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Home Compostable Heat Sealable Coating for Paper-based Flexible Packaging

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Mémoire présenté en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

Génie chimique

Novembre 2024

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POLYTECHNIQUE MONTRÉAL

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Ce mémoire intitulé :

Home Compostable Heat Sealable Coating for Paper-based Flexible Packaging

présenté par **Azadeh SADEGHI**

en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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DEDICATION

“To my beloved mother”

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RÉSUMÉ

L'augmentation de la population mondiale entraîne une demande accrue pour la nourriture et son emballage, le principal défi étant de préserver la qualité des aliments et d'allonger leur durée de conservation. L'emballage flexible, préféré pour sa légèreté et son coût abordable, domine le marché, en particulier dans l'industrie alimentaire. Bien que les plastiques soient largement utilisés pour l'emballage en raison de leur faible coût et de leur disponibilité, leur nature non biodégradable soulève des préoccupations environnementales et une dépendance vis-à-vis des ressources pétrolières. Le papier et le carton sont des matériaux biodégradables populaires pour l'emballage alimentaire, avec une migration de substances dans les aliments inférieure à celle des plastiques. Cependant, ils rencontrent des défis en raison de leur mauvaise scellabilité à chaud due à une faible conductivité thermique, rendant le scellage difficile. Pour améliorer leur fonctionnalité, des revêtements comme l'aluminium ou le plastique sont souvent appliqués, mais ceux-ci peuvent migrer dans les aliments, poser des risques pour la santé et compliquer le recyclage, contribuant ainsi à l'augmentation des déchets en décharge.

Cette étude se concentre sur l'utilisation de revêtements compostables à domicile, comme les amidons modifiés, en particulier le succinate d'octényle de sodium (SSOS) et la maltodextrine (MAL), combinés avec des plastifiants tels que le sorbitol et la glycérine, afin d'améliorer la scellabilité à chaud de l'emballage en papier. Grâce à une conception composite centrale (CCC) et à une méthodologie de surface de réponse (RSM), des formulations optimales ont été identifiées, entraînant une réduction significative de la température de début de scellage (SIT) et de la température de déchirure des fibres (FTT). Par le biais d'intervalles de prédiction (IP) et de courses de confirmation, il a été confirmé que les résultats expérimentaux correspondaient aux plages prédites, prouvant ainsi la fiabilité et la précision du modèle.

L'analyse a montré que les plastifiants avaient un impact notable sur la SIT et la FTT, avec de forts coefficients de corrélation démontrant le pouvoir prédictif fiable du modèle. De plus, des techniques analytiques, y compris la FTIR, la DSC et les évaluations rhéologiques, ont confirmé l'amélioration des performances de ces revêtements. Enfin, les effets du temps de séjour et de la pression sur la scellabilité à chaud ont été évalués pour les échantillons optimaux. L'approche expérimentale soigneusement structurée devrait offrir des perspectives prédictives pour des systèmes similaires et approfondir la compréhension des facteurs qui améliorent la scellabilité à

chaud des emballages en papier. Ce produit est spécifiquement conçu pour minimiser l'impact environnemental et garantir la sécurité alimentaire, le distinguant ainsi des autres options compostables ou biodégradables disponibles sur le marché.

ABSTRACT

The increasing global population drives higher demand for food and packaging, with a key challenge being to preserve food quality and extend shelf life. Flexible packaging, preferred for its light weight and cost-effectiveness, dominates the market, especially in the food industry. While plastics are widely used for packaging due to their low cost and availability, their non-biodegradable nature raises environmental concerns and reliance on petroleum resources. Paper and cardboard are popular biodegradable materials for food packaging, with lower substance migration into food compared to plastics. Nevertheless, paper and paper-based flexible packaging exhibits inadequate heat sealability. To improve their functionality, coatings like aluminum or plastic are often applied, but these can leach into food, pose health risks, and complicate recycling, contributing to landfill waste.

The study focuses on using home compostable coatings like modified starches, specifically sodium starch octenyl succinate (SSOS) and maltodextrin (MAL), combined with plasticizers such as sorbitol and glycerol, to enhance the heat sealability of paper packaging.

Through a central composite design (CCD) and response surface methodology (RSM), optimal formulations were identified, significantly lowering the seal initiation temperature (SIT) and fiber tear temperature (FTT). Through prediction intervals (PI) and confirmation runs, confirming that the experimental results matched the predicted ranges, proving the model's reliability and accuracy.

The analysis showed that plasticizers had a notable impact on SIT and FTT, with strong correlation coefficients demonstrating the model's reliable predictive power.

Moreover, Analytical techniques, including FTIR, DSC, and rheological assessments, confirmed the improved performance of these coatings. Finally, the effects of dwell time and pressure on heat sealability were evaluated for the optimal samples.

The carefully structured experimental approach is expected to offer predictive insights for similar systems and deepen the understanding of factors that enhance the heat sealability of paper-based packaging. This product is specifically designed to minimize environmental impact and ensure food safety, setting it apart from other compostable or biodegradable options available on the market.

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LISTE OF SYMBOLS AND ABBREVIATIONS

ANOVA	Analysis of variance		
Bio-PBS	Bio-polybutylene succinate	SPS	Sweet potato starch
CA	Citric acid	SSOS	Sodium starch octenyl succinate
CCD	Central Composite Design	T_m	Melting temperature
CI	Confidence interval	T_{pi}	Plateau initiation temperature
CV	Coefficient of variation	TS	Tapioca Starch
DSC	Differential scanning calorimetry	δ	Solubility parameter
F_p	Maximum peak	ΔC_p	Heat capacity change
FTIR	Fourier transform infrared analysis		
FTT	Fiber tear temperature		
GLY	Glycerol		
I	Wear index		
LEO	lemongrass essential oil		
MAL	Maltodextrin		
MBS	Mung bean starch		
MOW	Municipal organic waste		
OSA	Octenyl succinic anhydride		
PCL	Polycaprolactone		
PE	Polyethylene		
PVA	Polyvinyl alcohol		
R^2 Adj	Adjusted R-squared		
R_a	Surface roughness average		
RH	Relative humidity		
R_q	Root mean square roughness		
RSM	Response Surface Methodology		
SOR	Sorbitol		
SIT	Seal initiation temperature		

CHAPTER 1 INTRODUCTION

1.1 Context

Companies evaluate packaging materials based on the specific requirements of their products, considering some factors such as heat sealability, processability, strength, printability, and barrier properties against water, oil, and gas. The cost-efficiency, sustainability, and legal compliance are pondered as well. Various materials, including plastic, paper, wood, glass, aluminum, or combinations thereof, are employed in packaging development, with each material chosen based on its respective advantages and disadvantages [1]. On the other hand, in relation to environmental pollution and increased landfill waste, companies, especially those in the food industry, face escalating demands to minimize their dependence on plastic packaging [2]. Consequently, consumers are increasingly motivated to mitigate environmental pollution and decrease the use of plastic packaging by opting for biodegradable alternatives [3, 4].

Paper serves as an excellent alternative packaging material, effectively reducing the reliance on plastic and coatings. In 2000, approximately 47% of the global production of paper and paperboard was allocated for packaging purposes [5]. The paper and paperboard segment accounts for 31% of the global packaging market, finding extensive application in food packaging to ensure the preservation of manufactured food products, with fulfillment of functional requirements during transportation, warehousing, and consumption phases, and also providing crucial marketing information to consumers [1, 6]. Notably, paper is recognized for its environmentally friendly characteristics, rendering it a preferred choice for the food industry [5]. Specifically, paper and paperboard are extensively utilized in the packaging of milk, ice-cream, baking goods, microwave popcorn, etc. [1].

Conversely, conventional paper inherently exhibits suboptimal barrier properties, limited mechanical strength, and insufficient heat sealability. These limitations pose challenges for its use in packaging materials [7]. Therefore, to enhance its functional capabilities, it is necessary to incorporate suitable additives or apply surface coatings of aluminum oxide, and polymers, including EVOH, PE, PVDC, FKM acrylic, and latex [8-10]. However, additives and coatings applied on paper can migrate into food products, potentially causing significant health hazards for

humans, contingent upon the extent of migration and consumption. Furthermore, the agents used to improve the paper can interfere during the recycling phase of the paper [1]. Therefore, using biodegradable/compostable (industrial or home compostable) food-safe materials is necessary to reduce environmental issues and landfill waste. It is important to note that certain bioplastic packaging may be biodegradable but not compostable like Polycaprolactone (PCL) [11]. Biodegradable materials are primarily engineered to decompose under specific conditions, typically found in industrial composting facilities (based on the EN 13432 standard). These facilities provide optimal conditions for microbial growth, including controlled moisture levels (between 50% and 60%), oxygen concentrations (over 5%), carbon-to-nitrogen ratios (ranging from 20:1 to 40:1), and temperatures reaching up to 60 °C [12]. In addition, biodegradation rates of biodegradable materials are often not as high as predicted from standardized laboratory testing, and the degradation of end-products under realistic conditions in receiving environments remains largely unexplored [13].

On the contrary, on a smaller scale, composting can be undertaken at home without specific conditions, a process that has been explored less from a technical and scientific perspective. Home composting, also known as backyard composting, involves composting biowaste and using the resulting compost in a private garden. This method offers several potential benefits over industrial composting [14]. Home composting material eliminates the need to collect a significant portion of municipal solid waste, thereby reducing the economic, material, and energy investments required for waste management infrastructure [15-17]. It requires less land use and allows for more precise control over the composting process and the organic materials being treated [14].

Therefore, while industrial composting offers controlled conditions for biodegradation, home composting presents a viable alternative that empowers individuals to contribute to waste reduction. By adopting home composting practices, consumers can play an active role in mitigating environmental pollution and reducing reliance on plastic packaging, ultimately fostering a more sustainable future.

As a result, replacing conventional coatings with home compostable polymer coatings could be a more eco-friendly and cost-effective solution.

1.2 General objective

The objective of this research is to develop a home-compostable, sealable coating for paper that decomposes effectively under ambient home composting conditions, leveraging natural microbial populations to address limitations in paper packaging. This study aims to reduce environmental impact while ensuring food safety by focusing on environmentally friendly materials and providing clear selection criteria for the most efficient materials used in the coating process.

1.3 Plan of dissertation

This thesis is composed of six chapters. Chapter 1 serves as the introduction, elucidating the main aspects of this study. Chapter 2 provides a concise literature review of heat sealing, encompassing its definition, mechanisms, and influential parameters. Additionally, the examination covers influential parameters in heat sealing failures and the interaction between paper properties and sealing efficacy and failure modes. Following this, a detailed analysis of polymers and key parameters that enhance sealing performance in paper-based packaging is provided. Chapter 3 delineates the methodological approach utilized and furnishes comprehensive details regarding the execution of the experimental design. Chapters 4 and 5 will present the two articles that report the main results of this project. Chapter 6 provides a general discussion of the key findings. Chapter 7 will present the conclusions and recommendations.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

The effectiveness of paper and paperboard packaging relies heavily on achieving a perfect seal, particularly in applications where sealing is expected. This literature review commences by providing a succinct overview and comparison of various sealing methodologies employed globally. Emphasizing the pivotal role of adhesion and wetting in ensuring sealability, the initial section elucidates the mechanisms and associated theories governing the establishment of adhesion among disparate substrates. Moreover, an examination of the influential parameters contributing to heat sealing failures and the interplay between paper properties and sealing efficacy and failure modes is presented. The subsequent segment delves into an in-depth analysis of polymers and essential parameters instrumental in augmenting sealing performance in paper-based packaging. A notable focus of this inquiry lies in the exploration of compostable heat-sealing coating polymers, underscoring their significance within the context of this project.

2.2 Mechanisms of heat sealing

Various techniques have been employed to connect plastic components. These methods range from using screws for mechanical fastening to adhesive bonding and welding (heat sealing) processes. [18]. The enhancement of molecular mobility and fusion in the joining of plastic materials can generally be attributed to either internal or external sources of heat [19]. Internal heating methods encompass ultrasonic sealing, induction sealing, vibration, and laser welding, whereas external heating techniques include heat bar sealing, impulse sealing, hot wire sealing, and the use of heated tools [18]. Given that the hot bar is a relatively low-cost apparatus compared to other options, this study will utilize hot bar sealing. It is worth noting that a hot bar or heat jaw is applied to a wide range of products [20]. The two sides of the seal are positioned between two bars that are heated electrically. In fact, heat sealing entails the sealing of two components through the application of heat and pressure for a specified duration. Typically, thermoplastic materials are preferred for heat sealing due to their capacity to be heated to temperatures ranging from 20 to 100°C above their melting points, followed by subsequent cooling, thereby facilitating complete sealing [20].

The steps outlined below describe the mechanism of a heat-sealing process. (I) Melting temperature and wetting at the sealant interface: Upon melting and applying pressure, the two surfaces establish effective contact (wetting) across the seal area. (II) Diffusion and adhesion: Diffusion constitutes another crucial stage in the heat-sealing process [21]. It is noteworthy that diffusion is influenced by various internal and external factors. For instance, the diffusion rate is contingent upon both molecular weight and long-chain branching. Adhesion plays a pivotal role in bolstering the strength at the seal interface [22]. In the case of amorphous polymers, the attainment of sufficient seal strength primarily hinges on self-adhesion and diffusion dynamics rather than crystallization induced by cooling [22, 23]. (III) Entanglement and recrystallization: Within a very short timeframe, chain diffusion occurs across the interface, resulting in the formation of entanglements between polymer chains, primarily due to chain reptation [22, 24]. Following the sealing process, segments undergo recrystallization, which not only binds the surfaces but also enhances the strength of the seal. It is necessary to emphasize that in semicrystalline polymers, the sealing process involves a recrystallization stage alongside other primary sealing mechanisms, including melting, wetting, interdiffusion, adhesion, and entanglement [22]. The rate of cooling significantly influences crystal growth during recrystallization, with slower cooling resulting in the formation of fewer but larger crystals [25]. A visual representation of these stages is provided in Figure 2.1 [22].

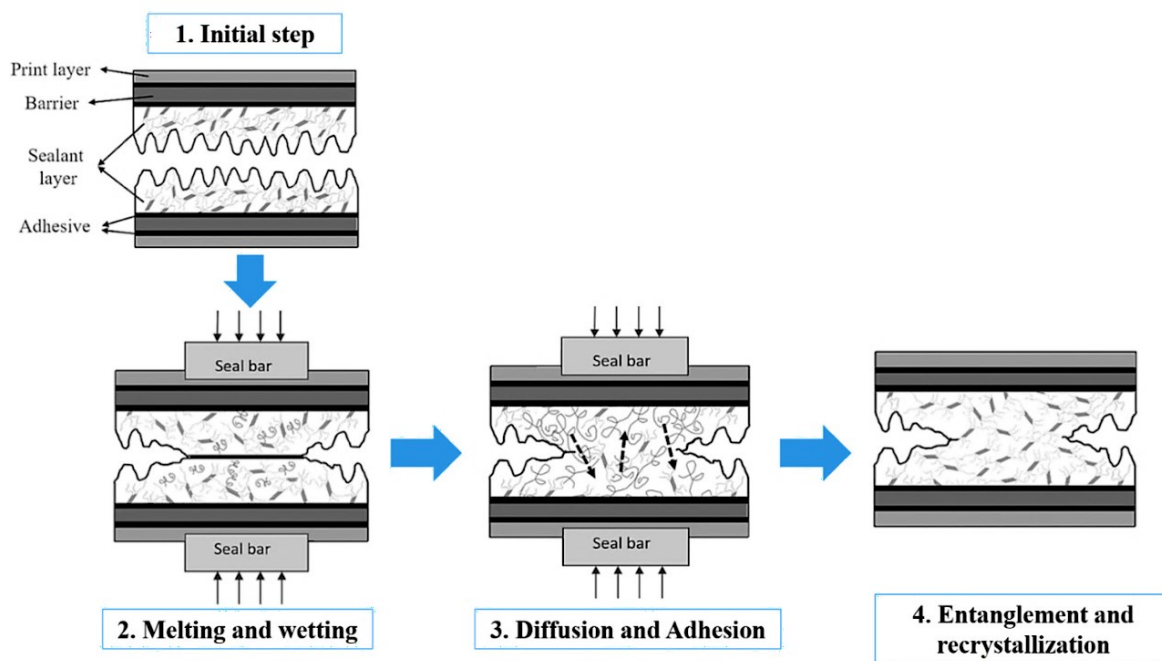


Figure 2.1 Various steps in a heat-sealing procedure [22].

Thus, as previously mentioned, temperature is a crucial factor in heat-sealing processes. All heat-sealing techniques rely on achieving a specific temperature range to guarantee optimal material bonding [26]. The critical role of temperature in heat sealing stems from its influence on polymer behavior. Insufficient temperatures hinder polymer melt flow, leading to weak and inadequate seals. Conversely, excessive heat exposure can induce material degradation, burning, or even combustion, compromising seal integrity [26].

These critical temperature thresholds are defined as the seal initiation temperature (T_{Si} or SIT) and the plateau initiation temperature (T_{Pi}), respectively.

- The seal initiation temperature represents (T_{Si}) the onset temperature at which the sealability experiences a notable escalation, precipitating enhanced adhesive sealing efficacy as the compound's temperature rises [18, 24]. Consequently, the initiation temperature plays a crucial role in determining the ultimate strength of the final seal [27].
- The plateau initiation temperature (T_{Pi}) the seal attains peak strength and optimal sealability. Subsequent temperature increments beyond this point lead to a diminution in both the seal and adhesion strength [18, 24, 28].

Figure 2.2 offers a simplified depiction of the impact of temperature on the seal strengths of thermoplastic films [26].

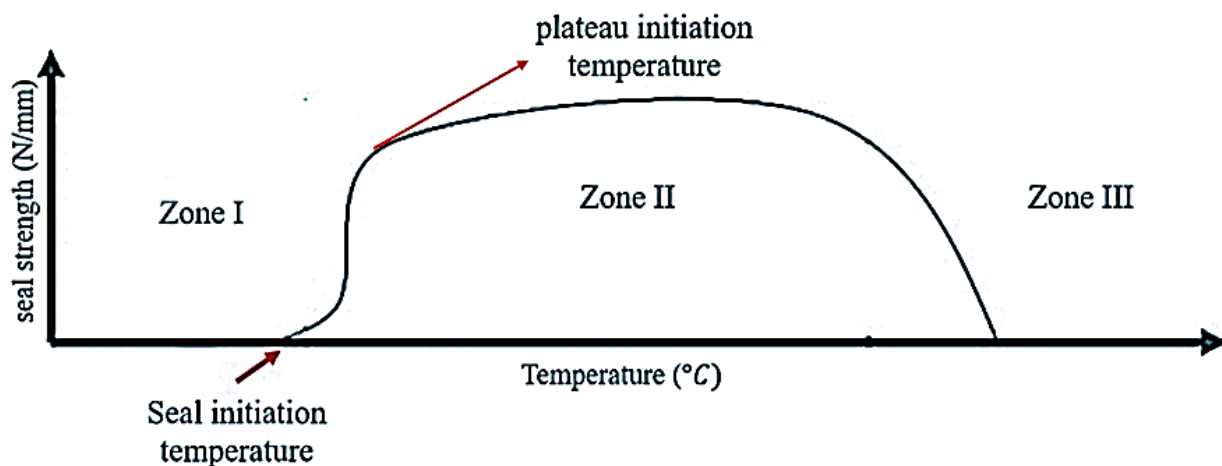


Figure 2.2 Relationship between temperature variations and seal strengths [26].

In thermoplastic sealing, temperatures in zones I and III are considered unsuitable because they weaken seal integrity. In contrast, zone II represents a temperature range that supports effective sealing. The boundary between the unsuitable and suitable temperature zones (I and II) is influenced by the rate of polymer diffusion. When the mobility of polymer chains at the seal interface increases, this boundary tends to shift to the left. This behavior is linked to the thermal transition properties of thermoplastics, with the glass transition temperature (T_g) and melting temperature (T_m) being significant for amorphous and semi-crystalline polymers, respectively. It's important to note that techniques like copolymerization, adding plasticizers, or blending can lower the temperature threshold needed to initiate the sealing process [26, 29].

2.3 Paper and polymer interaction

Interactions between the polymer coating and the paper are crucial for achieving adhesion and other sealing functions. The nature of the interactions can vary depending on the characteristics of the components involved and their surrounding environment. The interaction between the sealable surfaces is primarily governed by the principles of adhesion. In numerous industrial applications, the adhesion of polymers to paper and other cellulosic materials is of paramount importance [30]. There are various adhesion theories, including mechanical interlocking, adsorption, and diffusion theories, that explain the phenomena. These are briefly elaborated below [31].

2.3.1 Mechanical interlocking

In this theory, adhesion between two substrates occurs due to the penetration of one substrate into the surface irregularities of the other, as illustrated in Figure 2.3-a. Paper, as a porous surface, is necessary for this theory since pores in the paper allow the adhesive (as the mobile phase) to flow into the paper, thereby providing high strength [32]. It is noteworthy that there is a positive correlation between surface area and adhesion strength, meaning that as the surface area increases, the adhesion strength typically increases as well. Previous studies have demonstrated that increasing surface roughness enhances surface porosity. Consequently, rougher surfaces provide more space for adhesives to flow, thereby improving adhesion strength [33, 34].

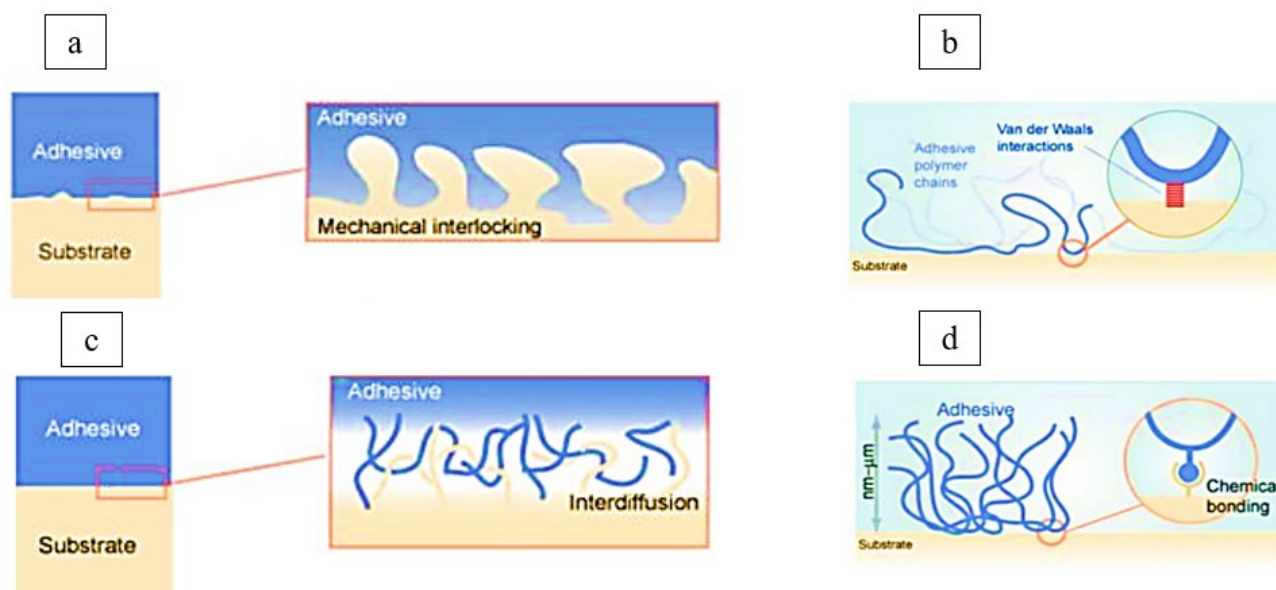


Figure 2.3 Type of adhesion theory. mechanical interlocking (a), Adsorption (b), Diffusion (c), and Chemical Bonding (d) [31].

2.3.2 Adsorption (wetting) theory

In adsorption theory, also known as wetting theory, macromolecules from the mobile phase adhere to the surface, creating surface forces between them. These adsorption forces typically manifest as van der Waals or secondary interactions, as illustrated in Figure 2.3-b. Wetting, determined by the equilibrium contact angle, is considered a necessary prerequisite for the onset of adhesion. Figure 2.4 illustrates both partial and incomplete wetting of a surface by a droplet [35].

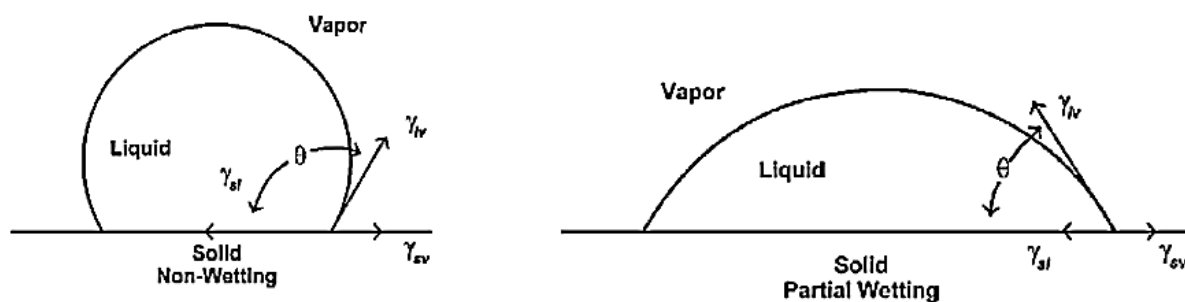


Figure 2.4 Wettability of adhesive and contact angle [35].

Moreover, surface-free energy plays a significant role in the wetting behavior of a material. When two surfaces come into contact, their interaction potential increases if both surfaces possess high surface free energy. This energy can be quantified through contact angle calculations [22]. It is important to highlight that the contact angles of materials are significantly influenced by their surface characteristics, including roughness, as well as their hydrophilic or hydrophobic properties. Furthermore, during the sealing process, materials begin to melt almost instantly in addition to the wetting behavior [22].

Utilizing Young's equation allows for the estimation of the wetting behavior of sealants, as demonstrated by the following equation [35]:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \quad (2.1)$$

Dupre's equation is employed to amount of energy bound through wetting, formulated as follows [36]:

$$w_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \quad (2.2)$$

Where γ_{sv} is the surface energy of the solid, γ_{sl} the interfacial tension between the solid and the liquid, γ_{lv} the surface energy at the liquid-vapor interface, θ the contact angle between the solid and the liquid, and w_a the work of adhesion.

2.3.3 Diffusion theory

This theory primarily concerns polymeric surfaces and their behavior under certain conditions. According to diffusion theory, when subjected to elevated pressure and temperatures exceeding the T_g , the molecular chains of two polymer surfaces interpenetrate. Consequently, this process leads to the dissolution of the initial boundary between the surfaces, as illustrated in Figure 2.3-c. Adhesion is achieved by moving polymer chains at the interface toward the opposing surface. Diffusion occurs when the two surfaces are composed of the same polymer. However, when fabricated from different polymers, diffusion occurs based on their chemical compatibility, indicating that the polymers must be soluble in each other [37-39]. In other words, bond strength reaches its maximum level when the solubility parameter (δ) between the adhesive and substrate is matched [40].

2.3.4 Chemical Bonding

This theory relates the formation of an adhesion bond to surface chemical forces, as shown in Figure 2.3-d. The hydrogen, covalent, and ionic bonds created between the adhesive and the adherends exhibit greater strength compared to the attractive forces arising from dispersion interactions. In general, the process of chemical bonding entails four distinct types of interactions: covalent bonds, hydrogen bonds, Lifshitz-van der Waals forces, and acid-base interactions. It is worth noting that the precise nature of these interactions is contingent upon the chemical composition of the interface. In Table 2.1, examples of the energy values associated with Lifshitz-van der Waals interactions and various chemical bonds are presented. [40].

Table 2.1 Magnitudes of Lifshitz-van der Waals Interactions and Chemical Bonds [40].

<i>Type</i>	<i>Covalent</i>	<i>Ion-Ion</i>	<i>Ion-Dipole</i>	<i>London dispersion</i>	<i>Dipole- dipole</i>	<i>Hydrogen bonding</i>
<i>Example</i>	C-C	$\text{Na}^+ \dots \text{Cl}^-$	$\text{Na}^+ \dots \text{CF}_3\text{H}$	$\text{CF}_4 \dots \text{CF}_4$	$\text{CF}_3\text{H} \dots \text{CF}_3\text{H}$	$\text{H}_2\text{O} \dots \text{H}_2\text{O}$
<i>E (KJ/mol)</i>	350	450	33	2	2	24

Covalent and ionic bonds yield much stronger adhesion than secondary forces, as illustrated in Table 2.1. Secondary valence bonding, which includes weaker interactions like hydrogen bonds, is more prevalent in polar materials, such as carboxylic acids, compared to nonpolar ones like polyolefins. Adhesion can also be enhanced through mechanical interlocking, diffusion, or electrostatic interactions. Covalent bonds are often formed at interfaces in cross-linked adhesives and thermoset coatings, requiring compatible reactive groups to be present. Surfaces such as wood and certain plastics can achieve these bonds through intentional surface treatments like corona or flame treatment.

Here are the definitions of various intermolecular interactions summarized:

Dipole-Dipole Interactions: These are intermolecular forces arising from the alignment of polar molecules, where the positive end of one molecule is positioned near the negative end of another.

Hydrogen Bonding: A strong dipole-dipole force where hydrogen bonded to F, O, N, or S interacts with lone electron pairs on another molecule.

Hydrogen bonding, a specific type of acid-base interaction, occurs among water molecules due to their dual acidic and basic properties. As shown in Table 2.1, hydrogen bonds, though weaker than ionic or covalent bonds, are among the most critical secondary interactions.

London Dispersion Forces: Weak attractions caused by temporary dipoles from fluctuating electron distributions [40].

2.3.5 Weak Boundary Layer Theory

Following the weak boundary layer theory, bond failure occurs at the interface of materials, giving rise to a weak boundary layer [37]. Specifically, the migration of contaminants, additives, or additional surface treatments induces the disruption of polymer chain structures, consequently yielding a layer characterized by relatively low molecular weight and exhibiting fragile boundaries.

As mentioned, the adhesion of polymers to paper and other cellulosic materials is critically significant. The adhesion properties of paper are generally explained by its surface energy and surface chemistry characteristics, such as contact angle, composition, and the presence of acidic and alkaline functional groups, particularly when considered from a macroscopic perspective. The equation, known as Dupre's equation, referenced in wetting theory, can be derived from the thermodynamic work of adhesion between a paper surface and a polymer adhesive. However, this advantage for the work of adhesion does not represent the actual adhesion. Instead, it indicates the ideal adhesion, which is dependent on chemical bonding within surface chemistry. In practical terms, adhesion pertains to the mechanical energy necessary to separate bonded components. Conversely, ideal adhesion refers to the formation of bonds.

Previous studies have indicated that the adhesion of coated papers is largely influenced by the nature of the coating composition. For example, research by Welander et al. [41] demonstrated that polyethylene (PE) combined with calcium carbonate (CaCO_3) and styrene-butadiene (SB) exhibited stronger adhesion compared to polyvinyl alcohol (PVA) combined with clay. The polarity of a polymer, particularly influenced by its carboxyl content, significantly affects the adhesion strength between paper (cellulose) and the polymer. This relationship is illustrated in

Figure 2.5, which shows that as the COOH content of the polymer increases, the peel strength nearly triples.

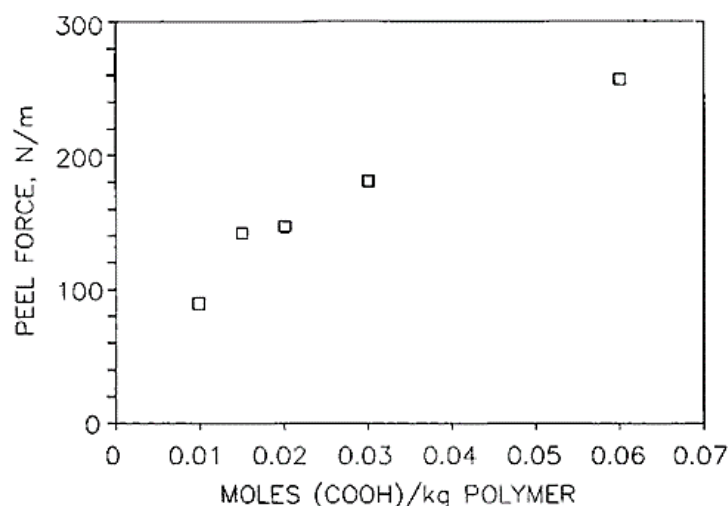


Figure 2.5 Influence of polarity on vinyl co-polymer adhesion to cellulose strips [41].

2.4 Seal strength

2.4.1 Peel test

After the sealing process, the peeling test distinguishes the grade of polymer adhesion bonds. The evaluation of heat seals between thin films is typically conducted using T-peel tests. As demonstrated in Figure 2.6 (A), the two ends of a test specimen are pulled at a constant rate, resulting in a force versus extension curve. The maximum force per unit width recorded during this test, as shown in Figure 2.6 (B), is commonly referred to as the seal strength. When subjected to sufficiently high extension, the test piece eventually fails. The elongation at the point of failure, known as seal elongation, and the area under the force-extension curve, referred to as seal energy, are commonly used as indicators of the seal's toughness [20, 42].

It is worth noting when the interfacial forces form a seal that does not penetrate deeply into the substrate, it is considered a peel seal. However, If the seal has dipped into the surface of substrates more deeply and made a strong cohesion between the components, the seal is known as a tear seal.

Tearing occurs outside the seal area because of the cohesive bond, which demonstrates good strength with resistance to get broken [20, 42].

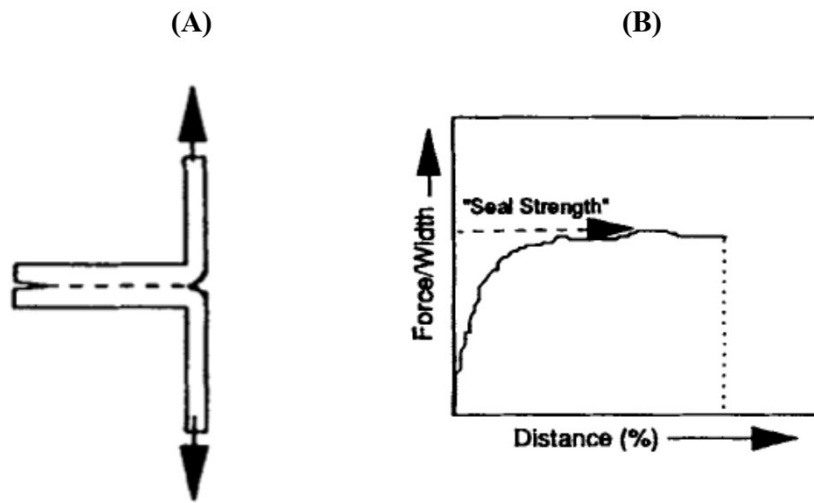


Figure 2.6 Schematic showing the T-peel test [42].

2.4.2 Hand test

Hand tests, as the name suggests, are performed manually. The process requires no machinery other than a sealing machine. Once the seal is formed, the samples are allowed to cool, and then the amount of fiber tears is measured. As shown in Table 2.2, the amount of fiber tear corresponds to the level of adhesion assigned to the seal [43].

Table 2.2 Sealability assessment scale for hand tests [43].

Adhesion value	0	1	2	3	4	4,5	5
Evaluation of the value	No Seal	Weak adhesion	Adhered but no tear	Under 50 % fibre tear	Over 50% fibre tear	Over 90% fibre tear	100% fibre tear

As shown in Table 2.2, the hand test does not quantify seal strength using specific units. Instead, it serves as a practical and efficient method for rapidly evaluating and comparing seals across various materials and surface pairings. For the hand tests, adhesion values were determined visually through manual evaluation [44]. Each adhesion value corresponds to a specific level of adhesion

performance, defined by the behavior of the materials during peeling. For example, at adhesion value 0, no adhesion is observed between the materials. The bonded layers separate effortlessly without any resistance, indicating a failure to form a seal. At adhesion value 3, the adhesion is moderate, with less than 50% of the fibre or coating material tearing during peeling. While this shows some adhesion, it may require further optimization to achieve better performance. At adhesion value 5, the strongest adhesion is observed, with a complete fibre tear (100%) occurring during peeling. This cohesive tear indicates excellent bonding and seal integrity, ideal for applications requiring high reliability. More precise values can be derived from the peel and tear seal tests, as previously discussed.

2.5 Failure modes

An essential consideration in heat sealing analysis is the failure of the joint. The integrity of the entire package is compromised if any part of the seal structure is damaged. In many cases, failure occurs outside the actual seal area. Consequently, any thermo-mechanical factors that could weaken adjacent regions must be carefully evaluated. When two materials are heat-sealed, it is possible to identify three areas simultaneously: the seal, the area close to the seal, and the untouched film region far from the seal bond. The failure modes based on the ASTM F88/F88M standard are classified as shown in Figure 2.7 [45].

- **Adhesive peel** (figure 2.7-a): The heat-sealed bond peels apart. This failure mode occurs when the seal is weak.
- **Cohesive peel** (figure 2.7-b): In this case, the joint is adequately strong to transfer the stress to the bulk of the sealing layer of the film.
- **Delamination** (figure 2.7-c): This occurs through the tensile breaking of the sealing layer, which is fragile and weak, followed by its separation from the support layer.
- **Material break** (figure 2.7-d): This is caused by the weakening of the seal at its edge as the substance melts or the breakdown of the laminate structure.
- **Material break (remote)** (figure 2.7-e): This failure occurs far from the sealed area and might result from faults in the composition or edges of the film.
- **Material elongation** (figure 2.7-f): The seal is strong, but the other components of the film are not sufficiently strong to withstand stress and yielding.

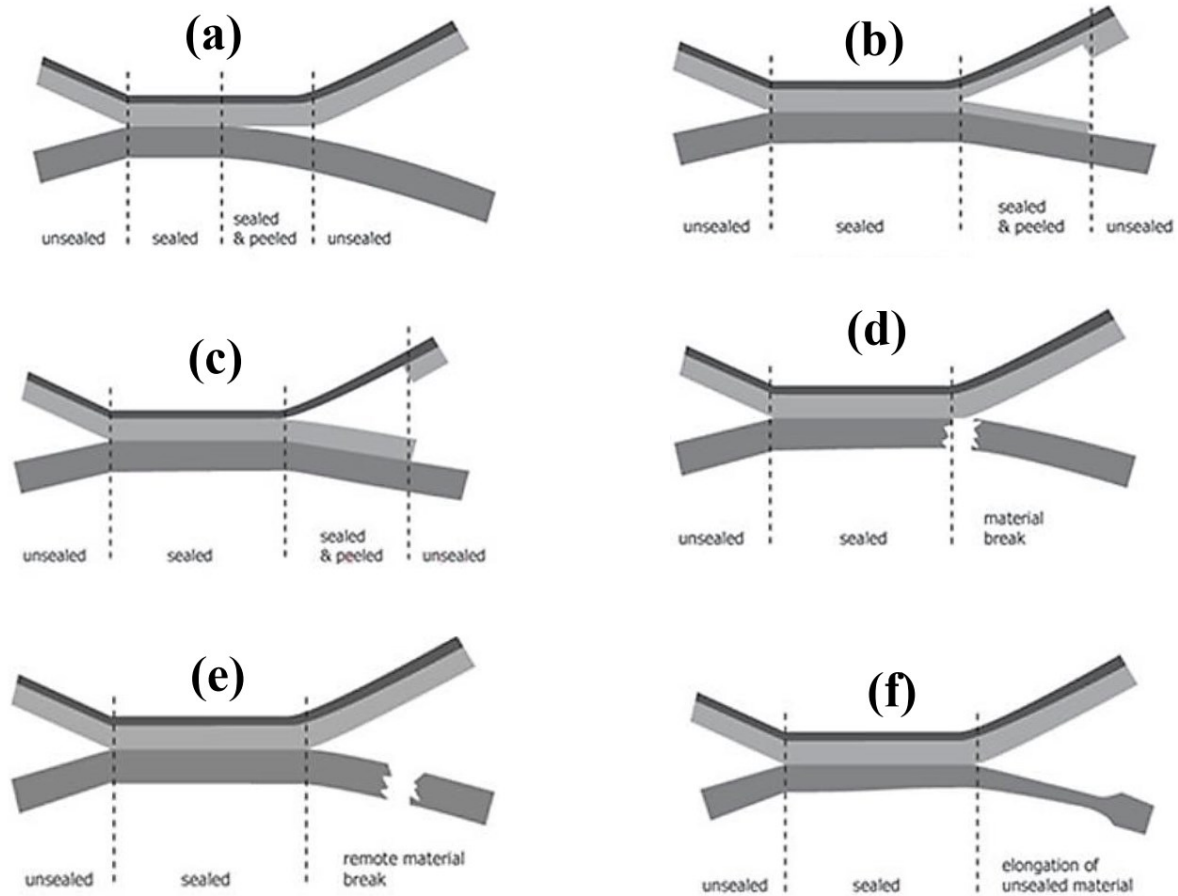


Figure 2.7 Test Strip Failure Modes [45].

2.6 Failure modes of paper/adhesive layers

As mentioned, the role of adhesion bonds in withstanding different mechanical stresses, such as failure stress and the separation of the bonded system imposed by mechanical energy indexed as bond strength and practical adhesion, respectively determines the quality of polymer adhesion to paper. Paper is a weak substrate due to its layered network structure, making it susceptible to tearing and delamination. This susceptibility renders paper a fragile substrate. Consequently, the laminates of paper/polymer do not typically split at the interface [46]. The remaining cellulose particles, either as free materials or connected components to the packaging after opening, are referred to as fiber tears [47]. Figure 2.8 represents the changes in the peel force of mixed and interfacial failure versus peel distance for adhesive/paper layers.

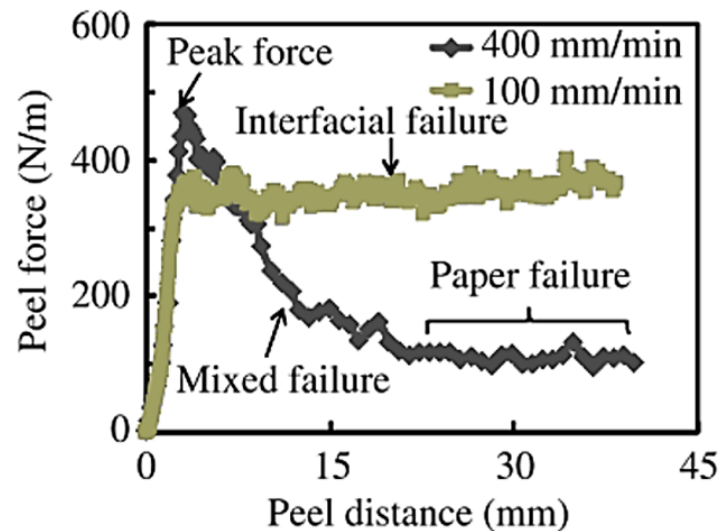


Figure 2.8 Curve of peel force of mixed and interfacial failure versus peel distance for adhesive/paper layers [46].

The graph has two curves: one shows the regular curve when an interfacial failure occurs, and another indicates the typical curve when a paper failure happens. Both curves have distinct peel rates: 100 mm/min and 400 mm/min. The former as the lower rate one illustrates interfacial failure occurrence which is noisier but fairly constant.

In contrast, the former initially reaches its maximum peak (F_p), followed by a decline from a low to a steady value, representing paper delamination. Upon peeling, at least one fibre layer is on the tape. Such failure commonly begins from a spot with a more fragile structure on the line of contact leading to the tape peeling due to the expansion and merge of the area [46].

Oni et al. [47] examined the process of fibre tear through heat-sealing papers with polymer films composed of multiple layers. Based on the results of the study, excessive fibre tears occurred in specimen combinations when there were no imprints of paper fibres on the surface of the film. Fibre tears are caused by the mechanical interlocking theory. Several factors dictate the level of interlocking:

- The physical composition of the paper.
- The chemical alteration of the paper surface.
- The formulation and molecular structure of the polymer sealant film.

Furthermore, their results indicate that fibre tear occurs beyond a certain seal strength value for a particular paper/film formulation.

2.7 Effect of processing factors

Numerous factors, such as the temperature employed for sealing, dwell time, and applied pressure, influence the efficacy of heat sealing in the context of polymeric films. As previously discussed, the sealing temperature is a critical parameter in the heat-sealing process and must be meticulously controlled to ensure desirable seal properties [18]. The strength of the heat seal primarily depends on the maximum temperature attained at the interface during the heat-sealing process. Ideally, the temperature at the film interface should be considered the primary controlling factor. However, directly measuring this temperature is practically challenging due to the unavailability and high cost of the required equipment [26].

Najarzadeh et al. [48] research indicates that raising the sealing temperature improves seal strength. This improvement is due to the higher energy levels of chain ends and increased free volume, which promote the diffusion of chain ends across the interface. As the temperature at the interface nears the melting point of the sealant materials, molecular diffusion significantly intensifies, resulting in more intermolecular connections forming across the interfaces. When under tension, these connections stretch into fibrils until they break. Elevated temperatures enhance both the strength and quantity of these links, thereby boosting seal strength. Ultimately, the widespread formation of these links across the surface contributes to a lock-seal effect.

Dwell time is the period during which the heated bars keep the two films in close contact at the interface. This direct contact allows for effective heat transfer to the interface. For strong seal strength or hot tack strength to be achieved, two critical phenomena must take place during this dwell time [49] :

- The temperature at the interface between the seal layers must rise to a level that allows the chain ends to diffuse across the boundary.
- The Brownian motion of the chain ends across the interface must occur, resulting in entanglement on a sufficient length scale.

Consequently, both the rate of heat flow and the dwell time directly impact seal strength. However, extending the dwell time beyond a certain limit does not significantly enhance seal strength. This occurs as the interface temperature nears the jaw temperature, causing the diffusion length to approach the critical scale necessary for entanglement. Thus, determining an optimal dwell time is essential for achieving a strong seal and should be tailored to each specific application [26, 50].

Applying pressure is essential to ensure sufficient contact between the surfaces of the films, facilitating interfacial penetration. Nonetheless, excessive pressure may result in the undesired expulsion of molten film from the sealed region. In most heat-seal components, pressure assumes a relatively minor role compared to temperature and dwell time [24, 49, 50]. It is noteworthy that in industrial production lines, increased pressure may be required in situations where pressure control is imprecise, film thickness is inconsistent, or heated bars are misaligned [26].

According to Merabtene et al. [51] the sealing pressure and sealing temperature were optimized with a set dwell time for paper-based flexible packaging with a polyethylene (PE) coating (Paper 70 + 15 PE and Paper 90 + 30 PE). They reported that the initiation sealing temperature for the Paper 90 + 30% PE sample was 80 °C, whereas the sealing initiation temperature for the Paper 70 + 15% PE specimen was 90 °C. Moreover, the maximum observed temperatures were 220 °C and 190 °C for the Paper 90 + 30 PE and Paper 70 + 15 PE, respectively. Beyond these temperatures, the samples turned brown. Figure 2.9 illustrates the influence of seal strength with different sealing pressure and temperature values (with a maximum temperature of 100°C) at a fixed dwell time for the paper-based material.

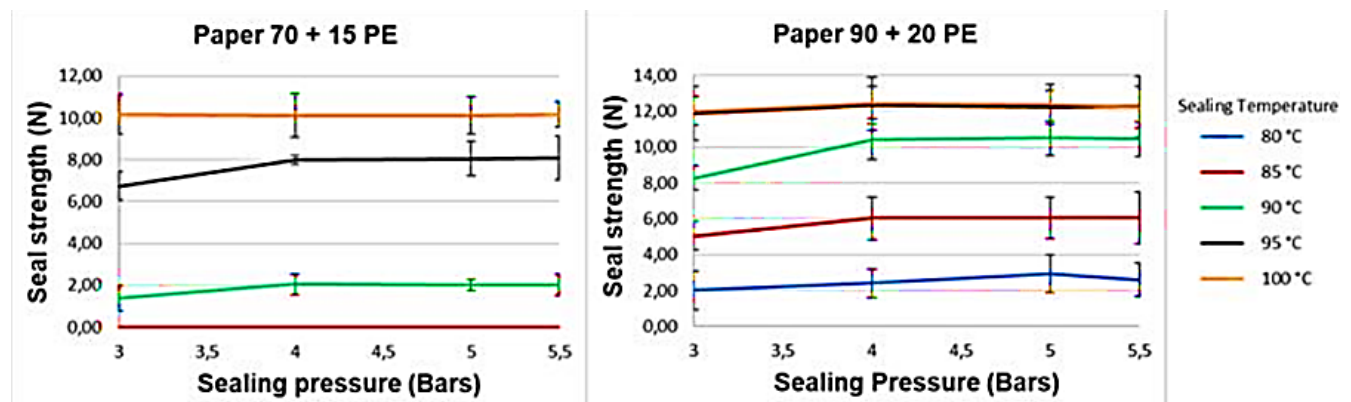


Figure 2.9 Seal strength effects on Paper 70 + 15 PE and Paper 90 + 30 PE specimens [51].

The seal strength of the paper-based material did not change significantly with varying sealing pressures, considering the significant effect of thickness on sealing strength [52]. Therefore, the influence of PE as a sealant layer with different thicknesses $78 \pm 5\%$ (Paper 70 + 15% PE) and $124 \pm 5\%$ (Paper 90 + 30% PE) on heat seal strength for paper packaging was examined. The seal strength of Paper 90 + 30% PE was higher than that of Paper 70 + 15% PE because a thicker sealant layer allowed for more inter spreading of polymer chains, leading to strong liaison through polymer recrystallization [51].

2.8 Heat sealing of compostable/biodegradable material coating on paper-based packaging

As previously discussed, paper packaging offers the advantage of being derived from biological sources, as well as being biodegradable and compostable. According to a study conducted by the Institute for Energy and Environmental Research in Germany, paper-based packaging exerts a considerably lower environmental impact compared to other forms of packaging. Globally, paper-based packaging helps mitigate marine litter and reduces the environmental impact of packaging. This is especially crucial given the increasing volume of packaging, driven by market expansion, urbanization, and a growing global population [53]. In fact, Paper-based packaging is primarily derived from wood pulp, a renewable resource. The raw material for paper production, trees, can be replanted and regrown, thereby supporting a sustainable cycle of production.

In contrast, materials such as plastics are derived from petroleum, a non-renewable resource that is finite and requires substantial energy for extraction and processing. Conversely, paper is unsuitable for food packaging due to its inadequate barrier properties, poor heat sealability, and low strength [1]. Moreover, due to paper's low thermal transfer coefficient, effective sealing is challenging, necessitating either a longer sealing time or a higher sealing temperature [54].

To address the limitations of paper, researchers have employed various techniques, including extrusion, dispersion, and solvent coating (as illustrated in Figure 2.10), as well as incorporating different polymers in multilayer packaging to enhance the sealing performance of paper [55].

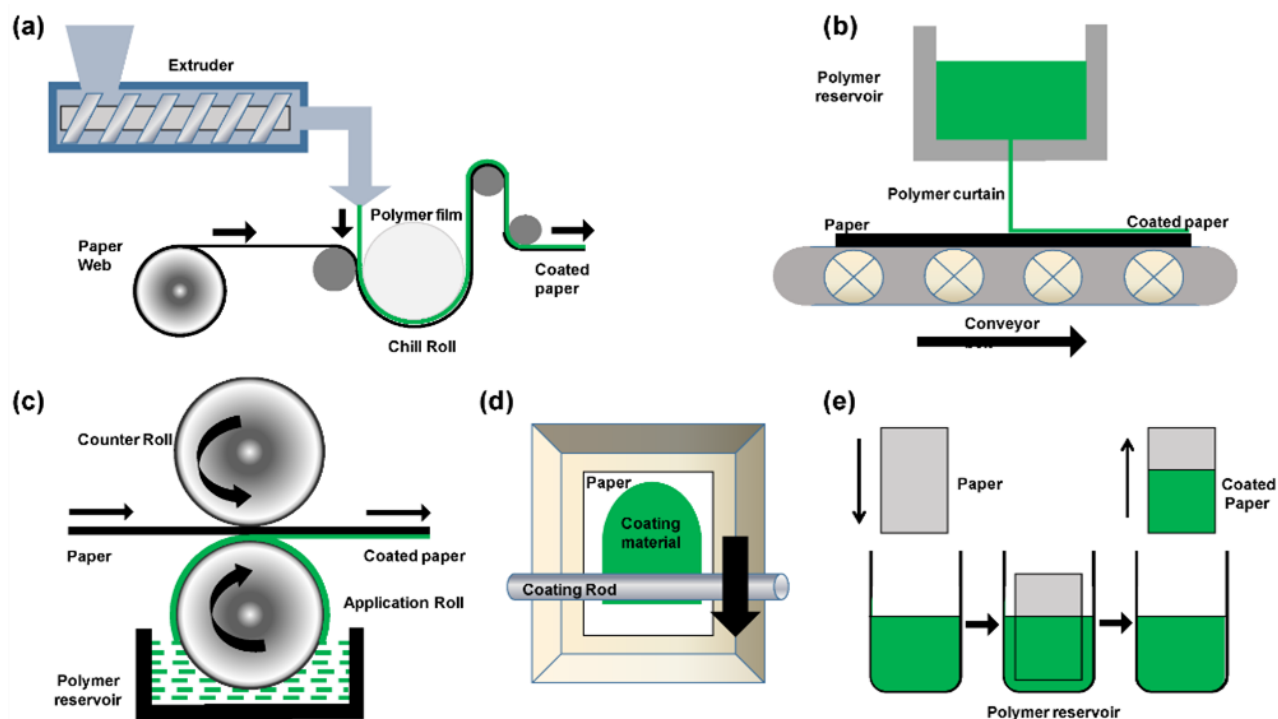


Figure 2.10 Processes for coating paper, extrusion coating(a), curtain coating (b), size press coating (c), bar coating (d) and dip coating (e) [55].

In theory, all thermoplastic polymers can be extruded and used as coatings for paper. However, polymers that do not possess thermoplastic properties, such as polysaccharides, proteins, and lipids, can also serve as coatings by being dissolved or dispersed in a suitable solvent. Additionally, the same methods can be applied to thermoplastic polymers that cannot be extruded [55].

The extrusion technique (Figure 2.10-a) is the most widely utilized method for coating paper due to its numerous advantages, such as continuous processing, uniform coating, and reduced cracking. However, achieving the required properties for high coat weight can be challenging due to polymer melt flow instabilities and certain material-relevant characteristics being limited. In addition, dispersion and solvent-based coating methods including surface sizing, curtain coating, bar or rod coating, and dip coating (illustrated in Figure 2.10-b and e) are employed to attain desired characteristics. These techniques typically use low coat weights, approximately around $10 \frac{g}{m^2}$. Considering the advantages outlined in this study, particularly regarding coating weight, the solvent coating method, specifically bar coating, will be utilized.

As noted, biodegradable or compostable heat-sealing coatings on paper-based flexible packaging have garnered attention due to their potential for reducing environmental issues and landfill waste. Consequently, this section of the literature review will focus on the use of compostable and biodegradable polymers as heat seal coatings in paper-based packaging.

Initially, to clarify the terms 'compostable' and 'biodegradable' and distinguish between them, the definitions of each concept will be provided. Subsequently, the discussion will focus on compostable and biodegradable polymers that have been employed as heat seal coatings in paper packaging. The following definitions are based on the standard EN 13432:

- **Biodegradable:** A process where microorganisms such as bacteria and fungi break down organic matter into natural components, primarily carbon dioxide (CO₂), water, and biomass, under specific environmental conditions.
- **Compostable:** Refers to materials that biodegrade during a composting process through the action of naturally occurring microorganisms, achieving a high degree of breakdown within a specified timeframe. These biological processes yield carbon dioxide (CO₂), water, inorganic compounds, and biomass. To qualify as compostable, the material must leave no visible contaminants or toxic residues, ensuring the resulting compost is safe for plant growth and soil health. Compostable materials may degrade under industrial composting conditions or in home composting systems, depending on their certification.
- **Home composting:** Also referred to as backyard composting, this process involves the biodegradation of organic waste, including municipal organic waste (MOW), through the action of naturally occurring microorganisms in a household setting. Unlike industrial composting, home composting occurs at ambient temperatures and less controlled conditions. Materials and components of home compostable products are specifically designed to fully decompose in soil within a defined timeframe, leaving no toxic residues and producing nutrient-rich compost that can be applied to household gardens.

The primary difference between compostable and biodegradable products, as defined by EN 13432, is that compostable items must degrade completely within a specified timeframe under controlled conditions, such as those found in industrial or home composting systems. Compostable materials must also disintegrate, leaving no visible residues or toxic substances, and produce nutrient-rich compost. Biodegradable products, on the other hand, can naturally break down into simpler

substances over time but may not meet the strict timeframes, residue-free requirements, or environmental safety criteria outlined in the standard. Let me investigate various materials utilized as coatings on paper to enhance its sealability.

In 2020, the heat-sealing properties of gelatin/palm wax coatings with varying concentrations of lemongrass essential oil (LEO) on paper were investigated [56]. The results indicated that adding a high concentration of LEO decreased seal strength. Specifically, the coated paper without LEO exhibited the greatest seal strength (1.6 kN/m), while the addition of 12% LEO resulted in the weakest sealing ability (0.9 kN/m). This reduction in seal strength is likely due to the hydrophobic nature of lemongrass essential oil, which may react with the hydroxyl groups in the paper and gelatin. This interaction can cause the gelatin network to become more rigid and lose its ability to melt effectively.

In another study examining the impact of protein on seal strength, Shao et al. [57] the heat-sealing capability of soy protein-coated celery composite paper was examined. The optimal seal strength was achieved within a temperature range of 110–130 °C, with a dwell time of 5–7 seconds for all specimens. The interaction between the soy protein and celery fiber facilitated the sealing of the paper, with the viscoelastic properties of soy protein combining both solid and liquid characteristics enhancing the heat-sealing performance. As the soy protein concentration increased from 10% to 13.75%, the seal strength improved from 114.9 N/m to 160.6 N/m. In contrast, pure celery paper did not exhibit desirable sealability.

Furthermore, Keyriläinen et al. [52] explored cellulose esters as a bio-based material and demonstrated that cellulose esters with controlled molecular weights and varying side chain lengths (C6-C16) significantly enhanced the seal strength of kraft paper when used as coatings. Additionally, PLA and bio-LDPE were used as reference materials. The cellulose esters with side chain lengths of C6 and C16 produced the most resilient seals, whereas those with C10 and C12 side chains were not sealable. Moreover, the reference materials, bio-LDPE and PLA, exhibited the highest sealing strengths of 228 N/m and 649 N/m, respectively, due to their thicker coatings compared to the cellulose esters.

PLA represents another significant commercially available compostable polymer. Several researchers have examined the use of PLA-coated paper and paperboard packaging [8, 58-60]. For instance, PLA-coated paperboards were fabricated using a solution casting technique, and the

impact of the coating on enhancing the heat seal properties of paperboard intended for manufacturing one-way paper cups was assessed [61]. The study observed that coated paperboards with PLA casting solutions containing less than 0.5 w/v% were unable to seal, likely due to insufficient thickness. This finding underscores the influence of coating thickness on heat-sealing strength. Moreover, low concentrations of PLA led to uneven or incomplete coating layers, exacerbating the issue. Consequently, samples were coated with PLA concentrations exceeding 1 w/v%. Within this range, the heat-sealing strength exhibited a linear increase with increasing PLA concentration until reaching 4 w/v%, beyond which it plateaued. Additionally, during all T-peel tests conducted with PLA coating solutions exceeding 1 w/v%, it was observed that the PLA layer adhered securely to the paperboard, suggesting the occurrence of fiber tears.

In a different study, a PLA-based polymer coating with mineral fillers (0–10 wt% loading), including talc, kaolin, and calcium carbonate, was used [8]. The results showed that all specimen points were effectively sealed at temperatures between 160 and 200 °C, leading to complete fiber tear. While there was no notable difference in the temperatures needed for full fiber tear, the presence of fillers influenced sealability. Consequently, higher temperatures were found to be beneficial for sealing.

Considering that the primary objective of this project is to investigate the use of home-compostable, heat-sealable coatings on paper, the literature review indicates that polymers with these properties can be categorized into three types: polysaccharides (e.g., cellulose, chitosan, starch), proteins (e.g., whey protein, gelatin), and home-compostable polyesters (e.g., bio-polybutylene succinate (bio-PBS)), as shown in Figure 2.11.

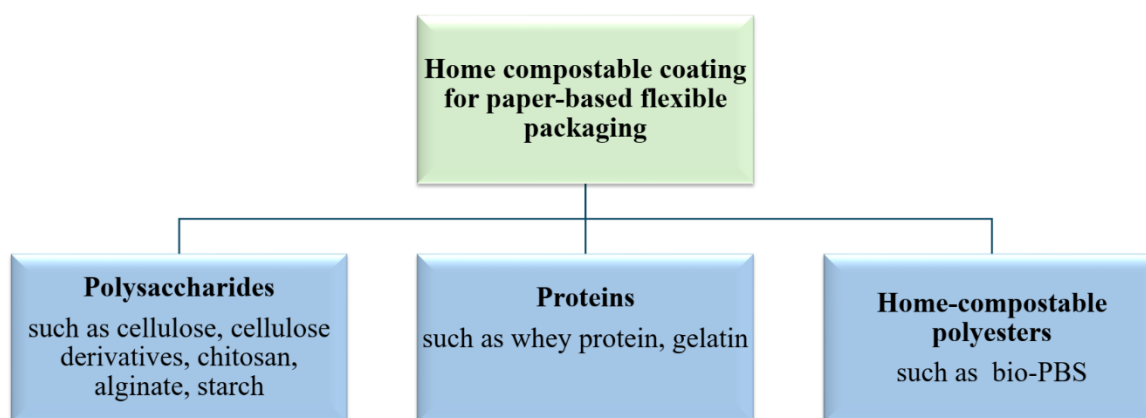


Figure 2.11 Chart of proper home-compostable heat sealable materials for paper-based packaging.

Among these materials, cellulose, its derivatives, chitosan, and home-compostable polyesters are insoluble in water, with some requiring pretreatment to achieve solubility [62]. Additionally, the formation of pectin and alginate films requires calcium ions to create ionic bonds with the carboxylic groups on polysaccharides [62, 63]. Furthermore, proteins and gelatin present certain limitations, such as potential allergenic reactions (particularly with wheat gluten), considerations related to religious beliefs (notably when pigskin gelatin is used), and dietary restrictions of vegans [64, 65]. Consequently, water-soluble starch emerges as a promising candidate for paper coating.

2.9 Starch and Modification of Starch

Starch is a natural polymer and the most abundant form of carbohydrate on Earth. It is primarily produced by plants and some cyanobacteria. Not only is starch industrially compostable, but it is also one of the few polymers that can be composted at home [66].

The structure of starch consists of amylose and amylopectin, both of which significantly influence film formation and the properties of the resulting films. Amylose, with its relatively long and linear chains, forms a high number of hydrogen bonds between molecules, contributing to a crystalline structure. In contrast, amylopectin, characterized by short and branched chains, leads to weaker intermolecular bonding. Consequently, films rich in amylose are denser and stiffer compared to those rich in amylopectin [70, 71]. The paper industry extensively utilizes starch due to its abundance and cost-effectiveness, enabling large-scale applications [67]. Indeed, the majority of non-food applications for starch are dominated by the paper industry [68]. In this industry, starch is primarily used in surface applications such as surface sizing, pigment binding, and coating [67]. Its substantial molecular weight allows for controlled depolymerization. Additionally, starch's ability to form hydrogen bonds enables it to dissolve in water, which facilitates pigment binding and adhesion to cellulose fibers due to its hydrophilic nature. Moreover, the reactivity of starch's hydroxyl groups allows for extensive oxidation or substitution reactions, which can alter its rheological properties and potentially reduce retrogradation [67, 69].

Despite these remarkable properties, there is currently no information available on starch-based heat seal coatings for flexible paper packaging. Therefore, this section will focus on investigating the heat seal properties of starch-based films.

2.9.1 Effect of plasticizer on heat sealing of Starch film

Starch films without plasticizers exhibit a dense network with high cohesive energy density, resulting in a fragile structure due to the extensive hydrogen bonding between multiple chains [70]. The introduction of a plasticizer disrupts these intermolecular connections by competing with the hydrogen bonds within the starch network. This interaction reduces hydrogen bonding between starch polymers, increasing the free volume and space between them, which diminishes the binding force within the network [71, 72]. As a result, the weakening of intermolecular bonds reduces brittleness and enhances both flexibility and extensibility. The use of a plasticizer promotes the formation of strong plasticizer-plasticizer or plasticizer-water bonds, further improving the performance of biodegradable films [72]. Figure 2.12 illustrates a schematic representation of the hydrogen bonds formed during the plasticization of starch with glycerol and sorbitol [73].

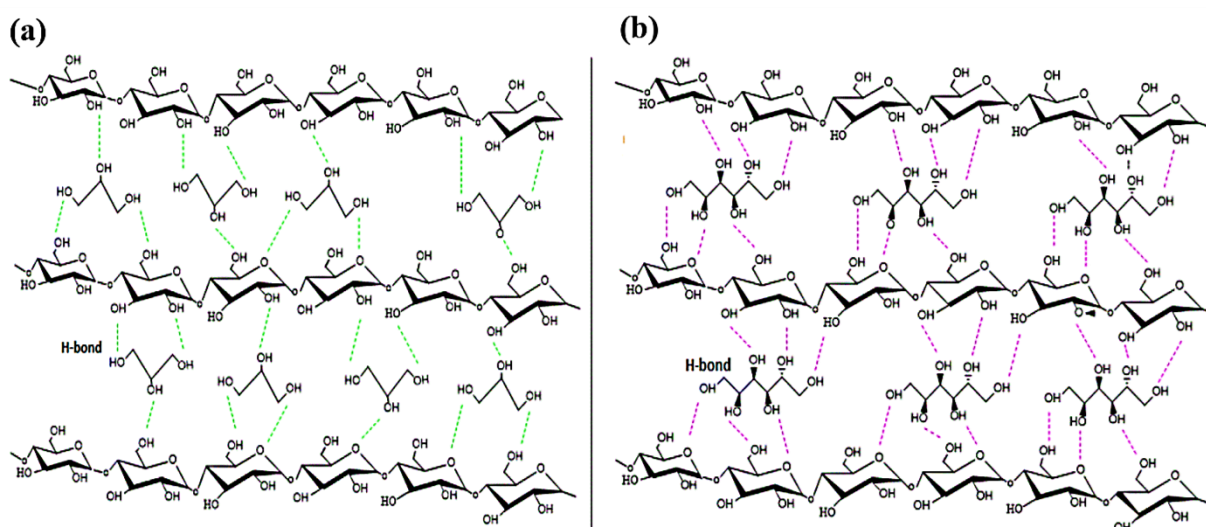


Figure 2.12 Schematic of hydrogen bonds created during starch plasticization with (A) glycerol and (B) sorbitol [73].

Numerous studies have investigated the effect of plasticizers on starch films. A study published in 2017 explored the influence of varying concentrations of starch and different plasticizer concentrations glycerol (0–30% w/w) and sorbitol (0–60% w/w) on the seal performance of mung bean starch (MBS) films [74]. The results indicated that increasing plasticizer concentration generally enhanced the seal strength of MBS films. Specifically, at certain concentrations of plasticizers (20% glycerol, 30% sorbitol), the association of starch polymers during the dwell time could be influenced.

In specific concentrations of plasticizers, such as 20% glycerol and 30% sorbitol, the association of starch polymers during the dwell time can be affected. MBS films with 30% glycerol exhibited greater seal strength compared to those with sorbitol, indicating that glycerol is a more effective plasticizer than sorbitol for MBS films.

Furthermore, Table 2.3 summarizes several studies that explored various starches and plasticizers to determine the optimum sealing performance. The data in Table 2.3 suggest that the effectiveness of plasticizers in heat sealing films varies depending on the type of starch used.

Table 2.3 Summary of studies examining the sealing performance of films using various starches and plasticizers.

Type of starch	Type of plasticizer	Method of preparation	Heat-sealing result		Ref.
			Concentration of plasticizer	Seal strength (N/m)	
Sago starch	GLY, SOR	Solution casting	30 % GLY	50	[75]
			30 % SOR	75	
			75%SOR / 25%GLY	375	
Mung bean starch	GLY, Citric acid (CA)	Solution casting	30% GLY and 3% CA	455	[62]
Banana starch	GLY, SOR	Solution casting	40 % GLY	102	[76]
			40% SOR	213	
Mango kernel starch	GLY, SOR	Solution casting	40 % GLY	153	[77]
			40 % GLY	126	
			70% GLY	358	

2.9.2 Effect of moisture content on heat sealing of Starch film

Starch, as a natural biopolymer, exhibits hygroscopic behavior, meaning it can readily absorb and retain moisture from the environment. This moisture content significantly impacts the physical and mechanical properties of starch-based films, including their heat-sealing characteristics.

In their investigation, Heung Suh et al. [70] examined how varying moisture content and the type of starch, with different amylose contents, affect the sealing performance of starch films. They studied mung bean, water chestnut, sweet potato, and cassava starches, which have amylose contents of 30.87%, 22.10%, 21.70%, and 15.20%, respectively. Figure 2.13 illustrates the moisture contents of starch films under various relative humidity (RH%) storage conditions and shows their corresponding seal performance in these conditions.

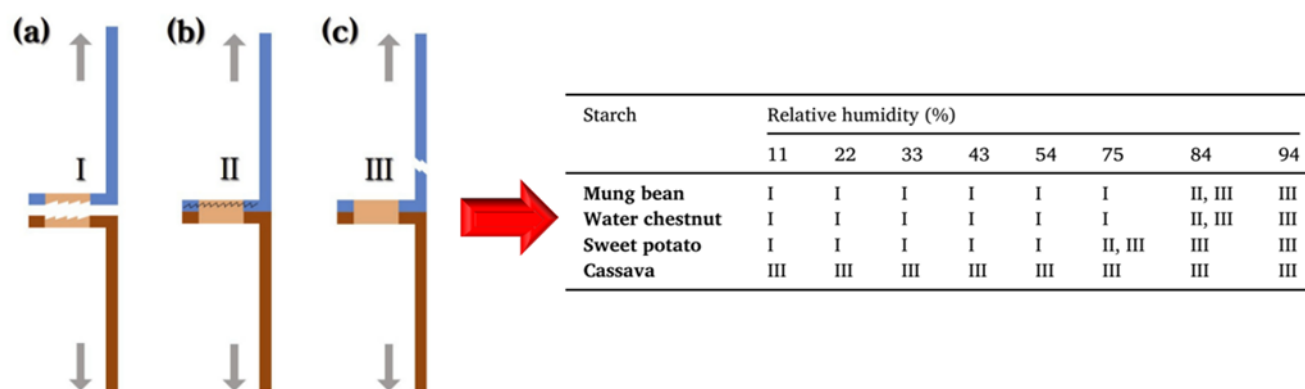


Figure 2.13 Mode of failure in the T-peeling test of the films of starch from various botanical sources after storage at different relative humidity [70].

Under conditions of 84% relative humidity (RH), all samples except cassava showed a Type-I failure mode, where the adhesive-sealed areas separated. Notably, cassava films maintained good adhesion across all RH storage conditions, likely due to their lower amylose content compared to other samples. In other starch films, higher amylose content impeded adhesion, even at higher temperatures, because crystal formation on the film surface limited molecular movement. Conversely, exposure to high RH levels may have enhanced molecular mobility due to water molecules acting as plasticizers, thus strengthening the adhesive bonds and improving sealing effectiveness.

Despite starch's advantageous properties, there is a significant gap in research on starch-based heat seal coatings for flexible paper packaging. This gap may result from the infrequent use of thermoplastic starch in paper coatings, due to issues like high solution viscosity, poor film formation, and retrogradation (the transition from liquid to gel) [78]. Therefore, using modified starches could be an effective strategy to boost starch performance on paper, enhancing attributes such as adhesion, solubility, and heat resistance [79].

2.10 Modification of Starch

Starch modifications can be achieved through various methods, including physical and chemical alterations. Physical modifications encompass thermal methods (such as heat treatment, hydrothermal treatment, and radiation treatment) and non-thermal methods (including mechanical treatment, pH adjustment, and annealing). Chemical modifications involve processes like oxidation, cross-linking, hydrolysis, cationization, etherification, and esterification [80].

While the physical modification of starch, whether through thermal or non-thermal methods, offers various advantages, it also presents several notable disadvantages. These limitations must be carefully considered when evaluating the suitability of such approaches. One key drawback is the potential destruction of the inherent integrity of the starch's molecular chain structure, which can lead to the formation of final products with more defects and compromised structural parameters [81, 82]. Additionally, it is energy-intensive, which can increase production costs and environmental impact [80, 82]. Moreover, the outcomes of physical modifications can vary depending on the specific conditions applied, such as temperature and moisture levels. This variability can lead to inconsistent product quality [80]. Furthermore, physical methods might not achieve the same level of modification as chemical methods, potentially leading to incomplete transformation of the starch's properties. This can limit the effectiveness of the modification in certain applications [80]. These disadvantages underscore the importance of a balanced evaluation of the trade-offs associated with the physical modification of starch. Considering these limitations, along with the potential benefits, it becomes evident that chemical modification is a more suitable option for our purposes.

On the other hand, certain chemical modification approaches to starch, such as oxidation, cross-linking, cationization, and etherification, exhibit notable drawbacks. These disadvantages must be

weighed alongside the potential benefits when evaluating the suitability of these techniques. A significant limitation is the need for the modified starch to be dissolved in hot water, typically at temperatures ranging from 85-90°C. This requirement for elevated temperatures can pose challenges in terms of energy consumption and processing efficiency. Additionally, the lack of commercial availability of these chemically modified starch products can hinder their widespread adoption and integration into various applications. Limited accessibility can restrict the scalability and market penetration of these modified starches.

Consequently, for our purposes, esterification and hydrolysis within the realm of chemical approaches present particularly attractive options. Sodium starch octenyl succinate (SSOS) is a chemical modification of starch achieved through esterification. In contrast, maltodextrin (MAL) is a different type of starch-derived ingredient, produced through the process of starch hydrolysis. While both SSOS and MAL are starch-based food additives, they are distinct in terms of their chemical structures and manufacturing processes, leading to differences in their functional properties and applications in the packaging industry. Notably, both dissolve in cold water, and SSOS contains functional groups and amphiphilic structure that influence its sealability, which will be further investigated in the next chapter (Chapter 5). Moreover, it seems that the α -D-glucose structure in MAL provides bonding potential with other substances in coatings, enhancing sealing performance.

In the compound sodium starch octenyl succinate (SSOS), starch is modified by the attachment of octenyl succinic anhydride (OSA), a hydrophobic compound that consists of an eight-carbon chain with one double bond [83], as shown in Figure 2.14 [84].

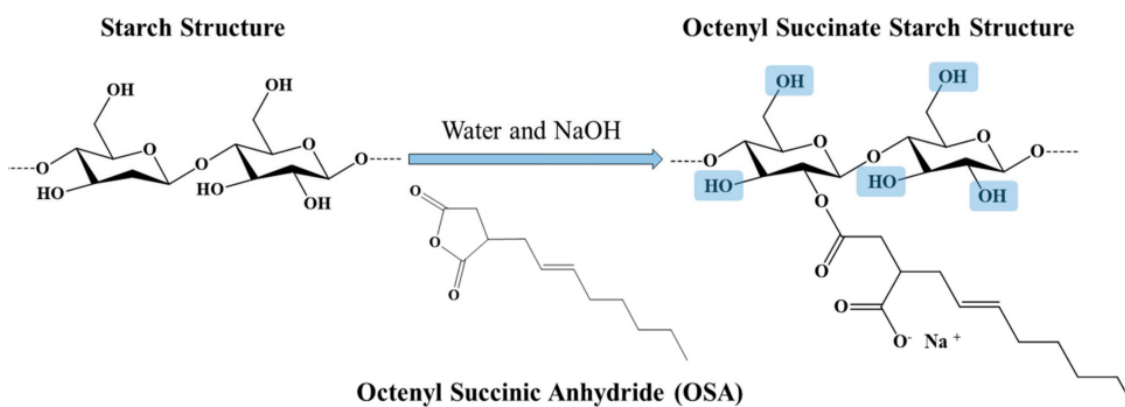


Figure 2.14 Diagram illustrating the production of octenyl succinate starch under alkaline conditions. The blue squares highlight the area where the OSA groups are incorporated [84].

In this reaction, the opening of the anhydride ring results in the formation of a sugar ester and the simultaneous development of a carboxyl group. These covalent substituents typically interact with any available hydroxyl groups on glucose monomers, imparting advantageous characteristics to the starch substrate. It is important to highlight that upon modification with OSA, starch, which conventionally exhibits hydrophilic properties, acquires a hydrophobic nature through the integration of octenyl groups, resulting in molecules characterized by amphiphilicity [83, 85].

On the other hand, maltodextrin (MAL) is derived from starch through partial enzymatic hydrolysis, resulting in a dextrose equivalent (DE) below 20 (see Figure 2.15) [86, 87]. This hydrolytic modification transforms starch into smaller molecules, facilitating its use in various applications [85]. Maltodextrin is primarily composed of α -D-glucose units linked predominantly by (1 $\rightarrow$ 4) glycosidic bonds, and it is characterized by the general chemical formula $[(C_6H_{10}O_5)_nH_2O]$ [88].

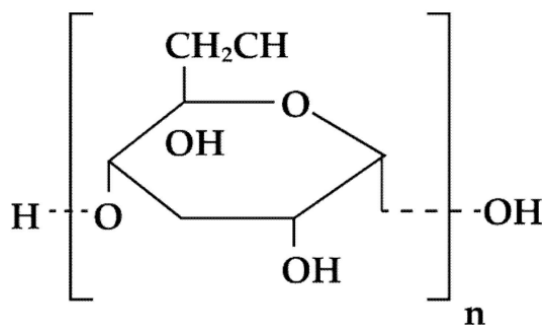


Figure 2.15 Schematic illustration of MAL structure [87].

2.11 Objective

Although paper is an excellent packaging material, its use is limited by certain inherent drawbacks. To address these issues, researchers have applied coatings, but this has raised environmental concerns. The primary aim of this study is to develop a home-compostable coating for paper that biodegrades under home composting conditions at room temperature with a natural microbial community. Additionally, the coating should enhance the heat sealability of paper, which is a major limitation for its use in packaging.

This study investigates the use of modified starch coatings (SSOS and MAL) combined with plasticizers (sorbitol and glycerol) to improve heat sealing properties. A central composite design (CCD) and response surface methodology (RSM) will be used to evaluate how different types of modified starch and plasticizer ratios affect Seal Initiation Temperature (SIT) and Fiber Tear Temperature (FTT). Furthermore, based on JMP recommendations for each modified starch, the study will characterize both favorable samples (with lower SIT and FTT) and unfavorable samples (with the highest SIT and FTT).

This research aims to generate a predictive model for optimizing sealability while minimizing environmental impact and ensuring food safety, setting it apart from current commercial compostable packaging solutions.

CHAPTER 3 EXPERIMENTAL METHODOLOGY

3.1 Experimental Section

3.1.1 Material

The sodium starch octenyl succinate (SSOS; E 1450) used in this study was procured from Chanjao Longevity Co., Ltd. Bangkok, Thailand (Myskinrecipes Co.). Maltodextrin (MAL), with a dextrose equivalent (DE) of 10, was sourced from the Toronto Brewing Company. Mung bean starch (MBS), sweet potato starch (SPS), and tapioca starch (TS) were acquired from a local grocery store in Montreal, Canada. Additionally, sorbitol (SOR) and glycerol (GLY) were obtained from Sigma-Aldrich (ON, Canada). Bleached paper with 5.5% moisture, a tensile strength (MD) of 20 lbf/in, and tear strengths (CD and MD) of 30 gf and 24 gf, respectively, was supplied by Prolamina Corp (U.S.).

3.1.2 Preparation of biopolymer Coatings on Paper

The coatings were formulated using modified starches, specifically SSOS and MAL, along with SOR and GLY as plasticizers. The formulation process involved stirring the mixture for 1.5 hours at room temperature, using distilled water as the solvent. The total biopolymer concentration was set at 25% (w/w) in the casting solution.

The plasticizer content was varied from 0 to 20% (w/w) of the polymer concentration, as outlined in Table 3.1 and 4.2 (a and b), according to the design of experiments (DOE) results generated with JMP statistical software (Version pro-17). The DOE assessed the effects of SOR, GLY, and their interactions to optimize the outcomes of the coating formulation.

After preparing the casting solution, it was left to stand for 1 hour to eliminate bubbles and ensure uniformity. The film solution was then applied to paper substrates using a bar coater machine (TQC Sheen AB4120) with a Mayer rod, producing a 2 μm wet film thickness, and the substrates were simultaneously dried for 2 minutes using an infrared (IR) dryer (Datous Boss, ZJ-SC-002, 2 kW, 220V) to set the coating, as shown in Figure 3.1. The process was then repeated under identical

conditions, applying a second layer with the Mayer rod to achieve a 4 μm wet film thickness, followed by simultaneous drying.



Figure 3.1 Coating process of modified starch films on paper substrates using SSOS, MAL, SOR, and GLY.

3.2 Characterization and Measurements

3.2.1 Heat sealing assessments

Heat sealing tests were conducted using an SL10 LakoTool laboratory hot-tack and seal tester, which was acquired from Lako Tool & Manufacturing Inc. These tests were performed under specific conditions of temperature, pressure, and dwell time. After sealing the samples, peel testing was conducted at 33 mm/sec speed to assess the quality of the seals. All samples were cut in 7 inches by 1 inch in dimensions and tested using an Instron machine (model number E3000). For each sample, the peel test was repeated 10 times, and the seal initiation temperature (SIT) and fiber tear temperature (FTT) results were reported. The temperature showed fiber tear was considered as FTT (fig. 3.2).

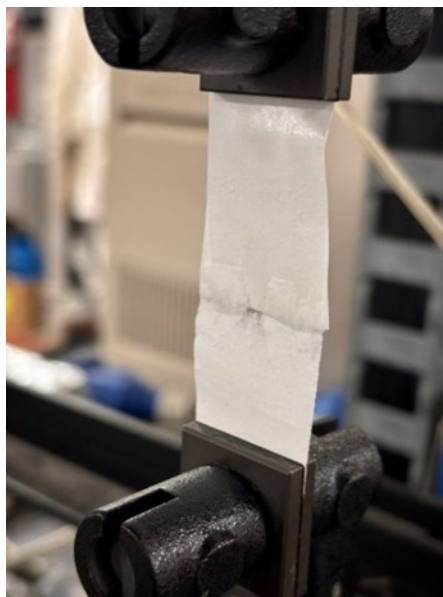


Figure 3.2 Fiber tear failure in paper-based packaging.

3.2.2 ATR-FTIR

Prior to the analysis, the samples (coating) were placed in a petri dish after preparation and then dried in an oven at 55 °C for 72 hours to eliminate water before analysis. ATR-FTIR measurements then were carried out to examine the chemical composition and the intensity of the chemical groups in the coating (without paper). The ATR-FTIR spectra of the samples were recorded in absorbance mode at ambient temperature using a Perkin Elmer ATR-FTIR spectrometer. The analysis was conducted over a wavenumber range of 600 to 4000 cm^{-1} .

3.2.3 Rheological characterization

The rheological properties of casting solution (SSOS and MAL with SOR and GLY), were conducted with an Anton-Paar rotational rheometer (MCR501), employing a Couette double gap (DG) flow geometry. A syringe was used to obtain the necessary volume of 8 mL for each geometry. Shear rate sweep experiments spanned from 0.01 s^{-1} to 800 s^{-1} , transitioning from low to high shear rates. All experiments were conducted at a temperature of 25 °C.

3.2.4 Physical properties and surface characterization

The coating weight of the coating layer was determined by measuring the mass of paper samples before and after the coating process (Quintix 224-1S, Sartorius Mechatronics). Surface roughness was analyzed by profilometer Dektak XT (Bruker Corporation). Two roughness parameters were assessed: Ra, representing the surface roughness average, and Rq, denoting the root mean square roughness. The measurements were conducted over a 4 mm length of the sample surface, utilizing a scanning stylus with an applied force of 3 mg. Each material underwent three replicate measurements to ensure sufficient accuracy.

3.2.5 Differential scanning calorimetry (DSC)

The glass transition temperatures of the films were appraised using a TA Instruments Q1000 calorimeter (TA Instruments, New Castle, DE) under a nitrogen atmosphere. The samples were heated from 0 °C to 130 °C at a rate of 10 °C/min. Notably, for greater accuracy in this analysis, only the coating (unmodified starch and plasticizers) without the substrate (paper) was used, as the presence of the paper substrate can potentially interfere with the Tg measurement of the coating material. The samples were dried at 55 °C for 72 hours to eliminate water before analysis.

3.2.6 Validation of adhesive performance

Abrasion resistance was evaluated using the Taber method with linear abrader model 5750 (Polytechnique Montreal, CA), according to ASTM D4060-10 Standard Test Method for Abrasion Resistance by the Taber Abraser. The test employed CS-10 abrasive wheels. Moreover, the load of 850 grams, a total of 3000 cycles, and a speed of 30 cycles per minute were considered. Weight losses were quantified in milligrams by measuring the difference in specimen weight before and after abrasion. The wear rate (wear index (I)) was calculated using Equations below (3.1) based on the measured weight loss in milligrams. All ASTM abrasion tests were conducted in triplicate, and the average values were reported.

$$I = \frac{(A - B)1000}{C} \quad (3.1)$$

Where, A represents the initial weight of the specimen before abrasion (mg), B denotes the weight of the specimen after abrasion (mg), and C indicates the recorded number of abrasion cycles.

Based on standard ASTM D918 – 99, the Blocking Resistance test procedure measures the effectiveness of flexible packaging materials in preventing blocking. This assessment includes various materials, such as paper combined with metallic foils and synthetic films, whether they are treated, coated, or laminated. The test is particularly significant for different types of paper where blocking is a major concern.

The procedure followed the standard with slight modifications. Specimens were prepared with dimensions of $50 \times 50 \text{ mm}^2$. The samples were folded with the coated sides facing each other and then with the coated side against the uncoated side. A 500 g weight was placed on the top plate to apply uniform pressure. The testing period lasted for 24 hours.

Testing was performed at ambient temperature under two relative humidity conditions (21% and 60%). After the test, the specimens were gently unfolded and inspected for any signs of adhesion or peeling of the sealant. The procedure was repeated three times to ensure the accuracy and reliability of the results.

3.3 Experimental design

3.3.1 Selection Criteria of Parameters

Numerous factors can influence seal strength and integrity during heat sealing, including material properties (such as branching, sealant thickness, and molecular weight) and process parameters (such as temperature, dwell time, and pressure) [22]. The current project's primary goal is to develop a home compostable heat-sealable coating for paper-based flexible packaging. To minimize overall energy consumption and reduce greenhouse gas emissions, it is crucial to reduce the coating weight. Implementing an experimental design that includes all these parameters is challenging due to time, material costs, and data analysis complexities. Therefore, we reduced the number of factors. Preliminary experiments were conducted to find an optimal condition for achieving a lower coating weight ($3\text{--}3.80 \frac{\text{g}}{\text{m}^2}$), as shown in Table 4.2 a and b (in chapter 4) for each modified starch, with bar coating speeds of 150 mm/s, specific wire sizes of 2 and 4 micron, and a total polymer concentration (both unmodified and modified starch) of 25% (w/w).

Pretests on the impact of plasticizer content revealed that increasing its percentage beyond 20% did not significantly affect sealing quality. Consequently, higher amounts of plasticizer were excluded from the experimental design. Our study focuses on examining plasticizer percentages within the range of 0-20% (w/w).

3.3.2 Optimization by Central Composite Design (CCD)

The Response Surface Methodology (RSM) was conducted using a rotatable and uniform precision central composite design (CCD) to identify the optimal conditions for minimizing both the SIT and the FTT. In fact, RSM encompasses a collection of mathematical and statistical techniques designed to model and analyze the relationships between a set of input and response variables [89]. By applying RSM, a polynomial equation can be fitted to the experimental data, allowing for the evaluation of interaction and quadratic effects among the tested factors. Additionally, RSM offers the advantage of reducing the number of experiments needed by eliminating those that are unnecessary [90, 91]. Moreover, the rotatability of the design ensures consistent prediction variance at all levels, as they are equidistant from the central point [92]. In addition, the uniform precision of the design provided for consistent prediction accuracy across the entire experimental space, enhances the reliability of the model. In this research, following the optimization of the coating weight, the influence of the percentage of SOR (X_1 , %) and the percentage of GLY (X_2 , %), as continuous independent input variables, on the minimum SIT (Y_1 , °C) and the minimum FTT (Y_2 , °C) was investigated via JMP software. It is noteworthy that the randomization of the experiments was carried out to ensure the minimization of unknown variability for the actual response which could be caused by uncharted factors. The coded variables (X_i) for the CCD were determined using Equation 3.2 [89]:

$$X_i = \left(\frac{x_i - x_0}{\Delta x} \right) \quad (3.2)$$

Where X_i denotes the dimensionless coded value of a variable; x_i represents the actual value of the variable; x_0 is the value of x at the center point; and Δx signifies the step change.

The coded levels of the two independent variables are detailed in Table 3.1. In this table, the values (+1) and (-1) correspond to the high and low levels of the two-level factorial design, respectively. (+1.41) and (-1.41) values represent the levels of axial point, while the value (0) indicates the center point of the experimental design.

Table 3.1 The input variables and their levels CCD employed.

Independent Variables	Type	Coded levels				
		-1.4	-1	0	+1	+1.41
X ₁ : Sorbitol (wt %)	Continuous	0	2.93	10	17.07	20
X ₂ : Glycerol (wt %)	Continuous	0	2.93	10	17.07	20

The CCD comprises a total of 10 experiments for each modified starch (SSOS and MAL), organized as follows: (i) four points by a two-level full factorial design experiment, (ii) four axial points, and (iii) two central points. To assess the pure error of the experiments, the latter experiments corresponding to the center point were replicated two times led to 20 tests in total.

The data obtained from the CCD were analyzed using a second-degree polynomial regression analysis to elucidate the system's behavior. This function was chosen to gain a proper fitness maintaining a high significance with a simple function possible. This analysis was conducted using the least squares regression methodology, as depicted in Equation 3.3 [93].

$$y_i = \beta_0 + \sum_{j=1}^K \beta_j x_{i,j} + \sum_{j=1}^{K-1} \sum_{K=j+1}^K \beta_{ijK} x_{i,j} x_{i,k} + \sum_{j=1}^K \beta_{jj} x_{i,j}^2 \quad (3.3)$$

In which y_i is the response of SIT and FIT, K represents the number of continuous variables; β_0 , β_j , β_{ijK} and β_{jj} are the estimated constant, linear, interaction, and quadratic coefficients effects, respectively. The factors are represented by actual variables, such as $x_{i,j}$, $x_{i,k}$, $x_{i,j}^2$.

2.3.3 Statistical optimization and validation

To identify the optimal levels of the two independent variables (x_1 and x_2) for achieving the desired response goals, both individual and comprehensive optimization procedures were performed. The former represented the condition where only one of the output variables (SIT and FTT) was at its optimum amount while the latter described optimization of both variables, simultaneously. Additionally, the adequacy of the regression equations was assessed by comparing the experimental data to the predicted values from these equations. The results were analyzed using

analysis of variance (ANOVA), and surface responses were displayed. Moreover, the least squares regression method was employed to develop multivariate models for the responses. These reduced response models were visually represented as 3D surface plots, illustrating how the interaction between the independent variables affected SIT and FTT parameters.

To verify the optimized data two different approaches were implemented. First, a 95% prediction interval (PI) for each response was calculated by JMP using Equation 3.4 [94].

$$PI = \hat{Y} \pm t \times s \sqrt{(1 + x_0'(X'X)^{-1}x_0)} \quad (3.4)$$

In this formula, t represents the t -value of the predicted response from the t -distribution, s is the standard deviation of the predicted response, x_0 is vectors containing the model terms for each run, x_0' is its transpose form, X is the design matrix, and X' is also its transpose matrix. To validate the model, a single confirmation run was conducted for each set of optimal data using the input values recommended by the model, ensuring that they fell within the specified PI range.

In the second approach, more confirmation runs were carried out to check the occurrence of any alterations between the initial experiment and follow-up runs that could lead to a shift in the response defined as block effect [95]. Furthermore, statistical confidence interval (CI) at a 99% confidence level for the mean response was calculated through a method suggested by Antony using Equation 3.5 [96].

$$CI = \bar{y} \pm 3 \left\{ \frac{SD}{\sqrt{n}} \right\} \quad (3.5)$$

Where $\bar{y}$ represents the mean response obtained from confirmation trials or runs, SD is the standard deviation of the response derived from these trials, and n denotes the number of samples (or confirmation runs) conducted. This step is essential for providing the necessary parameters to assess the variability and reliability of the mean response in the context of the experimental data.

CHAPTER 4 ARTICLE 1 : IMPROVING PAPER-BASED PACKAGING WITH HOME COMPOSTABLE MODIFIED STARCH COATINGS: A FOCUS ON HEAT SEAL OPTIMIZATION.

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Abstract

Development of sustainable food packaging solutions seems essential in response to the increasing global demand driven by world population growth. The study focused on enhancing the heat sealability of paper-based flexible packaging by applying eco-friendly coatings derived from sodium starch octenyl succinate (SSOS) and maltodextrin (MAL) as modified starches. These materials were selected for their home-compostability and potential to improve the functional properties of paper, which is favored for its lightweight and cost-effectiveness. Two plasticizers, Sorbitol (SOR) and glycerol (GLY), with variable concentrations up to 20% (w/w) were chosen to achieve optimal seal initiation temperature (SIT) and fiber tear temperature (FTT) through a central composite design (CCD) and response surface methodology (RSM). A binomial model for each of the outcome temperatures was developed, thereby, SIT and FTT were predicted using different compositions of the plasticizers. Statistical analyses showed strong effects of plasticizers on SIT and FTT, with correlation coefficients (R^2) of 0.89 and 0.86 in SSOS, and 0.88 and 0.93 in MAL, indicating robust predictive capabilities. The model explained a substantial amount of variability, and the low coefficients of variation indicated a high level of precision and reproducibility. A formulation of 10% SOR and 20% GLY in SSOS, and 20% SOR and 5% GLY in MAL, yielded the most favorable sealing properties, with the lowest SIT and FTT values. The strong correlation between predicted and observed outcomes further confirmed the models' reliability and predictive

capability. The optimal conditions were also validated by performing confirmation runs with two different approaches.

Keywords: sodium starch octenyl succinate (SSOS), maltodextrin (MAL), heat sealable, optimization, paper-based flexible packaging,

4.1 Introduction

With the ongoing increase in the global population, there is a corresponding rise in the demand for food products and their packaging. A crucial challenge in food packaging is ensuring the preservation of quality, enhancing safety, and extending the shelf life of food items [1]. Packaging must shield its contents from environmental influences like microorganisms, light, and external gases to prevent microbial and biochemical degradation. Thus, packaging should remain sealed until it is opened by the consumer for use [2]. Indeed, the product's shelf life is contingent upon the sealing quality of the flexible material [3]. Flexible packaging is typically favored over rigid packaging due to its lighter weight and lower cost [4]. Lightweight materials like paper, plastic, and composites are suitable for flexible food packaging [5]. Due to their lightweight nature, less energy is required for transportation. Flexible packaging holds approximately 30% of the global market share, with food packaging being its primary application [2].

In the food industry, plastic is predominantly employed for packaging purposes due to its cost-effectiveness, ease of processing, and widespread availability [6]. In general, petroleum-based synthetic polymers are extensively utilized in various packaging applications. However, their non-biodegradable nature leads to environmental challenges and heightens reliance on petroleum resources [7].

Paper and cardboard are currently considered as the most widely used biodegradable materials for food packaging. Structurally, paper is simpler than plastic, suggesting migration of substances from the packaging into the food is likely to be lower compared to similar plastic counterparts [6]. Nevertheless, paper and paper-based flexible packaging exhibits inadequate heat sealability [8]. The low thermal conductivity of paper complicates effective sealing, requiring either prolonged sealing times or increased sealing temperatures [9]. These limitations present significant challenges for its utilization in packaging applications. Therefore, applying a coating (such as aluminum foil,

plastic, and polymers) is the most straightforward method to enhance the functional properties of paper. However, these coatings can leach into food products, posing potential health risks, and interfere with the recycling process, thereby contributing to landfill waste increase [8, 10].

In order to select an appropriate coating for paper-based packaging, it is essential to consider both environmental concerns and heat-sealing properties of the coating. Heat sealing acts as a safeguard against microbial penetration through films and enhances both the barrier characteristics and mechanical strength of the films. In the heat-sealing process, the polymer is heated to high temperatures until it melts and is then compressed under pressure [11]. The heat-sealing characteristics of polymers are influenced by surface chemistry of the materials [12]. Moreover, the interaction between functional groups, such as -OH, -CHO, and -COOH, on a film affects seal strength [13]. Seal strength is evaluated based on sealing temperature, pressure, and dwell time, all of which are crucial factors influencing its effectiveness. Among them, temperature is a very important parameter as using an incorrect sealing temperature can lead to a reduction in seal strength [14]. Therefore, it is essential to properly adjust the temperature.

Starch, a very popular compound, recognized for its status as a highly renewable and biodegradable natural polymer, is of particular academic interest due to its abundant availability, economic viability, non-toxic properties, and water solubility, rendering it a compelling candidate for diverse applications [15, 16]. Despite its potential, thermoplastic starch is less frequently employed due to challenges associated with solution viscosity, film formation, and retrogradation [17]. As a result, the use of modified starches is advocated to improve characteristics such as adhesion, solubility, and thermal resistance [18]. Among the various modified starches, sodium starch octenyl succinate (SSOS) and maltodextrin (MAL) are particularly advantageous. They not only enhance the sealability of paper but also qualify as home-compostable materials.

SSOS, a derivative obtained through the esterification of native starch, has received approval from both the United States Food and Drug Administration (FDA) and the European Food Safety Authority (EFSA) for use in food products due to its non-toxic nature and biodegradability [19-21]. This esterification process introduces the hydrophobic characteristics of the octenyl group while preserving the hydrophilic nature of the starch backbone, resulting in an amphiphilic molecule [21, 22]. MAL, synthesized through the acid or controlled enzymatic hydrolysis of starch, consists of D-glucose polymers linked by α -(1,4) and α -(1,6) bonds, and is characterized by its high

water solubility and dispersibility [23, 24]. The degree of starch degradation in MAL is measured by the dextrose equivalent (DE) value, which assesses the concentration of reducing-end groups and is inversely related to the average degree of polymerization (DP) of the dehydrated glucose units [25]. With a DE value ranging from 3 to 20, MAL is characterized by long carbohydrate chains and a complex mix of high and low molecular weight substances [26, 27]. Consequently, films made from this starch derivative can resemble multicomponent films in their properties [21].

Absence of plasticizers in starch films provokes a network with high cohesive energy caused by hydrogen bonds, resulting in a brittle structure [28]. The incorporation of plasticizers disrupts intermolecular forces, increasing free volume and lowering the glass transition temperature (T_g), thus, enabling sealing at lower temperatures than conventional methods [29-31]. The efficacy of the film is profoundly affected by the specific type and concentration of plasticizer employed [13, 28]. In particular, the synergistic use of high molecular weight plasticizers, such as sorbitol (SOR), in conjunction with low molecular weight plasticizers, like glycerol (GLY), markedly enhances the functional properties of starch-based films [32, 33].

As stated, temperature is a critical parameter in heat sealing. The initiation temperature significantly affects seal strength, and a low seal initiation temperature (SIT) is regarded advantageous for a sealant layer [34, 35]. However, if the seal temperature is too low, it can result in weak seals [36]. Additionally, the layered network structure of paper makes it prone to fiber tearing, primarily due to mechanical interlocking. This occurs when the polymer sealant penetrates and intervenes in cellulose fibers, leading to their fracture and separation when seals are opened [37]. Achieving complete fiber tear is crucial for strong adhesive bonding in paper packaging [38], and monitoring fiber tear temperature (FTT) ensures quality by verifying seal strength and paper properties. Both SIT and FTT are essential for reliable heat sealing, impacting the performance and quality of final product in the packaging industry.

In this study, a central composite design (CCD) with rotatable and uniform precision, along with response surface methodology (RSM), was employed to examine how varying percentages of SOR and GLY affect the heat-sealing process (SIT and FTT) for each type of modified starch (SSOS and MAL) applied to paper. This investigation aims to examine the varying concentrations of plasticizers (SOR and GLY) in modified starches (SSOS and MAL) for enhancement in the sealability of paper-based packaging. Additionally, the rigorously designed experimental

framework is anticipated to furnish predictive capabilities for analogous systems and contribute to a more comprehensive understanding of the multifactorial interactions that improves the heat sealability of paper-based packaging materials. In fact, this product is engineered to mitigate environmental impact and uphold food safety standards, thereby highlighting it among other commercially available compostable or biodegradable alternatives.

4.2 Experimental Section

4.2.1 Materials

The sodium starch octenyl succinate (SSOS; E 1450) used in this study was purchased from Chanjao Longevity Co., Ltd. Bangkok, Thailand (Myskinrecipes Co.). Maltodextrin (MAL), with a dextrose equivalent (DE) of 10, was sourced from the Toronto Brewing Company, ON, Canada. Additionally, sorbitol (SOR) and glycerol (GLY) were obtained from Sigma-Aldrich, ON, Canada. Bleached paper with 5.5% moisture, a tensile strength (MD) of 20 lbf/in, and tear strengths (CD and MD) of 30 gf and 24 gf, respectively, was supplied by Prolamina Corp (U.S.).

4.2.2 Preparation of biopolymer Coatings on Paper

The coatings were formulated using modified starches, specifically SSOS and MAL, along with SOR and GLY as plasticizers. The formulation process involved stirring the mixture for 1.5 hours at room temperature, using distilled water as the solvent. The total biopolymer concentration was set at 25% (w/w) in the casting solution. The plasticizer content was varied from 0 to 20% (w/w) of the polymer concentration, as outlined in Table 3.1 and 4.2 (a and b), according to the design of experiments (DOE) results generated with JMP statistical software (Version pro-17). The DOE assessed the effects of SOR, GLY, and their interactions to optimize the outcomes of the coating formulation.

After preparing the casting solution, it was left to stand for 1 hour to eliminate bubbles and ensure uniformity. The film solution was then applied to paper substrates using a bar coater machine (TQC Sheen AB4120) with a Mayer rod, producing a 2 μ m wet film thickness, and the substrates were simultaneously dried for 2 minutes using an infrared (IR) dryer (Datous Boss, ZJ-SC-002, 2 kW, 220V) to set the coating. The process was then repeated under identical conditions, applying a

second layer with the Mayer rod to achieve a 4 μm wet film thickness, followed by simultaneous drying.

4.2.3 Evaluation of Heat Sealing

Heat sealing evaluations were carried out utilizing an SL10 LakoTool laboratory hot-tack and seal tester, sourced from Lako Tool & Manufacturing Inc. The tests were executed at a pressure of 40 psi with a dwell time of 1.5 seconds (1500 ms) across various temperatures. Following the sealing process, peel tests were conducted at a speed of 33 mm/sec to evaluate the seal quality. Each sample, measuring 7 inches by 1 inch, was tested using an Instron machine (model E3000). The peel test for each sample was conducted 10 times, with results for the seal initiation temperature (SIT) and fiber tear temperature (FTT) documented.

4.2.4 Physical properties

The coating weight of the coating layer was determined by measuring the mass of paper samples before and after the coating process (Quintix 224-1S, Sartorius Mechatronics).

4.3 Experimental design

4.3.1 Selection Criteria of Parameters

Numerous factors can influence seal strength and integrity during heat sealing, including material properties (such as branching, sealant thickness, and molecular weight) and process parameters (such as temperature, dwell time, and pressure) [39]. The primary goal of the current project is to develop a home compostable heat-sealable coating for paper-based flexible packaging. To minimize overall energy consumption and reduce greenhouse gas emissions, it is crucial to decrease the coating weight. Implementing an experimental design that includes all these parameters is challenging due to time constraints, material costs, and the complexities of data analysis. Therefore, we reduced the number of factors. Preliminary experiments were conducted to find an optimal condition for achieving a lower coating weight (3-3.80 g/m²), as shown in Table 2a and 2b for each modified starch, with bar coating speeds of 150 mm/s, specific wire sizes of 2

and 4 microns, and a total polymer concentration (both unmodified and modified starch) of 25% (w/w).

Pretests on the impact of plasticizer content revealed that increasing its percentage beyond 20% did not significantly affect sealing quality. Consequently, higher amounts of plasticizer were excluded from the experimental design. Our study focuses on examining plasticizer percentages within the range of 0-20% (w/w).

4.3.2 Optimization by Central Composite Design (CCD)

The Response Surface Methodology (RSM) was conducted using a rotatable and uniform precision central composite design (CCD) to identify the optimal conditions for minimizing both the SIT and the FTT. In fact, RSM encompasses a collection of mathematical and statistical techniques designed to model and analyze the relationships between a set of input and response variables [40]. By applying RSM, a polynomial equation can be fitted to the experimental data, allowing for the evaluation of interaction and quadratic effects among the tested factors. Additionally, RSM offers the advantage of reducing the number of experiments needed by eliminating those that are unnecessary [41, 42]. Moreover, the rotatability of the design ensures consistent prediction variance at all levels, as they are equidistant from the central point [43]. In addition, the uniform precision of the design provided for consistent prediction accuracy across the entire experimental space, enhances the reliability of the model. In this research, following the optimization of the coating weight, the influence of the percentage of SOR (X_1 , %) and the percentage of GLY (X_2 , %), as continuous independent input variables, on the minimum SIT (Y_1 , °C) and the minimum FTT (Y_2 , °C) was investigated via JMP software. It is noteworthy that the randomization of the experiments was carried out to ensure the minimization of unknown variability for the actual response which could be caused by uncharted factors. The coded variables (X_i) for the CCD were determined using Equation 4.1 [40]:

$$X_i = \left(\frac{x_i - x_0}{\Delta x} \right) \quad (4.1)$$

Where X_i denotes the dimensionless coded value of a variable; x_i represents the actual value of the variable; x_0 is the value of x at the center point; and Δx signifies the step change.

The coded levels of the two independent variables are detailed in Table 4.1. In this table, the values (+1) and (−1) correspond to the high and low levels of the two-level factorial design, respectively. (+1.41) and (−1.41) values represent the levels of axial point, while the value (0) indicates the center point of the experimental design.

The CCD comprises a total of 10 experiments for each modified starch (SSOS and MAL), organized as follows: (i) four points by a two-level full factorial design experiment, (ii) four axial points, and (iii) two central points. To assess the pure error of the experiments, the latter experiments corresponding to the center point were replicated two times led to 20 tests in total.

Table 4.1 The input variables and their levels CCD employed.

Independent Variables	Type	Coded levels				
		-1.4	-1	0	+1	+1.41
X ₁ : Sorbitol (wt %)	Continuous	0	2.93	10	17.07	20
X ₂ : Glycerol (wt %)	Continuous	0	2.93	10	17.07	20

The data obtained from the CCD were analyzed using a second-degree polynomial regression analysis to elucidate the system's behavior. This function was chosen to gain a proper fitness maintaining a high significance with a simple function possible. This analysis was conducted using the least squares regression methodology, as depicted in Equation 4.2 [44].

$$y_i = \beta_0 + \sum_{j=1}^K \beta_j x_{i,j} + \sum_{j=1}^{K-1} \sum_{K=j+1}^K \beta_{ijK} x_{i,j} x_{i,k} + \sum_{j=1}^K \beta_{jj} x_{i,j}^2 \quad (4.2)$$

In which y_i is the response of SIT and FIT, K represents the number of continuous variables; β_0 , β_j , β_{ijK} and β_{jj} are the estimated constant, linear, interaction, and quadratic coefficients effects, respectively. The factors are represented by actual variables, such as $x_{i,j}$, $x_{i,k}$, $x_{i,j}^2$.

4.3.3 Statistical optimization and validation

To identify the optimal levels of the two independent variables (x_1 and x_2) for achieving the desired response goals, both individual and comprehensive optimization procedures were performed. The

former represented the condition where only one of the output variables (SIT and FTT) was at its optimum amount while the latter described optimization of both variables, simultaneously. Additionally, the adequacy of the regression equations was assessed by comparing the experimental data to the predicted values from these equations. The results were analyzed using analysis of variance (ANOVA), and surface responses were displayed. Moreover, the least squares regression method was employed to develop multivariate models for the responses. These reduced response models were visually represented as 3D surface plots, illustrating how the interaction between the independent variables affected SIT and FTT parameters.

To verify the optimized data two different approaches were implemented. First, a 95% prediction interval (PI) for each response was calculated by JMP using Equation 4.3 [45].

$$PI = \hat{Y} \pm t \times s\sqrt{(1 + x_0'(X'X)^{-1}x_0)} \quad (4.3)$$

In this formula, t represents the t -value of the predicted response from the t -distribution, s is the standard deviation of the predicted response, x_0 is vectors containing the model terms for each run, x_0' is its transpose form, X is the design matrix, and X' is also its transpose matrix. To validate the model, a single confirmation run was conducted for each set of optimal data using the input values recommended by the model, ensuring that they fell within the specified PI range.

In the second approach, more confirmation runs were carried out to check the occurrence of any alterations between the initial experiment and follow-up runs that could lead to a shift in the response defined as block effect [46]. Furthermore, statistical confidence interval (CI) at a 99% confidence level for the mean response was calculated through a method suggested by Antony using Equation 4.4 [47].

$$CI = \bar{y} \pm 3 \left\{ \frac{SD}{\sqrt{n}} \right\} \quad (4.4)$$

Where $\bar{y}$ represents the mean response obtained from confirmation trials or runs, SD is the standard deviation of the response derived from these trials, and n denotes the number of samples (or confirmation runs) conducted. This step is essential for providing the necessary parameters to assess the variability and reliability of the mean response in the context of the experimental data.

4.4 Statistical analysis

4.4.1 Experimental design fitting

Table 4.2 (a and b) presents the actual values of for SSOS and MAL level, respectively, as well as all experimental (20 runs) with related observed and predicted data for SIT (Y_1), FTT (Y_2), and corresponding desirability scores based on the predicted data. It is important to highlight that the least squares regression method was utilized to develop multivariate models for the responses.

The results show the predicted values are generally close to the observed values, suggesting good accuracy of the predictive model. For instance, in SSOS (Table 4.2a) for run 1, 5, 9, 14, 15, 17, 18 and 20, the difference between predicted and observed values were below 5 °C for both SIT and FTT. This alignment in the results was also reflected in MAL data (Table 4.2b) where runs number 6, 7, 8, 9, 18, 17, and 18 represented the less than 5 °C difference between the values. In both modified starches, there was no run with more than 10 °C variation between the model outcomes and actual data. This strong match indicates that the model not only fits the data well but also has predictive validity.

The desirability score indicates the suitability of each experimental condition, with values closer to 1 representing more favorable outcomes. For SSOS results, scores range from 0.18 to 0.91, indicating varying levels of desirability for the conditions tested. Higher scores (e.g., 0.91 for Run 8 or run 15) suggest more optimal conditions with lower related SIT and FTT values, while lower scores (e.g., 0.18 for Runs 4 (or run 11)) indicate less favorable outcomes and higher SIT and FTT. Similarly, for MAL results, scores range from 0.22 to 0.98 where the highest score (0.98) occurred for Run 2 or Run 13, and the lowest scores (0.22) achieved in Runs 4 or Run 11 reflecting maximum and minimum desirability of outcomes, respectively.

The closeness of observed and predicted values was statistically analyzed using ANOVA in Table 4.3 to confirm the significance of the variables. A second order polynomial model was fitted in which the interaction effects of the various variables on the studied responses were examined by comparing their estimated coefficients. This analysis aimed to elucidate how variations in the factors influence both SIT (Y_1) and FTT (Y_2). The results, summarized in Table 4.3 (a and b) for SSOS and MAL respectively, illustrate the relationships between these factors and the coating formulation's properties.

Table 4.2a CCD with two input variables (%SOR and %GLY), two output variables (SIT and FTT), desirability score, and coating weight for SSOS.

Run	Variables		Coating weight ($\frac{g}{m^2}$)	Response				Desirability score
	X_1 (%)	X_2 (%)		SIT (°C)		FTT (°C)		
				Observed	Predicted	Observed	Predicted	
1	0	10	3.52 ± 0.004	160	167	190	195	0.27
2	20	10	3.51 ± 0.003	160	153	175	168	0.57
3	2.93	17.07	3.28 ± 0.004	130	128	180	170	0.72
4	2.93	2.93	2.80 ± 0.008	190	187	210	202	0.18
5	10	10	3.23 ± 0.005	160	161	180	183	0.42
6	10	10	3.19 ± 0.001	170	161	185	183	0.42
7	17.07	17.07	3.66 ± 0.007	135	142	155	155	0.69
8	10	20	3.58 ± 0.006	125	120	140	146	0.91
9	10	0	3.21 ± 0.009	155	157	180	179	0.46
10	0	10	3.43 ± 0.006	160	167	190	195	0.27
11	2.93	2.93	2.59 ± 0.002	190	187	210	202	0.18
12	17.07	2.93	3.68 ± 0.008	140	144	160	166	0.63
13	20	10	3.23 ± 0.003	160	153	175	168	0.57
14	10	10	3.49 ± 0.02	165	161	180	183	0.42
15	10	20	3.28 ± 0.008	125	120	140	146	0.91
16	2.93	17.07	3.55 ± 0.005	130	128	180	170	0.72
17	17.07	17.07	3.58 ± 0.008	135	142	155	155	0.69

18	10	0	3.71 ± 0.008	155	157	180	179	0.46
19	17.07	2.93	3.28 ± 0.008	140	144	160	166	0.63
20	10	10	3.51 ± 0.005	160	161	180	183	0.42

Table 4.2b CCD with two input variables (%SOR and %GLY), two output variables (SIT and FTT), desirability score, and coating weight for MAL.

Run	Variables		Coating weight ($\frac{g}{m^2}$)	Response				Desirability score
	X_1 (%)	X_2 (%)		SIT (°C)		FTT (°C)		
				Observed	Predicted	Observed	Predicted	
1	0	10	3.45 ± 0.008	165	170	190	200	0.48
2	20	10	3.41 ± 0.007	125	118	135	129	0.98
3	2.93	17.07	3.38 ± 0.001	150	140	180	173	0.74
4	2.93	2.93	2.71 ± 0.006	230	224	255	245	0.22
5	10	10	3.28 ± 0.004	140	146	160	165	0.73
6	10	10	3.59 ± 0.001	140	146	160	165	0.73
7	17.07	17.07	3.56 ± 0.007	140	141	160	161	0.77
8	10	20	3.20 ± 0.003	140	142	170	173	0.71
9	10	0	3.01 ± 0.005	170	175	200	200	0.48
10	0	10	3.33 ± 0.005	165	170	190	200	0.48
11	2.93	2.93	2.81 ± 0.008	230	224	255	245	0.22
12	17.07	2.93	3.65 ± 0.005	135	128	150	145	0.88
13	20	10	3.43 ± 0.007	125	118	129	135	0.98
14	10	10	3.29 ± 0.01	140	146	160	165	0.73
15	10	20	3.40 ± 0.008	140	142	170	173	0.71
16	2.93	17.07	3.35 ± 0.001	150	140	180	173	0.74
17	17.07	17.07	3.38 ± 0.005	140	141	160	161	0.77
18	10	0	3.31 ± 0.006	170	175	200	200	0.48
19	17.07	2.93	3.85 ± 0.008	135	128	150	145	0.88
20	10	10	3.59 ± 0.001	140	146	160	165	0.73

Table 4.3a ANOVA results for SIT and FTT by SSOS optimization. Significant effects ($p < 0.05$) are highlighted in bold.

ANOVA source (SSOS)	Sum of squares	D.F.	Mean square	F-ratio	<i>p</i> -value
SIT					
x_1 : Sorbitol	506.25	1	506.25	9.349	0.0080
x_2 : Glycerol	2885.108	1	2885.108	53.282	<0.0001
$x_1 \cdot x_2$	1512.5	1	1512.5	27.932	<0.0001
x_1^2	-	-	-	-	-
x_2^2	1508.928	1	1508.928	27.867	<0.0001
Lack of fit	712.213	4	178.053	19.585	
Pure error	100.00	11	9.091		
Total error	812.213	15			<0.0001
FTT					
x_1 : Sorbitol	2314.245	1	2314.245	35.048	<0.0001
x_2 : Glycerol	2096.199	1	2096.199	31.746	<0.0001
$x_1 \cdot x_2$	312.500	1	312.500	4.732	0.0460
x_1^2	-	-	-	-	-
x_2^2	1160.357	1	1160.357	17.573	0.0008
Lack of fit	971.698	4	242.925	142.515	
Pure error	18.750	11	1.705		
Total error	990.448	15		<0.0001	

Table 4.3b ANOVA results for SIT and FTT by MAL optimization. Significant effects ($p < 0.05$) are highlighted in bold.

ANOVA source (MAL)	Sum of squares	D.F.	Mean square	F-ratio	<i>p</i> -value
SIT					
x_1 : Sorbitol	6526.098	1	6526.098	50.714	<0.0001
x_2 : Glycerol	3447.240	1	3447.240	26.788	0.0001
$x_1 \cdot x_2$	3612.500	1	3612.500	28.073	<0.0001
x_1^2	-	-	-	-	-
x_2^2	788.928	1	788.928	6.130	0.025
Lack of fit	1930.232	4	482.558		
Pure error	0.0000	11	0.0000		
Total error	1930.232	15			
FTT					
x_1 : Sorbitol	10280.109	1	10280.109	103.854	<0.0001
x_2 : Glycerol	2885.108	1	2885.108	29.146	<0.0001
$x_1 \cdot x_2$	3612.500	1	3612.500	36.495	<0.0001
x_1^2	-	-	-	-	-
x_2^2	2117.500	1	2117.500	21.392	0.0003
Lack of fit	1484.782	4	371.196		
Pure error	0.0000	11	0.0000		
Total error	1484.782	15			

In Table 4.3 (a and b), x_1 and x_2 indicate the level of SOR and GLY, respectively, for each modified starch. Combined with the ANOVA results, the least significant variables were excluded from the model. In fact, only the first order terms (x_1 and x_2), GLY binomial term (x_2^2), and their interaction ($x_1 \cdot x_2$) demonstrated a significant effect on SIT and FTT with a very low p -value for both MAL

and SSOS. In contrast, due to the insignificant impact ($p\text{-value} > 0.1$) of SOR quadratic term (x_1^2) on the responses for both types of starch, this term was eliminated from the model.

The regression coefficients and the fit models for SIT(y_1) and FTT(y_2) based on %SOR and %GLY in the SSOS and MAL quadratic model are shown in Equation 5 (a and b) for SSOS, and Equation 6 (a and b) for MAL as follow:

$$y_1 = 161.78 - 5.625 x_1 - 13.428 x_2 + 13.75 x_1 x_2 - 11.607 x_2^2 \quad (4.5\text{-a})$$

$$y_2 = 183.392 - 12.026 x_1 - 11.446 x_2 + 6.25 x_1 x_2 - 10.178 x_2^2 \quad (4.5\text{-b})$$

$$y_1 = 146.785 - 20.196 x_1 - 14.678 x_2 + 21.25 x_1 x_2 + 8.392 x_2^2 \quad (4.6\text{-a})$$

$$y_2 = 165 - 25.347 x_1 - 13.428 x_2 + 21.25 x_1 x_2 + 13.75 x_2^2 \quad (4.6\text{-b})$$

Based on the model, for SSOS, Equation 4.5, both SIT and FTT (y_1 and y_2 , respectively) indicate that increasing either SOR (x_1) or GLY (x_2) could decrease the respective outcomes, with GLY exerting a more substantial negative influence in SIT value (Equation 4.5-a). The positive interaction term ($x_1 x_2$) in both equations suggests that when both variables are elevated, they can somewhat offset their individual negative impacts, although the diminishing returns from GLY with the negative coefficient of its quadratic term (x_2^2) highlight the stronger impact of higher GLY concentrations on SIT and FTT reduction for this starch.

For MAL, Equation 4.6, the coefficients show an even stronger negative influence of SOR concentration on SIT and FTT values, while the interaction term remains significant, highlighting the importance of optimizing both variables together to minimize the response. Nevertheless, despite SSOS, the positive quadratic term for GLY (x_2^2) suggests that keeping its amount low may be required to achieve the lowest possible SIT and FTT levels, yet careful management of both variables is essential to meet the objective of achieving the lowest SIT and FTT outputs.

For SSOS results, the findings indicate a robust design performance for predicting the relevant responses, demonstrated by a relatively high correlation coefficient $R^2 = 0.89$ and 0.86 for SIT and FTT, respectively, as shown in figure 4.1 (a and b). The closer the R^2 value to 1.00, the higher the quality of the model [48].

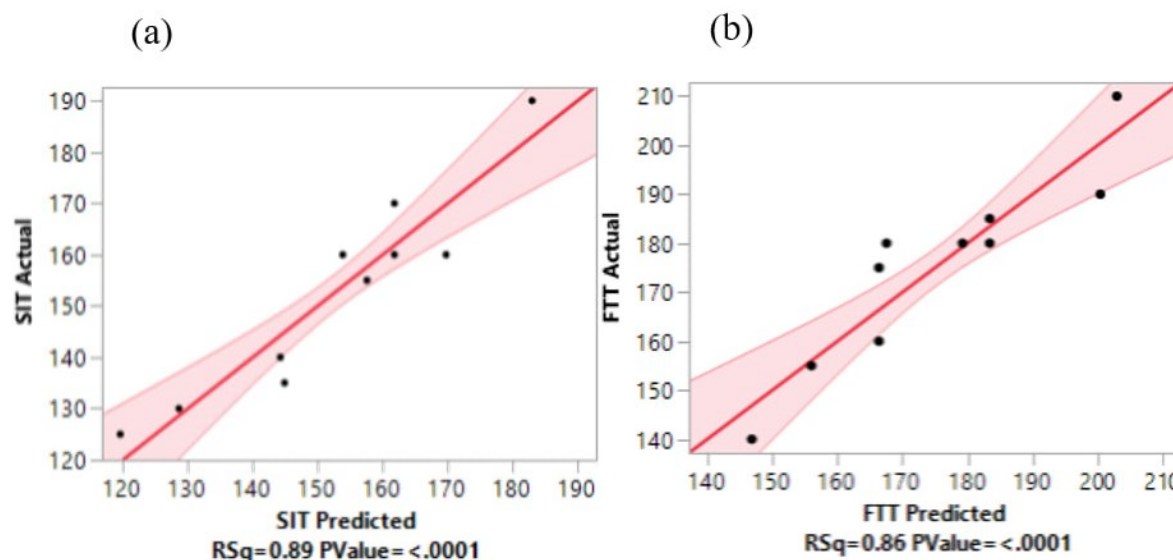


Figure 4.1 Analysis of SIT and FTT for SSOS family, (a) actual SIT response versus SIT predict, (b) actual FTT response versus FTT predict.

This figure (Figure 4.1a and b) indicates the correlation between the predicted values from Equation (4.5-a and 4.5-b) and experimental ones for SSOS starch. The data points show variations close to the diagonal line, suggesting that the model effectively predicts the experimental outcomes and can assist in parameter optimization [48]. To illustrate the interactions between the two independent variables and each response variable, response surface methodologies were developed for each fitted model.

The interaction effects of SOR and GLY on the SIT and FTT are depicted in Figure 4.2.a and b, respectively, using the response surface analysis. In SSOS, the minimum SIT (100 °C) is obtained when SOR and GLY are 0% and 20%, respectively, while the lowest FTT (147 °C) is acquired in 20% of both SOR and GLY. However, the model exhibits a relatively high level of FTT (151 °C) and SIT (139 °C) for the former and latter, respectively, highlighting them as unfavorable situations. To aim better saleability, both SIT and FTT are crucial to be at their lowest possible level, leading to importance of considering them in the simultaneously.

As shown in the response surface in Figure 4.2, by evaluating the impact of SOR and GLY levels on SIT (Figure 4.2a) and FTT (Figure 4.2b), two analogous types of parabolas are achieved.

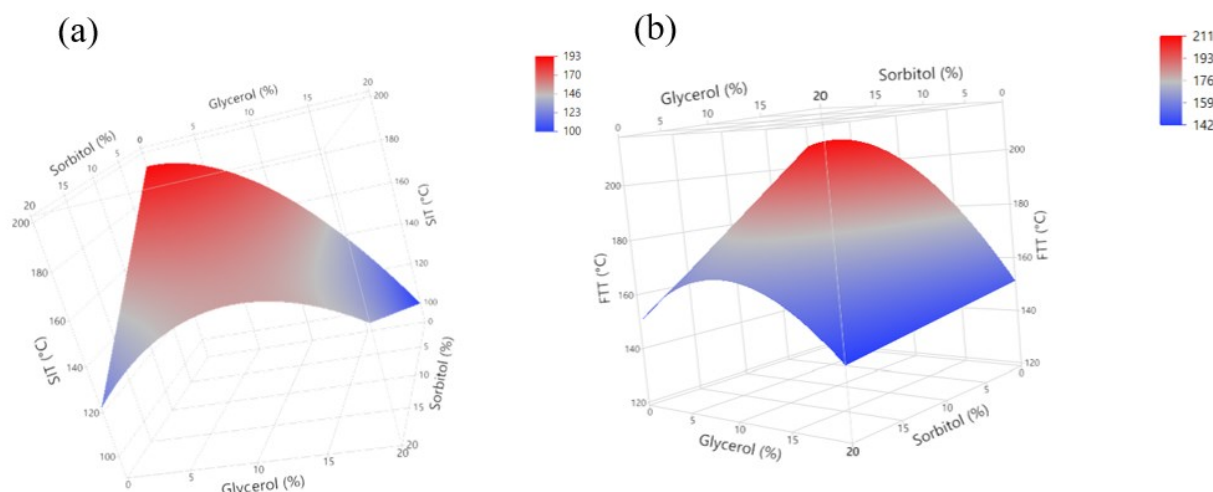


Figure 4.2 Analysis of SIT and FTT for SSOS family, (a) response surface for SIT, (b) response surface for FTT.

These parabolic surfaces indicate that by increasing the level of each additive (SOR and GLY) while the other level was maintained, the outcome parameters (SIT and FTT) varied; thereby, in most cases they increased initially and then dropped by adding further amount of the agent. Nonetheless, the reduction part of this pattern was not followed equally by the whole surface and for some additive levels, where SIT or FTT decreased faster comparing to the other ones. Moreover, in case of changing one factor while the other one was also changing, the parabolas indicated different scenarios for each response and every condition. In SSOS, although the impact of GLY ($p\text{-value} < 0.0001$) was slightly more significant than SOR ($p\text{-value} < 0.0080$) for SIT, these factors indicate similar effects for FTT. Hence, it was essential to find a situation in which both SIT and FTT were at their lowest possible levels.

For MAL, similarly, the results indicate a strong predictive capability of the design, with high correlation coefficients of $R^2 = 0.88$ for SIT and $R^2 = 0.93$ for FTT (figure 5 (a and b)). Figure 5 shows this high level of prediction accuracy.

More specifically, Figure 4.3 (a) and (b) illustrate the strong correlation between the predicted values from Equations (4.6-a and 4.6-b) and the experimental data. The points in the figures hover around the diagonal line, supporting the fact that the model effectively predicts experimental outcomes and is reliable for parameter optimization.

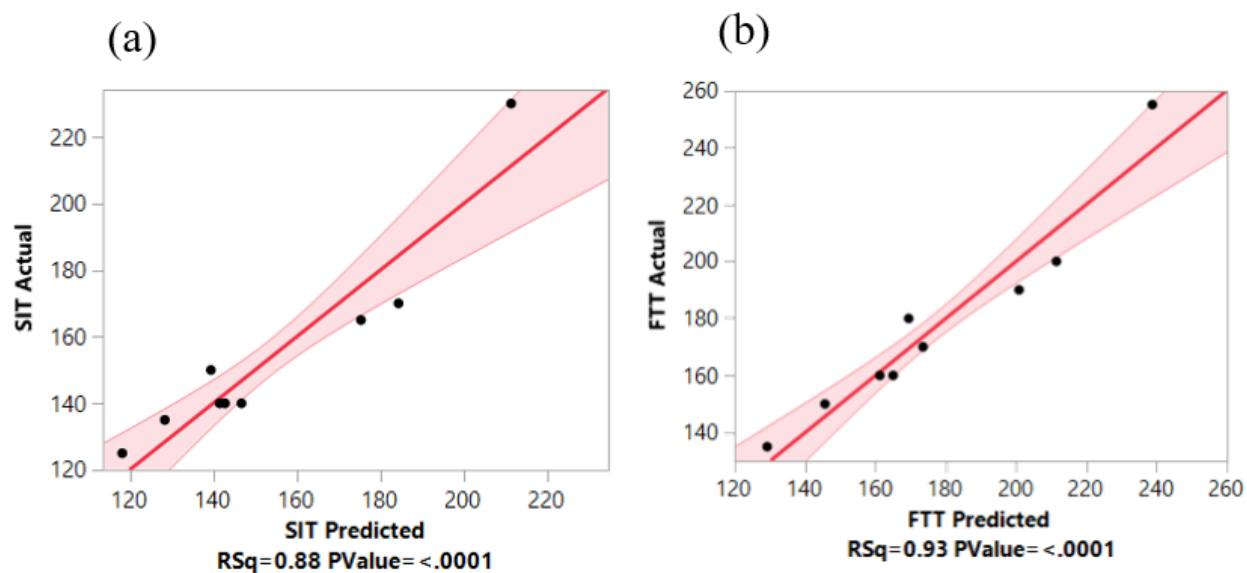


Figure 4.3 Analysis of SIT and FTT for MAL family, (a) actual SIT response versus SIT predict, (b) actual FTT response versus FTT predict.

Moreover, the effect of SOR and GLY on SIT and FTT in MAL as coating solution is demonstrated in Figure 4.4 (a) and Figure 4.4 (b), respectively. The response surface depicted in Figure 5 illustrates the effects of varying levels of SOR and GLY on SIT (Figure 5.c) and FTT (Figure 5.d), resulting in two similar parabolic shapes.

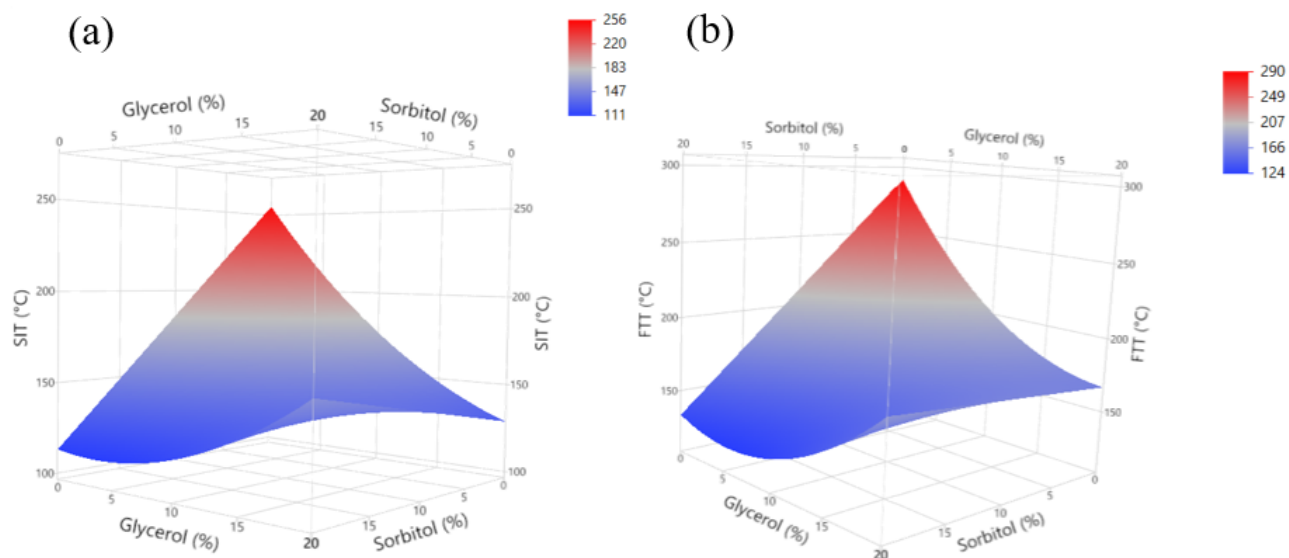


Figure 4.4 Analysis of SIT and FTT for MAL family, (a) response surface for SIT, (b) response surface for FTT.

Although the parabolas were reasonably alike, they followed different pattern comparing to the observations in SSOS section.

When MAL was utilized, the increase in amount of one plasticizer led to consistent decline in both SIT and FTT levels while the amount of another agent was hold around zero. However, for high concentrations (around 20%) this trend was reversed in which by increasing the amount of another additive, except for a slight reduction in the outcomes by adding GLY up to 5% when SOR was maintained at 20%, both SIT and FTT values were escalated.

Furthermore, when one agent amount was adjusted alongside the other, the surfaces revealed distinct outcomes for each response under varying conditions. The quadratic term of SOR amount played a slightly less significant role comparing to other terms especially in case of SIT level (P-value=0.025). Therefore, also in MAL family, identification of a condition where both SIT and FTT reached their minimum levels was vital.

The adjusted R-squared (R^2 Adj) values were 0.85 for SIT of SSOS and MAL, and 0.81 and 0.92 for FTT of SSOS and MAL, respectively. This implies that approximately 85%, 81%, and 92% of the variability in the dependent variable can be explained by the independent variables included in the CCD. Indeed, the high R^2 Adj values indicate a strong explanatory power of the regression models, suggesting that the independent variables included in the CCD analysis are effective in predicting the dependent variables (STI and FTT).

In our study, the coefficient of variation (CV%) were 4.825% and 4.636% for SIT and FTT of SSOS, respectively. Additionally, for MAL, CV% were 7.390% and 5.652% for SIT and FTT, respectively. Generally, a CV value below 10% is preferred, as it indicates high precision and low variability within the dataset [44]. Consequently, these results demonstrate the high precision and reproducibility of CCD in optimizing and analyzing the effects of our formulation.

4.4.2 Optimization of coating formulation and experimental validation

The optimization of the coating formulation on paper packaging using CCD aimed to simultaneously minimize the SIT (%) and FTT (%) as much as possible using the desirability score, as shown in Figure 4.5 and 4.6 for SSOS and MAL, respectively. The highest desirability of model was determined to be 99.0% for the SSOS and MAL family (see Fig. 4.5 and 4.6).

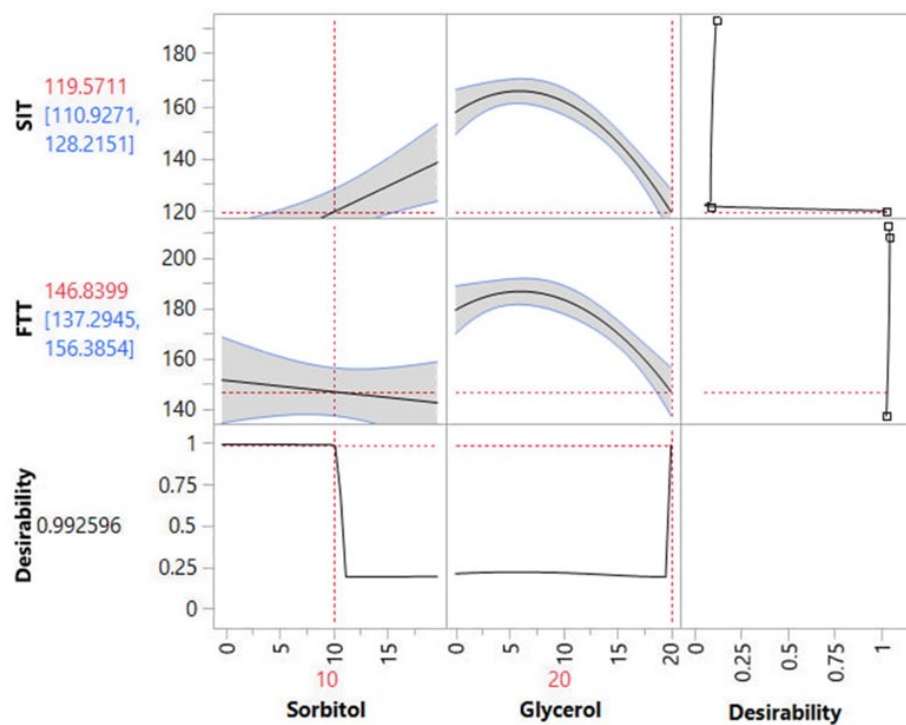


Figure 4.5 Profiler and desirability graph for the combined optimization of SIT and FTT in the SSOS.

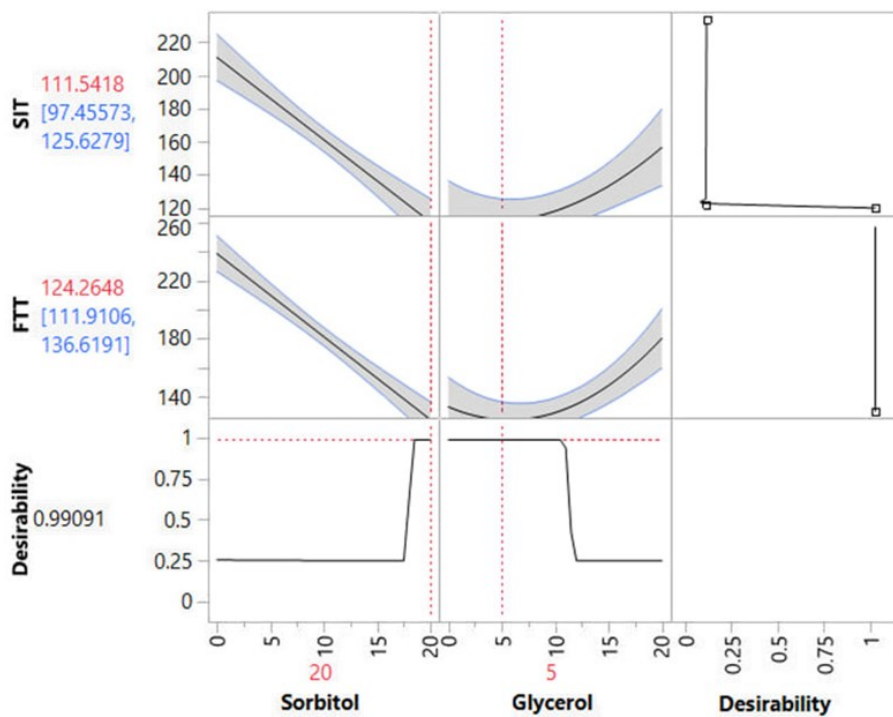


Figure 4.6 Profiler and desirability graph for the combined optimization of SIT and FTT in the MAL.

In general, the Y-axis displays the response (or desirability), while the X-axis shows the factors. The blue numbers indicate the response ranges achievable with the optimal settings for each factor, and the red number represents. Furthermore, the regions shaded in gray between the blue lines indicate the confidence interval for each graph. The plots at the bottom illustrate the change of desirability score with different level of each factor [49].

The objective was to minimize both SIT and FTT reflected through the maximum desirability scores. For SSOS, the fitting model suggested a coating formulation of 10% SOR and 20% GLY with predicted SIT of 120 °C and FTT of 147 °C which interestingly the percentages of GLY and SOR were the same as in run 2 (or 13). In addition, the most desire predicted results for MAL showed 20% SOR and 5% GLY with SIT of 112 °C and FTT of 125 °C. In order to verify the model's predictions, the samples were retested using the optimized levels of SOR and GLY for each modified starch family.

The ranges indicated under SIT and FTT for the optimal point represent the 95% PIs for each response in MAL and SSOS in Fig. 4.5 and 4.6, respectively. For SSOS with 10% SOR and 20% GLY, SIT was predicted to be in range of 110.9 to 128.2 °C, while FTT was anticipated to be between 137.3 and 156.4 °C. For the other modified starch, MAL, with 20% SOR and 5% GLY as the optimum point, the intervals for SIT and FTT were obtained to be between 97.5 to 125.4 °C and 111.9 to 136.6 °C, respectively. Initially, a single confirmation run for each of the two optimum points was performed to measure their FTT and SIT. The results are summarized in Table 4.4.

Table 4.4 Validation of the optimum data using 95% PI and single confirmation run.

Modified starch	Variable			Predicted values (°C)	Predicted interval (PI) (°C)	Single confirmation run (°C)
	SOR	GLY				
	%	%				
SSOS	10	20	SIT	119.6	110.9 – 128.2	120
			FTT	146.8	137.3 – 156.4	145
MAL	20	5	SIT	111.6	97.5 – 125.6	115
			FTT	124.3	111.9 – 136.6	120

As shown in Table 4.4, all the SIT and FTT results achieved from the one-time confirmation, fell within the PI suggested by the regression. Thus, the model demonstrated high consistency with the experimental values closely matching the predicted ones.

In the second step, as summarized in Table 4.5, the modified starches, with optimized level of SOR and GLY, were prepared and evaluated with 4 more replications (5 in total) to measure their SIT and FTT and obtain the mean and standard deviation of the confirmation runs.

Table 4.5 Empirical verification of the predicted optimal parameters.

Modified starch	Variable		Predicted values (°C)	Mean of confirmation runs (°C), N=5	Standard deviation of confirmation runs (°C)	Confidence interval (99% confidence)	
	SOR %	GLY %					
SSOS	10	20	SIT	119.6	121.0	4.2	± 5.6
			FTT	146.8	145.0	5.0	± 6.7
MAL	20	5	SIT	111.6	114.0	4.2	± 5.6
			FTT	124.3	123.0	4.5	± 6.0

No block effect was detected, as there was no significant shift in the outcomes of the confirmation runs. All SIT and FTT values remained well within their respective PI ranges, indicating a stable model performance across different conditions. In addition, the confidence intervals calculated using a 99% confidence limit, further validated the accuracy of the model. Notably, all predicted values fell within the interval surrounding the mean of the confirmation runs. This alignment reinforces the reliability of the model, demonstrating high consistency between the experimental values and the predicted outcomes. Overall, the results illustrate a strong correlation, confirming that the model accurately reflects the underlying processes being studied.

The optimal samples for SSOS and MAL with other favorable samples with relatively acceptable SIT and FTT, and some unfavourable ones with very high SIT and FTT, will be characterized, compared and assessed more in a future study.

4.5 Conclusion

The potential of using modified starches, specifically SSOS and MAL, as home compostable coatings to enhance the heat sealability of paper-based food packaging was thoroughly evaluated. Through a designed experimental framework using CCD and RSM, the use of plasticizers, SOR and GLY, was assessed to improve sealing properties. The optimal formulation for SSOS involved 10% SOR and 20% GLY, achieving a SIT of 120 °C and an FTT of 147 °C. For MAL, the ideal formulation was 20% SOR and 5% GLY, with SIT and FTT values of 112 °C and 125 °C, respectively. These conditions were validated through PI following by single confirmation runs and CI around mean of multiple confirmation runs, verifying that the experimental outcomes fell within the predicted intervals, thereby demonstrating the model's reliability and accuracy. The reasons leading to the observed SIT and FTT amounts as a result of the changes in plasticizer levels will be thoroughly investigated in Chapter 5.

Statistical analyses revealed significant effects of the plasticizers on SIT and FTT, with high correlation coefficients ($R^2 = 0.89$ for SIT and 0.86 for FTT in SSOS, and $R^2 = 0.88$ for SIT and 0.93 for FTT in MAL), indicating robust predictive capabilities. The adjusted R-squared values further supported the models' explanatory power, with 85% and 81% of the variability in SIT and FTT for SSOS, and 92% for FTT in MAL, were accounted for by the independent variables. The low coefficients of variation (CV%), with values of 4.825% and 4.636% for SIT and FTT in SSOS, and 7.390% and 5.652% for SIT and FTT in MAL, obtained in this study indicated the high precision and reproducibility of the experimental design.

These findings highlighted the potential of the modified starch coatings to serve as sustainable alternatives to traditional plastic packaging. The interactions between plasticizer concentrations and sealing performance provided a valuable foundation for future research and commercial applications, promoting the development of packaging solutions that are both environmentally friendly and functionally robust. Overall, this research contributed significantly to advancing sustainable packaging technologies in the food industry, aligned with global sustainability purposes.

4.6 References

1. Jahdkaran, E., et al., *The effects of methylcellulose coating containing carvacrol or menthol on the physicochemical, mechanical, and antimicrobial activity of polyethylene films*. Food Science & Nutrition, 2021. **9**(5): p. 2768-2778.
2. Bamps, B., M. Buntinx, and R. Peeters, *Seal materials in flexible plastic food packaging: A review*. Packaging Technology and Science, 2023. **36**(7): p. 507-532.
3. Merabtene, M., et al., *Heat sealing evaluation and runnability issues of flexible paper materials in a vertical form fill seal packaging machine*. BioResources, 2022. **17**(1): p. 223.
4. Dudbridge, M., *Handbook of seal integrity in the food industry*. 2016.
5. Piergiovanni, L. and S. Limbo, *Food packaging materials*. 2016: Springer.
6. Ganjizadeh Zavareh, S., M. Javanmard Dakheli, and B. Tajeddin, *Optimization of biodegradable paper cup packaging coated with whey protein isolate and rice bran wax as potential popcorn package*. Food Science & Nutrition, 2021. **9**(12): p. 6762-6775.
7. Salwa, H., et al., *Green bio composites for food packaging*. Int. J. Recent Technol. Eng, 2019. **8**(2): p. 450-459.
8. Deshwal, G.K., N.R. Panjagari, and T. Alam, *An overview of paper and paper based food packaging materials: health safety and environmental concerns*. Journal of food science and technology, 2019. **56**: p. 4391-4403.
9. Hauptmann, M., et al., *The effect of flexible sealing jaws on the tightness of pouches made from mono-polyolefin films and functional papers*. Packaging Technology and Science, 2021. **34**(3): p. 175-186.
10. Henry, T., *Suitability of poly (butylene succinate) as a coating for paperboard convenience food packaging*. 2020.
11. Lim, W.S., et al., *Heat-sealing property of cassava starch film plasticized with glycerol and sorbitol*. Food Packaging and Shelf Life, 2020. **26**: p. 100556.
12. Allen, K., *A review of contemporary views of theories of adhesion*. The journal of Adhesion, 1987. **21**(3-4): p. 261-277.
13. Rompothi, O., et al., *Development of non-water soluble, ductile mung bean starch based edible film with oxygen barrier and heat sealability*. Carbohydrate polymers, 2017. **157**: p. 748-756.
14. Das, M. and T. Chowdhury, *Heat sealing property of starch based self-supporting edible films*. Food Packaging and Shelf Life, 2016. **9**: p. 64-68.
15. Apriyanto, A., J. Compart, and J. Fettke, *A review of starch, a unique biopolymer–Structure, metabolism and in planta modifications*. Plant Science, 2022. **318**: p. 111223.
16. Zamani, Z. and S.M.A. Razavi, *Steady shear rheological properties, microstructure and stability of water in water emulsions made with basil seed gum and waxy corn starch or high pressure-treated waxy corn starch*. LWT, 2023. **174**: p. 114453.

17. Nechita, P. and M. Roman, *Review on polysaccharides used in coatings for food packaging papers*. Coatings, 2020. **10**(6): p. 566.
18. Kushwaha, R. and D. Kaur, *Recent techniques used in modification of starches: A review*. Food Technology From Health to Wealth & Future Challenges; Bharti Publication: Delhi, India, 2018: p. 1-15.
19. Sajilata, M. and R.S. Singhal, *Specialty starches for snack foods*. Carbohydrate polymers, 2005. **59**(2): p. 131-151.
20. Coggins, T.L., *Print No More: US Code, Code of Federal Regulations, and the Federal Register*. Virginia Lawyer, 2000. **49**(3): p. 53.
21. Liu, Z., et al., *Edible starch sodium octenyl succinate film formation and its physical properties*. Journal of applied polymer science, 2013. **127**(4): p. 2922-2927.
22. Wang, X., et al., *Preparation and characterisation of octenyl succinate starch as a delivery carrier for bioactive food components*. Food Chemistry, 2011. **126**(3): p. 1218-1225.
23. Du, Q., et al., *Whey protein and maltodextrin-stabilized oil-in-water emulsions: Effects of dextrose equivalent*. Food Chemistry, 2021. **339**: p. 128094.
24. Garnero, C., C. Aloisio, and M.R. Longhi, *Ibuprofen-maltodextrin interaction: study of enantiomeric recognition and complex characterization*. 2013.
25. Xiao, Z., et al., *Maltodextrin as wall material for microcapsules: A review*. Carbohydrate polymers, 2022. **298**: p. 120113.
26. Parikh, A., S. Agarwal, and K. Raut, *A review on applications of maltodextrin in pharmaceutical industry*. system, 2014. **4**(6).
27. Saavedra-Leos, Z., et al., *Technological application of maltodextrins according to the degree of polymerization*. Molecules, 2015. **20**(12): p. 21067-21081.
28. Suh, J.H., et al., *Effect of moisture content on the heat-sealing property of starch films from different botanical sources*. Polymer Testing, 2020. **89**: p. 106612.
29. Jiménez, A., et al., *Phase transitions in starch based films containing fatty acids. Effect on water sorption and mechanical behaviour*. Food Hydrocolloids, 2013. **30**(1): p. 408-418.
30. Basiak, E., A. Lenart, and F. Debeaufort, *How glycerol and water contents affect the structural and functional properties of starch-based edible films*. Polymers, 2018. **10**(4): p. 412.
31. Alves, V.D., et al., *Effect of glycerol and amylose enrichment on cassava starch film properties*. Journal of Food Engineering, 2007. **78**(3): p. 941-946.
32. Muscat, D., et al., *Comparative study of film forming behaviour of low and high amylose starches using glycerol and xylitol as plasticizers*. Journal of Food Engineering, 2012. **109**(2): p. 189-201.
33. Mohammadi Nafchi Abdorreza, M.N.A., L. Cheng, and A. Karim, *Effects of plasticizers on thermal properties and heat sealability of sago starch films*. 2010.

34. Morris, B., *Thermoforming, Orientation, and Shrink*. The Science and Technology of Flexible Packaging: Multilayer Films from Resin and Process to End Use Plastics Design Library, 2017: p. 401-433.
35. Herrera, N., et al., *Functionalized blown films of plasticized polylactic acid/chitin nanocomposite: Preparation and characterization*. Materials & Design, 2016. **92**: p. 846-852.
36. Morris, B.A., *The science and technology of flexible packaging: multilayer films from resin and process to end use*. 2022: William Andrew.
37. Frihart, C.R., *Adhesive bonding and performance testing of bonded wood products*. 2005.
38. Kavčič, U., G. Lavrič, and I. Karlovits, *Alternative Fiber-Based Paperboard Adhesion Evaluation with T-and Y-Peel Testing*. Applied Sciences, 2023. **13**(17): p. 9779.
39. İlhan, I., et al., *Understanding the factors affecting the seal integrity in heat sealed flexible food packages: A review*. Packaging technology and science, 2021. **34**(6): p. 321-337.
40. Jadaa, W., A. Prakash, and A.K. Ray, *Modeling of degradation of Diazo dye in swirl-flow photocatalytic reactor: Response surface approach*. Catalysts, 2020. **10**(12): p. 1418.
41. Sudarjanto, G., B. Keller-Lehmann, and J. Keller, *Optimization of integrated chemical–biological degradation of a reactive azo dye using response surface methodology*. Journal of hazardous materials, 2006. **138**(1): p. 160-168.
42. Bagheri, A.R., et al., *Modeling and optimization of simultaneous removal of ternary dyes onto copper sulfide nanoparticles loaded on activated carbon using second-derivative spectrophotometry*. Journal of the Taiwan Institute of Chemical Engineers, 2016. **65**: p. 212-224.
43. Myers, R.H., D.C. Montgomery, and C.M. Anderson-Cook, *Response surface methodology: process and product optimization using designed experiments*. 2016: John Wiley & Sons.
44. Moussa, H., et al., *Definitive screening design and I-optimal design for optimization of ultrasound-assisted extraction of phenolic content and antioxidant capacity from Salvia officinalis L. leaves*. Sustainable Chemistry and Pharmacy, 2022. **29**: p. 100820.
45. Montgomery, D.C., *Design and analysis of experiments*. 2017: John wiley & sons.
46. Mee, R.W., *A comprehensive guide to factorial two-level experimentation*. 2009: Springer.
47. Antony, J., *Design of experiments for engineers and scientists*. 2023: Elsevier.
48. Zhang, S., et al., *Modelling and optimization of electrodeposited amorphous Fe-P alloys using central composite design and response surface method*. International Journal of Electrochemical Science, 2024. **19**(7): p. 100644.
49. Malci, K., L.E. Walls, and L. Rios-Solis, *Rational design of CRISPR/Cas12a-RPA based one-pot COVID-19 detection with design of experiments*. ACS Synthetic Biology, 2022. **11**(4): p. 1555-1567.

CHAPTER 5 ARTICLE 2 : INNOVATIVE HOME COMPOSTABLE HEAT SEALABLE COATING BY MODIFIED STARCH FOR PAPER- BASED FLEXIBLE PACKAGING

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Abstract

This research undertook an in-depth analysis of the creation and evaluation of home compostable, heat-sealable coatings for flexible packaging made from paper. The study employed both unmodified starches, with modified starches such as Sodium starch octenyl succinate (SSOS) and Maltodextrin (MAL), in combination with plasticizers like sorbitol and glycerol. Pure SSOS improved the heat sealability of paper, whereas pure MAL did not exhibit this behavior. Adding different concentrations of SOR and GLY to the SSOS and MAL coatings significantly affected the seal initiation temperature (SIT) and fiber tear temperature (FTT). In the case of SSOS, GLY had a more pronounced effect on SIT, while SOR notably enhanced tackiness in MAL, underscoring their essential roles in optimizing sealing performance. Fourier transform infrared analysis (FTIR), differential scanning calorimetry (DSC), rheological characterization, and the physical and chemical properties of the coatings were analyzed.

The effect of pressure and dwell time on the optimal samples showed that longer dwell times typically reduced the SIT and FTT due to improved molecular interactions, except at high pressure (140 psi). Additionally, while increasing pressure enhanced sealing by improving layer contact, excessive pressure had minimal impact on performance. The findings suggest that these home compostable coatings represent a viable alternative to conventional plastic packaging, contributing to reduced landfill waste and promoting sustainability in food packaging applications.

Keywords: Home-compostable coatings, heat sealability, paper-base packaging, modified starches, plasticizer.

5.1 Introduction

In recent years, urbanization and globalization have driven a rise in food production and consumption, resulting in more complex and extended food supply chains. The growing demand for food has also spurred the expansion of related industries, particularly the packaging sector, which is a key player in the food value chain [1]. In developed countries, the packaging industry contributes around 2% to the gross national product, with approximately half of this production dedicated to food packaging [2, 3]. With a global annual growth rate of 5%, the consumption of packaged foods estimated to reach from \$1.9 trillion in 2020 to \$3.4 trillion by 2030 [4].

As global demand for packaged food grows, the production of non-degradable and non-renewable materials places increasing strain on Earth's environmental resources. Packaging constitutes the largest market for plastics and is a major contributor to solid waste in landfills and marine environments across the U.S. [5, 6]. In 2018, containers and packaging accounted for 28.1% of the total municipal solid waste (MSW) generated [7]. Traditional food packaging, primarily made from petroleum-based plastics, has a short service lifetime and provokes environmental pollution. Contamination reduces recyclability, exacerbating landfill accumulation [8, 9]. Additionally, plastic packaging offers limited protection against microbial contamination, potentially reducing the food safety and shelf life [10]. Consequently, consumers are increasingly motivated to mitigate environmental pollution and decrease the use of plastic packaging by opting for biodegradable alternatives.

Paper serves as an excellent alternative, effectively reducing reliance on plastics and coatings. In 2000, approximately 47% of global paper and paperboard production was allocated for packaging purposes [11]. The paper and paperboard segment accounts for 31% of the global packaging market, extensively used in food packaging to ensure the preservation of manufactured food products during transportation, warehousing, and consumption phases, while also providing crucial marketing information to consumers [11, 12]. As a result, the ability to compost post-consumer waste instead of sending it to landfills contributes the environment by reducing the potential for accumulation [6].

However, conventional paper has insufficient heat sealability [11]. Effective sealing is challenging due to paper's low thermal transfer coefficient, requiring either a longer sealing time or a higher sealing temperature [12]. These limitations pose challenges for its use in packaging materials [10].

To enhance its functional capabilities, it is necessary to incorporate suitable additives or apply surface coatings of aluminum foil, plastic, and polymers, including Ethylene-vinyl alcohol (EVOH), Polyethylene (PE), Polyvinylidene Chloride (PVDC), latex and etc. [13-15]. However, these additives and coatings can migrate into food products, potentially causing health hazards, and disrupt the recycling process, increasing landfill accumulation [9, 11]. Using biodegradable or compostable materials such as poly (lactic acid), poly (butylene succinate), polycaprolactone (PCL), and starch seems a promising alternative to reduce environmental issues and landfill waste. It is important to note that certain bioplastic packaging may be biodegradable but not compostable [16]. Biodegradable materials are primarily engineered to decompose under specific conditions found in industrial composting facilities, which provide optimal conditions for microbial growth, including controlled moisture levels, oxygen concentration, carbon-to-nitrogen ratio, and high temperatures [17]. However, biodegradation rates under realistic conditions remain largely unexplored [18].

Home composting, or backyard composting, involves composting biowaste and using the resulting compost in a private garden, offering benefits over industrial composting [19]. It reduces the need for municipal solid waste collection, economic and material investments in waste management infrastructure, and allows for more precise control over the composting process [19-22]. Replacing traditional coatings with home compostable polymer coatings could be an eco-friendly and cost-effective solution.

Given the advantages of home-compostable materials, this study examines the decomposition of home-compostable polymers under typical home composting conditions, including ambient temperatures and a naturally occurring microbial population. Additionally, the selected materials are expected to enhance the heat sealability of paper, addressing one of the significant shortcomings of paper packaging. Polymers that are both home-compostable and possess heat-sealing properties for paper coatings include polysaccharides (e.g., cellulose, chitosan, starch), proteins (e.g., whey protein, gelatin), and home-compostable polyesters (e.g., polycaprolactone (PCL), bio-polybutylene succinate (bio-PBS)). Among these, cellulose, its derivatives, chitosan, and home-compostable polyesters are insoluble in water, with some requiring pretreatments [23]. Pectin and alginate films require calcium ions to create ionic bonds with the carboxylic groups on polysaccharides [23, 24]. Proteins and gelatin present limitations, such as potential allergenic reactions, considerations related to religious beliefs, and dietary restrictions [25, 26]. Starch

emerges as a promising candidate for paper coating due to its abundance and cost-effectiveness, facilitating its large-scale application [27]. Starch is composed of amylose and amylopectin, both significantly impacting film formation and characteristics. The paper industry extensively utilizes starch in surface applications, including surface sizing, pigment binding, and practical coating [28]. However, thermoplastic starch is less commonly used due to issues with solution viscosity, film formation, and retrogradation [29]. Therefore, using modified starches can improve properties such as adhesion, solubility, and heat resistance [30].

Sodium starch octenyl succinate (SSOS) is a chemically modified starch achieved through esterification, resulting in a hydrophobic nature through the integration of octenyl groups [31, 32]. Maltodextrin (MAL), derived from starch through partial enzymatic hydrolysis, is composed of α -D-glucose molecules predominantly connected through glycosidic bonds [33, 34].

Starch films without plasticizers exhibit a high density of cohesive energy within their network due to hydrogen bonds which create a brittle structure [35]. Plasticizers interfere with intermolecular interactions, reducing hydrogen bonding, increasing free volume and distance between polymers, and lowering the glass transition temperature (T_g). Therefore, sealing can be achieved at lower temperatures compared to traditional thermal bonding methods [36-38]. The type and amount of plasticizer influence polymer interactions, resulting in different performance outcomes [35, 39]. For instance, researchers explored how different concentrations of glycerol (0–30% w/w) and sorbitol (0–60% w/w) affect the seal strength of mung bean starch (MBS) films [74]. It was found that higher concentrations of plasticizers generally improved the seal strength. Specifically, MBS films with 30% glycerol showed superior seal strength compared to those with sorbitol, suggesting glycerol is more effective for enhancing seal performance in MBS films [39]. Combining high molecular weight (Mw) plasticizers like sorbitol with low Mw plasticizers like glycerol significantly enhances starch-based films' functional properties [40, 41].

This study aims to develop a home-compostable, heat-sealable coating for paper-based flexible packaging by fabricating environmentally friendly modified starch (SSOS and MAL) coatings with various plasticizers (sorbitol and glycerol) and evaluating their impact on the sealing properties. This product aims to reduce environmental impact and ensure food safety, setting it apart from commercially compostable or biodegradable alternatives.

5.2 Experimental Section

5.2.1 Material

For this study, sodium starch octenyl succinate (SSOS; E 1450) was sourced from Chanjao Longevity Co., Ltd. in Bangkok, Thailand (Myskinrecipes Co.). Maltodextrin (MAL), with a dextrose equivalent (DE) of 10, was acquired from the Toronto Brewing Company. Mung bean starch (MBS), sweet potato starch (SPS), and tapioca starch (TS) were obtained from a local grocery store in Montreal, Canada. Additionally, sorbitol (SOR) and glycerol (GLY) were procured from Sigma-Aldrich (ON, Canada). Prolamina Corp (U.S.) provided bleached paper samples containing 5.5% moisture, a tensile strength of 20 lbf/in (MD), and tear strengths of 30 gf (CD) and 24 gf (MD).

5.2.2 Preparation of biopolymer Coatings on Paper

The coatings using both unmodified and modified starches as well as, SOR, and GLY as plasticizers were prepared by stirring for 1.5 hours at room temperature with distilled water as the solvent. A total biopolymer concentration of 25% (w/w) was considered, which included one of the unmodified starches such as MBS, SPS, and TS, or the modified starches (SSOS and MAL). Plasticizer content (SOR and GLY) ranged from 0 to 20% (w/w) relative to the polymer concentration.

The casting solution was left undisturbed for 1 hour to remove air bubbles and ensure consistency. A Mayer rod on a bar coater (TQC Sheen AB4120) was then used to apply the film solution onto paper substrates, forming a wet film with a thickness of 2 μm . The coated substrates were dried for 2 minutes using an infrared (IR) dryer (Datous Boss, ZJ-SC-002, 2 kW, 220V) to set the layer. The process was repeated under identical conditions to add a second layer, resulting in a combined wet film thickness of 4 μm , followed by drying again.

Samples made by the modified starches were selected based on the Design of Experiments (DOE) results obtained using JMP statistical software (in previous research article) for characterization of their properties. The optimal coating formulation for SSOS included 10% SOR and 20% GLY, while for MAL, it consisted of 20% SOR and 5% GLY which were labeled as O-SSOS and O-MAL, respectively. Additionally, samples 7-SSOS (17.07% SOR / 17.07% GLY), 2-MAL (20%

SOR / 10% GLY), and 12-MAL (17.07% SOR / 2.93% GLY), which displayed favorable SIT and FTT observed in that study, were selected for the analysis. To provide a comparison, the two most unfavorable samples with the highest SIT and FTT, 4-SSOS and 4-MAL, with compositions of 2.93% SOR and 2.93% GLY, were also included in the study. The naming convention for favorable and unfavorable samples corresponds to their original run number listed in the previous article. To provide a clearer understanding, Table 5.1 specifies all the samples that supposed to be characterized, along with their respective plasticizer percentages.

Table 5.1 Composition of coating solutions.

	Sample name	SOR%	GLY%	SIT (°C)	FTT (°C)	Coating weight ($\frac{g}{m^2}$)
Optimal	O-SSOS	10	20	120	147	3.58 ± 0.006
	O-MAL	20	5	110	120	3.51 ± 0.005
Favorable	7-SSOS	17.07	17.07	135	155	3.66 ± 0.007
	2-MAL	20	10	125	135	3.41 ± 0.007
	12-MAL	17.07	2.93	135	150	3.65 ± 0.005
Unfavorable	4-SSOS	2.93	2.93	190	210	2.80 ± 0.008
	4-MAL	2.93	2.93	230	255	2.71 ± 0.006

5.3 Characterization and Measurements

5.3.1 Heat sealing assessments

Heat sealing tests were conducted using an SL10 LakoTool laboratory hot-tack and seal tester, which was acquired from Lako Tool & Manufacturing Inc. These tests were performed under specific conditions of temperature, pressure, and dwell time. After sealing the samples, peel testing was conducted at 33 mm/sec speed to assess the quality of the seals. All samples were cut in 7 inches by 1 inch in dimensions and tested using an Instron machine (model number E3000). For each sample, the peel test was repeated 10 times, and the seal initiation temperature (SIT) and fiber

tear temperature (FTT) results were reported. The temperature showed fiber tear was considered as FTT (fig. 5.1).

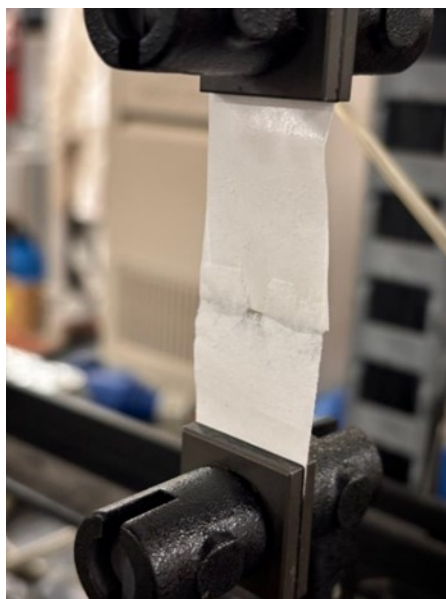


Figure 5.1 Fiber tear failure in paper-based packaging.

5.3.2 ATR-FTIR

Prior to the analysis, the samples (coating) were placed in a petri dish after preparation and then dried in an oven at 55 °C for 72 hours to eliminate water before analysis. ATR-FTIR measurements then were carried out to examine the chemical composition and the intensity of the chemical groups in the coating (without paper). The ATR-FTIR spectra of the samples were recorded in absorbance mode at ambient temperature using a Perkin Elmer ATR-FTIR spectrometer. The analysis was conducted over a wavenumber range of 600 to 4000 cm^{-1} .

5.3.3 Rheological characterization

The rheological properties of casting solution (SSOS and MAL with SOR and GLY), were conducted with an Anton-Paar rotational rheometer (MCR501), employing a Couette double gap (DG) flow geometry. A syringe was used to obtain the necessary volume of 8 mL for each

geometry. Shear rate sweep experiments spanned from 0.01 s^{-1} to 800 s^{-1} , transitioning from low to high shear rates. All experiments were conducted at a temperature of $25\text{ }^{\circ}\text{C}$.

5.3.4 Physical properties and surface characterization

The coating weight of the coating layer was determined by measuring the mass of paper samples before and after the coating process (Quintix 224-1S, Sartorius Mechatronics). Surface roughness was analyzed by profilometer Dektak XT (Bruker Corporation). Two roughness parameters were assessed: R_a , representing the surface roughness average, and R_q , denoting the root mean square roughness. The measurements were conducted over a 4 mm length of the sample surface, utilizing a scanning stylus with an applied force of 3 mg. Each material underwent three replicate measurements to ensure sufficient accuracy.

5.3.5 Differential scanning calorimetry (DSC)

The glass transition temperatures of the films were appraised using a TA Instruments Q1000 calorimeter (TA Instruments, New Castle, DE) under a nitrogen atmosphere. The samples were heated from $0\text{ }^{\circ}\text{C}$ to $130\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$. Notably, for greater accuracy in this analysis, only the coating (unmodified starch and plasticizers) without the substrate (paper) was used, as the presence of the paper substrate can potentially interfere with the T_g measurement of the coating material. The samples were dried at $55\text{ }^{\circ}\text{C}$ for 72 hours to eliminate water before analysis.

5.3.6 Validation of adhesive performance

Abrasion resistance was evaluated using the Taber method with linear abrader model 5750 (Polytechnique Montreal, CA), according to ASTM D4060-10 Standard Test Method for Abrasion Resistance by the Taber Abraser. The test employed CS-10 abrasive wheels. Moreover, the load of 850 grams, a total of 3000 cycles, and a speed of 30 cycles per minute were considered. Weight losses were quantified in milligrams by measuring the difference in specimen weight before and after abrasion. The wear rate (wear index (I)) was calculated using Equations below based on the measured weight loss in milligrams. All ASTM abrasion tests were conducted in triplicate, and the average values were reported.

$$I = \frac{(A - B)1000}{C} \quad (5.1)$$

Where, A represents the initial weight of the specimen before abrasion (mg), B denotes the weight of the specimen after abrasion (mg), and C indicates the recorded number of abrasion cycles.

Based on standard ASTM D918 – 99, the Blocking Resistance test procedure measures the effectiveness of flexible packaging materials in preventing blocking. This assessment includes various materials, such as paper combined with metallic foils and synthetic films, whether they are treated, coated, or laminated. The test is particularly significant for different types of paper where blocking is a major concern.

The procedure followed the standard with slight modifications. Specimens were prepared with dimensions of $50 \times 50 \text{ mm}^2$. The samples were folded with the coated sides facing each other and then with the coated side against the uncoated side. A 500 g weight was placed on the top plate to apply uniform pressure. The testing period lasted for 24 hours.

Testing was performed at ambient temperature under two relative humidity conditions (21% and 60%). After the test, the specimens were gently unfolded and inspected for any signs of adhesion or peeling of the sealant. The procedure was repeated three times to ensure the accuracy and reliability of the results.

5.4 Results and Discussion

5.4.1 Performance of unmodified starch

The use of unmodified starches, such as MBS, SPS, and TS, in paper-based flexible packaging presented several technical challenges. First, effective dissolution of these starches required elevated temperatures and extended heating times, complicating the production process and increasing energy consumption. Secondly, these starches were susceptible to retrogradation and gelatinization, often occurring within 5 minutes, which limited their functional stability and effectiveness as coating materials. Lastly, when unmodified starch was directly applied to paper substrates, it exhibited poor adhesion properties. This weak adhesion caused the starch coating to detach from the paper surface, often resulting in a powdery residue that compromises the integrity

and appearance of the packaging. Consequently, these issues prevented the study of seal strength in such applications.

5.4.2 Heat sealing evaluation

The quality of a heat seal is assessed by analyzing several factors, including the integrity of the joint, the behavior of the seal strength at various times and temperatures, the SIT, failure modes, and the uniformity of the seal [42]. Specifically, the seal strength is influenced by the initiation temperature, and a low SIT is considered a beneficial characteristic for a sealant layer [43, 44]. Seal temperature should not be too low because it leads to weak seals [45].

On the other hand, paper, with its layered network structure, is prone to fiber tearing. The primary cause of fiber tear in paper substrates is mechanical interlocking, which occurs when the polymer sealant penetrates into the paper structure, becoming interwoven with the cellulose fibers. During the opening of seals, this excessive interlocking causes the paper's cellulose fibers to fracture and break apart [46]. Achieving complete fiber tear when the adhesive joint is pulled apart is crucial for ensuring strong adhesive bonding in paper packaging products [47]. Moreover, monitoring FTT helps in quality assurance ensuring the seals are not only strong but also the paper maintains its intended properties for the end user. Therefore, both the SIT and the FTT are critical for achieving strong and reliable seals in heat sealing processes. They influence the effectiveness, efficiency, and quality of the final product, making them key parameters in the packaging industry.

To investigate the seal performance by determining SIT and FTT of the films, sealing experiments were conducted across a broad range of temperatures with 40 psi pressure and dwell time of 1.5 seconds (1500 ms).

Based on the results of the heat seal tests, it was found that pure SSOS on the paper demonstrated successful sealing behavior, with a SIT observed at 180°C. At 210°C, the paper experienced fiber tear failure, indicating a strong adhesive bond. Conversely, pure MAL on the paper did not achieve effective sealing within the tested temperature range, extending up to 220°C.

Figure 5.2 illustrates the effects of SSOS with varying percentages of SOR and GLY on the SIT and FTT of paper, and Figure 5.3 demonstrates the effects of MAL with varying percentages of SOR and GLY on SIT and FTT of the paper.

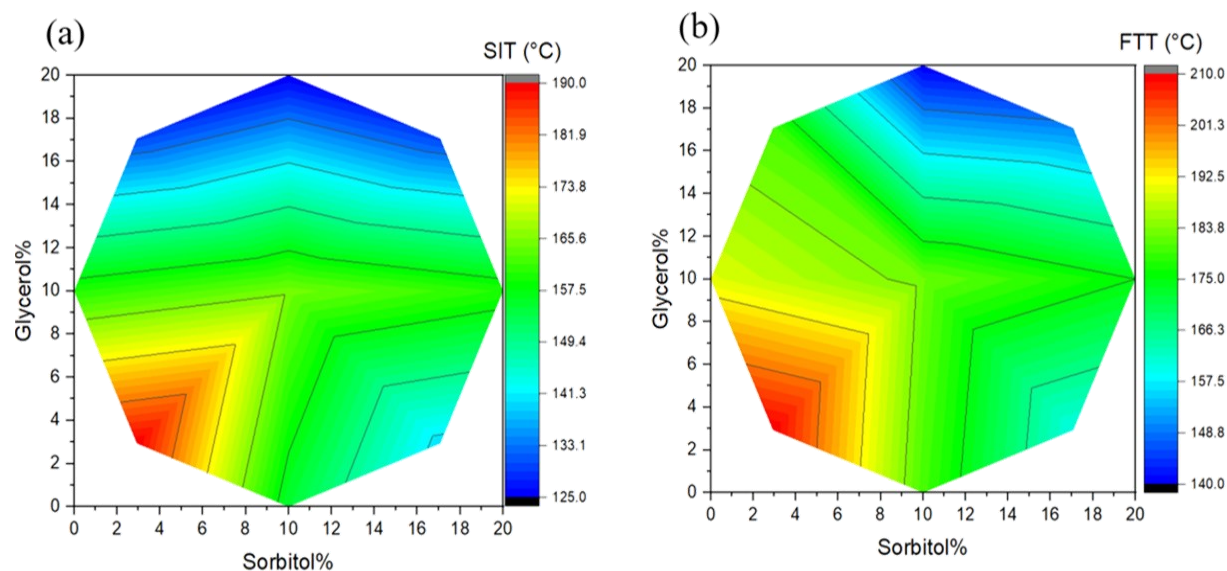


Figure 5.2 (a) SIT of SSOS samples as functional of sorbitol% and Glycerol%, (b) FTT of SSOS samples as functional of sorbitol% and Glycerol%.

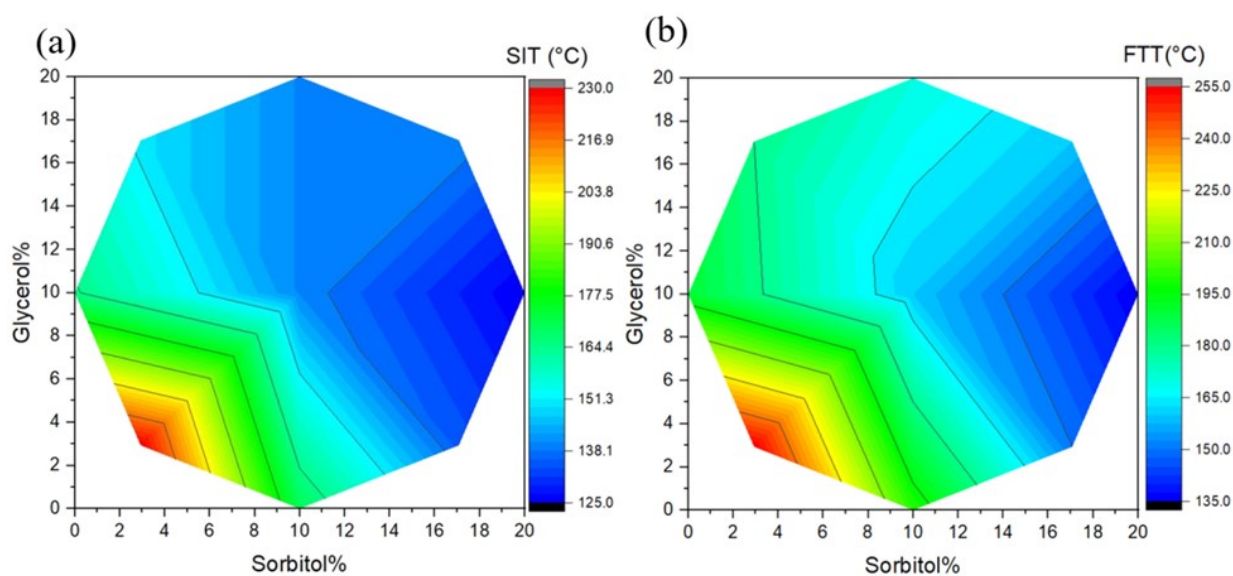


Figure 5.3 (a) SIT of MAL samples as functional of sorbitol% and Glycerol%, (b) FTT of MAL samples as functional of sorbitol% and Glycerol%.

As shown in Fig. 5.2, adjusting the proportions of SOR and GLY in SSOS led to a marked decrease in both SIT and FTT. For example, formulations with 2.93% SOR and 2.93% GLY (seen in the reddish regions), demonstrated SIT and FTT values of 190°C and 210°C, respectively. Increasing the plasticizer levels to 10% SOR and 10% GLY improved the paper's sealing properties, reflected by a shift towards blue and green regions, with SIT and FTT values dropping to 160°C and 180°C, respectively. Whereas simultaneous increase in GLY and SOR content resulted in reduction in SIT and FTT, elevation of a solo plasticizer quantity did not always lead to change in SIT and FTT outcomes, more especially, when GLY concentration was more than 10%, SIT of the modified starch was regardless of SOR content. For FTT, this phenomenon was observed when both GLY and SOR were bigger than 10% meaning in those conditions, FTT level changed only based on GLY percentage.

In addition, in Fig. 5.2 formulation of SSOS, the minimum SIT (125 °C) was observed when the SSOS contained 10% SOR and 20% GLY, which was associated with FTT of 140 °C. Other samples were also examined, specifically those with 17.7% SOR and 17.07% GLY and 2.93% SOR and 17.07% GLY. They achieved SIT of 135 °C and 130 °C, respectively, indicating relatively low SIT level. However, these formulations were associated with significantly high FTT of 155 °C and 180 °C, respectively. The results of this analysis suggested that in the context of SSOS, the presence of GLY has a slightly more pronounced effect on SIT compared to SOR. This observation implies that adjustments in the GLY concentration may lead to more favorable outcomes in terms of seal integrity.

As illustrated in Fig. 5.3, the incorporation of varying percentages of SOR and GLY into MAL aroused a significant change in both the SIT and the FTT. For instance, MAL formulations containing 2.93% SOR and 2.93% GLY (reddish colors) exhibited SIT and FTT values of 230°C and 255°C, respectively. An increase in the concentrations of plasticizers to 10% SOR and 10% GLY enhanced the sealing performance of the paper (shifting towards blue and green), yielding SIT and FTT values of 140°C and 160°C, respectively. These results suggested that, despite SOSS, in MAL, GLY and SOR content impacted on SIT and FTT level in all concentrations. Furthermore, in MAL, Similar to SOSS observations, simultaneous increase in proportion of the plasticizers in MAL, in most cases, enhanced the seal integrity by reduction in recorded SIT and FTT. Despite SOSS results, increasing only one plasticizer also declined SIT and FTT values except for two small regions. For SIT, when SOR was higher than 11%, and for FTT, when SOR was bigger than

9%, adding more than 10% GLY inspired slightly reverse seal quality, represented by shifting back from dark blue toward light blue or green regions. Nevertheless, as the SOR percentage increased, both SIT and FTT dropped significantly (shifting toward dark blue). For instance, when GLY is 10%, adding SOR up to 20%, reduced SIT and FTT from 165 and 190 to 125 and 135 °C, respectively.

In contrast, a different sample containing 10% SOR and 20% GLY yielded better values for both SIT and FTT, measuring 140 °C and 170 °C, respectively. The findings from these samples highlighted the differential roles that SOR and GLY play in affecting the performance metrics. Specifically, SOR appeared to exert a more substantial influence on FTT, indicating that higher concentrations may meaningfully enhance the tackiness of the material. However, when it comes to SIT, the impact of SOR was less pronounced, suggesting that other factors might be more critical in determining seal integrity.

5.4.3 Chemical functional groups of the coating

Figure 5.4 illustrates the FTIR spectra for both neat SSOS and neat MAL.

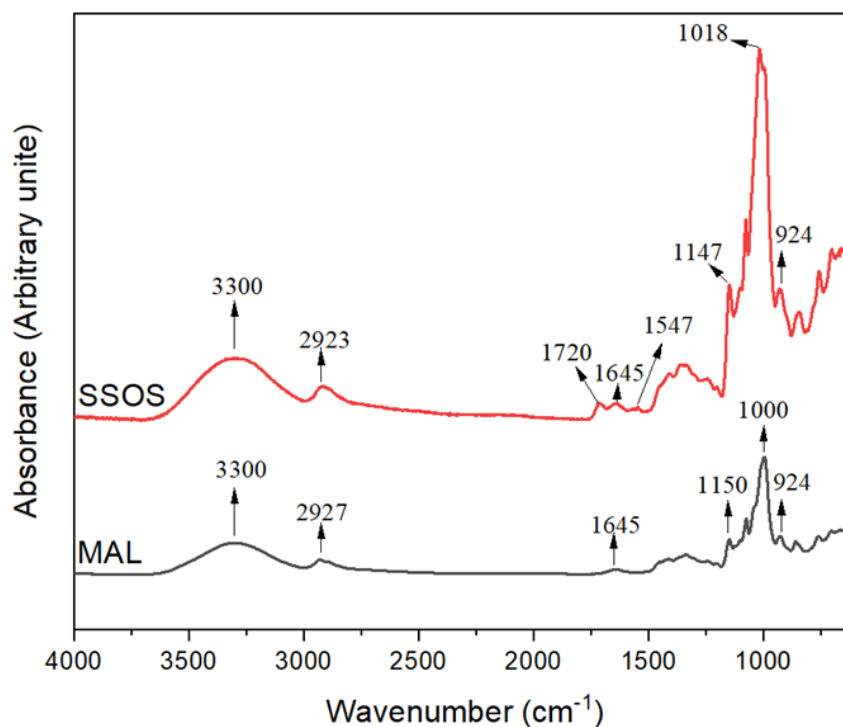


Figure 5.4 Fourier-transform infrared spectra (FTIR) obtained for the pure SSOS and MAL coatings.

In synthesis of SSOS, starch molecules undergo modification through the attachment of octenyl succinate groups, leading to formation of both an ester and a carboxyl group. This process involves the replacement of the hydroxyl groups present in the starch with ester carbonyl and carboxyl groups derived from octenyl succinic anhydride (OSA) [48, 49]. Conversely, in the production of MAL, starch undergoes degradation into smaller molecules without any substitution reactions [33].

As shown in figure 5.4, it is typical for many of the peaks observed in MAL and SSOS to exhibit similarities, as both substances were modified derivatives of starch. The absorption peaks associated with hydroxyl (OH) groups were observed at 3300 cm^{-1} in both SSOS and MAL. The peak at 2923 and 2927 cm^{-1} is linked to the C–H stretching vibration present in SSOS and MAL respectively [50-52]. Additionally, in both instances, the distinct bands observed at 924 cm^{-1} (in SSOS and MAL), 1147 cm^{-1} in SSOS, 1150 cm^{-1} in MAL, 1018 cm^{-1} in SSOS, and 1000 cm^{-1} in MAL are linked to the C–O stretching of C–O–C within the anhydroglucose ring, the C–O stretching of C–O–H groups, and the C–O stretching of C–O–C in the polysaccharide, respectively [53-55]. Moreover, in both cases, the band at 1645 cm^{-1} seemed to be linked to the bending vibration of water [53, 55].

SSOS and MAL displayed nearly identical spectra; however, two distinct peaks were identified in SSOS profile. Notably, the prominent peak at 1720 cm^{-1} is attributed to the C=O bond stretching vibration of an ester carbonyl group [49, 56]. Generally, the absorption attributed to carbonyl bonds in esters manifests as peaks within the spectral range of 1750 cm^{-1} , while carboxylic acids exhibit a singular band at 1712 cm^{-1} . Due to considerable overlap between these two bands, a consolidated peak emerges around 1718 cm^{-1} [57]. Furthermore, the band at 1547 cm^{-1} may be associated with the asymmetric stretching of the C=O bond in the carboxylate group (RCOO-) [54].

Therefore, these FTIR findings align with the theory suggested by Kim and Ustunol [28] through electron spectroscopy for chemical analysis (ESCA). They indicated that the increase in hydrogen and covalent bonds, particularly those involving C–O and could be the primary factors driving the formation of sealed joints in the films. As a result, pure SSOS demonstrated superior performance in SIT and FTT compared to MAL (as mentioned in Section 5.4.2).

Figure 5.5 illustrates the analysis of the effects of varying percentages of SOR and GLY on the coating solutions (SSOS and MAL) through normalized FTIR spectra ducted through the most intense peak ($\approx 1000\text{ cm}^{-1}$). The interactions between SOR, GLY, and SSOS are depicted in Figure

5.5(a), and those between SOR, GLY, and MAL, are shown in Figure 5.5(b). After adding plasticizers (SOR and GLY) to SSOS and MAL, two main variations in the normalized absorbance spectra are observed.

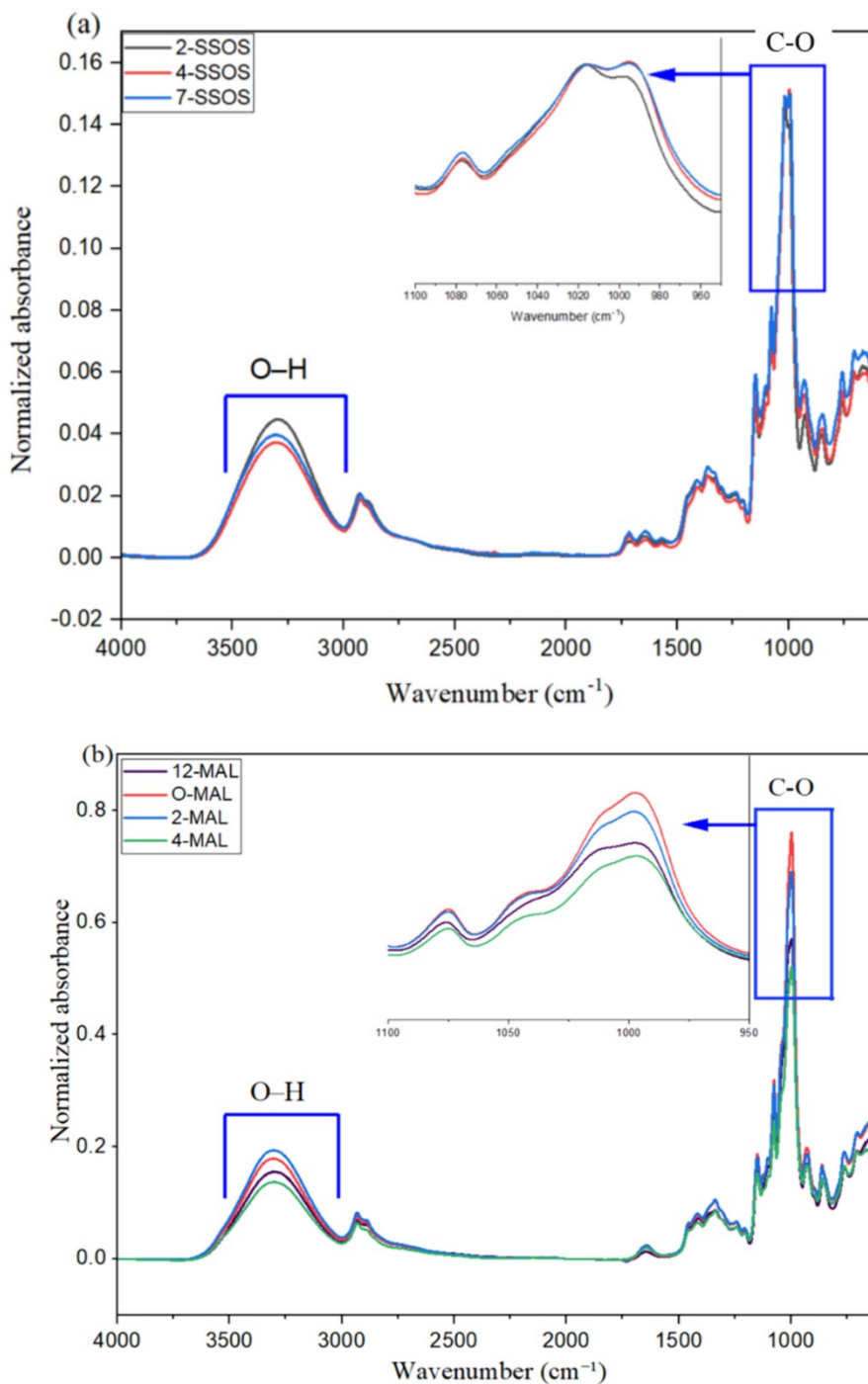


Figure 5.5 Normalized FTIR spectra for optimal, favorable, and unfavorable samples a) for SSOS family and b) for MAL family.

First, the one related to the O–H stretching vibration is observed in the range of 3000–3500 cm^{-1} (in SSOS and MAL families). A stronger O–H peak indicates a higher concentration of hydroxyl groups within the coatings. For instance, in SSOS case, intensity of O–H peak in O-SSOS is higher than 4-SSOS. Moreover, in MAL instance, in the region 3000–3500, increase of the absorbance signal in O-MAL and 2-MAL is more than 4-MAL.

The second variation involves C–O stretching vibrations, typically found in the range of 950–1000 cm^{-1} . Differences in the C–O peak intensity among the samples may stem from variations in the interactions between SOR and GLY with the samples.

A higher intensity could indicate stronger interactions that enhance the overall performance of the coatings. In O-MAL, the intensity was higher compared to the other samples, while in the SSOS samples, this area did not change significantly, suggesting that the O–H stretching had a more pronounced effect.

As previously mentioned, the differences in adhesion strengths of the films can be attributed to changes in functional groups, including hydroxyl, aldehyde, and carboxylic acids [58]. Consequently, the optimal samples demonstrate superior adhesion performance compared to the others (as discussed in Section 5.4.2). A similar phenomenon was reported in polyethylene films by Possart and Deckhoff, where improved seal strength was associated with increased chain interactions due to the incorporation of nitrogen- and oxygen-containing functional groups [59].

5.4.4 Rheology of coating solutions

Understanding of rheology is essential for optimizing seal performance [60]. Figure 5.6 reveals the investigation into the effects of varying percentages of SOR and GLY on steady rheology of the coating solutions (SSOS and MAL). The interactions among SOR, GLY, and SSOS, and those with MAL were depicted in Figure 5.6(a) and Figure 5.6(b), respectively.

Our observations elucidated a nonlinear relationship between viscosity and shear rate across all solutions. At low shear rates (approximately $<1\text{s}^{-1}$), the solutions exhibited shear-thinning behavior, transitioning to Newtonian fluid behavior at shear rates greater than 1s^{-1} . This result aligns with previous studies [61] likely due to changes in hydrogen bonding interactions among plasticizers, SSOS and MAL, during shear [62].

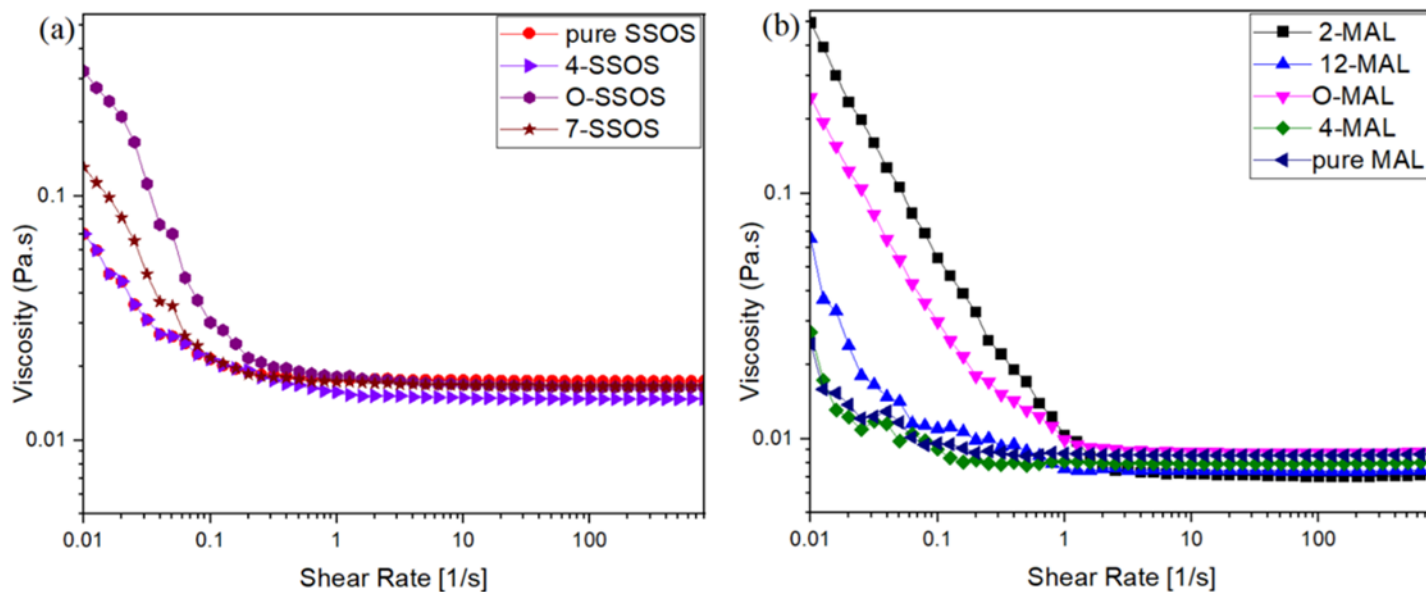


Figure 5.6 a) Viscosity behavior of coating solution of a) SSOS, and b) MAL.

In SSOS family (Fig. 5.6(a)) during low shear rates, the viscosity of pure SSOS and 4-SSOS were not significantly different (overlapped on each other). However, with increasing the percentage of plasticizer in O-SSOS and 7-SSOS, the viscosity raised, comparing to that of pure and 4-SSOS. This can be explained by the presence of hydroxyl groups on the outer surface of the amylose helices, which can establish hydrogen bonds through engagement with the hydroxyl groups of the plasticizers. Thus, this interaction enhances the hydrodynamic volume of the amylose molecules, leading to an increase in viscosity [63]. Furthermore, SSOS exhibits an amphiphilic structure, wherein the hydrophilic regions are capable of forming hydrogen bonds with water and plasticizers, while the hydrophobic segments facilitate the interactions that contribute to the formation of a structured network.

It seems that the carboxyl groups in SSOS interacted with glycerol, provoked increase in rigidity of the SSOS structure and consequently, elevating the viscosity of the system. Hence, a higher concentration of glycerol correlated with increased viscosity. This occurrence can be seen in viscosity enhancement from 7-SSOS with lower glycerol content (17.7%GLY) to O-SSOS with higher glycerol amount (20%GLY).

Having explored the rheological behavior of the SSOS family, MAL family was then examined. Similar to SSOS, the viscosity at low shear rates (Fig. 5.6(b)) shows minimal differences between pure MAL and 4-MAL. Nevertheless, higher percentage of the plasticizers led to an increase in viscosity confirmed by the positive correlation between sorbitol concentration and viscosity, more specifically for O-MAL and 2-MAL which exhibited the highest viscosities. Analogous to SSOS results, formation of hydrogen bonds between hydroxyl groups presents in the plasticizers and outer layer of the amylose helices, prompted the viscosity enhancement [63]. It is noteworthy that, due to non-amphiphilic nature of MAL, the amount of glycerol did not highly impact on viscosity as what was observed for SSOS data. Consequently, in the context of MAL, the overall amount of plasticizer was the most critical factor affecting viscosity.

The viscosity of sealant materials is a critical factor influencing sealing quality [64]. Rheological properties, such as the viscosity-shear rate relationship, play a pivotal role in optimizing seal performance by determining how the material flows and behaves under different mechanical conditions. Specifically, the viscosity vs. shear rate curves is crucial as they reveal the material's response to shear stresses, which directly impacts both application and sealing.

Our results indicated that both SSOS and MAL families generally exhibited low viscosity, which was advantageous for enhancing caulkability. Lower viscosity facilitates the filling of gaps and helps encapsulate contaminants, ensuring a more effective seal [60].

However, an exponential decrease in viscosity, as shown in the viscosity-shear rate curves, can lead to the squeeze-out phenomenon. Squeeze-out occurs when the material flows out of the seal area under applied pressure, compromising seal integrity and potentially causing defects in the sealing region [65]. This issue was evident in pure SSOS, MAL, 4-SSOS, and 4-MAL, where the viscosity was insufficient to resist squeeze-out during sealing.

In contrast, samples such as O-SSOS and 2-MAL and O-MAL demonstrated higher viscosities, which effectively prevented squeeze-out and maintained seal integrity under pressure. As a result, these samples showed improved performance in the SIT and FTT, underscoring the importance of rheological optimization (as discussed in Section 5.4.2).

5.4.5 Thermal studies

Increased mobility of polymer chains at the seal interface generally leads to higher seal strength [66]. T_g reflects the temperature dependence of molecular mobility [67, 68]. Hence, evaluation of T_g is vital to analyze the seal performance. Heat capacity change (ΔC_p) at the glass transition is another important parameter, as it can indicate the degree of molecular organization within the glass. Additionally, ΔC_p can reflect the nature of intermolecular interactions, including hydrogen bonds, within the glass [69]. Table 5.2 presents T_g and ΔC_p values for each analyzed sample.

Table 5.2 Glass transition (T_g) and heat capacity change (ΔC_p) for each sample.

	Sample name	T_g (°C)	ΔC_p (J g ⁻¹ °C ⁻¹)
SSOS	O-SSOS	64.32±2.0	0.60±0.06
	7-SSOS	68.14±1.2	0.58±0.02
	4-SSOS	74.80±1.8	0.53±0.01
MAL	O-MAL	54.29±0.7	0.66±0.03
	2-MAL	51.65±1.4	0.69±0.07
	12-MAL	64.73±2.2	0.62±0.06
	4-MAL	69.13±0.9	0.45±0.02

Based on the results, among the samples, 4-SSOS and 4-MAL, which are considered as the least favorable samples, exhibited the highest T_g values of 74.80±1.8 °C and 69.13±0.9 °C, respectively, along with the lowest ΔC_p values of 0.53±0.01 J g⁻¹ °C⁻¹ and 0.45±0.02 J g⁻¹ °C⁻¹, respectively. Notably, as the percentage of plasticizer increased in each sample, a corresponding decrease in T_g and an increase in ΔC_p were observed when compared to the values for 4-SSOS and 4-MAL. For instance, in O-SSOS sample, T_g and ΔC_p were 64.32±2.0 °C and 0.60±0.06 J g⁻¹ °C⁻¹, respectively. Similarly, the O-MAL also showed T_g and ΔC_p values of 54.29±0.7 °C and 0.66±0.03 J g⁻¹ °C⁻¹, respectively.

The incorporation of a plasticizer into the polymer matrix generally leads to a reduction in T_g and an increase in the free volume surrounding the polymer chains. In addition, plasticizers typically enhance the flexibility of stiff polymer chains, facilitating their diffusion [44].

The plasticizer acts as a lubricant, reducing frictional forces between the polymer chains and thereby enhancing the flexibility of the polymer films [70]. Mali et al. indicated that the addition of a plasticizer, such as glycerol or water, enhances the mobility of polymer chains, resulting in a decrease in T_g [71].

Regarding enhancement in mobility of the polymer chains and seal strength improvement as a result of reduction in T_g and rise in ΔC_p , therefore, the thermal observations are also consistent with our findings on sealing performance, particularly regarding SIT and FTT, as elaborated in Section 5.4.2.

5.4.6 Surface roughness measurement

Mechanical interlocking theory plays a crucial role in understanding the adhesion properties of paper, particularly in relation to surface roughness [72]. This theory posits that the physical anchoring of one material into the surface irregularities of another enhances adhesion by increasing the contact area and providing mechanical resistance to separation [73]. Elevated surface roughness improves adhesion performance by creating a larger surface area for bonding [74, 75].

Figure 5.7 (a and b) graphically illustrates the average surface roughness (R_a), and the root mean square roughness (R_q) of the produced coatings with SSOS and MAL on paper, as measured by the profilometer.

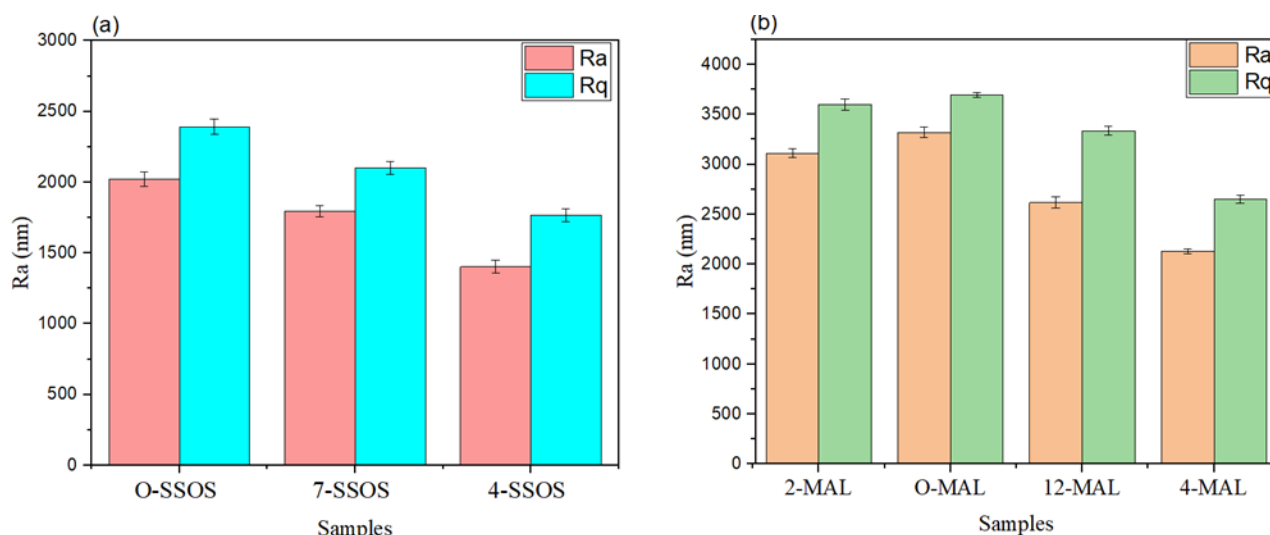


Figure 5.7 Average mean roughness (R_a) and Root mean square roughness (R_q) for SSOS samples (a) and MAL samples (b).

As shown in Figure 5.7 (a and b), the Ra and Rq values for 4-SSOS (Ra: 1402.97 ± 46.10 nm and Rq: 1767.29 ± 45.11 nm) and 4-MAL (Ra: 2131.01 ± 23.94 nm and Rq: 2653.02 ± 39.90 nm) as unfavorable samples were significantly lower than those of the other samples.

Conversely, the optimal formulations and favorable families exhibited the highest average surface roughness and root mean square roughness. This observation suggests that the optimal and favorable samples, which contained a higher concentration of plasticizer compared to 4-SSOS and 4-MAL, exhibited increased mobility of polymer chains due to the reduction of intermolecular forces. This enhanced mobility might result in a less ordered arrangement of the polymer matrix, leading to surface irregularities and increased roughness [76].

Owing to these findings, the samples with the highest Ra and Rq values, specifically, O-SSOS (Ra: 2024.10 ± 50.73 nm and Rq: 2392.58 ± 53.73 nm) were anticipated to demonstrate superior adhesion properties compared to 4-SSOS, which exhibits the lowest surface roughness. A similar trend was observed for O-MAL (Ra: 3320.12 ± 51.94 nm and Rq: 3696.45 ± 25.94 nm) and 2-MAL (Ra: 3110.37 ± 45.10 nm and Rq: 3599.13 ± 55.10 nm), which were also expected to show enhanced adhesion properties relative to 4-MAL.

Consequently, these findings were consistent with our sealing performance results, specifically adhesion strength (SIT and FTT, as discussed in Section 5.4.2), and aligned with previous research indicating that increased surface roughness enhances adhesion strength [74, 77].

5.4.7 Verification of adhesion: abrasion test and blocking resistance assessment

The main failure in printed packaging, like paper and laminates, is abrasion, which can result from both resonant frequencies and low-stress vibrations. This occurs when surfaces move against each other in a vibrating environment, leading to significant damage such as material wear and microflex cracks, particularly in food and medical device packaging [78]. Therefore, it is crucial to evaluate coatings on paper, as effective coatings can enhance the durability and longevity of packaging. The assessment of coating performance under conditions of mechanical damage and abrasion was conducted through the measurement of wear index (I). Figure 5.8 illustrates the wear index for optimal, favorable, and unfavorable samples.

Generally, a reduced wear index signifies enhanced resistance to abrasion. As indicated in Fig. 5.8, SSOS family demonstrated better performance in terms of abrasion resistance compared to MAL

family. Research indicates that hybrid materials can enhance abrasion resistance [79]. Furthermore, the optimal samples in both SSOS and MAL showed a greater capacity to withstand a higher number of abrasion cycles before failure. For instance, the wear index for O-SSOS was 3.25 ± 0.25 , while for 4-SSOS, it was 6.53 ± 0.48 . This suggests that an increased percentage of plasticizer improved abrasion performance.

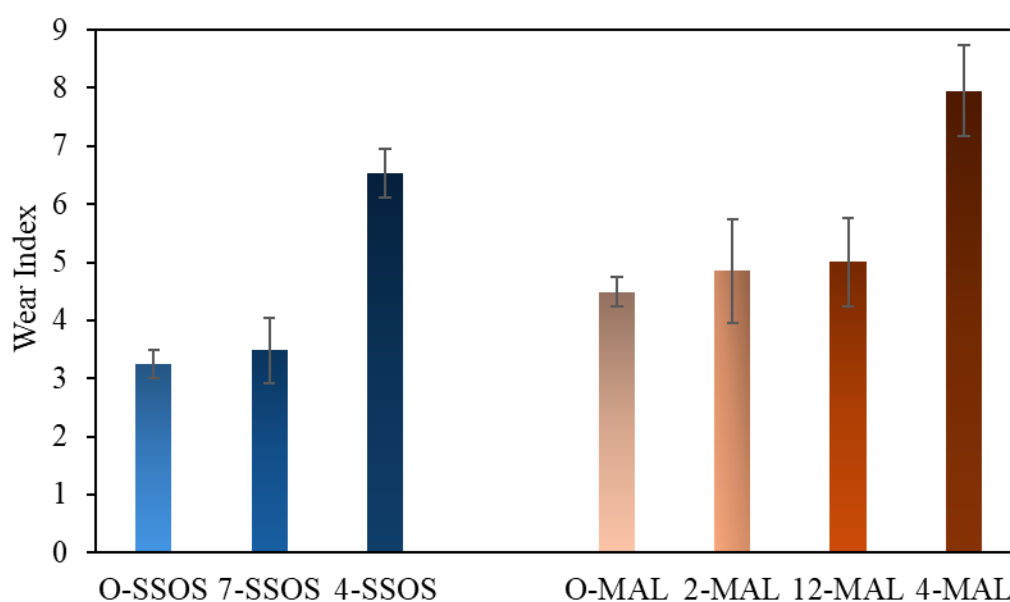


Figure 5.8 Wear index for optimal, favorable, and unfavorable samples.

Conversely, no significant difference was observed between the optimal and favorable samples. For example, in the case of MAL, the wear indices were 4.49 ± 0.26 for O-MAL and 4.85 ± 0.89 for 2-MAL, respectively.

Blocking presents a critical challenge in the realm of coated paper packaging. This phenomenon involves the unintended adhesion of two surfaces, which can occur in coated paperboard under certain conditions, particularly when temperature and pressure are conducive to such interactions [80]. The results showed that not only did the optimal samples (O-SSOS and O-MAL) and the favorable samples (7-SSOS, 2-MAL, and 12-MAL) pass the blocking resistance test, but the unfavorable samples (4-SSOS and 4-MAL) also achieved successful outcomes. There was no evidence of adhesion or cohesion between the adjacent surfaces (coated sides facing each other and then the coated side against the uncoated side) in both relative humidity conditions (21% and 60%).

This suggests that all specimens effectively maintained their quality during manufacturing and storage, thus highlighting a low risk of damage or deterioration.

5.4.8 Effect of pressure and dwell time of sealing for optimal formulation

Multiple factors, such as dwell time and pressure affect the efficiency of heat sealing. Final sealing properties can be optimized by managing and modifying these two parameters [81]. Since processing time is a factor that affects costs, identifying the minimum dwell time required for the sealing process is crucial [64]. In fact, it is essential to identify an optimal dwell time that guarantees a robust seal while also facilitating a high production rate for any specific application [65]. It is important to highlight that all the tests conducted in this section utilized dwell times of 0.5, 1, and 1.5 seconds (500, 1000 and 1500 ms).

Figures 5.9 (a, b, c and d) displays SIT and FTT change in different dwell times under three pressures of 40, 70, and 140 psi for optimal samples (O-SSOS and O-MAL).

Except under 140 psi, both SIT and FTT decreased with longer dwell times (at constant pressure), as this promoted the development of entanglements within the material. This observation suggests that extended dwell times allow for greater molecular interaction and alignment, which can enhance the overall sealing properties [64].

For instance, in the case of O-SSOS at 70 psi pressure, increasing the dwell time from 0.5 to 1.5 seconds significantly dropped both SIT (115 to 100 °C) and FTT (125 to 115 °C). In addition, when examining O-MAL at the same pressure, extending the dwell time from 0.5 seconds to 1.5 seconds remarkably impacted SIT, decreased from 105°C to 90°C, and the FTT, which dropped from 115°C to 100°C. As noted by Najarzadeh et al. and Ajji, there is a linear relationship between seal strength and the square root of dwell time. Additionally, the slope of the graph plotting $t^{(1/2)}$ against seal strength tends to rise when sealing occurs at elevated temperatures. This indicates that higher temperature levels lead to achieving maximum seal strength more rapidly [82].

Conversely, at high pressure (140 psi), variations in dwell time do not influence the SIT and FTT for both optimal samples. For instance, in the case of O-MAL, increasing the dwell time from 0.5 to 1.5 seconds neither affected SIT, remained at 90°C across all three dwell times, nor the FTT, stayed constant at 100°C for the same durations.

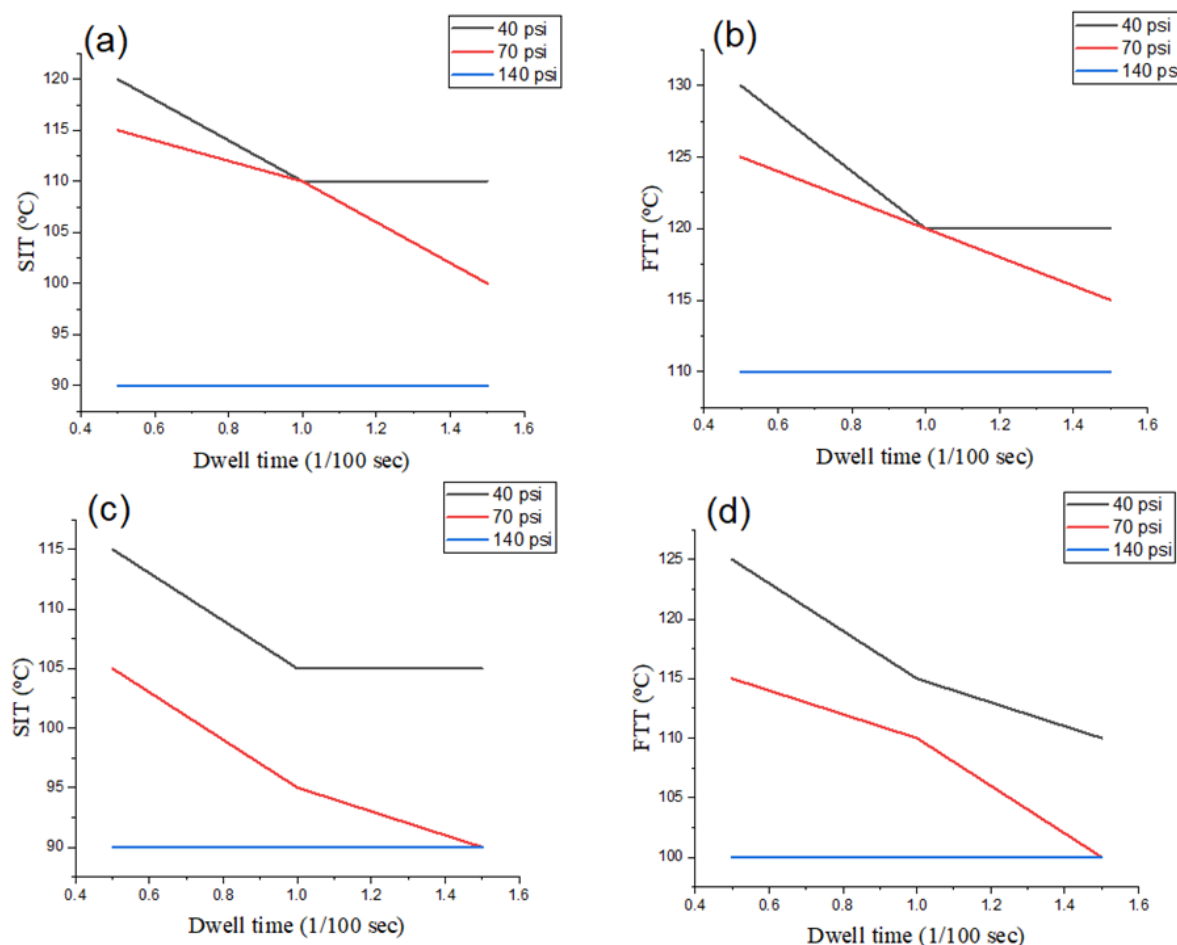


Figure 5.9 a) SIT and b) FTT for SSOS samples, c) SIT and d) FTT for MAL samples illustrating as functions of dwell time at varying pressures (40 psi, 70 psi, and 140 psi).

Sealing pressure is essential for ensuring that the seal layers are brought into close contact, allowing them to overcome any microroughness present on the surfaces. This process improves wetting and facilitates molecular diffusion at the interface [83]. As shown in Figures 5.9 (a, b, c and d), raising the pressure for both O-SSOS and O-MAL led to some alterations in SIT and FTT. For O-MAL, at dwell time of 1.5 seconds, increasing the pressure from 40 to 70 psi resulted in a decrease in SIT from 105°C to 90°C and in FTT from 110°C to 100°C. A comparable pattern was seen with O-SSOS, where the SIT and FTT decreased from 110°C to 100°C and from 120°C to 115°C, respectively. Previous research demonstrated that elevating sealing pressure from a very low baseline reduces the seal initiation temperature [82].

In contrast, at higher pressures, there was no effect on SIT and FTT in both scenarios. Many studies indicated that increasing sealing pressure beyond the optimal level adequate for achieving complete contact between layers does not significantly influence sealing temperature or strength [84, 85]. This can be explained by a decrease in free volume under compression, which may restrict chain movement. Therefore, during the interdiffusion phase, raising the pressure does not promote entanglement or improve mechanical strength in sealing [82].

5.5 Conclusion

This study conducted a comprehensive examination on development and characterization of home compostable, heat-sealable coatings for paper-based flexible packaging. Unmodified starches (such as MBS, SPS, TS) and modified starches like SSOS and MAL, were utilized combined with plasticizers such as sorbitol and glycerol. In the first step, using the unmodified starches due to their high energy demand for dissolution, instability, and exhibition of poor adhesion, led to detachment and residue on paper surfaces; therefore, they were not considered suitable for coating on paper. In the next step, it concluded that varying levels of SOR and GLY in SSOS and MAL coatings significantly influenced SIT and FTT. In SSOS, GLY had a stronger impact on SIT, while in MAL, SOR notably improved tackiness, highlighting their crucial roles in optimizing seal performance.

In the third step, the experimental approach employed a variety of analytical techniques to assess the physical and chemical properties of the optimal, favorable, and unfavorable coating formulations for SSOS and MAL. Techniques such as FTIR, DSC, rheological characterization and surface roughness provided a comprehensive understanding of how these coatings perform under different conditions. Increased O–H and C–O peak intensities were observed in the FTIR spectrum, particularly in O-SSOS and O-MAL compared to other samples. The DSC test demonstrated less favorable properties for samples with higher T_g and lower ΔC_p , like 4-SSOS and 4-MAL owing to restricted polymer chain mobility and higher molecular organization. In contrast, samples such as O-SSOS and O-MAL, with lower T_g and higher ΔC_p , showed improved seal performance thanks to increased chain mobility and flexibility. Roughness investigation revealed that samples with higher plasticizer concentrations, such as O-SSOS and O-MAL, had increased polymer chain mobility, resulting in a less ordered matrix and greater surface roughness.

In the fourth step, the impact of processing parameters, specifically pressure and dwell time, on heat sealing for optimal samples was analyzed. The results indicated that optimizing these parameters was crucial for effective heat sealing. The tests demonstrated longer dwell times generally reduced the SIT and FTT because of enhanced molecular interactions, except at high pressure (140 psi), where dwell time had no effect. Additionally, pressure increase improved sealing by ensuring better contact between layers; however, beyond a certain threshold, further increases in pressure did not significantly affect the sealing performance. Therefore, this study highlighted home compostable coatings as a sustainable alternative to plastic packaging through heat sealability improvement and reliance reduction on non-degradable materials. This advancement supports eco-friendly packaging and sets the stage for further research and commercialization in the packaging industry.

5.6 References

1. Zhang, M., et al., Recent advances in polymers and polymer composites for food packaging. *Materials Today*, 2022. 53: p. 134-161.
2. Vignali, G., Life-cycle assessment of food-packaging systems. *Environmental Footprints of Packaging*, 2016: p. 1-22.
3. Robertson, G., Legislative and Safety Aspects of food packaging. *Food Packaging, Principles and Practices*; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2013.
4. Kan, M. and S.A. Miller, Environmental impacts of plastic packaging of food products. *Resources, Conservation and Recycling*, 2022. 180: p. 106156.
5. Geyer, R., J.R. Jambeck, and K.L. Law, Production, use, and fate of all plastics ever made. *Science advances*, 2017. 3(7): p. e1700782.
6. Thurber, H. and G.W. Curtzwiler, Suitability of poly (butylene succinate) as a coating for paperboard convenience food packaging. *International Journal of Biobased Plastics*, 2020. 2(1): p. 1-12.
7. <https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/containers-and-packaging-product-specific>. 2023.

8. Yin, Y. and M.W. Woo, Transitioning of petroleum-based plastic food packaging to sustainable bio-based alternatives. *Sustainable Food Technology*, 2024. 2(3): p. 548-566.
9. Henry, T., Suitability of poly (butylene succinate) as a coating for paperboard convenience food packaging. 2020.
10. Shi, S.-C., S.-W. Ouyang, and D. Rahmadiawan, Erythrosine–Dialdehyde Cellulose Nanocrystal Coatings for Antibacterial Paper Packaging. *Polymers*, 2024. 16(7): p. 960.
11. Deshwal, G.K., N.R. Panjagari, and T. Alam, An overview of paper and paper based food packaging materials: health safety and environmental concerns. *Journal of food science and technology*, 2019. 56: p. 4391-4403.
12. Hauptmann, M., et al., The effect of flexible sealing jaws on the tightness of pouches made from mono-polyolefin films and functional papers. *Packaging Technology and Science*, 2021. 34(3): p. 175-186.
13. Helanto, K., R. Talja, and O.J. Rojas, Mineral-filled biopolyester coatings for paperboard packaging materials: barrier, sealability, convertability and biodegradability properties. *Nordic Pulp & Paper Research Journal*, 2022. 37(1): p. 212-221.
14. Aloui, H., et al., Effect of glycerol and coating weight on functional properties of biopolymer-coated paper. *Carbohydrate polymers*, 2011. 86(2): p. 1063-1072.
15. Dixon, J., *Packaging materials: 9. multilayer packaging for food and beverages*. 2011.
16. Raźniewska, M., Compostable packaging waste management—Main barriers, reasons, and the potential directions for development. *Sustainability*, 2022. 14(7): p. 3748.
17. Folino, A., et al., Biodegradation of wasted bioplastics in natural and industrial environments: A review. *Sustainability*, 2020. 12(15): p. 6030.
18. Rujnić Havstad, M., et al., Influence of home composting on tensile properties of commercial biodegradable plastic films. *Polymers*, 2021. 13(16): p. 2785.
19. Colón, J., et al., Environmental assessment of home composting. *Resources, Conservation and Recycling*, 2010. 54(11): p. 893-904.
20. Jasim, S., *The practicability of home composting for the management of biodegradable domestic solid waste*. 2003, Imperial College London (University of London).

21. Ligon, P.J. and G. Garland, Analyzing the costs of composting strategies. 1998.
22. McGovern, A., Home composting makes major impact. *BioCycle (USA)*, 1997. 38(12).
23. Yao, S., B.-J. Wang, and Y.-M. Weng, Preparation and characterization of mung bean starch edible films using citric acid as cross-linking agent. *Food Packaging and Shelf Life*, 2022. 32: p. 100845.
24. Ngo, T.M.P., et al., Effects of zinc oxide nanoparticles on the properties of pectin/alginate edible films. *International Journal of Polymer Science*, 2018. 2018.
25. Lim, W.S., et al., Heat-sealing property of cassava starch film plasticized with glycerol and sorbitol. *Food Packaging and Shelf Life*, 2020. 26: p. 100556.
26. Guazzotti, V., et al., Bio-based coatings as potential barriers to chemical contaminants from recycled paper and board for food packaging. *Food Additives & Contaminants: Part A*, 2014. 31(3): p. 402-413.
27. Apriyanto, A., J. Compart, and J. Fettke, A review of starch, a unique biopolymer—Structure, metabolism and in planta modifications. *Plant Science*, 2022. 318: p. 111223.
28. Li, H., et al., Starch and its derivatives for paper coatings: A review. *Progress in Organic Coatings*, 2019. 135: p. 213-227.
29. Nechita, P. and M. Roman, Review on polysaccharides used in coatings for food packaging papers. *Coatings*, 2020. 10(6): p. 566.
30. Kushwaha, R. and D. Kaur, Recent techniques used in modification of starches: A review. *Food Technology From Health to Wealth & Future Challenges*; Bharti Publication: Delhi, India, 2018: p. 1-15.
31. Jin, Y., J.Z. Li, and A.M. Nik, Starch-based microencapsulation, in *Starch in food*. 2018, Elsevier. p. 661-690.
32. Sweedman, M.C., et al., Structure and physicochemical properties of octenyl succinic anhydride modified starches: A review. *Carbohydrate polymers*, 2013. 92(1): p. 905-920.
33. Parikh, A., S. Agarwal, and K. Raut, A review on applications of maltodextrin in pharmaceutical industry. *system*, 2014. 4(6).

34. Dziedzic, S. and M. Kearsley, Handbook of starch hydrolysis products and their derivatives. 2012: Springer Science & Business Media.
35. Suh, J.H., et al., Effect of moisture content on the heat-sealing property of starch films from different botanical sources. *Polymer Testing*, 2020. 89: p. 106612.
36. Jiménez, A., et al., Phase transitions in starch based films containing fatty acids. Effect on water sorption and mechanical behaviour. *Food Hydrocolloids*, 2013. 30(1): p. 408-418.
37. Basiak, E., A. Lenart, and F. Debeaufort, How glycerol and water contents affect the structural and functional properties of starch-based edible films. *Polymers*, 2018. 10(4): p. 412.
38. Alves, V.D., et al., Effect of glycerol and amylose enrichment on cassava starch film properties. *Journal of Food Engineering*, 2007. 78(3): p. 941-946.
39. Rompothi, O., et al., Development of non-water soluble, ductile mung bean starch based edible film with oxygen barrier and heat sealability. *Carbohydrate polymers*, 2017. 157: p. 748-756.
40. Muscat, D., et al., Comparative study of film forming behaviour of low and high amylose starches using glycerol and xylitol as plasticizers. *Journal of Food Engineering*, 2012. 109(2): p. 189-201.
41. Abdorreza, M.N., L. Cheng, and A. Karim, Effects of plasticizers on thermal properties and heat sealability of sago starch films. *Food hydrocolloids*, 2011. 25(1): p. 56-60.
42. Kanani Aghkand, Z., Effect of Sealant Structure and Sealing Condition on Heat Sealing Performance of Polyethylene Films. 2021, Polytechnique Montréal.
43. Herrera, N., et al., Functionalized blown films of plasticized polylactic acid/chitin nanocomposite: Preparation and characterization. *Materials & Design*, 2016. 92: p. 846-852.
44. Morris, B.A., 7 - Heat Seal, in *The Science and Technology of Flexible Packaging*, B.A. Morris, Editor. 2017, William Andrew Publishing: Oxford. p. 181-257.
45. Morris, B.A., *The science and technology of flexible packaging: multilayer films from resin and process to end use*. 2022: William Andrew.
46. Frihart, C.R., *Adhesive bonding and performance testing of bonded wood products*. 2005.

47. Kavčič, U., G. Lavrič, and I. Karlovits, Alternative Fiber-Based Paperboard Adhesion Evaluation with T-and Y-Peel Testing. *Applied Sciences*, 2023. 13(17): p. 9779.
48. Zhang, J., et al., Impact of octenyl succinic anhydride (OSA) esterification on microstructure and physicochemical properties of sorghum starch. *LWT*, 2021. 152: p. 112320.
49. Abiddin, N.Z., A. Yusoff, and N. Ahmad, Effect of octenylsuccinylation on physicochemical, thermal, morphological and stability of octenyl succinic anhydride (OSA) modified sago starch. *Food Hydrocolloids*, 2018. 75: p. 138-146.
50. Durmus, Y., et al., Physical, Barrier, Mechanical, and Biodegradability Properties of Modified Starch Films with Nut By-Products Extracts. 2020.
51. Vargas-Muñoz, D.P. and L.E. Kurozawa, Influence of combined hydrolyzed collagen and maltodextrin as carrier agents in spray drying of cocona pulp. *Brazilian Journal of Food Technology*, 2020. 23: p. e2019254.
52. Lai, W., et al., Preparation and evaluation of microcapsules containing *Rimulus Cinnamon* and *Angelica Sinenis* essential oils. *Journal of Dispersion Science and Technology*, 2023. 44(14): p. 2639-2650.
53. Wu, D.D., et al., Preparation and characterization of maltodextrin-based polyurethane. *Carbohydrate Polymers*, 2018. 194: p. 236-244.
54. Leon-Bejarano, M., et al., Physical, barrier, mechanical, and biodegradability properties of modified starch films with nut by-products extracts. *Foods*, 2020. 9(2): p. 226.
55. Wang, Y., et al., Octenyl succinic acid starch-stabilized vanilla essential oil pickering emulsion: preparation, characterization, antioxidant activity, and storage stability. *Foods*, 2022. 11(7): p. 987.
56. Lai, C., et al., Effects of different alcohol and ultrasonic treatments on thermal and structural properties of zein-starch sodium octenyl succinate composite nanoparticles. *Journal of Food Science*, 2021. 86(8): p. 3574-3588.
57. Mohammadi, S., S. Abbasi, and M. Scanlon, Development of emulsifying property in Persian gum using octenyl succinic anhydride (OSA). *International Journal of Biological Macromolecules*, 2016. 89: p. 396-405.

58. López, O.V., et al., Biodegradable packages development from starch based heat sealable films. *Journal of Food Engineering*, 2011. 105(2): p. 254-263.
59. Possart, W. and S. Dieckhoff, Adhesion mechanisms in a cyanurate prepolymer on silicon and on aluminium. *International Journal of adhesion and adhesives*, 1999. 19(6): p. 425-434.
60. Bamps, B., M. Buntinx, and R. Peeters, Seal materials in flexible plastic food packaging: A review. *Packaging Technology and Science*, 2023. 36(7): p. 507-532.
61. Du, Q., et al., Whey protein and maltodextrin-stabilized oil-in-water emulsions: Effects of dextrose equivalent. *Food Chemistry*, 2021. 339: p. 128094.
62. Cao, L., et al., An edible oil packaging film with improved barrier properties and heat sealability from cassia gum incorporating carboxylated cellulose nano crystal whisker. *Food hydrocolloids*, 2020. 98: p. 105251.
63. Mantzari, G., S.N. Raphaelides, and S. Exarhopoulos, Effect of sorbitol addition on the physicochemical characteristics of starch–fatty acid systems. *Carbohydrate Polymers*, 2010. 79(1): p. 154-163.
64. Ilhan, I., et al., Understanding the factors affecting the seal integrity in heat sealed flexible food packages: A review. *Packaging technology and science*, 2021. 34(6): p. 321-337.
65. Ajji, A., et al., Heat Sealing in Packaging: Materials and Process Considerations. 2023: Walter de Gruyter GmbH & Co KG.
66. Rakesh, P.K. and J.P. Davim, *Polylactic Acid Composites: Sustainable Biocomposites*. Vol. 18. 2023: Walter de Gruyter GmbH & Co KG.
67. Moynihan, C.T., Correlation between the width of the glass transition region and the temperature dependence of the viscosity of high-T_g glasses. *Journal of the American Ceramic Society*, 1993. 76(5): p. 1081-1087.
68. Hancock, B.C., et al., A pragmatic test of a simple calorimetric method for determining the fragility of some amorphous pharmaceutical materials. *Pharmaceutical research*, 1998. 15: p. 762-767.
69. Selmin, F., et al., Aminoacids as non-traditional plasticizers of maltodextrins fast-dissolving films. *Carbohydrate polymers*, 2015. 115: p. 613-616.

70. Cadogan, D.F. and C.J. Howick, Plasticizers. Kirk-Othmer Encyclopedia of Chemical Technology, 2000.
71. Mali, S., et al., Effects of controlled storage on thermal, mechanical and barrier properties of plasticized films from different starch sources. Journal of food engineering, 2006. 75(4): p. 453-460.
72. Vähä-Nissi, M. and J. Kuusipalo, Wetting and adhesion in paper and paperboard converting, in Paper and paperboard converting. Papermaking science and technology series, book 12. 1998. p. 24-59.
73. Allen, K., Current theories of adhesion and their relevance to adhesive technology. Le Journal de Physique IV, 1993. 3(C7): p. C7-1511-C7-1516.
74. Sanchis, M., et al., Surface modification of low density polyethylene (LDPE) film by low pressure O₂ plasma treatment. European Polymer Journal, 2006. 42(7): p. 1558-1568.
75. Paul, S., Physico-chemical interpretation of paint film adhesion. 1982.
76. Ucpinar Durmaz, B. and A. Aytac, Effects of polyol-based plasticizer types and concentration on the properties of polyvinyl alcohol and casein blend films. Journal of Polymers and the Environment, 2021. 29(1): p. 313-322.
77. Steffnec, N.O.E., R. Dickson, and P. LePoutre, Mechanical interlocking in coated paper. Nordic Pulp & Paper Research Journal, 1995. 10(1): p. 80-82.
78. Ge, C. and L. Pan, Vibration damage rate curves for quantifying abrasion of printed packaging in accelerated random vibration test. Packaging Technology and Science, 2018. 31(2): p. 71-81.
79. Wang, J., Y. Zhu, and Y. Fu, Abrasion resistance of biaxially oriented polypropylene films coated with nanocomposite hard coatings. Applied surface science, 2013. 285: p. 697-701.
80. Riekkki, A., Oil and grease resistant paperboard-factors affecting barrier properties and an evaluation of the test methods. 2019.
81. Sadeghi, A., et al., Heat-sealing properties of polylactic acid and polylactic acid composites. 2024.

82. Najarzadeh, Z. and A. Ajji, A novel approach toward the effect of seal process parameters on final seal strength and microstructure of LLDPE. *Journal of Adhesion Science and Technology*, 2014. 28(16): p. 1592-1609.
83. Theller, H., Heatsealability of flexible web materials in hot-bar sealing applications. *Journal of Plastic Film & Sheeting*, 1989. 5(1): p. 66-93.
84. Nase, M., et al., Adhesive properties of heat-sealed EVAc/PE films in dependence on recipe, processing, and sealing parameters. *Journal of Adhesion Science and Technology*, 2014. 28(12): p. 1149-1166.
85. Yuan, C. and A. Hassan, Effect of bar sealing parameters on OPP/MCPP heat seal strength. *Express Polym Lett*, 2007. 1(11): p. 773-779.

CHAPTER 6 GENERAL DISCUSSIONS

The global shift towards sustainable practices has placed significant emphasis on developing alternatives to conventional petroleum-based packaging materials. Biodegradable coatings, particularly those derived from renewable resources, have emerged as promising candidates in addressing environmental concerns and reducing plastic waste. This study focuses on the development and evaluation of home-compostable, heat-sealable coatings for paper-based flexible packaging, exploring their potential to replace traditional plastic-based solutions.

This study explored the development and evaluation of home-compostable, heat-sealable coatings for paper-based flexible packaging using modified starches (SSOS and MAL) in combination with plasticizers such as SOR and GLY. The findings represent a significant step toward sustainable packaging solutions, offering practical contributions and insights into future research and applications.

The research has several main contributions to the advancement of sustainable packaging technology. Firstly, it provides a viable alternative to conventional plastic coatings by introducing home-compostable solutions that enhance the heat sealability of paper-based packaging. By employing CCD and RSM, the study identified optimal formulations, such as 10% SOR and 20% GLY for SSOS, and 20% SOR and 5% GLY for MAL. These formulations successfully minimized SIT and FTT. Additionally, the coatings improved sealing performance, adhesion, and flexibility of the paper substrates, demonstrating their potential for food packaging applications. Furthermore, the study integrated rheological, thermal, and chemical analyses, providing a comprehensive understanding of the factors influencing seal performance.

The formulations developed in this study have potential applicability to existing paper-based packaging systems, though several considerations must be addressed. While the optimized coatings demonstrated promising heat-sealing properties and biodegradability under home composting conditions, further testing is required to ensure compliance with industry standards for barrier properties, mechanical strength, and food safety. The viscosity and thermal behavior of the coatings suggest they can integrate well with industrial coating techniques such as bar coating and drying; however, scalability and long-term storage stability need to be validated. Additionally, while the coatings enhance sealing, they may not fully meet the moisture and gas barrier requirements of

certain applications without additional modifications or layering with other biodegradable materials.

The study also faced challenges and limitations that highlight areas for improvement and guide future research. Some formulations exhibited high SIT and FTT values, limiting their practical applicability. The initial use of unmodified starches demonstrated insufficient adhesion and structural integrity, emphasizing the necessity of chemical modification. The interplay between SOR and GLY concentrations required extensive statistical modeling, underscoring the complexity of achieving optimal sealing properties. Moreover, the variability in home composting conditions may influence the degradation rates of the coatings.

While this study demonstrates significant progress, a critical review reveals areas that require further attention. The combination of experimental design and advanced characterization techniques provided robust and reproducible results. The coatings achieved substantial reductions in SIT and FTT, enhancing sealing performance while maintaining compostability. This aligns with global sustainability goals by contributing to plastic waste reduction. However, limited exploration of multilayered or hybrid coating systems to address moisture and gas permeability remains a weakness. Challenges in maintaining uniform coating thickness and adhesion on industrial scales also pose potential issues. Additionally, the study primarily focused on sealing properties, with less emphasis on mechanical durability and compatibility with various paper grades.

Despite these challenges, the project provided invaluable insights into the development of sustainable packaging solutions. The findings emphasized the critical role of precise material design in achieving both functional and environmental objectives. By combining experimental results with industrial feedback, the study highlighted the potential for starch-based coatings to replace conventional plastic coatings while meeting stringent environmental regulations. However, it also became clear that successful implementation at scale would require addressing the identified challenges through collaborative efforts with industrial stakeholders and further refinement of the formulations.

Future work and recommendations will be explored in detail in the next chapter, where an in-depth discussion of potential advancements, scaling strategies, and industrial applications will be presented.

CHAPTER 7 CONCLUSION AND RECOMMENDATIONS

7.1 Conclusions

This study provided a thorough investigation into the development and characterization of home compostable, heat-sealable coatings for paper-based flexible packaging. By employing both unmodified and modified starches, such as SSOS and MAL, in combination with plasticizers like sorbitol SOR and GLY, the research thoroughly evaluated the potential of these materials to enhance the seal performance of packaging.

Initially, unmodified starches were found unsuitable due to their high energy demands, instability, and poor adhesion, leading to detachment and residue on paper surfaces.

The focus then shifted to modified starches, where the levels of SOR and GLY in SSOS and MAL coatings were shown to significantly influence the SIT and FTT. Through a designed experimental framework using CCD and RSM, the use of plasticizers, SOR and GLY, was assessed to improve sealing properties. The optimal formulation for SSOS involved 10% SOR and 20% GLY, achieving a SIT of 120 °C and an FTT of 147 °C. For MAL, the ideal formulation was 20% SOR and 5% GLY, with SIT and FTT values of 112 °C and 125 °C, respectively. These conditions were validated through PI following by single confirmation runs and CI around mean of multiple confirmation runs, verifying that the experimental outcomes fell within the predicted intervals, thereby demonstrating the model's reliability and accuracy.

Statistical analyses revealed significant effects of the plasticizers on SIT and FTT, with high correlation coefficients ($R^2 = 0.89$ for SIT and 0.86 for FTT in SSOS, and $R^2 = 0.88$ for SIT and 0.93 for FTT in MAL), indicating robust predictive capabilities. The adjusted R-squared values further supported the models' explanatory power, with 85% and 81% of the variability in SIT and FTT for SSOS, and 92% for FTT in MAL, were accounted for by the independent variables. The low coefficients of variation (CV%), with values of 4.825% and 4.636% for SIT and FTT in SSOS, and 7.390% and 5.652% for SIT and FTT in MAL, obtained in this study indicated the high precision and reproducibility of the experimental design.

In the next step, the experimental approach employed a variety of analytical techniques to assess the physical and chemical properties of the optimal, favorable, and unfavorable coating

formulations for SSOS and MAL. Techniques such as FTIR, DSC, rheological characterization and surface roughness provided a comprehensive understanding of how these coatings perform under different conditions. Increased O–H and C–O peak intensities were observed in the FTIR spectrum, particularly in O-SSOS and O-MAL compared to other samples. The DSC test demonstrated less favorable properties for samples with higher T_g and lower ΔC_p , like 4-SSOS and 4-MAL owing to restricted polymer chain mobility and higher molecular organization. In contrast, samples such as O-SSOS and O-MAL, with lower T_g and higher ΔC_p , showed improved seal performance thanks to increased chain mobility and flexibility. Roughness investigation revealed that samples with higher plasticizer concentrations, such as O-SSOS and O-MAL, had increased polymer chain mobility, resulting in a less ordered matrix and greater surface roughness.

Moreover, the impact of processing parameters, specifically pressure and dwell time, on heat sealing for optimal samples was analyzed. The results indicated that optimizing these parameters was crucial for effective heat sealing. The sets demonstrated longer dwell times generally reduced the SIT and FTT because of enhanced molecular interactions, except at high pressure (140 psi), where dwell time had no effect. Additionally, pressure increase improved sealing by ensuring better contact between layers; however, beyond a certain threshold, further increases in pressure did not significantly affect the sealing performance.

These findings highlighted the potential of the modified starch coatings to serve as sustainable alternatives to traditional plastic packaging. The interactions between plasticizer concentrations and sealing performance provided a valuable foundation for future research and commercial applications, promoting the development of packaging solutions that are both environmentally friendly and functionally robust. Overall, this research contributed significantly to advancing sustainable packaging technologies in the food industry, aligned with global sustainability purposes.

7.2 Recommendations

The following areas could be explored in future studies:

- It is recommended to explore the performance of these coatings on a variety of paper and paperboard types. This will ensure their broad applicability across diverse packaging requirements and industries.
- Investigating the mechanical properties of these coatings when applied to paper-based packaging materials is crucial. This will help assess their durability, strength, and overall suitability for protecting the contents.
- Conducting long-term studies to evaluate the compostability rates of these coatings in both industrial and home composting environments is highly recommended. These studies will provide valuable data on their environmental impact and degradation rates.
- It is important to test the optimal formulations on various food products.
- A comprehensive life cycle assessment (LCA) should be conducted to quantify the environmental impact of these coatings. Comparing the environmental footprint of these coatings with traditional plastics and other biodegradable alternatives will provide critical insights for future improvements and informed policy decisions.
- Studying the biodegradation of the coatings through microbial activity, including the types of microorganisms that affect the coatings, could provide a more detailed understanding of their environmental impact.
- Examining the effect of different relative humidity (RH) levels on SIT and FTT for the optimal formulations.

Declaration of AI and AI-assisted technologies in the writing process

In the preparation of this work, the authors utilized Chat-GPT to rephrase and summarize certain texts. Following the use of this tool, the author thoroughly reviewed and edited the content as necessary and accepted full responsibility for the thesis content.

REFERENCES

1. Deshwal, G.K., N.R. Panjagari, and T. Alam, *An overview of paper and paper based food packaging materials: health safety and environmental concerns*. Journal of food science and technology, 2019. 56: p. 4391-4403.
2. Fauza, A.N., et al., *The influence of processing temperature on the mechanical properties of recycled PET fibers*. Teknomekanik, 2023. 6(1): p. 21-28.
3. Jiang, A., et al., *Chitosan based biodegradable composite for antibacterial food packaging application*. Polymers, 2023. 15(10): p. 2235.
4. Nurdin, H., et al., *The investigation of physical dan mechanical properties of Nipah-based particle board*. Teknomekanik, 2023. 6(2): p. 94-102.
5. Khwaldia, K., E. Arab-Tehrany, and S. Desobry, *Biopolymer coatings on paper packaging materials*. Comprehensive reviews in food science and food safety, 2010. 9(1): p. 82-91.
6. Jones, P. and D. Comfort, *The forest, paper and packaging industry and sustainability*. International Journal of Sales, Retailing and Marketing, 2017. 6(1): p. 3-21.
7. Shi, S.-C., S.-W. Ouyang, and D. Rahmadiawan, *Erythrosine–Dialdehyde Cellulose Nanocrystal Coatings for Antibacterial Paper Packaging*. Polymers, 2024. 16(7): p. 960.
8. Helanto, K., R. Talja, and O.J. Rojas, *Mineral-filled biopolyester coatings for paperboard packaging materials: barrier, sealability, convertability and biodegradability properties*. Nordic Pulp & Paper Research Journal, 2022. 37(1): p. 212-221.
9. Aloui, H., et al., *Effect of glycerol and coating weight on functional properties of biopolymer-coated paper*. Carbohydrate polymers, 2011. 86(2): p. 1063-1072.
10. Dixon, J., *Packaging materials: 9. multilayer packaging for food and beverages*. 2011.
11. Raźniewska, M., *Compostable packaging waste management—Main barriers, reasons, and the potential directions for development*. Sustainability, 2022. 14(7): p. 3748.
12. Folino, A., et al., *Biodegradation of wasted bioplastics in natural and industrial environments: A review*. Sustainability, 2020. 12(15): p. 6030.
13. Rujnić Havstad, M., et al., *Influence of home composting on tensile properties of commercial biodegradable plastic films*. Polymers, 2021. 13(16): p. 2785.
14. Colón, J., et al., *Environmental assessment of home composting*. Resources, Conservation and Recycling, 2010. 54(11): p. 893-904.
15. Jasim, S., *The practicability of home composting for the management of biodegradable domestic solid waste*. 2003, Imperial College London (University of London).
16. Ligon, P.J. and G. Garland, *Analyzing the costs of composting strategies*. 1998.
17. McGovern, A., *Home composting makes major impact*. BioCycle (USA), 1997. 38(12).
18. Ajji, A., et al., *Heat Sealing in Packaging: Materials and Process Considerations*. 2023: Walter de Gruyter GmbH & Co KG.
19. Vogel, J., *Sealing and cutting of PLA bio-plastic*. 2011, Iowa State University.

20. Hishinuma, K., *Heat sealing technology and engineering for packaging: Principles and applications*. 2009: DEStech Publications, Inc.
21. Halle, R. *Polymer and processing parameters influencing the heat seal sealability of polyethylene*. in *Laminations and Coatings Conference*. 1989. TAPPI Press Orlando.
22. Ilhan, I., et al., *Understanding the factors affecting the seal integrity in heat sealed flexible food packages: A review*. *Packaging technology and science*, 2021. 34(6): p. 321-337.
23. Boiko, Y.M., et al., *Healing of interfaces of amorphous and semi-crystalline poly (ethylene terephthalate) in the vicinity of the glass transition temperature*. *Polymer*, 2001. 42(21): p. 8695-8702.
24. Stehling, F.C. and P. Meka, *Heat sealing of semicrystalline polymer films. II. Effect of melting distribution on heat-sealing behavior of polyolefins*. *Journal of Applied Polymer Science*, 1994. 51(1): p. 105-119.
25. Grady, A., et al., *Crystallization of polypropylene at various cooling rates*. *Materials Science and Engineering: A*, 2005. 413: p. 442-446.
26. Rakesh, P.K. and J.P. Davim, *Polylactic Acid Composites: Sustainable Biocomposites*. Vol. 18. 2023: Walter de Gruyter GmbH & Co KG.
27. Herrera, N., et al., *Functionalized blown films of plasticized polylactic acid/chitin nanocomposite: Preparation and characterization*. *Materials & Design*, 2016. 92: p. 846-852.
28. Morris, B.A., *The science and technology of flexible packaging: multilayer films from resin and process to end use*. 2022: William Andrew.
29. Bamps, B., M. Buntinx, and R. Peeters, *Seal materials in flexible plastic food packaging: A review*. *Packaging Technology and Science*, 2023. 36(7): p. 507-532.
30. Borch, J., *Thermodynamics of polymer-paper adhesion: a review*. *Journal of adhesion science and technology*, 1991. 5(7): p. 523-541.
31. Hurnanen, M., *Heat Sealing Paper with Polymer Film*. 2016.
32. Frihart, C.R., *Adhesive bonding and performance testing of bonded wood products*. 2005.
33. Gardner, D.J., et al., *Adhesion theories in wood adhesive bonding*. *Progress in adhesion and adhesives*, 2015: p. 125-168.
34. Steffnec, N.O.E., R. Dickson, and P. LePoutre, *Mechanical interlocking in coated paper*. *Nordic Pulp & Paper Research Journal*, 1995. 10(1): p. 80-82.
35. Schuler, P. and W. Haas, *The wettability of sealing materials and its effect on sealing performance: part I*. *Sealing Technology*, 2016. 2016(5): p. 9-12.
36. Schuler, P. and W. Haas, *The wettability of sealing materials and its effect on sealing performance: Part II*. *Sealing Technology*, 2016. 2016(6): p. 7-11.
37. Petrie, E.M., *Handbook of adhesives and sealants*. 2000.
38. Brewis, D. and I. Mathieson, *Adhesion and bonding to polyolefins*. Vol. 12. 2002: iSmithers Rapra Publishing.

39. Comyn, J., *Adhesion science*. 2021: Royal Society of Chemistry.
40. Ebnesajjad, S., *Handbook of adhesives and surface preparation: technology, applications and manufacturing*. 2010: William Andrew.
41. Welander, M. and M. Rigdahl, *Determination of the adhesion between low density polyethylene and coated paper*. Nordic Pulp & Paper Research Journal, 1987. 2(2): p. 61-65.
42. Meka, P. and F.C. Stehling, *Heat sealing of semicrystalline polymer films. I. Calculation and measurement of interfacial temperatures: Effect of process variables on seal properties*. Journal of Applied Polymer Science, 1994. 51(1): p. 89-103.
43. Lahti, J., J. Kuusipalo, and S. Auvinen. *Novel equipment to simulate hot air heat sealability of packaging materials*. in *TAPPI European PLACE Conference*. 2017. TAPPI Press.
44. Tiitola, M., *Heat sealability of paperboard and factors affecting sealability*. 2021.
45. Astm, F. 88-00. *Standard test method for seal strength of flexible barrier materials*. in *The American Society for Testing and Materials*. 2015.
46. Zhao, B. and H.J. Kwon, *Adhesion of polymers in paper products from the macroscopic to molecular level—an overview*. Journal of adhesion science and technology, 2011. 25(6-7): p. 557-579.
47. Oni, Y., et al. *Towards the Understanding of Fiber Tear*. 2012. ANTEC.
48. Najarzadeh, Z. and A. Ajji, *A novel approach toward the effect of seal process parameters on final seal strength and microstructure of LLDPE*. Journal of Adhesion Science and Technology, 2014. 28(16): p. 1592-1609.
49. Theller, H., *Heatsealability of flexible web materials in hot-bar sealing applications*. Journal of Plastic Film & Sheeting, 1989. 5(1): p. 66-93.
50. Hassan, A. and S.Y. Cheng, *Effect of bar sealing parameters on OPP/MCPP heat seal strength*. eXPRESS Polymer Letters, 2007. 1(11): p. 773-779.
51. Merabtene, M., et al., *Heat sealing evaluation and runnability issues of flexible paper materials in a vertical form fill seal packaging machine*. BioResources, 2022. 17(1): p. 223.
52. Willberg-Keyriläinen, P., et al., *Cellulose fatty acid ester coated papers for stand-up pouch applications*. Journal of Applied Polymer Science, 2018. 135(48): p. 46936.
53. Oloyede, O.O. and S. Lignou, *Sustainable paper-based packaging: A consumer's perspective*. Foods, 2021. 10(5): p. 1035.
54. Hauptmann, M., et al., *The effect of flexible sealing jaws on the tightness of pouches made from mono-polyolefin films and functional papers*. Packaging Technology and Science, 2021. 34(3): p. 175-186.
55. Rastogi, V.K. and P. Samyn, *Bio-based coatings for paper applications*. Coatings, 2015. 5(4): p. 887-930.
56. Nurul Syahida, S., et al., *Development and characterisation of gelatine/palm wax/lemongrass essential oil (GPL)-coated paper for active food packaging*. Packaging Technology and Science, 2020. 33(10): p. 417-431.

57. Shao, C., et al., *Characterization of soy protein–celery composite paper sheet: Rheological behavior, mechanical, and heat-sealing properties*. Journal of Applied Polymer Science, 2012. 125(S2): p. E255-E261.
58. Auras, R., B. Harte, and S. Selke, *An overview of polylactides as packaging materials*. Macromolecular bioscience, 2004. 4(9): p. 835-864.
59. Lahtinen, K., et al., *Characterization for water vapour barrier and heat sealability properties of heat-treated paperboard/polylactide structure*. Packaging Technology and Science: An International Journal, 2009. 22(8): p. 451-460.
60. Ai, X., et al., *The mechanical, thermal, rheological and morphological properties of PLA/PBAT blown films by using bis (tert-butyl dioxy isopropyl) benzene as crosslinking agent*. Polymer Engineering & Science, 2019. 59(S1): p. E227-E236.
61. Rhim, J.W. and J.H. Kim, *Properties of poly (lactide)-coated paperboard for the use of 1-way paper cup*. Journal of Food Science, 2009. 74(2): p. E105-E111.
62. Yao, S., B.-J. Wang, and Y.-M. Weng, *Preparation and characterization of mung bean starch edible films using citric acid as cross-linking agent*. Food Packaging and Shelf Life, 2022. 32: p. 100845.
63. Ngo, T.M.P., et al., *Effects of zinc oxide nanoparticles on the properties of pectin/alginate edible films*. International Journal of Polymer Science, 2018. 2018.
64. Lim, W.S., et al., *Heat-sealing property of cassava starch film plasticized with glycerol and sorbitol*. Food Packaging and Shelf Life, 2020. 26: p. 100556.
65. Guazzotti, V., et al., *Bio-based coatings as potential barriers to chemical contaminants from recycled paper and board for food packaging*. Food Additives & Contaminants: Part A, 2014. 31(3): p. 402-413.
66. Apriyanto, A., J. Compart, and J. Fettke, *A review of starch, a unique biopolymer–Structure, metabolism and in planta modifications*. Plant Science, 2022. 318: p. 111223.
67. Li, H., et al., *Starch and its derivatives for paper coatings: A review*. Progress in Organic Coatings, 2019. 135: p. 213-227.
68. Whistler, R.L., J.N. BeMiller, and E.F. Paschall, *Starch: chemistry and technology*. 2012: Academic Press.
69. Maurer, H.W. and R.L. Kearney, *Opportunities and challenges for starch in the paper industry*. Starch-Stärke, 1998. 50(9): p. 396-402.
70. Suh, J.H., et al., *Effect of moisture content on the heat-sealing property of starch films from different botanical sources*. Polymer Testing, 2020. 89: p. 106612.
71. Alves, V.D., et al., *Effect of glycerol and amylose enrichment on cassava starch film properties*. Journal of Food Engineering, 2007. 78(3): p. 941-946.
72. Basiak, E., A. Lenart, and F. Debeaufort, *How glycerol and water contents affect the structural and functional properties of starch-based edible films*. Polymers, 2018. 10(4): p. 412.

73. Surendren, A., et al., *A review of biodegradable thermoplastic starches, their blends and composites: recent developments and opportunities for single-use plastic packaging alternatives*. Green Chemistry, 2022. 24(22): p. 8606-8636.
74. Rompothi, O., et al., *Development of non-water soluble, ductile mung bean starch based edible film with oxygen barrier and heat sealability*. Carbohydrate polymers, 2017. 157: p. 748-756.
75. Abdorreza, M.N., L. Cheng, and A. Karim, *Effects of plasticizers on thermal properties and heat sealability of sago starch films*. Food hydrocolloids, 2011. 25(1): p. 56-60.
76. Orsuwan, A. and R. Sothornvit, *Effect of banana and plasticizer types on mechanical, water barrier, and heat sealability of plasticized banana-based films*. Journal of Food Processing and Preservation, 2018. 42(1): p. e13380.
77. Nawab, A., et al., *Innovative edible packaging from mango kernel starch for the shelf life extension of red chili powder*. International journal of biological macromolecules, 2018. 114: p. 626-631.
78. Nechita, P. and M. Roman, *Review on polysaccharides used in coatings for food packaging papers*. Coatings, 2020. 10(6): p. 566.
79. Kushwaha, R. and D. Kaur, *Recent techniques used in modification of starches: A review*. Food Technology From Health to Wealth & Future Challenges; Bharti Publication: Delhi, India, 2018: p. 1-15.
80. Emeje, M. and M. Blumenberg, *Chemical properties of starch*. 2020: BoD—Books on Demand.
81. Zia-ud-Din, H. Xiong, and P. Fei, *Physical and chemical modification of starches: A review*. Critical reviews in food science and nutrition, 2017. 57(12): p. 2691-2705.
82. Ashogbon, A.O. and E.T. Akintayo, *Recent trend in the physical and chemical modification of starches from different botanical sources: A review*. Starch-Stärke, 2014. 66(1-2): p. 41-57.
83. Jin, Y., J.Z. Li, and A.M. Nik, *Starch-based microencapsulation*, in *Starch in food*. 2018, Elsevier. p. 661-690.
84. Leon-Bejarano, M., et al., *Physical, barrier, mechanical, and biodegradability properties of modified starch films with nut by-products extracts*. Foods, 2020. 9(2): p. 226.
85. Sweedman, M.C., et al., *Structure and physicochemical properties of octenyl succinic anhydride modified starches: A review*. Carbohydrate polymers, 2013. 92(1): p. 905-920.
86. Parikh, A., S. Agarwal, and K. Raut, *A review on applications of maltodextrin in pharmaceutical industry*. system, 2014. 4(6).
87. Olechno, K., A. Basa, and K. Winnicka, *“Success depends on your backbone”—about the use of polymers as essential materials forming orodispersible films*. Materials, 2021. 14(17): p. 4872.
88. Dziedzic, S. and M. Kearsley, *Handbook of starch hydrolysis products and their derivatives*. 2012: Springer Science & Business Media.

89. Jadaa, W., A. Prakash, and A.K. Ray, *Modeling of degradation of Diazo dye in swirl-flow photocatalytic reactor: Response surface approach*. Catalysts, 2020. 10(12): p. 1418.
90. Sudarjanto, G., B. Keller-Lehmann, and J. Keller, *Optimization of integrated chemical–biological degradation of a reactive azo dye using response surface methodology*. Journal of hazardous materials, 2006. 138(1): p. 160-168.
91. Bagheri, A.R., et al., *Modeling and optimization of simultaneous removal of ternary dyes onto copper sulfide nanoparticles loaded on activated carbon using second-derivative spectrophotometry*. Journal of the Taiwan Institute of Chemical Engineers, 2016. 65: p. 212-224.
92. Myers, R.H., D.C. Montgomery, and C.M. Anderson-Cook, *Response surface methodology: process and product optimization using designed experiments*. 2016: John Wiley & Sons.
93. Moussa, H., et al., *Definitive screening design and I-optimal design for optimization of ultrasound-assisted extraction of phenolic content and antioxidant capacity from Salvia officinalis L. leaves*. Sustainable Chemistry and Pharmacy, 2022. 29: p. 100820.
94. Montgomery, D.C., *Design and analysis of experiments*. 2017: John wiley & sons.
95. Mee, R.W., *A comprehensive guide to factorial two-level experimentation*. 2009: Springer.
96. Antony, J., *Design of experiments for engineers and scientists*. 2023: Elsevier.