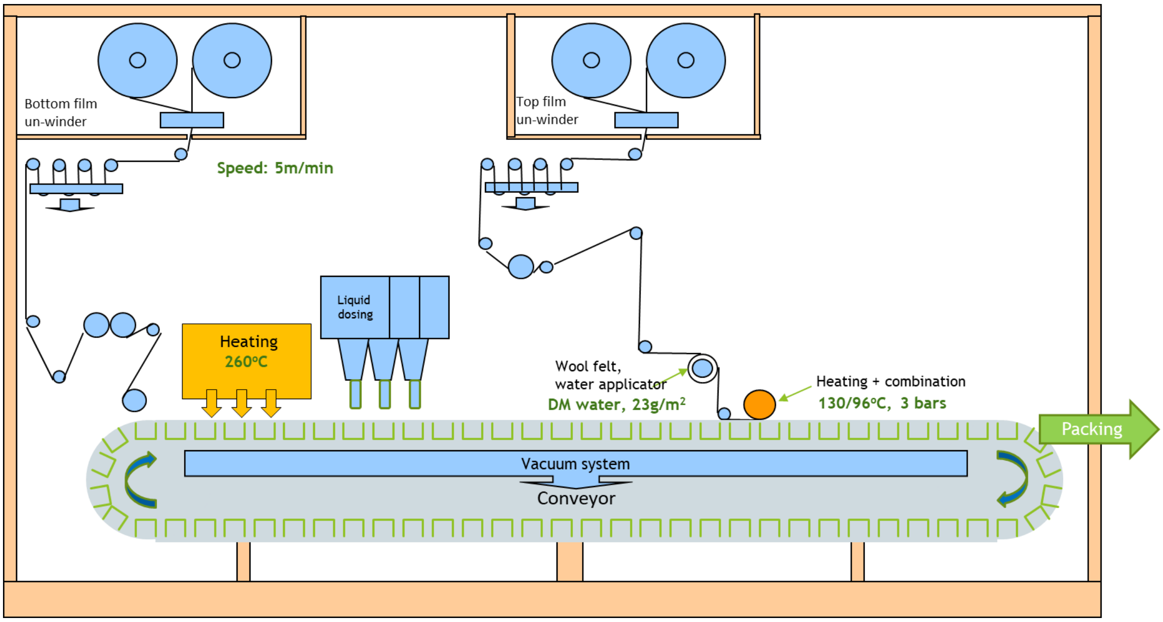


Figure 6-8 1-lane converting procedure.

- Bottom film was un-winded from the film roll and delivered to the conveyor;
- IR lamp heating was set at 260ºC to soften the film, followed by vacuum deformation of the film into the cavities;
- Liquid/powder detergents were dosed into the bottom film cavity;
- In the meantime, the top film was un-winded and coated with demineralized water through a wetted wool felt. The coat weight was set at $23g/m^2$;
- The wetted top film was combined with the bottom film via a heated roll that applied heat (set 130 ºC, real 96ºC) and pressure (3 bars) to seal the two films;
- Prepared pouches were delivered out from 1-lane converter and packed.

Observations:

- The film was fully deformed, and sealed very well with heat and solvent;

- 40 liquid detergent pouches and 40 powder detergent pouches were prepared successfully;
- Because of its high stiffness and low elasticity, Lactips extruded film showed uneven tension, which caused wrinkles throughout web-handling;
- Due to its high brittleness, the film could be cut by platen sometimes and film/bubbles were easily broken by hand;
- In the powder detergent pouches, the powder in the pouches was loose, not as compact as current PVA pouches due to the low elasticity of Lactips film;
- The film roll is especially sticky towards the core part, resulting in high blocking force. The film broke many times and couldn't be processed towards the end.

6.3.3 Stability tests

Liquid and powder detergent pouches made with Lactips film and reference liquid detergent pouches made with current commercial PVA film were packed in tubs - 4 pouches were put in 1 tub without compressing each other. Tubs were placed at 20°C, 40%RH for 2 days.

All Lactips liquid pouches leaked on the 2nd day. Leakages happened at the seal edges through large holes (**Figure 6-9**). We believe that because the film became the weakest with combination pressure and water in this area, this made it even more vulnerable to the juice. Leakage may be reduced if the film has a better elasticity.

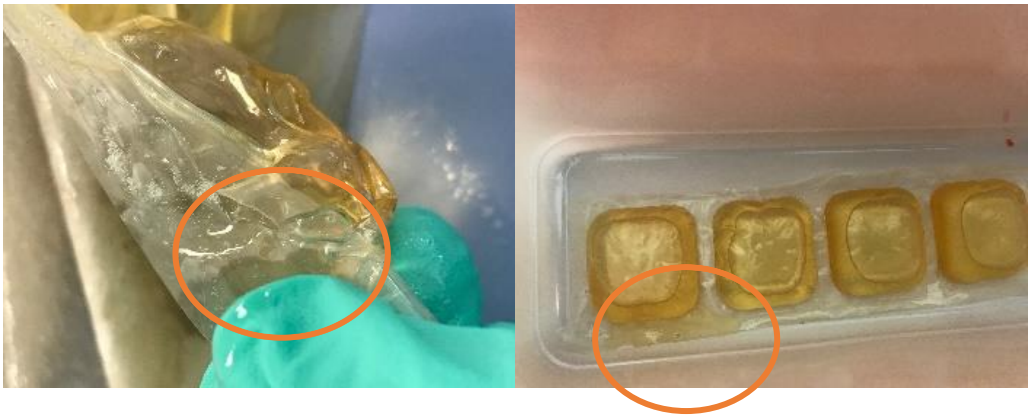


Figure 6-9 Lactips liquid pouches leaked.

Lactips powder pouches and PVA liquid pouches didn’t change during the 2-day storage. They were then sent to stability room to study the effect of temperature and humidity on the pouch. 2 case studies were conducted – one is to fix the humidity at 40%RH and study the impact of temperatures at 20, 35 and 50°C, and the other one is to fix the temperature at 35 °C and study the impact of humidities at 40%, 65%, 80%RH. In each condition, 6 pouches were packed individually, 3 top-side up, and 3 top-side down.

The results show that the way pouches were packed doesn’t affect pouch behavior as pouches of the same condition behaved all the same after 3-months storage. **Figure 6-10** exhibits the fresh pouches and pouches after 3-months stability tests. **Figure 6-10 a-0** shows the newly made Lactips powder pouch, the fine white powders are very well sealed inside the Lactips films, and the films are flexible. After 3-months storage at 20°C, 40%RH, powders become swollen (not significant), and the films remain flexible, as seen in **Figure 6-10 a-1**. **Figure 6-10 a-2** shows the Lactips powder pouch stored at 35°C, 40%RH, some parts of the powders change color because of oxidation, and the films are much drier. At 50°C, 40%RH (**Figure 6-10 a-3**), the powders changed color because of oxidation, and the films became so dry and brittle that they could be broken easily by touching. When stored at 35°C, 60%RH (**Figure**

6-10 a-4) the powders swell significantly, and yellow liquid are leaked out from the pouch, while the film is not broken, similar as **Figure 6-10 a-5** when stored at 35ºC, 80%RH. The leakage of yellow liquid is caused by hygroscopic material (Na_2CO_3) presented in the powder material. As for PVA liquid pouches, **Figure 6-10 b-0** shows the newly made PVA liquid pouch, the blue liquids are very well sealed inside the PVA films, and the films are flexible. After 3-months storage at 20ºC, 40%RH, liquids and the films almost remain the same, as seen in **Figure 6-10 b-1**. **Figure 6-10 b-2** shows the PVA liquid pouch stored at 35ºC, 40%RH, the liquids become darker because of oxidation, and the films are drier. At 50ºC, 40%RH **(Figure 6-10 b-3**), the liquids become much darker because of oxidation, and the films are drier, but are not easy to be broken. When stored at 35ºC, 60%RH (**Figure 6-10 b-4**) the liquids change color significantly, and the PVA films become much softer, similar as **Figure 6-10 b-5** when stored at 35ºC, 80%RH.

The Lactips powder pouches and PVA pouches behave similarly: both the Lactips powder pouches and PVA liquid pouches remained almost the same at 20ºC, 40%RH after 3-months storage. At higher temperature the powders/liquids get oxidized, and at higher humidity the powders leak out liquid due to hygroscopic material; while liquids change color. However, Lactips film has worse tensile properties after storage at high temperature compared with PVA - at 50 ºC for 3 months: the Lactips film becomes brittle and fragile.

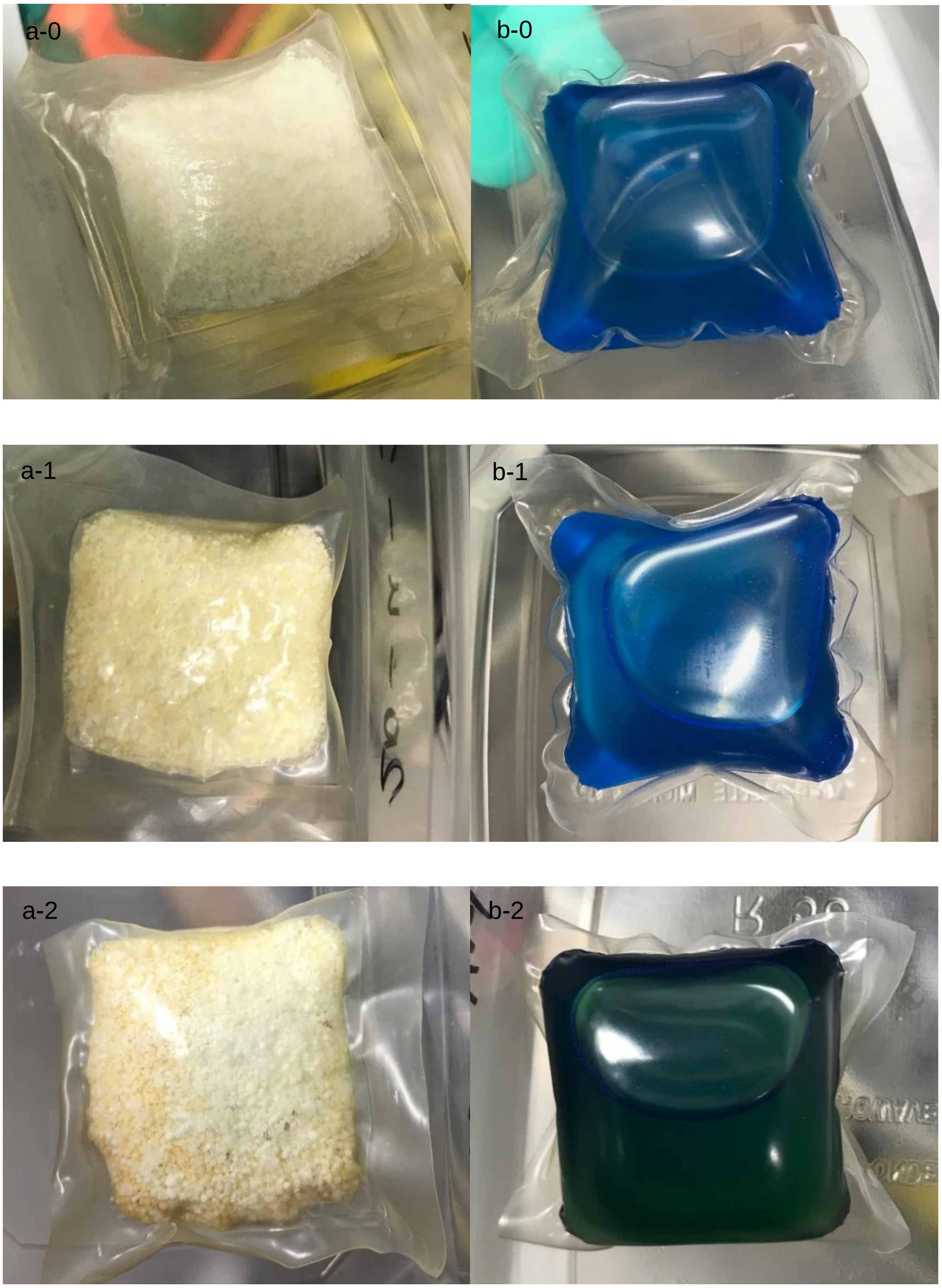

a-0
b-0
a-1
b-1
a-2
b-2

Figure 6-10 a. Lactips powder pouches and b. PVA liquid pouches stability test. Conditions: -0. Newly made; -1. 20ºC, 40%RH; -2. 35ºC,40%RH; -3. 50ºC, 40%RH; -4. 35ºC, 60%RH; -5 35ºC, 80%RH.

6.3.4 Pouch stain-removal performance test

Stain removal performance of Lactips film with detergent was tested and compared with detergent alone, and detergent with commercial PVA film. Stain removal index (SRI) was calculated by analyzing the stain colors before and after washing.

As can be seen in **Table 6-4**, Lactips film doesn't have any negative effect on stain-removal when used with detergent during a standard laundry cycle compared to detergent alone, and Lactips film has an obvious advantage over PVA film on clay removal: when detergent works alone in a laundry compliance, the SRI is at 69, when detergent works together with Lactips film, the SRI didn't change, however, when detergent works with PVA film, the SRI decreased by 13.7, which means that PVA film has a negative effect on clay removal, and Lactips film doesn't have this negative effect.

Table 6-4 Stain removal index comparison.

Paired Comparison vs. Detergent alone		**Detergent alone**	**Detergent+ Lactips**	**Detergent+ PVA**	
Stain	**Fabric**	**SRI**	**Diff**	**Diff**	**SD**
Overall Average		**55.2**	**-0.5**	**-0.4**	
Overall Net Wins vs. C (+/=/-)			**0 (0/25/0)**	**-1 (0/24/1)**	
AISE Group Average		**52.7**	**-0.4**	**-0.2**	**1.10**
AISE Group Net Wins vs. C (+/=/-)			**0 (0/14/0)**	**0 (0/14/0)**	
Cooked Beef GSRTCBE001 EQ021 AISE	WHITE A	64.4	-2.0	0.7	7.02
Red Wine Wolf Blas GSRTRW001 EQ185 AISE	WHITE A	63.7	-1.5	-0.2	2.47
AISE Blood Sheep EQ117	WHITE B	76.4	0.6	-0.9	2.44

AISE Carrot baby food EQ026	WHITE B	60.0	-1.8	-1.1	5.77
AISE Espresso Coffee EQ195	WHITE B	64.4	1.0	-0.5	2.21
AISE French Squeezy Mustard EQ087	WHITE B	42.4	-0.6	0.2	1.45
AISE Grass Mud EQ065	WHITE B	54.6	-0.1	0.1	2.87
AISE Lipton Tea EQ194	WHITE B	24.6	0.5	-0.2	7.86
AISE Tomato Puree EQ133	WHITE B	64.6	-0.6	-0.1	4.42
AISE Chocolate CS44	CFT 1	33.1	-0.6	-0.2	1.30
AISE Fruit juice CS15	CFT 2	61.7	-0.8	-0.4	3.16
AISE Grass CS08	CFT 2	35.0	-0.5	-1.7	1.91
AISE Makeup CS17	CFT 2	46.9	-0.2	0.5	3.07
AISE Unused motor oil C01	CFT 2	45.8	0.8	0.4	3.21
GSRT Group Average		**59.3**	**-0.8**	**-0.5**	**1.62**
GSRT Group Net Wins vs. C (+/=/-)			**0 (0/13/0)**	**-1 (0/12/1)**	
Bacon grease dyed GSRTBGD001	WHITE A	61.6	-1.0	1.7	2.41
Black Todd Clay GSRTBT001	WHITE A	69.0	0.1	-13.7	4.04
Burnt butter GSRTBB001	WHITE A	73.7	-2.4	0.4	3.67
Cooked Beef GSRTCBE001 EQ021 AISE	WHITE A	64.4	-2.0	0.7	7.02
CS 28 Rice Starch	WHITE A	87.0	0.0	-0.2	1.02
CS 45 Chocolate Soy Milk	WHITE A	32.9	1.6	0.3	3.97
Lipton Tea GSRTLIT001	WHITE A	25.0	-2.5	-0.1	4.17
Makeup Cover Girl GSRTCGM001	WHITE A	50.5	-5.3	4.1	12.07
PCS 132 Discriminating Sebum	WHITE A	48.8	0.8	0.6	2.37
PCS 94 ASTM Sebum	WHITE A	56.2	0.6	-0.8	2.79
Ragu Spaghetti Sauce GSRTSS001	WHITE A	80.1	0.6	1.1	2.89

Red Wine Wolf Blas GSRTRW001 EQ185 AISE	WHITE A	63.7	-1.5	-0.2	2.47
Scrubbed grass EQ062	WHITE A	57.6	0.5	0.1	3.16

Clay particles are stacked in layers, and each clay sheet is slightly separated from each other on either side with negative charge on it. These negative charges are balanced by positive charges. The -OH groups in the chains of PVA confers a certain negative charge to the polymer, so that PVA chain could interact with clay molecules and cover the clay molecules on the fabric, hindering the interaction between clay and surfactants. Although casein micelles also have negative charges on the surface, it is rather a macrostructure that doesn’t interact the same way with clay or fabric – in this sense the Lactips film has a benefit over PVA film on washing performance.

6.4 Conclusions

Lactips film can be converted into pouches in both lab scale and pilot plant scale; it is possible to be processed in a continuous operation. It can be used in auto dish washing pouch applications. Lactips film is very sensitive to water so that the liquid pouches need further investigation to improve the compatibility of detergent liquid and Lactips film. Performance-wise, Lactips film has advantage over PVA film in clay-removal.

References

[1] P. Frederic and A. Gilles, “Thermoplastic Granule Made of Casein and/or Caseinate, Composition and Manufacturing Method.,” FR2963013, 2012.

Chapter 7. Sodium Caseinate Film and its Blending with PVA

7.1 Introduction

Nowadays, sustainable, 100% bio-degradable and environmentally-friendly packaging is more and more interested[1]–[7]. Casein, as a milk protein, stands out for its great availability [8]; its salt caseinate, is soluble in water [9].Commercial caseinates are manufactured by adjusting acid-coagulated casein to pH 6.7 with the appropriate amount of calcium or sodium hydroxide. The acid and alkaline treatments disrupt the native structure of the casein particles, and caseinates have little similarity to the native casein micelles in milk. Adjustment of pH to 4.5 dissociates the colloidal phosphate structure and frees the casein precipitate of calcium. The alkaline treatment solubilizes the caseins by altering the net charge which overcomes hydrophobic interactions. Sodium caseinate (NaCAS) is highly soluble in water and can form stable colloidal dispersions rapidly in aqueous mixtures[10].

NaCAS can easily form films from aqueous solutions because of its random coil nature and its ability to form extensive intermolecular hydrogen electrostatic and hydrophobic bonds, resulting in an increase of the interchain cohesion [11]–[13].

As introduced in **Chapter 5**, casein films can form a good barrier to oxygen and other nonpolar groups [14], on the other hand, they possess low elasticity similar to other bio-sourced films, which could be improved using plasticizers such as glycerol and water, by increasing the free volume of the polymer network [13], [15]–[17]. However, in SUD applications the elasticity of casein film after addition of plasticizer is not enough.

PVA is a water-soluble polymer which is known to have excellent mechanical strength but relatively low ductility, which would complement with casein regarding tensile properties. Therefore, the blending of casein with PVA as a film-forming material is very interesting for the objective of this PhD project.

In this chapter, the dissolution, compatibility with detergent, water vapor permeability and mechanical properties of caseinate film and its blending with PVA are studied. The interaction between caseinate and PVA is discussed.

7.2 Experimental

7.2.1 Materials

Sodium caseinate and PVA Mowiol® 18-88 resin were purchased from Sigma Aldrich, and were used without further purification. Glycerol was used as received from Oleon and sorbitol was received from Sigma Aldrich and used as received.

7.2.2 Sample preparation

Films were prepared by a solution casting and vapor evaporation method, as explained in **Chapter 2**. NaCAS/PVA blended films were prepared by casting a solution of the mixture of NaCAS powder and PVA resin, incorporating 25% of plasticizer. Blended films of 100%NaCAS, 80%NaCAS, 60%NaCAS, 50%NaCAS, 40%NaCAS, and 20%NaCAS were prepared and characterized. PVA film and commercial M8630 film from MonoSol were used as reference.

7.2.1 Characterizations

7.2.1.1 Environmental scanning electron microscope (ESEM)

Film surface and cross-sectional morphologies were observed at 15kV with low-vacuum ESEM FEI 600 apparatus, without sputter coating. Film cross-sections were prepared by fracturing in liquid nitrogen.

7.2.1.2 Differential scanning calorimetry (DSC)

Calorimetric studies were performed with a Mettler DSC822e thermal analyzer, using about 5 mg of sample, nitrogen as a purge gas (100ml/min). The films were heated from -50ºC to 230ºC at the heating rate of 10ºC/min.

7.2.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded at room temperature using Fourier Transform Infrared Spectrometer 680 Plus from Jasco with a resolution of 4 cm^{-1} and scanning speed of 2 mm/s^{-1}, in transmittance mode. An attenuated total reflection (ATR) accessory with thermal control and a diamond crystal (a Golden Gate heated single reflection diamond ATR from Specac-Teknokroma) was used to obtain FTIR spectra.

7.2.1.4 Film property tests

Dissolution test, compatibility test with detergent, tensile stress-strain test and mono-pouch prototyping were conducted to study film properties. The detailed theories, procedures, and instruments are referred in **Chapter 2**.

7.3 Results and discussion

7.3.1 Film morphologies

ESEM images of the surface and cross-section of NaCAS, PVA, NaCAS/PVA blended films are shown in **Figure 7-1**. It is seen that all films are homogeneous, dense and flat. No phase separation is oserved on the blended film surface nor cross-section, meaning that NaCAS and PVA form a compatible polymer blend at microscopic scale.

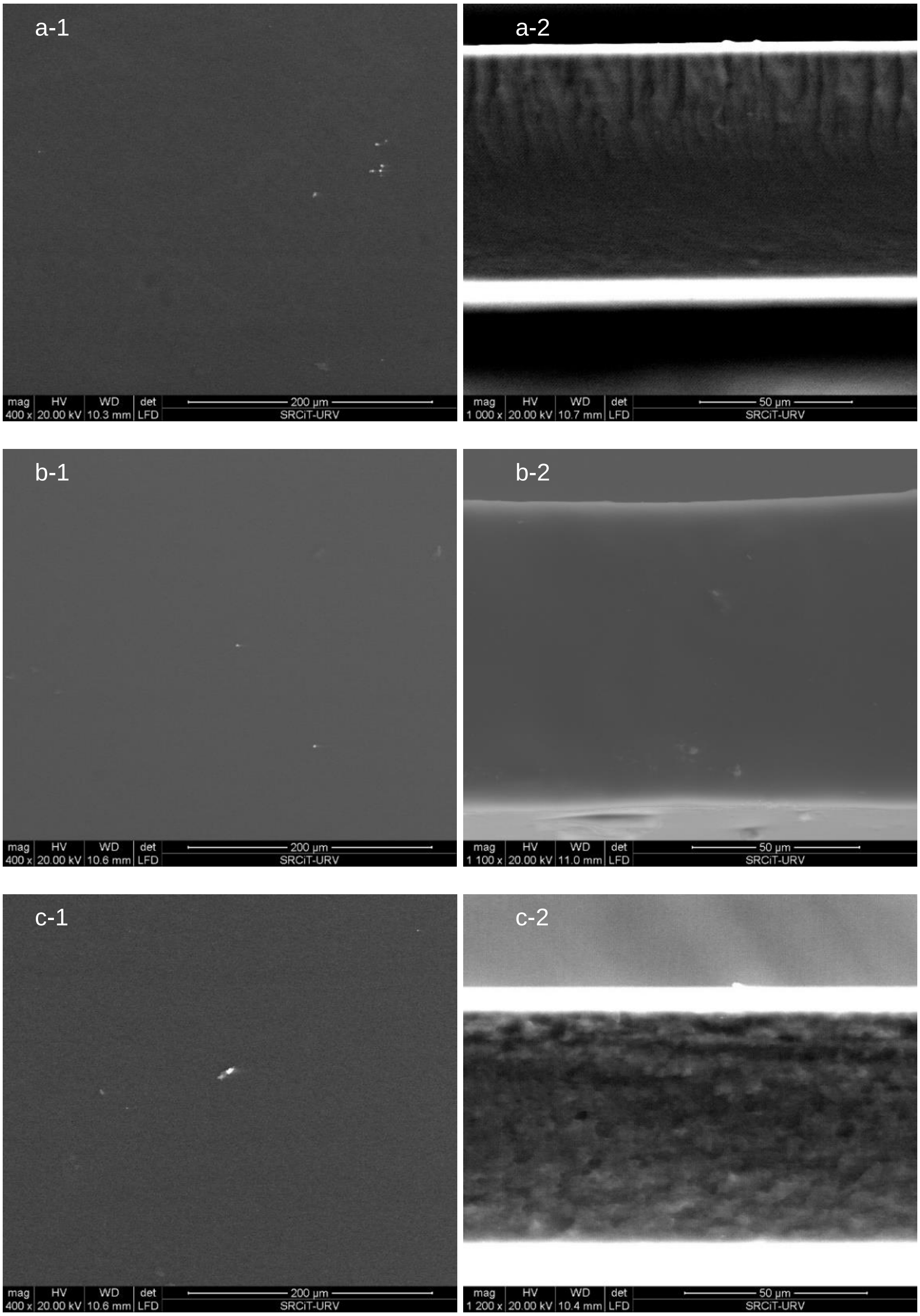
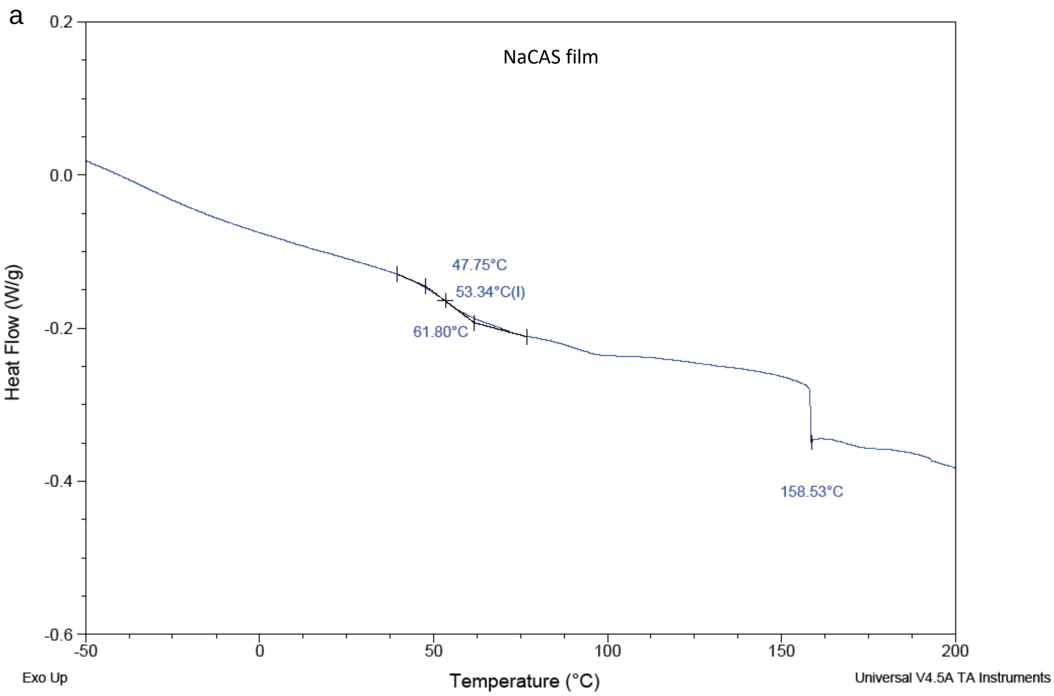


Figure 7-1 ESEM images of a. NaCAS film surface and cross-section, b.PVA film surface and cross-section, c. NaCAS/PVA blended film with 40%PVA; -1 surface and -2 cross-section.

7.3.2 Thermal behavior

As shown by the DSC curves in **Figure 5-6,** NaCAS has its glass transition temperature at 53ºC; PVA film is semi-crystalline with glass transition temperature at -15 ºC, a PVA melting transition in water phase at 58 ºC , and a melting point at 136 ºC ; NaCAS/PVA blended film (with 40% PVA) is semi-crystalline with a melting point at 133 ºC, similar to pure PVA film, and only one glass transition temperature at -4.5 ºC, in between the glass transition point of NaCAS and PVA, which means that these two polymers are miscible.



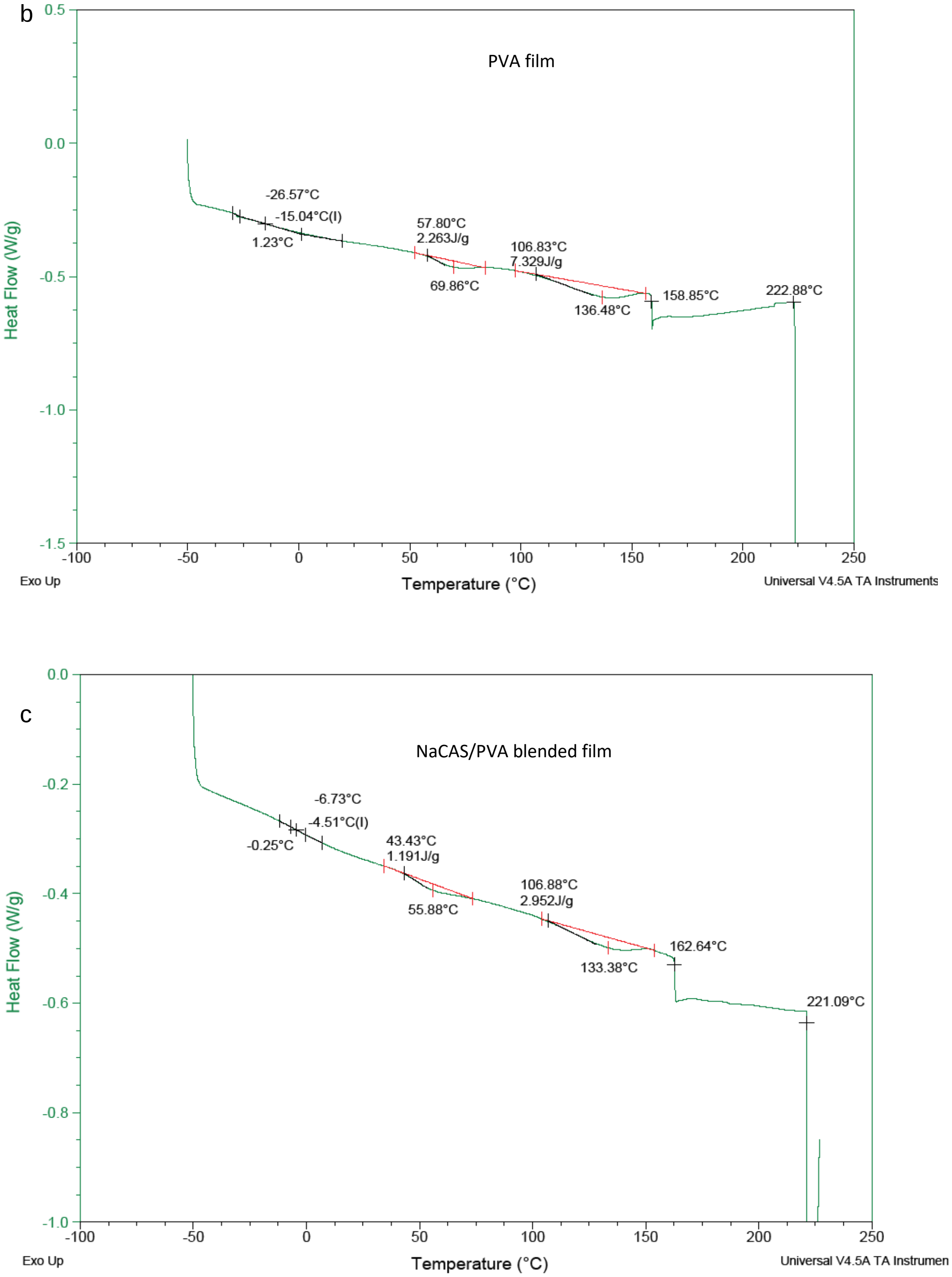


Figure 7-2 DSC curves of a. NaCAS film; b. PVA film and c. NaCAS/PVA blended film with 50%NaCAS.

7.3.3 Interactions between NaCAS and PVA

Based on FTIR study, as can be seen in **Figure 7-3**, in the spectrum of NaCAS film, a broad peak is seen at 3278cm^{-1}, which corresponds to the stretching of the hydroxyl groups (O-H). The characteristic absorption bands of NaCAS at 1630 and 1535 cm^{-1} indicate the bond stretching of amide (CONH) and associated with the protein network. The band at 1106cm^{-1} indicates C-O stretch.

In the PVA film spectrum, a broad O-H stretching band is seen at 3300cm^{-1}. Two peaks at 2946 and 2919cm^{-1} are related to C-H stretching. The spectrum of PVA film exhibits bands at 1732cm^{-1} for the carbonyl group (C=O). The band 1085 cm^{-1} indicates C-O stretch.

In the NaCAS/PVA blended film we can see the band at 3278 cm^{-1} was gradually broadened and shifted to higher wavenumber with increasing PVA, the band at 1630 and 1535 cm^{-1} of NaCAS shifted to higher wavenumber, the band at 1106 cm^{-1} shifted to a lower wavenumber, which all indicate the formation of hydrogen bonds.

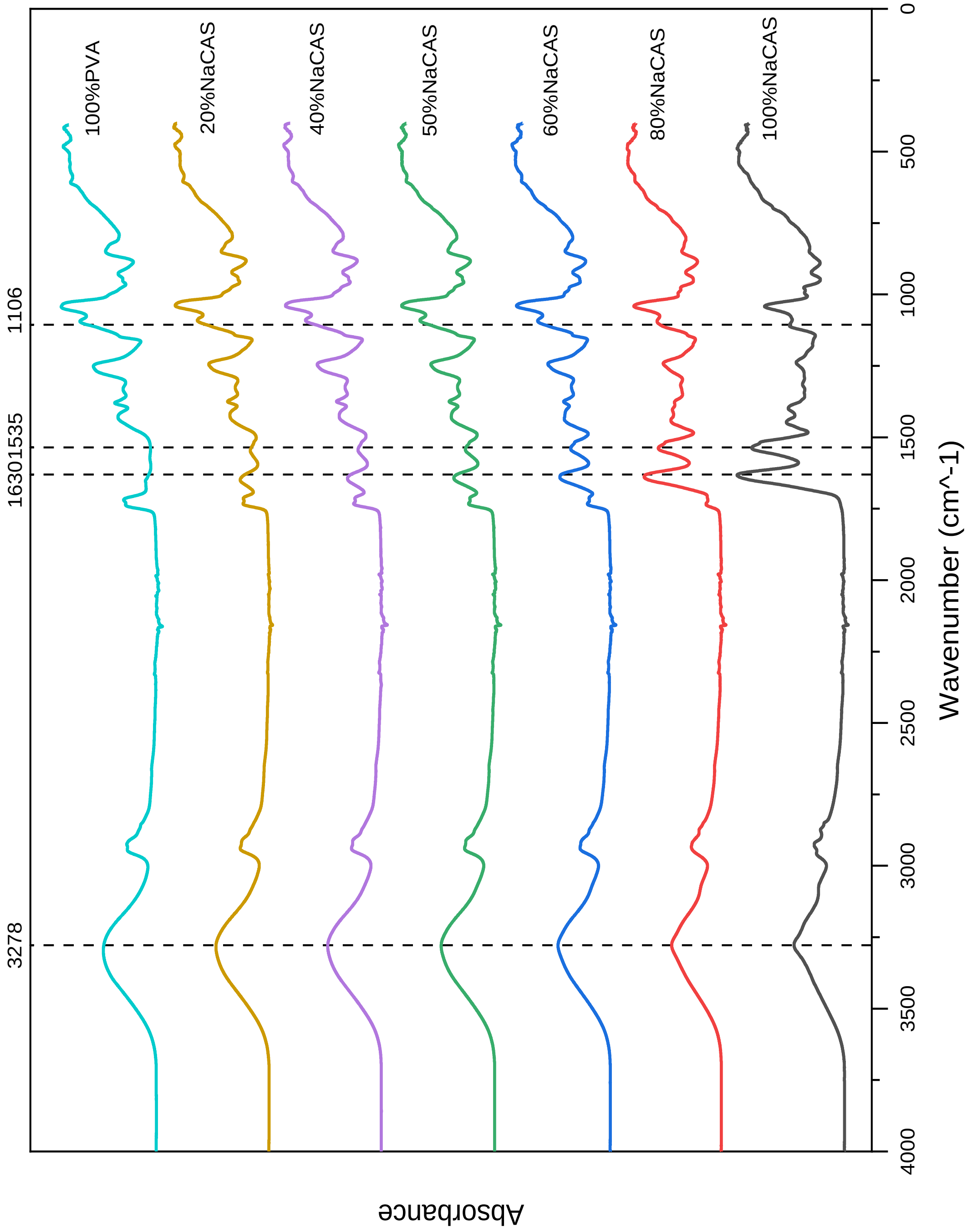


Figure 7-3 FTIR spectras of PVA, NaCAS and NaCAS/PVA blended films.

7.3.4 Dissolution properties

Slide frame test method **TMD_00719** was employed to study the rupture properties of the films. **Figure 7-4** shows that the pure NaCAS film ruptures at 48s, and PVA film ruptures at 42s, while the NaCAS/PVA blended films rupture slower than the pure polymer films up to 67s, which may be due to the hydrogen bonding formed between the NaCAS and PVA chains, which slows down the polymer chain disentanglement, and provides more space for water to bind into the polymer network and swell the film.

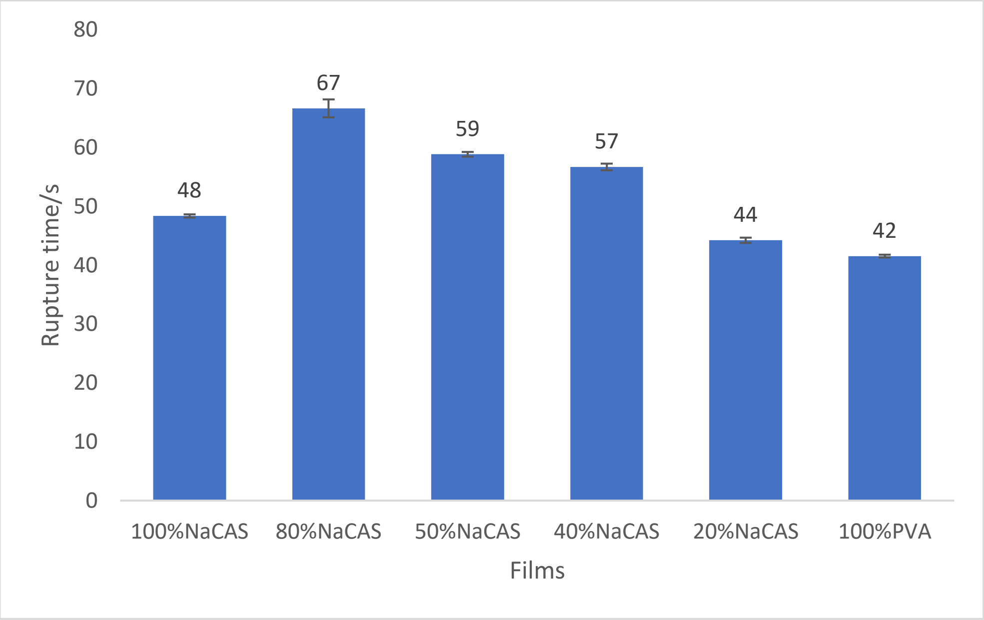


Figure 7-4 Slide frame test results of NaCAS film, NaCAS/PVA blended films and PVA film.

Standard test method for residue with dissolution chamber by MonoSol MSTM-119 was employed to test film dissolution properties. As shown in **Figure 7-5**, the NaCAS film totally dissolved after 10-min immersion in water, more than twice of PVA film (42%). The NaCAS/PVA blended films dissolved more than PVA film, proportionally with the amount of NaCAS component in the blended film. The dissolution of NaCAS film is faster due to its shorter polymer chain and micelle structure in water, where the phase breakage happens more easily than with the long PVA chains upon disentanglement.

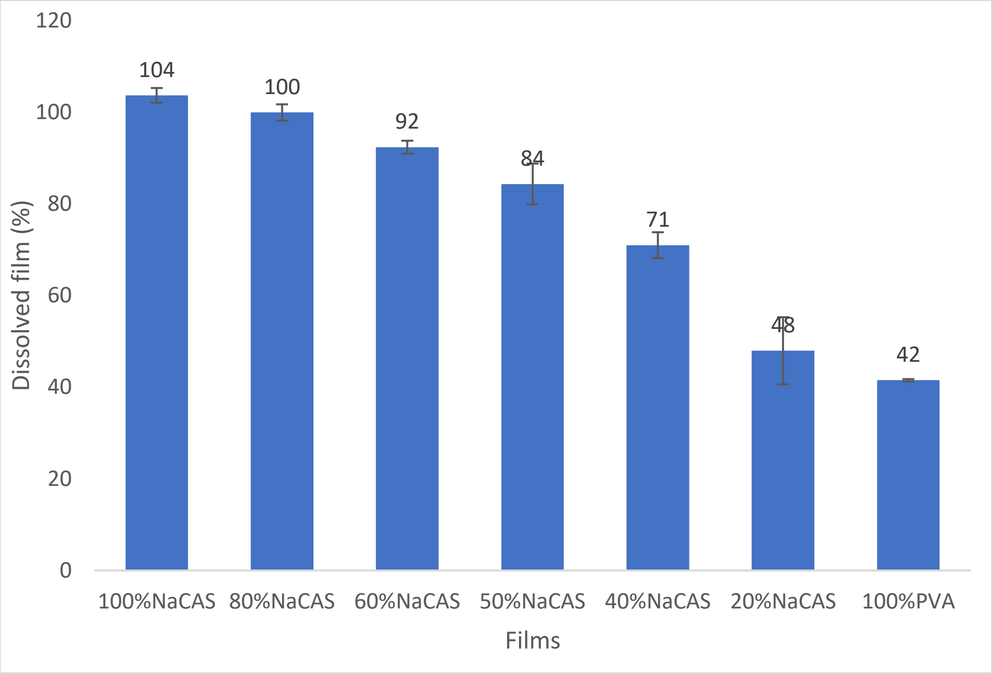


Figure 7-5 Dissolution chamber test results of NaCAS film, NaCAS/PVA blended films and PVA film.

7.3.5 Mechanical properties

Mechanical properties were tested using INSTRON using procedure **TMD_00543** to generate stress-strain profile at 21°C, 35% RH.

The results can be seen in **Figure 7-6**. The tensile strength of PVA film is 43 MPa, and it elongated to 425%. In comparison, the pure NaCAS material however was very stiff. It had poor tensile elongation at 6%, with a high tensile strength at 50MPa. The tensile properties of blended film with 80% PVA was similar to PVA film, with a tensile strength of 45 MPa, and a tensile strain at 400%. The blended film with 60% PVA had a lower tensile strength of 24MPa, and a tensile strain at 297%; the blended films with 50% and 40% PVA had similar tensile strength as the film with 60% PVA but lower elongation, at 256% and 191%, respectively. The blended film with 20% PVA had a tensile strength at 21MPa and a tensile strain at 161%. In other words, by blending it with PVA, the NaCAS material proportionally improved its elasticity to a significant extent.

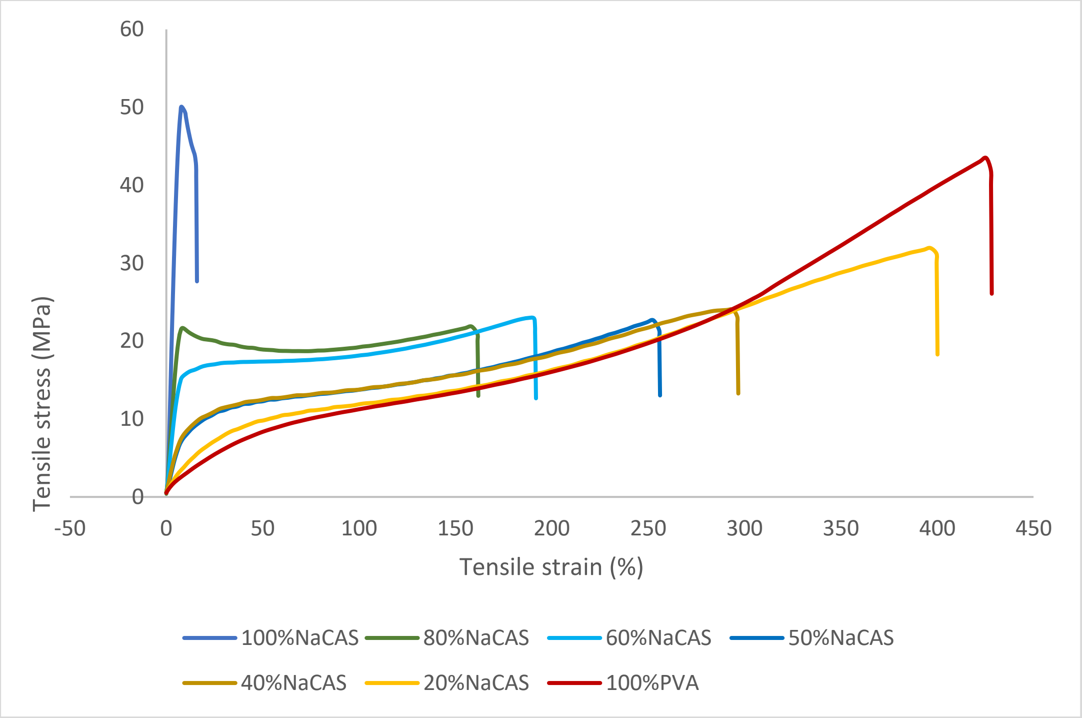


Figure 7-6 Mechanical stress-strain profiles of films (NaCAS film, NaCAS/PVA blended films with 20%-80% NaCAS, and PVA film).

7.3.6 Water Vapor Permeability

WVP of films was tested using a gravimetric sorption (dynamic vapor sorption) technique according to standard method **ASTM E96-95**. From **Figure 7-7** we can see that the WVP of all the films don't differ a lot. The pure NaCAS film has better water vapor barrier properties than the pure PVA film. For the NaCAS/PVA blended films, the water vapor barrier properties increase proportionally with the amount of NaCAS component.

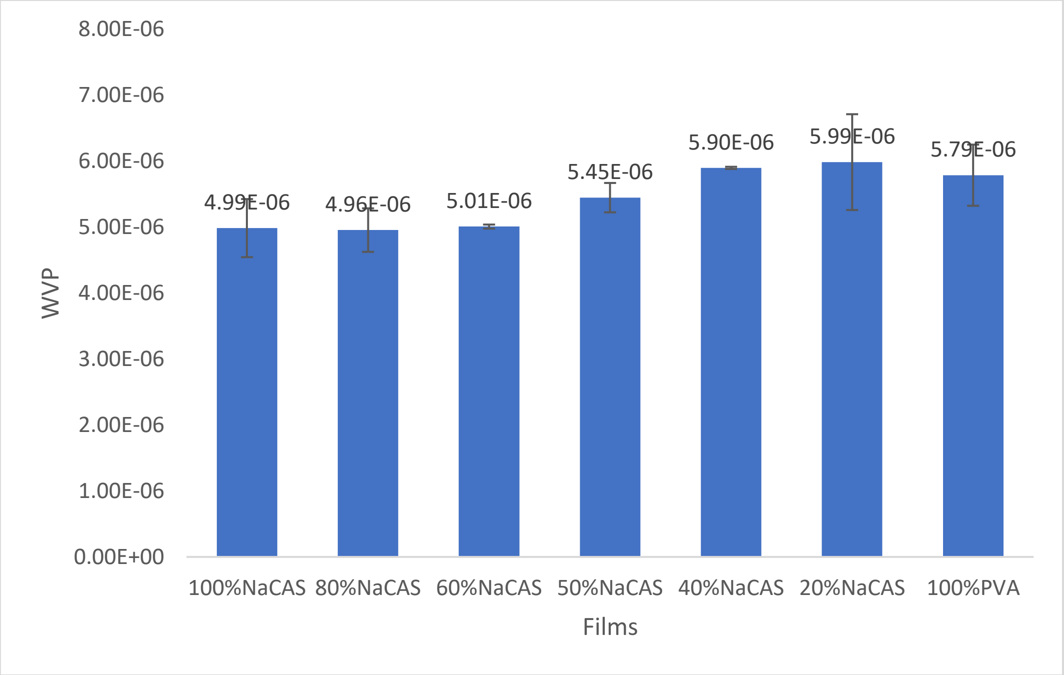


Figure 7-7 Water vapor permeability of NaCAS film, NaCAS/PVA blended film with 20%-80% NaCAS, and PVA film.

7.4 Conclusions

The NaCAS material blended with PVA can be a good candidate to form a film for SUD applications. NaCAS film is flat and dense, with excellent rupture and dissolution properties, although it may present several challenges for direct SUD applications, such as detergent compatibility, but the blended films with PVA shows very promising results while providing obvious benefits in terms of biodegradability, solubility and rupture properties in water.

References

[1] L. M. Bonnaillie, H. Zhang, S. Akkurt, K. L. Yam, and P. M. Tomasula, "Casein Films: The Effects of Formulation, Environmental Conditions and the Addition of Citric Pectin on the Structure and Mechanical Properties," *Polymers (Basel).*, pp. 2018–2036, 2014.

[2] M. P. Arrieta, M. A. Peltzer, J. López, C. Garrigós, A. J. M. Valente, and A. Jiménez, "Functional Properties of Sodium and Calcium Caseinate Antimicrobial Active Films Containing Carvacrol," *J. Food Eng.*, vol. 121, pp. 94–101, 2014.

[3] Y. R. Wagh and H. A. Pushpadass, "Preparation and Characterization of Milk Protein Films and Their Application for Packaging of Cheddar Cheese," *J. Food Sci. Technol.*, vol. 51, no. December, pp. 3767–3775, 2014.

[4] S. Am, G. Gopikrishna, P. Ac, and P. Aj, "Milk Protein Based Edible Films and Coatings – Preparation , Properties and Food Applications," *J. Nutr. Heal. Food Eng.*, vol. 8, no. 2, pp. 219–226, 2018.

[5] R. Thakur, P. Pristijono, C. J. Scarlett, M. Bowyer, S. P. Singh, and Q. V Vuong, "Starch-based Films : Major Factors Affecting Their Properties," *Int. J. Biol. Macromol.*, vol. 132, pp. 1079–1089, 2019.

[6] M. Carissimi, S. H. Flôres, and R. Rech, "Effect of Microalgae Addition on Active Biodegradable Starch Film," *Algal Res.*, vol. 32, pp. 201–209, 2018.

[7] A. Ramu, S. Munisamy, and R. Bhat, "Producing Novel Edible Films from Semi Refi ned Carrageenan (SRC) and Ulvan Polysaccharides for Potential Food Applications," *Int. J. Biol. Macromol.*, vol. 112, pp. 1164–1170, 2018.

[8] M. R. Ginger and M. R. Grigor, “Comparative Aspects of Milk Caseins,” *Comp. Biochem. Physiol. Part B*, vol. 124, pp. 133–145, 1999.

[9] A. R. Sarode, P. D. Sawale, C. D. Khedkar, S. D. Kalyankar, and R. D. Pawshe, *Casein and Caseinate: Methods of Manufacture*, 1st ed., no. December. Elsevier Ltd., 2015.

[10] J. E. Kinsella, C. V Morr, and J. E. Kinsella, “Milk proteins : Physicochemical and functional properties Author :,” *Crit. Rev. Food Sci. Nutr.*, vol. 0248, 2009.

[11] R.J.Avena-Bustillos and J. M. Krochta, “Water Vapor Permeability of Caseinate-Based Edible Films as Affected by pH , Calcium Crosslinking and Lipid Content,” *Food Sci.*, vol. 58, no. 4, pp. 904–907, 1993.

[12] D. Brault, G. D. Aprano, and M. Lacroix, “Formation of Free-Standing Sterilized Edible Films from Irradiated Caseinates,” *J. Agric. Food Chem.*, vol. 45, no. 8, pp. 2964–2969, 1997.

[13] L. J. Mauer, D. E. Smith, and T. P. Labuza, “Water Vapor Permeability , Mechanical , and Structural Properties of Edible b-casein Films,” *Int. Dairy J.*, vol. 10, pp. 353–358, 2000.

[14] P. M. Tomasula, W. C. Yee, and N. Parris, “Oxygen Permeability of Films Made from CO 2-Precipitated Casein and Modified Casein,” *J. Agric. Food Chem.*, vol. 51, pp. 634–639, 2003.

[15] O. A. Diak, B. Amro, D. Jones, and G. P. Andrews, “The Manufacture and Characterization of Casein Films as Novel Tablet Coatings,” *Food Bioprod. Process.*, vol. 85, no. C3, pp. 284–290, 2007.

[16] A. Longares, F. J. Monahan, E. D. O. Riordan, and M. O. Ã. Sullivan, “Physical

Properties of Edible Films Made from Mixtures of Sodium Caseinate and WPI," *Int. Dairy J.*, vol. 15, pp. 1255–1260, 2005.

[17] A. Ghosh, M. A. Ali, and G. J. Dias, "Effect of Cross-Linking on Microstructure and Physical Performance of Casein Protein," *Biomacromolecules*, vol. 10, pp. 1681–1688, 2009.

Chapter 8. General Conclusions and Future Work

8.1 General Conclusions

The conclusions of this research are summarized as follows:

- The dissolution times of the PEG film, PVA film and PEG/PVA blended film were studied, without noticing big differences: PEG film and blended film dissolve as fast as PVA film.
- PEG film exhibits less tensile strength and tensile strain compared to PVA film; by blending with PVA the tensile strength was improved, and by blending with glycerol, the maximum elongation was increased.
- PEG film presents low melting point, which was increased by reacting with glutaraldehyde, albeit not significantly sufficient to justify further efforts within SUD context.
- The dissolution times of sodium alginate film and the its blends are acceptable, though a bit slower than virgin PVA film.
- The stiffness of sodium alginate film is very high, and it was not decreased by blending with PVA and/or PEG.
- Lactips film is not compatible with current detergent Ambrosia 3.0 in SUD; by blending with PVA the compatibility improved, but not significantly enough.
- The dissolution times of Lactips film and its blends with PVA are acceptable, though a bit slower than PVA film. The LAC/PVA blended films rupture slower than that of PVA and Lactips films, probably due to hydrogen bonding between Lactips and PVA chains.
- The tensile strength and strain of Lactips film are not as high as PVA film; by blending the two materials together, better tensile strength and strain were achieved, and both parameters increased with more proportions of PVA.

- Glycerol was selected as plasticizer for the LAC/PVA blended film, which increased film elongation at break and decreased film stiffness.
- Lactips and LAC/PVA blended films present a bit lower water vapor barrier property as PVA film.
- Lactips commercial film can be successfully converted into pouches in both lab and pilot plant scale, and it is possible to be processed in a continuous operation.
- Lactips film behaves good when used to pack powder detergent; thus can be applied in auto dish washing pouch applications.
- Lactips film is sensitive to water, less water amount in the detergent can improve the film-detergent compatibility, and further investigation is still needed to have stable Lactips liquid pouch.
- Lactips film has advantage over PVA film in clay-removal in a laundry appliance.
- The dissolution times of NaCAS and NaCAS/PVA blended films are faster than PVA, after 10 min immersion in water, NaCAS film totally dissolved, more than twice than PVA film. The NaCAS/PVA blended films rupture slower than virgin NaCAS and PVA films probably due to hydrogen bonding.
- NaCAS film is very brittle. The tensile strength and strain of NaCAS are significantly improved when blended with PVA.
- NaCAS film and NaCAS/PVA blended films have similar water vapor barrier property as PVA film.

8.2 Future work

- Copolymerization of PEG and PVA could solve the melting point issue of PEG and become a promising candidate in the future.
- Blending SA with PBAT by hot extrusion may help to increase its mechanical properties significantly (inspired by Lactips film in **Chapter 5**).
- Detergent modification can help to improve the compatibility of casein based films with detergent; the key contributor may be water amount.
- More blending of NaCAS with more PVA copolymers is suggested, to broaden the scope and look for more benefits.
- Pouch prototyping of casein based films with modified detergent is necessary to test pouch stability and other properties such as pouch dissolution and pouch strength.

Appendices

Appendix Congresses and Contributions

Congresses

Authors: J. Ma, T. Gumi

Title: Water Soluble Sodium Alginate Film and its Blending with Poly(vinyl alcohol).

Congress: 15th Doctoral Day at University Rovira i Virgili

Format (poster or oral): poster

Dates: 23 May 2018 **Place**: Tarragona, Spain

Authors: J. Ma, T. Gumi

Title: Water Soluble Sodium Alginate Film and its Blending with Poly(vinyl alcohol).

Congress: Network Young Membrains (NYM) 2018

Format (poster or oral): oral

Dates: 5-7 July 2018 **Place**: Valencia, Spain

Authors: J. Ma, T. Gumi

Title: Water Soluble Sodium Alginate Film and its Blending with Poly(vinyl alcohol).

Congress: 21st Advanced Materials Congress

Format (poster or oral): poster

Dates: 3-6 September 2018 **Place**: Stockholm, Sweden

Authors: J. Ma, J. A. Reina

Title: Water Soluble Sodium Alginate Film and its Blending with Poly(vinyl alcohol).

Congress: 2019 MCAA General Assembly and Annual Conference

Format (poster or oral): poster

Dates: 24-25 February 2019 **Place**: Vienna, Austria

Stay abroad

Organization: Procter & Gamble Services Company NV

Department: Soluble Unit Dose

Supervisors: Florence Courchay

City: Brussels

Country: Belgium

Length: 20 months: January 2017-March 2017 / June 2018-December 2019

Patent

Inventors: J. Ma, F. Courchay

Field of the invention: Water-Soluble Film and Water-Soluble Unit Dose Article Made Therefrom.

Application N°: EP19217967.9

Year: 2019