Shape Memory Polyurethane Coating on the Polyester cloth for humidity control in crisper: Synthesis and Characterization

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A thesis submitted to the National University of Sciences and Technology, Islamabad,

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(2025)

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DEDICATION

"This thesis is dedicated to my beloved parents for their unwavering support and to my sisters for their constant encouragement. I am deeply grateful to my supervisor, Dr. Muhammad Irfan, my mentor, Dr. N. M. Butt and all my teachers for their invaluable guidance. goes to my BS institute, PINSAT (Preston Institute of Nanoscience and Technology), where my passion for research and discovery first took shape. To my mentors and friends, this work is a tribute to your wisdom, patience, and inspiration."

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allowed me to complete this journey. I could not have done this without your constant support.

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LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS

PU	**Polyurethane**
SMPU	**Shape memory polyurethane**
SMAs	**Shape memory alloys**
SMPs	**Shape memory polymers**
SMCs	**Shape memory ceramics**
PEG	**Polyethylene glycol**
CO	**Castor oil**
BDO	**Butanediol**
HMDI	**Hexamethylene diisocyanate**
FTIR	**Fourier-Transform Infrared Spectroscopy**
SEM	**Scanning electron microscope**
OP	**Optical profilometry**
TGA	**Thermogravimetric analysis**
XRD	**X-ray diffraction**
CA	**Contact angle**
DSC	**Differential Scanning Calorimetry**
WVPT	**Eater vapor permeability test**
WVTR	**Water vapour transmission rate**
MC	**Moisture content**
WS	**Water solubility**
Ra	**Average surface roughness**
PPI	**Picks per inch**

ABSTRACT

The purpose of this study is to investigate at how film compositions affect the production of fresh produce films for humidity control in crispers with increased temperature sensitivity for gas permeability. Shape-memory polyurethane (SMPU) formulations were created utilizing poly(ethylene glycol) (PEG), 1,6-hexamethylene diisocyanate, 1,4-butanediol, and castor oil (CO), and then cast into films on polyester cloth. The study focused on determining the thermal, shape-memory, and water vapor permeability of the synthesized coatings. The prepared SMPU films containing 40/60 CO/PEG, exhibited -outstanding shape-memory capabilities. These films had a shape recovery ratio greater than 96% which can contribute to play a significant role in the preservation of fresh produce in crisper up to 10 days. Moreover, the SMPU film with 40/60 CO/PEG demonstrated greater water vapor permeability, with cabbage leaves losing less than 6% of their water content. This new film formulation has great promise for the development of smart packaging solutions since it provides thermally responsive gas permeability which can help to preserve fresh foods longer. The findings pave the way for the development of packaging materials that can respond to changing conditions in the environment, providing the most effective preservation of food that is perishable.

Keywords: Shape Memory Polyurethane, coatings, food packaging, gas permeability, humidity control.

CHAPTER 1: INTRODUCTION

1.1 Introduction to the Research Problem

The food industry stands as a cornerstone of human civilization, offering sustenance and nourishment to populations worldwide. In this dynamic and critical sector, the preservation of food quality and safety during storage, transportation, and distribution is paramount. While various factors contribute to this preservation challenge, humidity control emerges as a key facet that cannot be overlooked. This thesis is devoted to addressing the intricate dilemma of [1-4].

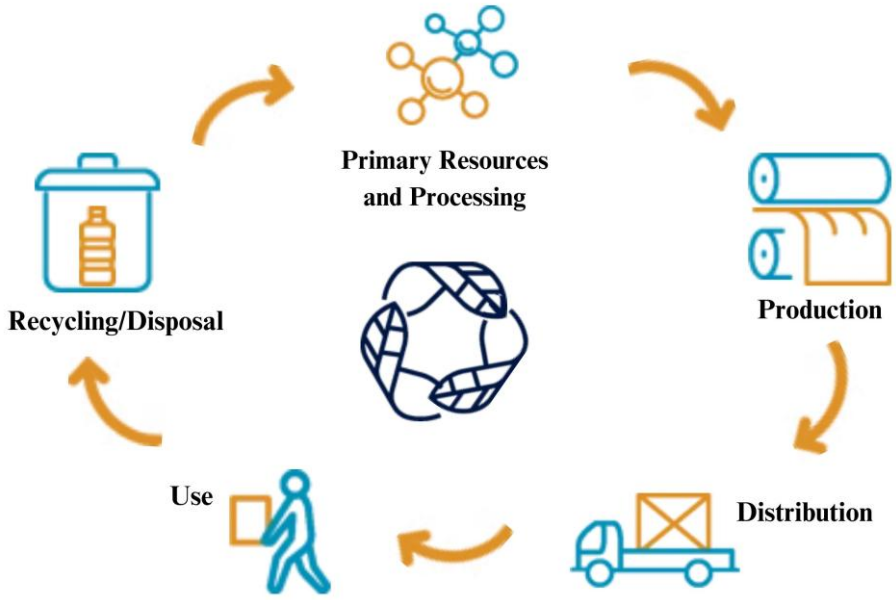

Figure 1.1: Life cycle of Food Packaging

Food packaging materials must not only protect perishable contents from contamination and external conditions, but also provide additional capabilities to ensure the food's quality. Modified atmosphere (MA) packaging for fresh fruits and vegetables is meant to adjust the composition of gases, keeping lower oxygen (O_2) and higher carbon dioxide (CO_2) levels within the package, particularly when stored at cold temperatures. [5]. However, issues can arise during these products' storage and transportation, leading to temperature fluctuations. This can disrupt the equilibrium modified atmosphere (EMA) within the packaging, resulting in a loss of product quality [6].

The reason for this disruption of EMA under temperature fluctuations is the higher sensitivity of the respiration rate of fresh products to temperature changes compared to the gas permeability characteristics of conventional packaging materials [7]. The food sector faces a significant difficulty in the lack of commercially accessible packaging films with gas permeability qualities that are more responsive to temperature changes [8].

1.2 Importance of Humidity Control in Food Packaging

The significance of humidity control in food packaging stems from its profound impact on the quality, safety, and shelf life of food products. Humidity, the water vapour content in the packaging environment, plays a pivotal role in determining packaged food's sensory and microbiological attributes. High humidity levels can encourage microbial growth and lead to spoilage, while low humidity levels may desiccate products, resulting in compromised texture, flavor, and consumer appeal [9]. As such, precise management of humidity in food packaging is vital for preventing food spoilage, extending product shelf life, reducing food waste, and ultimately ensuring the health and satisfaction of consumers [10].

1.3 Overview of the Research Objectives

This thesis endeavors to tackle the multifaceted issue of humidity control in food packaging through a comprehensive investigation and innovative solution development. The research objectives can be outlined as follows:

1.3.1 Primary Objective

The primary goal of this research is to design, synthesize, and evaluate a shape memory polyurethane coating for polyester cloth, specifically tailored to control humidity within food packaging.

1.3.2 Secondary Objectives

a. To examine the synthesis process of shape memory polyurethane, optimizing its properties for effective humidity regulation.

b. To develop and implement a robust methodology for applying the shape memory polyurethane coating to polyester cloth, ensuring a consistent and durable coating.

c. To comprehensively characterize the mechanical and thermal properties of the coated cloth, evaluating its suitability for use in food packaging.

d. To investigate the morphological changes that occur in the coated cloth during exposure to varying humidity conditions, thereby gaining insights into its behavior.

e. To assess the efficacy of the shape memory polyurethane-coated polyester cloth in actively controlling and maintaining desired humidity levels within food packaging.

f. To systematically analyze experimental data in order to draw useful findings and insights into the realm of food packaging and humidity control.

By addressing these research objectives, this study aspires to make a valuable contribution to the field of food packaging technology, improving the management of humidity, and enhancing the quality and safety of food products throughout their journey from production to consumption.

1.4 Research Questions and Hypotheses

Research Questions:

What are the optimal synthesis parameters for shape-memory polyurethane to synthesize durable shape-memory polyurethane thin films?

Can the developed shape memory polyurethane coating on polyester cloth actively regulate humidity within a crisper?

What are the mechanical and thermal properties of the coated cloth, and how do they influence its suitability for food packaging applications?

How do morphological changes in the coated cloth relate to its performance in maintaining desired humidity levels within food packaging?

Hypotheses:

The synthesis parameters of shape memory polyurethane can be optimized to achieve precise and effective humidity control in the crisper.

The shape memory polyurethane coating on the polyester cloth will actively regulate and maintain humidity levels within the crisper.

The mechanical and thermal properties of the coated cloth will meet the required standards for food packaging applications.

Morphological changes in the coated cloth will correspond to its performance in humidity control within food packaging.

1.5 Significance of the Study

This study holds significant importance on various fronts. Firstly, it addresses a pressing concern in the food industry by providing an innovative solution for humidity control, thus contributing to the preservation of food quality, reduction of food waste, and the overall safety of consumable products. Secondly, the development of shape-memory polyurethane coatings and their application on polyester cloth offers a potential breakthrough in materials science with broader applications beyond the food sector, such as in pharmaceuticals, textile, defense and electronics.

Furthermore, this research can stimulate advancements in sustainable packaging technologies, promoting eco-friendly practices in food preservation and reducing the environmental footprint of the industry. The findings of this study can inform future research endeavors in the field of materials science and food packaging.

1.6 Structure of the Thesis

This thesis is structured as follows:

Chapter 1: Introduction (as presented)

In this chapter, extensive background is presented on the use of shape memory polyurethane for humidity control in crispers, elucidating both their advantages and limitations. This section throws light on existing scientific understanding, discusses the research methodology, highlights unresolved gaps in current knowledge, and emphasizes the thesis's distinctive contribution to the body of knowledge in this specific topic. In addition, this chapter summarizes the thesis's key aims and research questions, laying the groundwork for future research.

Chapter 2: Literature Review

This chapter delves into the literature of the study, providing an extensive review of related research in the field of humidity control in food packaging. It covers key

concepts such as shape-memory materials, polyurethane coatings, and the role of polyester cloth in packaging. Furthermore, it examines previous studies on these topics, identifies gaps in current knowledge, and establishes the theoretical and conceptual framework upon which the research is built. This chapter sets the stage for the subsequent chapters, elucidating the context and theoretical foundations of the thesis.

Chapter 3: Materials and Methods

This chapter outlines the materials and methods used in the research. It describes the selection of materials, the processes involved in coating, and the various techniques employed for characterization. It provides insight into the experimental design, data collection, and analysis methods. Ethical considerations, if relevant, are also discussed, as well as the reliability and validity of the research methods. This chapter serves as a detailed guide to the practical aspects of the study, laying the foundation for the subsequent chapter on results and discussion.

Chapter 4: Results and Discussion

Chapter 4 delves into the results of the experiments conducted and initiates a discussion regarding the findings. It explores the mechanical and thermal properties of the coated cloth, morphological changes in the material, and the performance of humidity control. The chapter then delves into an in-depth discussion of the results, interpreting their meaning, comparing them with existing literature, and highlighting the implications. It addresses the research questions and hypotheses and acknowledges any limitations or potential sources of error. Furthermore, this chapter provides recommendations for future research and serves as a conclusion to the thesis, summarizing the key findings and their broader implications.

Each subsequent chapter will offer in-depth exploration and analysis in its respective area, contributing to a comprehensive understanding of the research and its implications for the field of food packaging technology and materials science

CHAPTER 2: LITERATURE REVIEW

2.1 Shape memory materials

Over time, nature has provided inspiration for scientists to design intelligent materials capable of adapting to various environments by modifying their inherent properties [5]. One such class of intelligent materials is shape-memory materials, which include shape-memory alloys, ceramics, and polymers (SMPs). SMPs have gained significant attention due to their exceptional qualities, such as their highly customizable molecular structures, flexibility, ease of processing, and lightweight nature. As a result, they hold considerable promise for a broad range of applications and have seen significant progress in recent decades [6].

The rapid advancements in artificial intelligence have sparked a global surge in SMP research [7]. SMPs, with their capacity for self-monitoring, self-repair, and self-adaptation, serve as fundamental materials for intelligent autonomous systems. However, the increasing demands for higher intelligence, the ability to thrive in more complex environments, and broader applications have raised the bar for SMPs. As a result, SMPs are not only presented with new opportunities but also face more significant challenges [8].

2.1.1 Shape Memory Alloys (SMAs):

Shape memory alloys are a type of smart material that has a unique property called the shape memory effect. When exposed to specific external stimuli, including temperature fluctuations or stress, some alloys have the ability to "remember" and return to a particular shape [9]. Common shape memory alloys include nickel-titanium (Ni-Ti or Nitinol), copper-aluminum-nickel, and iron-manganese-silicon [10]. SMAs are used in various applications, including medical devices (e.g., stents and orthodontic wires), actuators, and aerospace components due to their ability to undergo reversible phase transformations [11].

2.1.2 Shape Memory Ceramics:

Shape memory ceramics are relatively less common than shape memory alloys and polymers, but they share some similar characteristics. These ceramics can undergo reversible phase transitions in response to changes in temperature or stress. One well-known shape memory ceramic is lead zirconate titanate (PZT), which has applications in actuators and sensors. The field of shape memory ceramics is a niche area of research with potential for further development [12].

2.1.3 Shape Memory Polymers (SMPs):

Shape memory polymers are a subgroup of shape memory materials that have garnered significant attention due to their versatility and potential applications [13]. When subjected to an external stimulus, like heat, certain polymers can "remember" a specific shape and return to it. Unlike shape memory alloys, SMPs are lightweight, flexible, and easy to process. They can be synthesized to exhibit various responses to different triggers, making them suitable for diverse applications. Some common SMPs include thermoplastic polyurethanes, polycaprolactone, and epoxy-based polymers. SMPs are used in diverse fields, including biomedicine, robotics, aerospace, and smart textiles [14, 15].

2.1.4 Synthesis of SMPs:

Three main ingredients are used in the step-growth polymerization process to create polyurethanes (PUs): macrodiols, diisocyanates, and low molecular weight chain extenders, also known as cross-linkers. Repeating units of urethane moieties (-NH–COO–) make up the PU chain. [16].

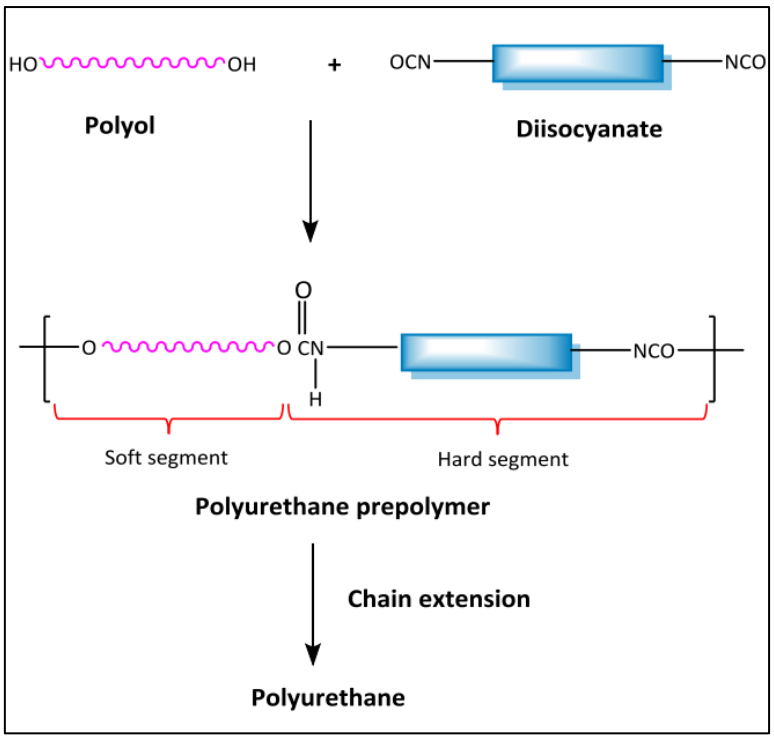

Figure 2.1: Schematic Illustration of synthesis of Polyurethane [17]

Polyurethanes can be made utilizing a variety of polymerisation techniques, including bulk, solution, emulsion, and suspension polymerisation [17]. Conventional PUs are typically created using bulk or solution polymerisation. Solution polymerisation provides fine control over reaction temperature, pace, and viscosity. However, the cost and difficulties involved with solvent cleanup have prompted concerns. As a result, there is an increasing trend in the synthesis of water-dispersible polyurethanes, which do not require organic solvents. Water-dispersible polyurethanes are produced using both suspension and emulsion polymerisation techniques. Water-dispersible PUs provide various advantages, including decreased viscosity at greater molecular weights and improved application when compared to conventional PUs [18].

PUs can be synthesized in one or two step processes, which are commonly referred to as "one-pot" or "two-steps" procedures. The one-pot synthesis mixes all of the materials at once, whereas the two-step prepolymer technique uses an excess of diisocyanate to react with the macrodiols, resulting in an NCO end-capped prepolymer. The prepolymer is subsequently chain-extended to form PU. The two-step reaction is chosen because it allows for better control over the reaction and produces PUs with well-defined structures and physical qualities [19].

2.1.5 Molecular Structure and Composition of SMPs:

SMPs have a molecular structure that consists of both soft and hard segments. The combination and arrangement of these segments play a crucial role in their shape memory behavior.

Soft Segments: Soft segments are typically composed of flexible and amorphous polymer chains. These segments contribute to the polymer's flexibility and deformability. Common materials used for soft segments include polyethene glycol (PEG) and polypropylene glycol (PPG) [18].

Hard Segments: Hard segments are composed of more rigid, crystalline, or semi-crystalline components. They provide strength and stability to the polymer. Examples of hard segments include diisocyanates and diols [20].

2.1.6 Influence of Soft and Hard Segments on Shape Memory Behavior:

The combination of soft and hard segments in SMPs results in a block copolymer structure. The interplay between these segments influences the material's shape memory behavior. Soft segments enable flexibility and deformability, while hard segments provide stability and fixity. The transition between temporary and permanent shapes occurs due to the reversible phase transitions in the material, guided by the combination of these segments [21].

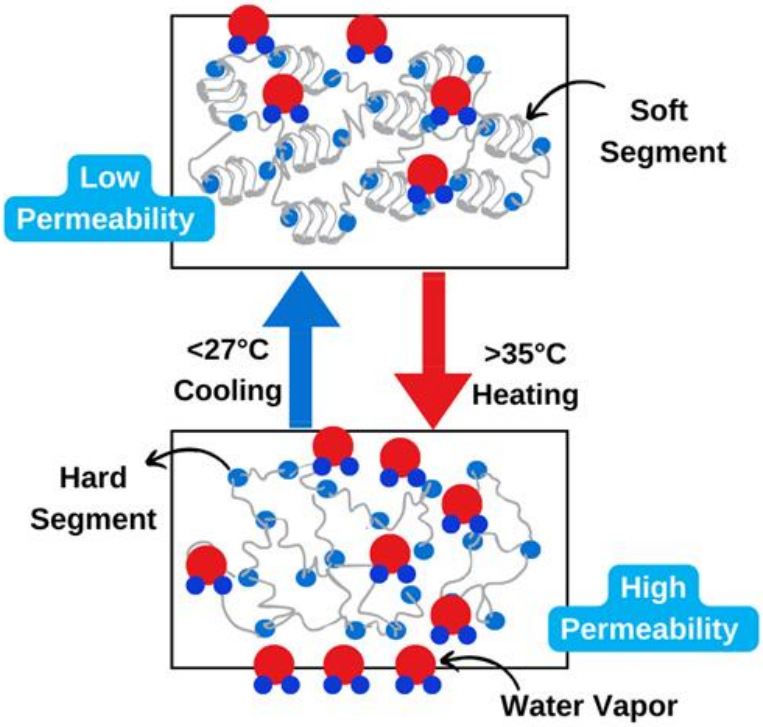

Figure 2.2: Schematic of molecular Thermoplastic Shape memory polyurethane for water-vapor Permeability

By adjusting soft and hard segments of the polyurethane we can adjust the wettability properties or water vapor permeability of polyurethane and wettability can be tested by contact angle measurements. By the wettability studies we can be able to determine whether SMPU coatings are hydrophilic (attracting water) or hydrophobic (repelling water) and to what degree. This information is vital in the food industry, as it can influence how liquids interact with the coating, affecting the shelf life and quality of food products. Additionally, the contact angle measurement can help optimize the design of SMPU coatings to enhance their wettability characteristics, ensuring their effectiveness in preserving and protecting food items [22].

2.4 Types of stimuli for shape memory behavior

SMPs exhibit their unique behavior by responding to specific stimuli. These stimuli trigger changes in the material's shape or properties, allowing it to "remember" a particular configuration and return to it [23]. There are several types of stimuli used for shape memory activation.

Environmental Stimuli for Shape Memory Response:

Temperature: Temperature is the most common and widely used stimulus for shape memory behavior in SMPs. These materials have distinct transition temperatures, such as the glass transition temperature (Tg) and the melting temperature (Tm), which enable them to undergo phase changes when exposed to heat [24]. As the material's temperature changes, it can transition between temporary and permanent shapes. Heating above the transition temperature typically allows the material to return to its original shape.

Light: Light-responsive SMPs have garnered attention for their ability to change shape upon exposure to specific wavelengths of light [25]. This type of stimulus is particularly useful in applications where precise control is required, as light can be manipulated with high accuracy.

Electric Fields: Some SMPs can be actuated by applying an electric field. This stimulus is especially useful in applications where electrical control is preferred, such as in the development of smart materials and devices [26].

Temperature-Responsive SMPs: Temperature-responsive SMPs are a prominent category within shape memory materials. They are known for their sensitivity to changes in temperature and exhibit shape memory behavior when exposed to temperature variations [26]. These SMPs have specific transition temperatures, such as Tg and Tm, which are characteristic of the polymer and dictate their behaviour. Temperature-responsive SMPs are particularly valuable in applications where temperature control can be easily managed and manipulated [27].

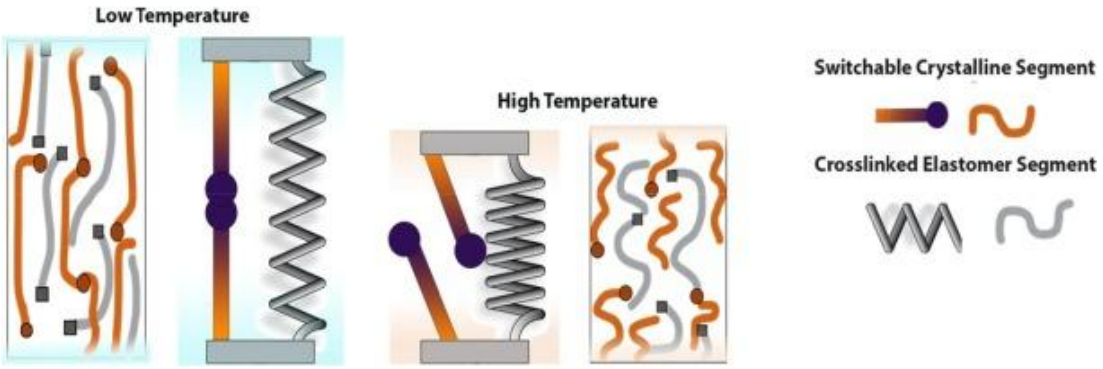

Figure 2.3: Switch Spring model at low and high temperature behavior [27]

2.5 Food packaging

Food packaging is a significant component of the modern food industry. It entails the design, manufacture, and application of various materials and containers to protect, store, and transport food products. Food packaging serves more than just one purpose: it preserves food quality, ensures safety, informs consumers, and improves convenience. The packaging industry is constantly evolving to satisfy changing consumer wants and preferences, while also addressing environmental and sustainability issues [28].

The Role of Packaging in Food Preservation:

One of the primary roles of food packaging is food preservation. It serves to extend the shelf life of perishable food items and maintain their quality and safety. Packaging materials and designs are carefully selected to create a protective barrier between the food product and the external environment. This barrier safeguards the food from factors that could cause deterioration, such as exposure to oxygen, moisture, light, temperature variations, and contaminants [29].

Key aspects of the role of food packaging in food preservation include:

Barrier Properties: Packaging materials are chosen for their ability to act as barriers against external elements. For instance, impermeable packaging prevents oxygen and moisture from entering, reducing the risk of spoilage and microbial growth [29].

Temperature Control: Insulated packaging can help maintain desired temperature conditions, crucial for products that require refrigeration or freezing [30].

Protection from Light: Packaging can shield food items from light, which can lead to undesirable chemical reactions and quality degradation, especially in products like dairy and beverages [31] .

Contamination Prevention: Packaging is designed to prevent contamination from external sources, ensuring the safety and hygiene of the food product [32].

Information and Labels: Packaging provides essential information to consumers, such as nutritional facts, ingredient lists, expiration dates, and preparation instructions. This information aids consumers in making informed choices and using the product safely.

Convenience: Packaging is also about convenience, offering features like resealable closures, portion control, and ease of handling and storage for consumers [33].

Sustainability: In recent years, there has been a growing emphasis on sustainable packaging solutions that minimize environmental impact. This includes recyclable, biodegradable, and eco-friendly packaging options [34].

2.6 Humidity control mechanisms for food preservation

Humidity is a critical factor that profoundly influences the shelf life and quality of fruits during storage. High humidity levels in storage environments can create a favourable breeding ground for molds, bacteria, and other microorganisms [35]. Excessive moisture on the fruit's surface can promote fungal infections, leading to spoilage and decay. Mold growth, surface softening, and alterations in the fruit's appearance and taste are common consequences. Therefore, controlling humidity is essential to prevent excessive moisture and microbial proliferation, ultimately extending the shelf life of fruits [36].

Conversely, low humidity levels can result in rapid moisture loss from fruits. Fruits, with their high-water content, can quickly dehydrate when exposed to dry air. This can lead to undesirable texture changes, loss of juiciness, and compromised quality. Fruits may become leathery, wilted, and less appealing to consumers. To maintain the desired texture and quality, it is vital to control humidity and minimize moisture loss during storage [37].

The optimal humidity levels for fruit storage can vary depending on the specific fruit variety. For instance, berries and grapes are highly sensitive to moisture and require

higher humidity levels (typically 85% to 95%) to prevent drying out due to their thin skin [38]. In contrast, fruits like apples and citrus, with thicker skins and natural wax layers, can tolerate lower humidity levels (typically 75% to 85%) to minimize moisture loss without promoting microbial growth.

Proper humidity control is achievable through various methods and technologies, including humidifiers and dehumidifiers in storage facilities. These systems can adjust and maintain the desired humidity levels based on specific fruit requirements. Additionally, packaging materials with moisture permeability properties can regulate humidity within individual fruit packages [39].

Crucially, humidity control should be complemented by effective ventilation to ensure adequate air circulation. Proper air circulation helps prevent the buildup of excess moisture and the formation of condensation, which can further contribute to microbial growth and spoilage. Balancing humidity and ventilation is key to preserving the freshness and quality of stored fruits [40].

Moisture plays a significant role in various factors that can affect the product's overall quality and stability, including:

Microbial Stability: Maintaining the right moisture levels is essential to prevent microbial proliferation. Excessive moisture can create a favorable environment for mold and bacteria growth, leading to spoilage and decay. A moisture barrier helps inhibit these microorganisms [41].

Chemical Changes: Moisture can trigger chemical reactions such as oxidation and enzymatic browning, which can deteriorate the food product's quality and appearance. A moisture barrier helps to mitigate these changes [42].

Physical and Sensory Properties: The texture, freshness, and overall sensory attributes of the food product can be influenced by moisture content. Excessive moisture can lead to softening, while moisture loss can result in undesired texture changes [43].

Water Activity: The water activity of a food product is a critical parameter for its stability and safety. Maintaining the appropriate level is necessary to ensure product quality and safety.

2.7 Food packaging materials

Food packaging materials are indispensable components of the modern food industry, serving multifaceted roles critical to food safety and consumer satisfaction. These materials are thoughtfully selected and engineered to possess essential properties. Mechanical attributes, like strength and flexibility, ensure that the packaging endures the challenges of production, transport, and consumer handling, safeguarding the product's integrity [44]. Barrier properties, which include protecting against oxygen, moisture, light, and undesired odors, are fundamental in preserving food freshness and prolonging shelf life. Meanwhile, thermal properties are crucial for products that require specific temperature maintenance, such as those needing refrigeration or insulation. These properties aid in keeping food items at the right temperature throughout the supply chain [45] .

Furthermore, food packaging materials must exhibit minimal chemical interactions with the food to prevent contamination or undesirable reactions. They should be chemically inert and compatible with various types of food. Microbiological considerations are of utmost importance, as these materials are expected to provide a microbial barrier, and some packaging solutions may incorporate antimicrobial features to enhance food safety. On the functional and aesthetic front, packaging should be easy to use, visually appealing, and eco-friendly to cater to consumer needs and align with growing sustainability concerns. Food packaging materials are the unsung heroes of the food industry, ensuring the safety, quality, and marketability of products, all while adapting to the evolving dynamics of the market [46]..

Table 2.1: Highlights of recent literature of Polymers used for food packaging application

Polymer composite	Properties	Application	Reference
Low-Density-Polyethylene, Thymol Halloysite Nanohybrid	• Natural and Bio-Based Materials, • Environmentally friendly,	• Enhance food preservation and safety for Meat	[47]
Polypropylene, Nanosilica	• Improved Mechanical Properties • Seal Strength • Overall Migration Control • Barrier Properties	• Packaging of both perishable and non-perishable food items • Flexible Packaging films • Ecofriendly	[48]
Polyethylene terephthalate (PET) trays with a film of polypropylene (PP), Moisture Adsorber.	• Excellent transparency and mechanical strength, • Heat-sealing in packaging • controlling moisture content	• Cape Gooseberry Fruit Packaging • Customized Packaging for Fruits and Vegetables • Sustainable Packaging • Controlled Atmosphere Packaging	[49]

Thymol/ Ethylene-vinyl alcohol copolymer (EVOH)	• Humidity-Responsive Release • Core-Shell Nanofiber Structure • Antimicrobial Activity • Biocompatibility	• Fresh produce packaging • Fruit Preservation • Sensory Appeal • Commercial Potential •	[50]
Essential oils in Polyurethane	• Antibacterial Activity, • Sustained Release, • Biodegradability, • UV Blocking, • Low Cell Toxicity, • Mechanical Properties	• Food Packaging of fresh produce, • Environmental Protection, • UV-resistant packaging, • Sustainable Food Preservation	[51]
Nano-CaCO3 into Polylactic acid (PLA)	• Thermal Stability • Temperature-Dependent Mechanical Properties	• Improved Shelf Life for Perishable Products • Sustainability • Alternative to Conventional Plastics • Reduced Dependency on Petrochemicals	[52]

		• Commercial Production	
Phloretin incorporated into Polyhydroxyalkanoates (PHA)	• Antioxidant Activity • Antimicrobial Properties • Morpho-Mechanical Features • Hydrophilicity	• Eco-Friendly Packaging, • Food Packaging, Freshness Preservation • Bioplastic Formulation • Renewable Resources • Sustainable Packaging	[53]
Montmorillonite (MMT) nanosheets coassembled with polyvinyl alcohol (PVA) to create a nanocoating layer on polyolefin (PO) substrates.	• Improved Barrier Properties • Highly Ordered Structure • Modified Surface Properties • Thin Film Vapor Barrier	• Food Packaging Material • Biomedical Devices • Thin Film Technology	[54]

2.9 Theoretical and Conceptual Framework

The theoretical and conceptual framework of this study is underpinned by several key theories and concepts, which provide the basis for the research design and investigation:

Shape Memory Properties

The theoretical framework is grounded in the principles of shape memory materials, with a specific emphasis on shape memory polyurethane [17]. This material exhibits the capacity to change its shape in response to external stimuli and return to its original form, a property that aligns with the study's aim of active humidity control.

Polyurethane Coatings

The concept of polyurethane coatings, their synthesis, properties, and potential applications are integral to the study. Understanding the nature of polyurethane and its adaptability is vital for customizing coatings suitable for food packaging [55].

Polyester Cloth Substrate

The theoretical framework involves the properties and versatility of polyester cloth as a substrate for coating applications. Its properties, including flexibility and moisture resistance, play a pivotal role in the success of the proposed solution.

Humidity Control Mechanisms

Central to the study's conceptual framework is the concept of humidity control mechanisms. It encompasses the principles and practices involved in maintaining optimal humidity levels within food packaging and the transition from passive to active control methods.

CHAPTER 3: MATERIALS AND METHODS

3.1 Introduction

3.1.1 Materials

The chemical which was used for the synthesis of SMP coatings are mentioned below:

- Castor Oil (CO) bought from Daejung, Korea which has hydroxyl number of 161.01 mg and functionality of 2.76. (Analytical Grade)
- • Sigma Aldrich Germany supplied PEG with a molecular weight of 15 00 g/mol. (Analytical grade)
- 1,6-Hexamethylene diisocyanate (HMD) was purchased from the Daejung, Korea. (Analytical Grade)
- 1,4 Butanediol (BDO) was purchased from Merck, USA. (Technical Grade).
- Polyester cloth

3.1.2 Apparatus Used

The apparatus used in the synthesis of SMP is listed below:

- Hot Plate with stirring.
- Beaker
- Thermometer
- Magnetic Stirrer
- Dropper
- Petri Dish
- Teflon Mold
- Aluminum foil
- Glass slabs

3.2 Selection of soft and hard segments for the synthesis of SMPU

3.2.1 Polyethylene Glycol (PEG) and Castor oil (CO) as soft segments

The incorporation of PEG in polyurethane films not only enhances their water retention properties but also imparts a degree of flexibility that is valuable in various applications. This improved flexibility can be particularly advantageous in scenarios where the films need to conform to the shape of fresh produce or packaging. Additionally, the expected enhancement of water vapour permeability makes PEG a valuable component in the pursuit of effective and efficient film materials for applications such as food preservation and packaging [56].

Castor oil, derived from the seeds of the castor oil plant, serves as the source of a natural-based polyol [57]. These polyols, rich in hydroxyl groups, impart remarkable flexibility to polyurethane films. The incorporation of castor oil into polyurethane films is expected to confer improved water vapour permeability, making it a promising candidate for enhancing the effectiveness of films designed for food preservation and packaging. This natural and sustainable method has the ability to increase the shelf life of perishable foods while preserving their quality and freshness, which is in line with the food industry's growing desire for eco-friendly materials [58].

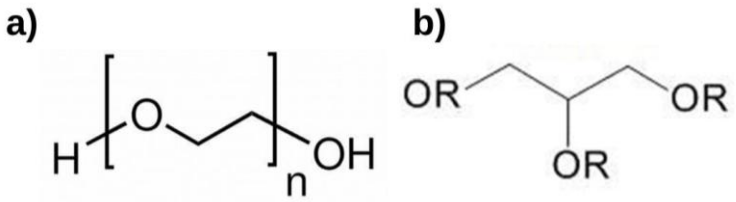

Figure 3.1: Chemical structures of a) PEG, b) Castor oil where R represents the fatty acid components

The combination of castor oil and PEG as soft segments in polyurethane synthesis offers a unique synergy, blending the natural-based flexibility of castor oil with the multifunctional and hydrophilic properties of PEG. This combination not only enhances the film's flexibility and water retention capabilities but also contributes to improved biodegradability and sustainable film production, aligning with eco-conscious and efficient packaging solutions.

3.2.2 1,4 Butanediol (BDO) and 1,6-Hexamethylene diisocyanate (HMD) as hard segments

Isocyanates play a pivotal role in instigating crosslinking within polyurethane films, conferring upon them attributes such as hardness, strength, and stiffness. In this study, the chosen isocyanate is 1,6 Hexamethylene Di-isocyanate (HMD), characterized by the presence of two or more N-C-O groups can be seen in figure 5. Hexamethylene Di-isocyanate (HMD) is widely favoured in polyurethane synthesis due to its reactivity and its capability to create robust polyurethane networks, making it an ideal choice for enhancing the film's structural integrity and performance [20].

Elevating the molecular weight of polyurethane is achieved through the introduction of chain extenders, short-chain molecules that hold the potential to enhance its mechanical characteristics. In this study, the selected chain extender is 1,4-Butanediol (BDO). Its interaction with facilitate groups and polyols facilitates the creation of a three-dimensional polyurethane network structure, as illustrated in Figure 5. This network structure reinforces the film's mechanical properties, making it well-suited for applications demanding resilience and durability while preserving its shape memory attributes [59].

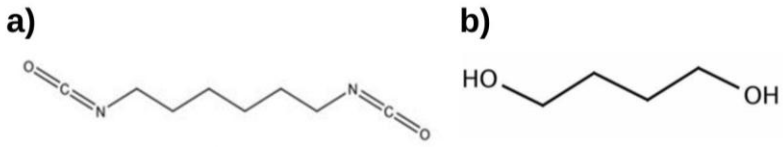

Figure 3.1: Structure of hard segments a) HMD, b) BDO

3.3 Polyester Cloth Selection

Different kinds of polyester clothes were purchased from the local market and then studied in terms of their picks per inch (PPI) number. As the PPI is higher in the fabric, that fabric is considered as finer. The PPI number of the fabric as well as the diameter of the single fiber of the fabric were studied to select the most suitable fabric for the coating. So, we got fabric of PPI numbers 42, 57 and 77. We have selected 77 as it is finer and can serve as a better substrate for coating [60].

Table 3.1: Single Fiber diameter of 44, 52 and 77 PPI polyester fabric taken by optical microscopy

	44 PPI	52 PPI	77 PP1
Sr. #	**Measurement(µm)**	**Measurement (µm)**	**Measurement (µm)**
1st Reading	330.69	335.98	349.21
2nd Reading	342.59	341.27	343.92
3rd Reading	346.56	314.81	333.33
Average	1019.84/3 =339.94µm	992.06/3= 330.68	1026.49/3=342.16

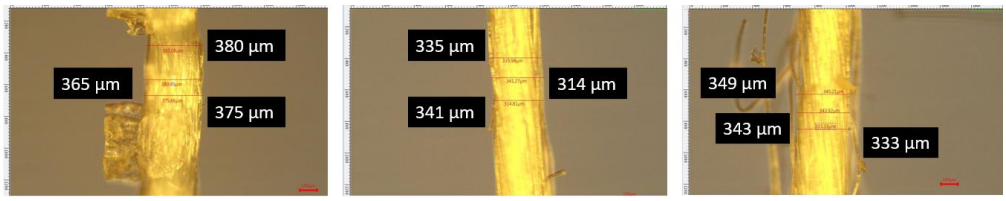

Figure 3.2: Single fiber diameter measurement from optical microscope of, 44, 52 and 77 PPI

3.4 SMPU Synthesis Approach

Synthesis of Shape memory polyurethane was done by one step bulk polymerization method which is also known as mass polymerization. It is the simplest approach to synthesize polymer as it does not use any solvents and is simple to begin with the monomer and initiator [61]. Chain growth reactions are exothermic in nature and involve a water bath to control the heat produced. The reaction becomes viscous with time.

- Different setups can be used to do one-step bulk polymerization but here we used a facile method which contains a bath (container) contains reaction vessel to maintain

the reaction temperature. The factors that were monitored carefully during the reaction were temperature, stirring speed, concentration of the reactants and time.

Figure 3.3: Setup for synthesis of one-step shape memory polyurethane

3.4.1 Synthesis of SMPU

First, PEG and Castor Oil were dried at 90 °C for the removal of any water vapors in the reactants to avoid contamination for 12 hours. BDO was dried at 50 °C for 12 hours. To get uniform, stable, and bubble-free SMPU free-standing film this step is crucial.

The reaction started with a homogeneous premixing of PEG, CO and HMD at 80 °C for two hours which aids the degassing of any volatile compounds and gases. The premixing step of HMD with polyols is essential to get uniform films. Then the reaction is followed by the addition of BDO. The reactants were then stirred with a magnetic stirrer at 300 RPM and heated simultaneously on a hot plate at 80 °C for about 10 minutes. After the reaction was completed, the reactant mixture was poured into petri dishes to get free-standing films. The thin coating was made with the help of a knife on polyester cloth which was stuck on glass slabs. Then both the Petri dishes and glass slabs containing polyester cloth were placed in the oven for post-treatment at 80 °C for 24 hours for further cross-linking.

3.4.2 Synthesis of free-standing SMPU films

The preparation of free-standing films allowed for shape memory testing of the synthesized SMPU, following a well-defined procedure. Freshly prepared SMPU was easily poured into a Teflon mold. Utilizing the Teflon mold provided a non-stick surface for consistent spreading, ensuring the creation of an even film.

Once poured into the respective mold, the curing process of the polyurethane began. The mold, infused with polyurethane, was placed inside a heated drying oven set at 80°C for effective hardening. The curing process extended for a minimum of two days, enabling the establishment of a strong and coherent coating through cross-linkage. Controlled curing in the drying oven at elevated temperatures facilitated the development of desirable mechanical properties in the film.

After the completion of the curing process, the film was promptly removed. A brief cooling period at room temperature was allowed, followed by cautious detachment from the Teflon mold, resulting in a free-standing film. In figure8 you can see the picture of Teflon mold and synthesized free-standing SMPU films.

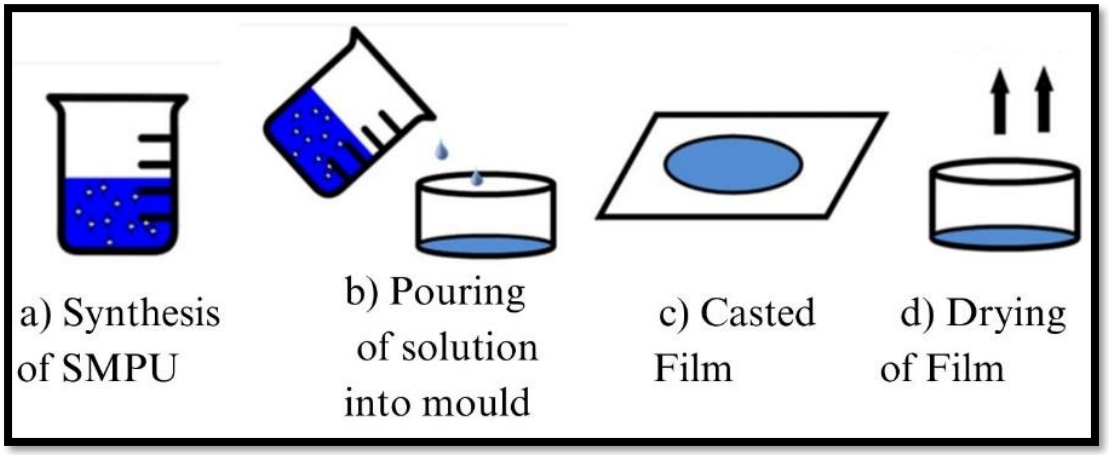

Figure 3.4: Systematic of synthesis shape memory polyurethane free-standing films.

Figure 3.5: Teflon mold and synthesis of free-standing shape memory polyurethane films

3.4.3 Pretreatment of Fabric for Coating

For the coating of SMPU, it is very important to do pretreatment on the fabric. The pre-treatment helps us to get better coating. First, we have washed the fabric to get rid of any dust. Then we bleached it for further purification. After drying the fabric was pressed to get a wrinkle-free fabric. It helps to get a more homogeneous and uniform

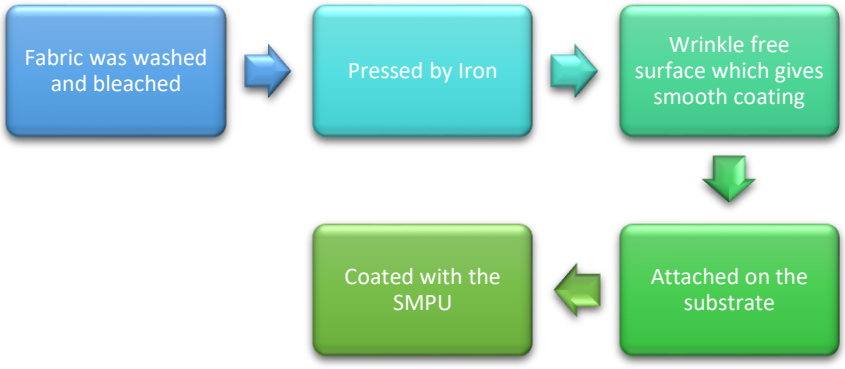

Figure 3.6: Graphical representation of pretreatment of fabric

coating. The fabric was then attached to the substrate with tape and then it was coated with SMPU.

3.4.4 Coating Process

To synthesize the uniform coating on the polyester cloth we followed a very facile approach known as screen printing process. Screen printing is a widely used technique that employs a mesh screen to transfer ink onto diverse substrates, including fabric, paper, and glass. It finds extensive applications in industries like textile printing, graphic arts, and various industrial uses.

In the context of synthesizing polyurethane films, this method entails the application of a polyurethane solution onto a flat surface, typically glass, and utilizes a doctor blade for an even and uniform coating [62]. By selectively blocking specific areas of the screen, precise design or pattern creation within the polyurethane films can be achieved, offering a versatile and controlled approach to film production. Below are the steps that we have followed for the uniform coating of SMPU on the polyester fabric:

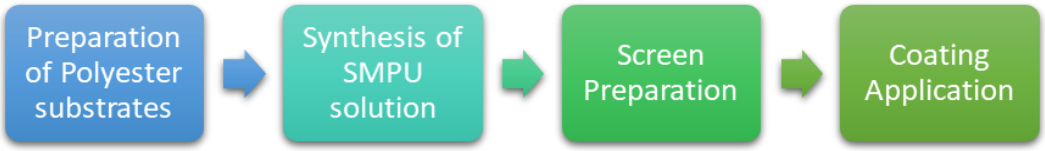

Figure 3.7: Graphical representation of stepwise coating process

To prepare the polyester substrates for SMPU coating, a meticulous process was employed involving the application of polyester cloth onto the glass surfaces. The polyester cloth was carefully affixed to the glass substrates to ensure a wrinkle-free and uniform surface using scotch tape. This step was vital to establish a smooth and consistent base for the subsequent screen printing of the SMPU solution, facilitating precise and high-quality film formation.

1. **Synthesis of SMPU solution**

The preparation of the SMPU solution for coating involved a meticulous process of combining the essential ingredients. By carefully mixing polyol, isocyanate and chain extender (mentioned in the detailed process earlier in 3.3.1), a homogenous solution was achieved. The key objective was to attain a specific viscosity suitable for coating, ensuring that the SMPU solution possessed the right consistency for smooth and controlled application during the screen-printing process.

2. **Screen Preparation**

The screen preparation was a crucial step in the SMPU coating process. The size of the mesh was thoughtfully chosen in accordance with the desired coating thickness. A finer or coarser mesh was selected to control the amount of SMPU solution passing through, thereby achieving the targeted film thickness during screen printing.

3 Coating Application of Polyurethane solution

The semi-viscous SMPU solution is then poured on the fabric attached to the glass slab. The solution was then filled into the screen's mesh with the help of Dr. Blade. To make the film of uniform thickness Dr. Blade was used with a certain amount of pressure at a little tilted angle.

3.5 Characterization Techniques

3.5.1 Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR is a technique that uses infrared light to analyze a material's chemical composition. The interaction between the light and the sample produces a unique spectrum representing the sample's molecular structure. FTIR is widely applied in various fields to identify substances, assess purity, and monitor chemical changes in samples. It operates in modes like transmission, reflection, and attenuated total reflectance (ATR), each offering specific advantages for its ability to provide information about functional groups, chemical bonds, and molecular vibrations. In the figure 9 gives the detailed fingerprint region of infrared absorption for specific functional groups.

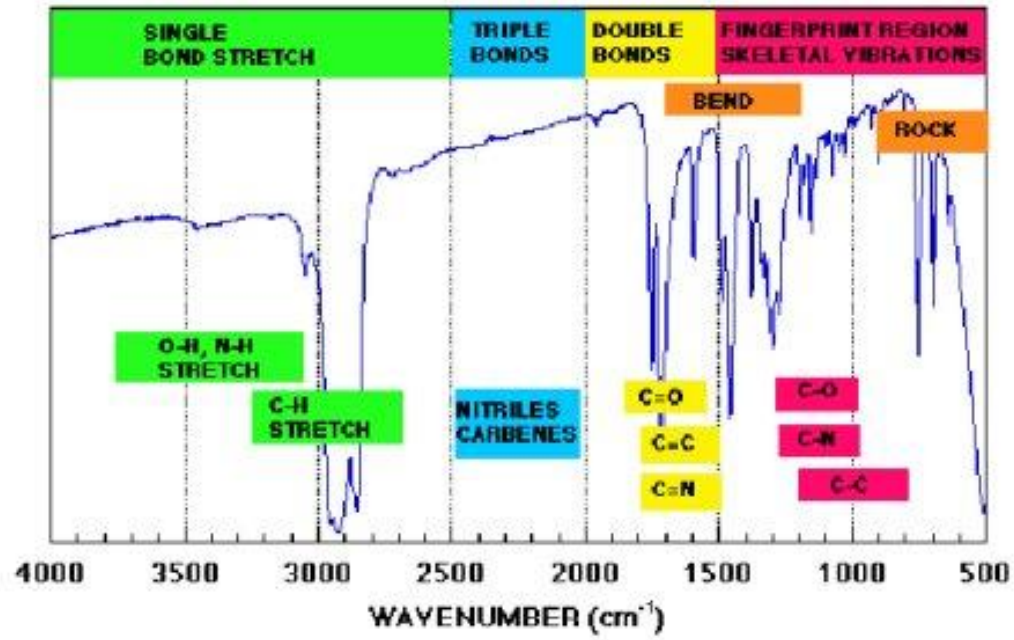

Figure 3.8: Absorption regions of different functional groups in mid and far infrared region

The FTIR analysis in this study was performed using a FTIR instrument Perkin Elmer USA Spectrum 10D, operating in the range of 4000 to 500 cm^{-1}. The samples were prepared by making KBr pallets with a small amount of coating in them. The obtained FTIR spectra provided valuable information about the chemical composition of the analyzed SMPU coatings.

3.5.2 Scanning electron microscopy (SEM)

SEM is a technique where a focused electron beam interacts with a specimen's surface, causing the emission of secondary electrons and backscattered electrons, along with X-rays. The output from a detector modulates the brightness of a cathode ray tube, creating an image of the material. SEM allows for easy sample preparation and provides information on morphology, chemistry, crystallography, and plane orientation at various magnifications, ranging from 10 to 500,000 times.

The SEM analysis in this study was carried out using a JEOL-JSM-6490LA scanning electron microscope operating at 10-20 kV, with a spot size of 35-60 and a working distance of 10 mm. The images were recorded in secondary electron mode at both low and high magnifications.

Samples for the study of cross-section were prepared by dipping the sample in liquid nitrogen and then tearing it and sputtering it with gold to make it conductive. Later examine through SEM to get the most accurate reading about the coating thickness and surface morphology.

3.5.3 Optical profilometry

To see the roughness of the coated films. We have done optical profilometry which tells us about the surface roughness of the coated films through optical profile measurements. The uniform surface of the coated films is essential as it can give us uniform properties of the film. And to achieve high functionality in the crisper the thickness needs to be uniform, so it gives us equal barrier properties on any part of the SMPU film [63].

Surface Roughness

The investigation of membrane surface roughness is a crucial parameter, particularly concerning fouling aspects. In this study, the surface roughness of the prepared membrane specimens was examined using optical profilometry. The emergence of surface roughness is commonly associated with processing methods and various influencing factors. Due to disparities in processing methods and materials, the imprints left on the processed surface vary in depth, density, shape, and texture. The primary parameter for assessing surface roughness is the contour arithmetic mean deviation (Ra), representing the arithmetic mean value of the distance from each point on the measured contour to the reference line within the defined sampling range according to ISO 4287 [64].

3.5.4 Thermogravimetric analysis

To evaluate the thermal stability and degradation behavior of the synthesized polyurethane films, one of the films were analyzed, thermal gravimetric analysis (TGA) was performed using a TGA Q500 (TA Instruments). For the analysis, little fragments of the polyurethane film samples (about 10 mg) were cut and put in a platinum pan. To stop oxidation, the samples were then heated from ambient temperature to 800°C in a nitrogen environment at a steady heating rate of 10°C/min. The nitrogen flow rate was maintained at 50 mL/min for the experiment.

3.5.5 X-ray diffraction analysis

The crystalline structure and phase composition of the PU1 sample were investigated using X-ray diffraction (XRD) techniques. The investigation was performed using an X-ray diffractometer (STOE Germany S/N 65022) with a Cu Kα radiation source (λ = 1.5406 Å). The samples were scanned at 1°/min over a 2θ range of 5° to 80°, with a step size of 0.02°. 30 mA and 40 kV were the operational parameters. The material's crystalline and amorphous areas were determined by analysing the diffraction patterns that resulted from data collection conducted under ambient settings. The degree of crystallinity was assessed by looking at the baseline and diffraction peaks.

3.5.6 Contact Angle

Contact angle measurement is a valuable technique employed to assess the wettability of surfaces, including SMPU coatings. The contact angle is the angle formed at the interface of water, air, and solid, and its magnitude indicates the potential of the surface being wetted by water. Low contact-angle values indicate that water spreads and adheres to the surface, whereas high contact-angle values indicate that the surface repels water. In the context of SMPU coatings, measuring the contact angle is crucial for understanding their interaction with liquids, such as water or food substances, which is essential for applications in food preservation [22].

Using a Dataphysics OCA 40 contact angle instrument and the sessile drop technique, the contact angle with water was measured to assess the wettability of the SMPU coated films. We cut our SMPU-coated clothing into 2 by 2 inch pieces and secured them to a frame in order to evaluate the contact angle. The contact angle value was the average of three measurements, and the water droplet volume was 5 μL [65].

3.5.7 Differential Scanning Calorimetry (DSC)

DSC is a powerful technique employed to study the phase changes in SMPU coatings. DSC measures the heat flow into or out of a sample as it undergoes controlled temperature changes. This method is particularly useful for understanding the thermal properties of materials, making it essential for investigating the behavior of SMPU coatings [66].

DSC can identify critical phase transitions, such as crystallization, glass transitions, melting points (Tm), and enthalpy changes (ΔH) (J/g). These phase transitions are crucial in influencing the thermal stability and performance of coatings, particularly when used in food preservation. The crystallinity and melting temperature of polymer films were measured using a differential scanning calorimeter (DSC) on a TA Instruments Trios V5.0.0.44616 USPCASE, NUST, Islamabad. The samples were first heated from -40 to 375°C at a rate of 10°C/min. The used sample weights were around 6 mg.

DSC analysis provides valuable insights into the SMPU coating's behavior under different temperature conditions, helping researchers assess its suitability for real-world applications. By studying phase changes, researchers can optimize the formulation and design of SMPU coatings to ensure they exhibit the desired characteristics for preserving and protecting food items effectively and getting the desired temperature transition.

3.5.8 Water Vapour Transmission Rate and water vapor Permeability Test

In accordance with ASTM E96B, the water vapour transfer rate (WVTR) of the synthetic Shape Memory Polyurethane (SMPU) films was determined using the desiccant method. Open-mouthed beakers containing silica gel were sealed with the manufactured SMPU films and kept at 23°C and 50% relative humidity. At regular intervals over a 4-hour period each test beaker was periodically weighed with the sealed film using a precise weighing scale. The changes in weight were carefully recorded and analyzed against time [67]. Upon reaching steady-state conditions, linear regression analysis was employed to fit a straight line to the plot. The slope of this line represented the rate of moisture transmission (G/t), from which the slope (G/t) was divided by the film's test area (A) to determine the water vapour transmission rate (WVTR). The WVTR was estimated with the following equation:

$$WVTR = \frac{G}{tA}$$

Where:

G is the change in beaker weight (in grams), t is the experiment duration (in days), and A is the surface area of the film (in square meters). Following the determination of the WVTR, the water vapour permeability (WVP) of the produced SMPU films was computed using Fick's First Law. The following formula was used to calculate the WVP:

$$WVP = d\frac{WVTR}{\Delta P}$$

where WVTR is the water vapor transmission rate in grams per day per square meter ($g/d/m^2$), t is the experiment's duration, and A is the film's surface area (in square meters, m^2) [68].

3.5.9 Moisture Content (MC)

Measuring the moisture content (MC) is an essential aspect of studying the phase changes in SMPU coatings, as it provides insights into the coatings' ability to interact with and retain moisture under different environmental conditions. The MC determination, performed through the gravimetric method, is a critical parameter to understanding the coatings' response to humidity and water vapour.

In this method, small film specimens (typically 2 cm x 2 cm) are initially weighed (Wi) to establish their dry weight. These specimens are then subjected to controlled conditions in an oven, and dried at 105°C for a specified period, usually 24 hours. After the drying process is complete, the specimens are reweighed (Wf) to determine their final weight [69].

The MC is then calculated using the following equation:

$$\boldsymbol{Moisture\ content}\ \% = \frac{(\boldsymbol{Wi - Wf})}{\boldsymbol{Wf}} \times \mathbf{100}$$

The MC data reveals how much moisture the SMPU coatings can absorb or release under the influence of environmental factors. By tracking MC changes under varying humidity and temperature conditions, researchers gain valuable insights into the

coatings' phase transitions, including swelling or shrinking. This information is crucial for optimizing the performance of SMPU coatings in food preservation applications, as it helps ensure the coatings' stability and effectiveness in managing moisture levels to extend the shelf life of food products.

3.5.10 Water Solubility

In previous studies, the solubility of the films (WS) in water was assessed using a standardized method [70, 71]. Initially, the PU film samples were subjected to drying at 100°C for 24 hours to eliminate any moisture content. Following this, the dried film samples were weighed to obtain their initial weight measurements (w_0). Subsequently, these dried film samples were immersed in distilled water for a duration of eight hours under constant magnetic stirring. After the immersion period, the films were carefully filtered and subsequently dried once again at 100°C for 24 hours to acquire their final weight (w_f) measurements. The solubility of the films (WS) was then calculated using Equation were MC represents the moisture content determined by Equation. To ensure the reliability and reproducibility of the results, three samples for each formulation were tested. This standardized approach allows for a comprehensive evaluation of the films' solubility in water, providing valuable insights into their potential applications and environmental implications.

$$WS = \frac{Wo \times (100 - MC) - Wf}{Wo \times (100 - MC)} \times 100$$

3.5.11 Shape Memory Test

By performing the shape memory tests, we could evaluate how the SMPU coatings respond to changes in temperature and understand the phase changes they undergo, offering insights into their practical applications and potential for shape memory functionality.

To conduct shape memory tests on the SMPU coatings, a well-defined procedure was followed. Transition temperatures for the tests were selected based on the melting temperature of the soft segments within the polymer. Film specimens were carefully cut into standardized dimensions, measuring 1mm in thickness, 50mm in length, and 15mm in width. These film specimens were then subjected to a series of controlled tests [72].

The shape memory test procedure involved the following steps:

1. The film specimens were initially placed in a drying oven set at 35 ºC for a period of 5 minutes. This heat conditioning allowed the polymer to adapt to a temporary shape.
2. After the heat conditioning, the film specimens were bent to an angle of 180 º (Θ_{max}), and a load of 3 kgs was applied to maintain this bent position.
3. The films, while maintaining the applied load, were placed in a refrigerator for 5 minutes. This step induced a phase change in the polymer's shape memory behavior.
4. Following refrigeration, the applied load was removed, and the angle (Θ_{fixed}) was measured, indicating the degree of shape recovery at this stage.
5. The film specimens were returned to the drying oven at the same temperature (35 ºC) for another 5 minutes.
6. Subsequently, the angle (Θ_{final}) was measured after the second heat conditioning step, providing information about the polymer's shape recovery.

The shape memory behavior of the films was assessed using the Shape Fixity Ratio (Rf) and Shape Recovery Ratio, which were determined using the following formulas:

$$\boldsymbol{Shape\ Fixity\ Ratio\ (Rf)} = \frac{\boldsymbol{\Theta fixed}}{\boldsymbol{\Theta max}} \times \mathbf{100}$$

$$\boldsymbol{Shape\ Recovery\ Ratio\ (Rr)} = \frac{\boldsymbol{\Theta fixed - \Theta final}}{\boldsymbol{\Theta fixed}} \times \mathbf{100}$$

3.5.12 Food Packaging Test

The evaluation of food packaging tests plays a pivotal role in understanding the practical application of SMPU coatings, particularly in scenarios like preserving fresh produce in a crisper. These tests provide insights into how well the coatings can maintain the quality and shelf life of food items in real-world storage conditions [73, 74]

The food packaging test aimed to simulate real-life scenarios, where maintaining freshness and preventing spoilage are essential. The SMPU coatings were assessed for their ability to act as a protective barrier, preserving the quality of the cabbage samples

under refrigeration conditions. Parameters such as moisture retention, temperature stability, and the prevention of external contamination were evaluated.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 FTIR analysis

The FTIR spectra depicted in Figure 13 highlight distinctive features of PU1, PU2, and PU3 formulations. Notably, the urethane ether linkage (NH-COO) is evident in PU1, PU2, and PU3 at 1101 cm^{-1} and 1137 cm^{-1}, respectively [75]. The presence of the NH stretching peak at 3422 cm^{-1}, coupled with the absence of a peak at approximately 2230 cm^{-1} (indicative of the NCO group), suggested the completion of polymerization. This observation aligns with established findings in polymer chemistry [18].

In PU1 and PU2, a notable feature in the spectra was the presence of vibration peaks related to the C=C in the aromatic ring, accompanied by CH out-of-plane bending, identified at wavenumbers of 1596 cm^{-1}. This characteristic is indicative of an aromatic polyurethane structure. Intriguingly, this feature is absent in PU3.

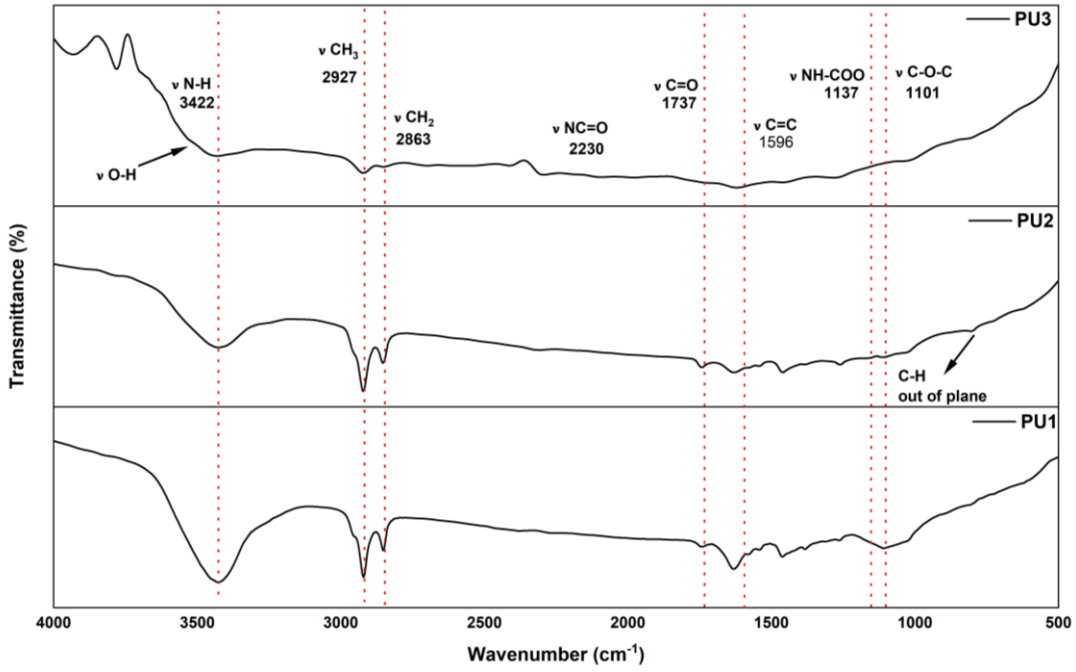

Figure 4.1: FTIR analysis of Synthesized Shape Memory polyurethanes

An essential consideration lies in the peaks associated with free carbonyl (C=O) vibrations at 1737 cm^{-1}, a significant parameter for assessing the degree of microphase mixing. The integral of the corresponding peak serves as a criterion for evaluating the extent of microphase mixing. Researchers have proposed equations to quantify this aspect, emphasizing the importance of these peaks in characterizing the polyurethane structures [8] .

4.2 SEM Analysis

The SEM analysis was employed to characterize the morphology of the synthesized PU membranes, as depicted in the figures. Cross-sectional SEM images revealed a dense structure across all three PU membrane samples. Both the cross-sectional Figure (a,d and g) and surface images Figure (c,f and i) collectively suggest the absence of surface defects that could compromise the functionality of the membranes. The thickness of the prepared membranes are around 97 -99 µm and comparison can be seen in PU1 a) with a coating thickness of 97.2 ± 14 µm, PU2 with coating thickness of 99.6 ± 2.8 µm Figure d and PU3 with coating thickness of 98.3 ± 6.1 µm in Figure g. The membranes observed are the robust and intact in nature supporting their potential effectiveness in fulfilling their intended purpose to provide better gas barrier properties in crisper.

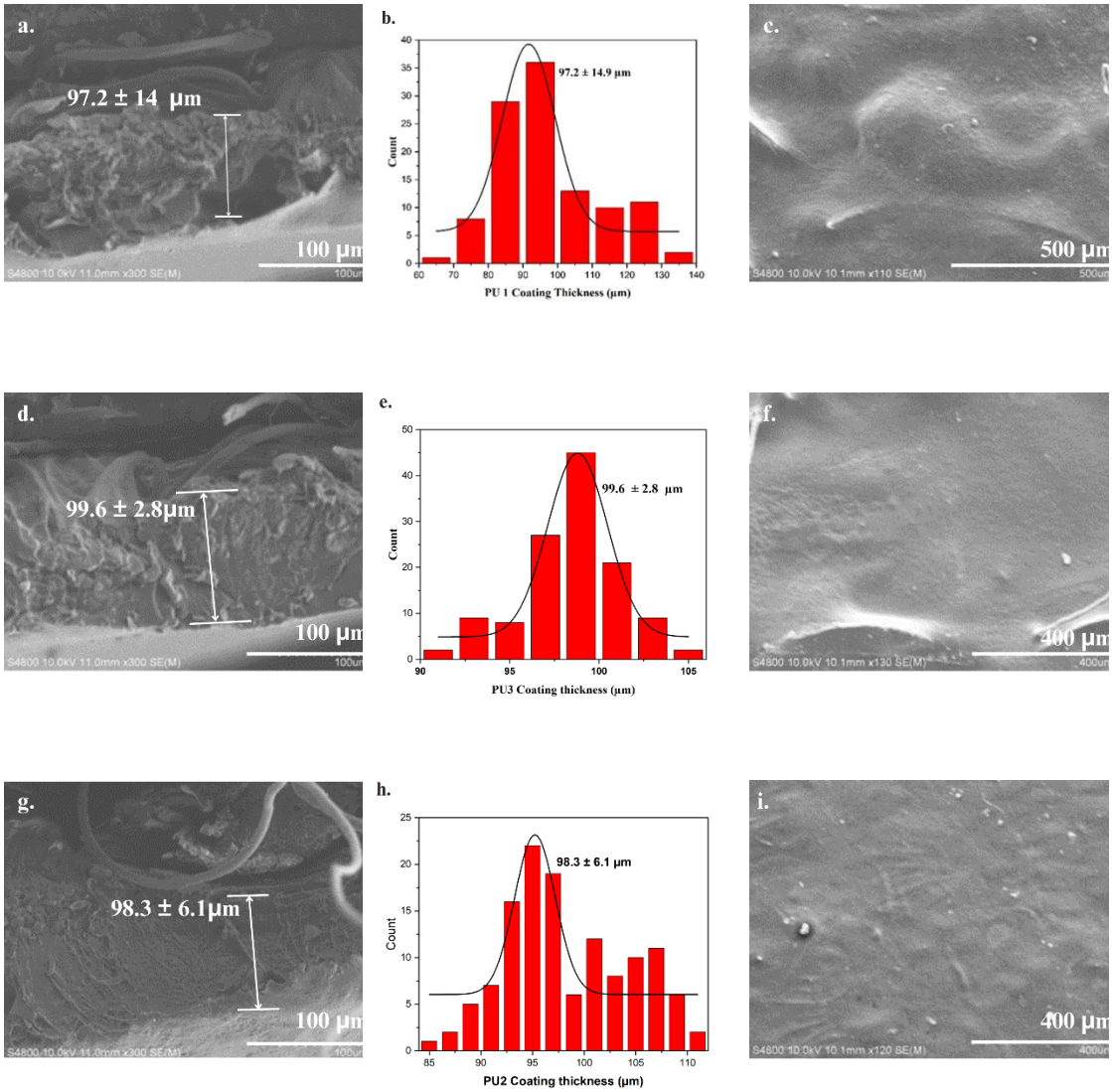

Figure 4.2: SEM analysis of SMPU coating on Polyester cloth. a,d,g) Cross-section of PU1, PU2 and PU3, b,e,h) average thickness measurement curves with standard deviation observed through SEM of PU1,PU2 and PU3, c,f,i) shows surface morphology of PU1, PU2 and PU3

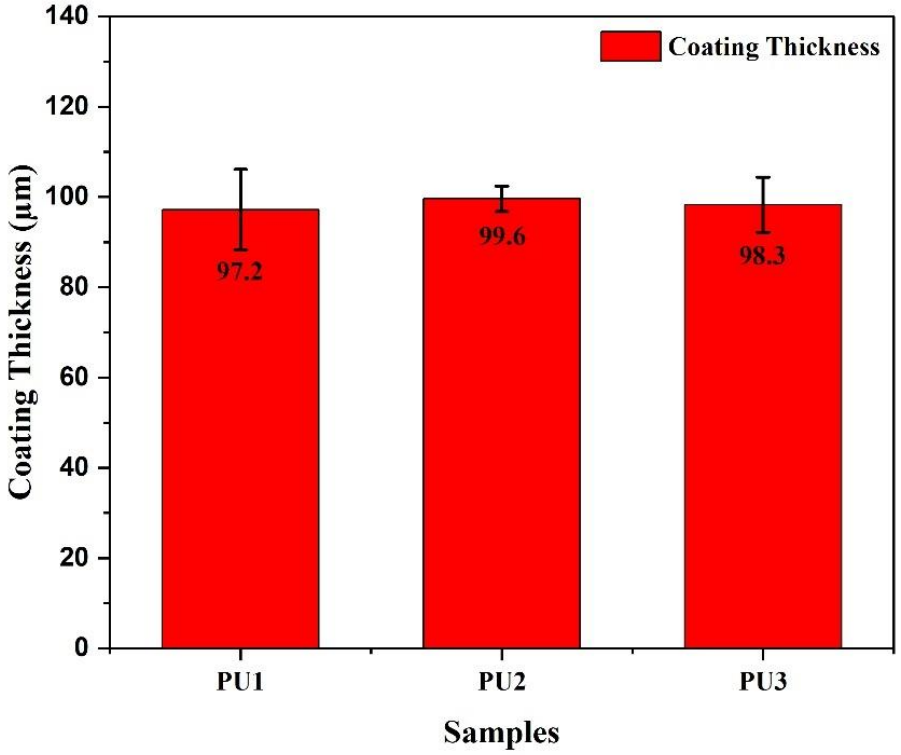

Figure 4.3: Bar graph representing SMPU coating thickness on Polyester Fabric analyzed by SEM.

4.3 Optical profilometry

In the case of the prepared SMPU coating on polyester cloth, the analysis focused on surface roughness for both the coated and uncoated sides. On the coated side of the three prepared coatings, an almost similar Ra value was observed between 3.05 - 3.86 can be seen in Figure 4.4, significantly lower due to the smooth nature of the resulting film, resulting in reduced roughness. Conversely, when comparing the uncoated side of all three membranes, higher roughness was noted. This is attributed to the fact that the coating did not penetrate to the other side of the cloth, leaving it near the polyester cloth without any protective coating also we have observed through SEM images in Figure 4.3.

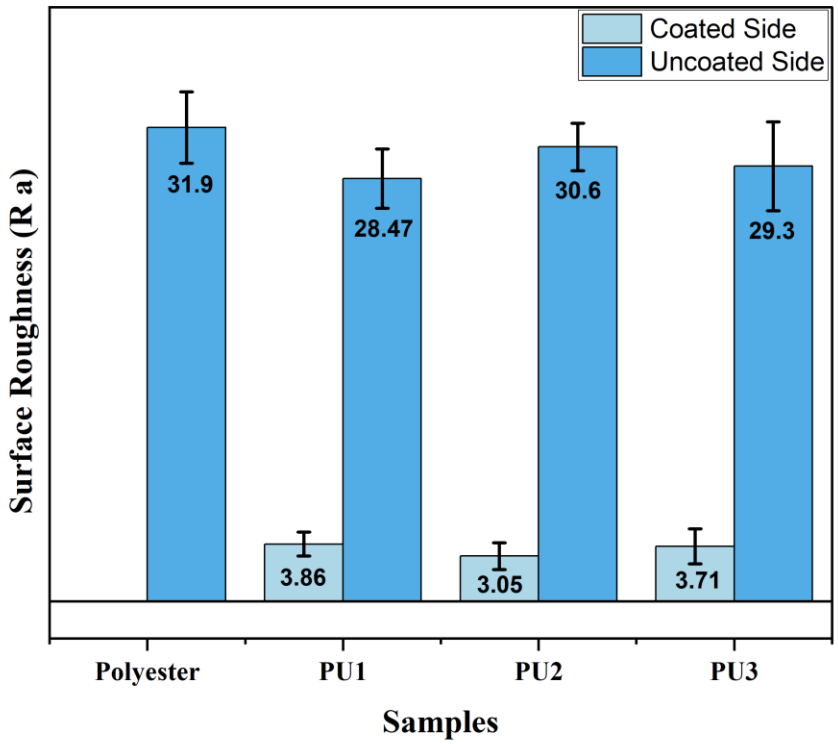

Figure 4.4: Bar graph represents surface roughness Ra from coated and uncoated

4.4 TGA Analysis

PU1 showed a multi-stage heat breakdown behavior according to TGA investigation. At 260°C, there was an initial 3% mass loss that was ascribed to moisture or volatile component removal. The degradation of the soft segments is linked to the first significant stage of decomposition, which started at 325°C and resulted in a 30% mass loss. At 372°C, a second significant decomposition stage was detected, accompanied by a 50% mass loss. This stage is probably related to the breakdown of hard segments and the crosslinked network. At 425°C, the final stage of disintegration produced an 80% mass loss, signifying the polymer's total breakdown. After 425°C, the residual weight indicates the presence of inorganic residue or stable char. These findings highlight PU1's comparatively strong thermal stability, which suggests that it is very stable to use for food packaging.

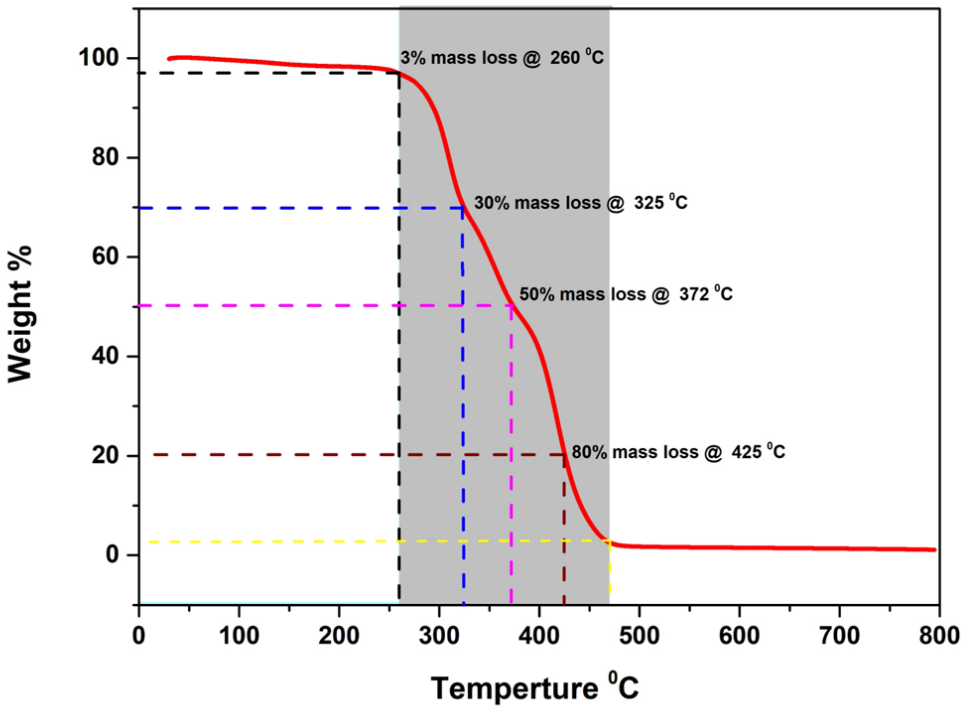

Figure 4.5: TGA analysis for the PU1 SMPU film

4.5 XRD analysis

The XRD pattern indicates that the SMPU film for PU1 sample is semi-crystalline. While the sharp peaks at particular 2θ values verify the existence of crystalline domains, the broad peak in the 10-30° 2θ range suggests the presence of amorphous regions. The crystalline structure of the hard segments in the SMPU, which are usually created by the ordered arrangement of urethane and urea connections, is responsible for the diffraction peaks. The degree of crystallinity and the size of the crystalline domains inside the SMPU film can be inferred from the relative intensity and sharpness of the peaks.

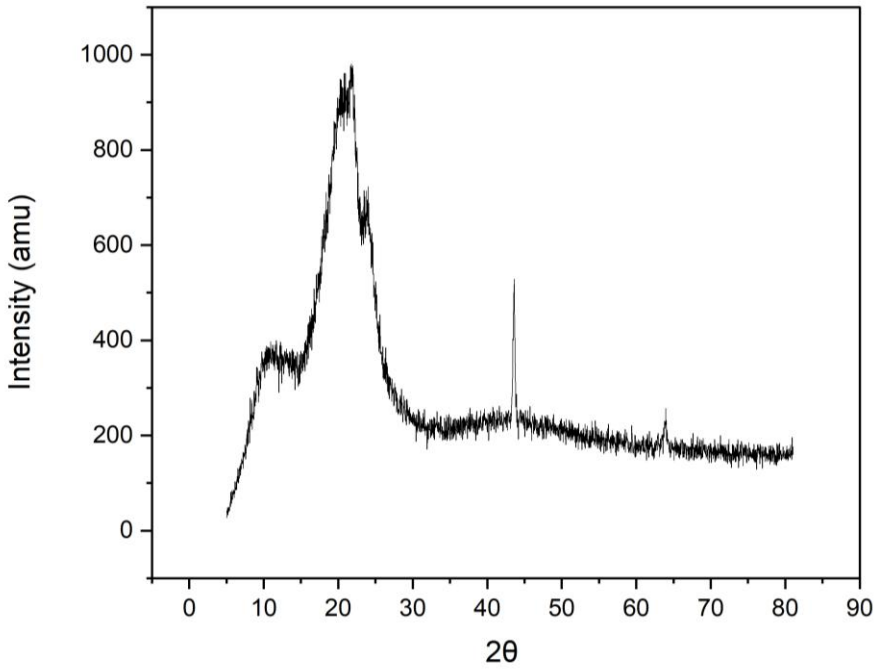

Figure 4.6: XRD pattern showing the crystalline phases present in PU1

4.6 Wettability Property Analysis

The analysis of the water contact angle serves as a fundamental parameter for evaluating the hydrophilic-hydrophobic characteristics of a membrane surface, particularly in relation to its antifouling properties. In Figure 17, the contact angle measurements of PU1, PU2, and PU3 are presented for both the coated and uncoated sides.

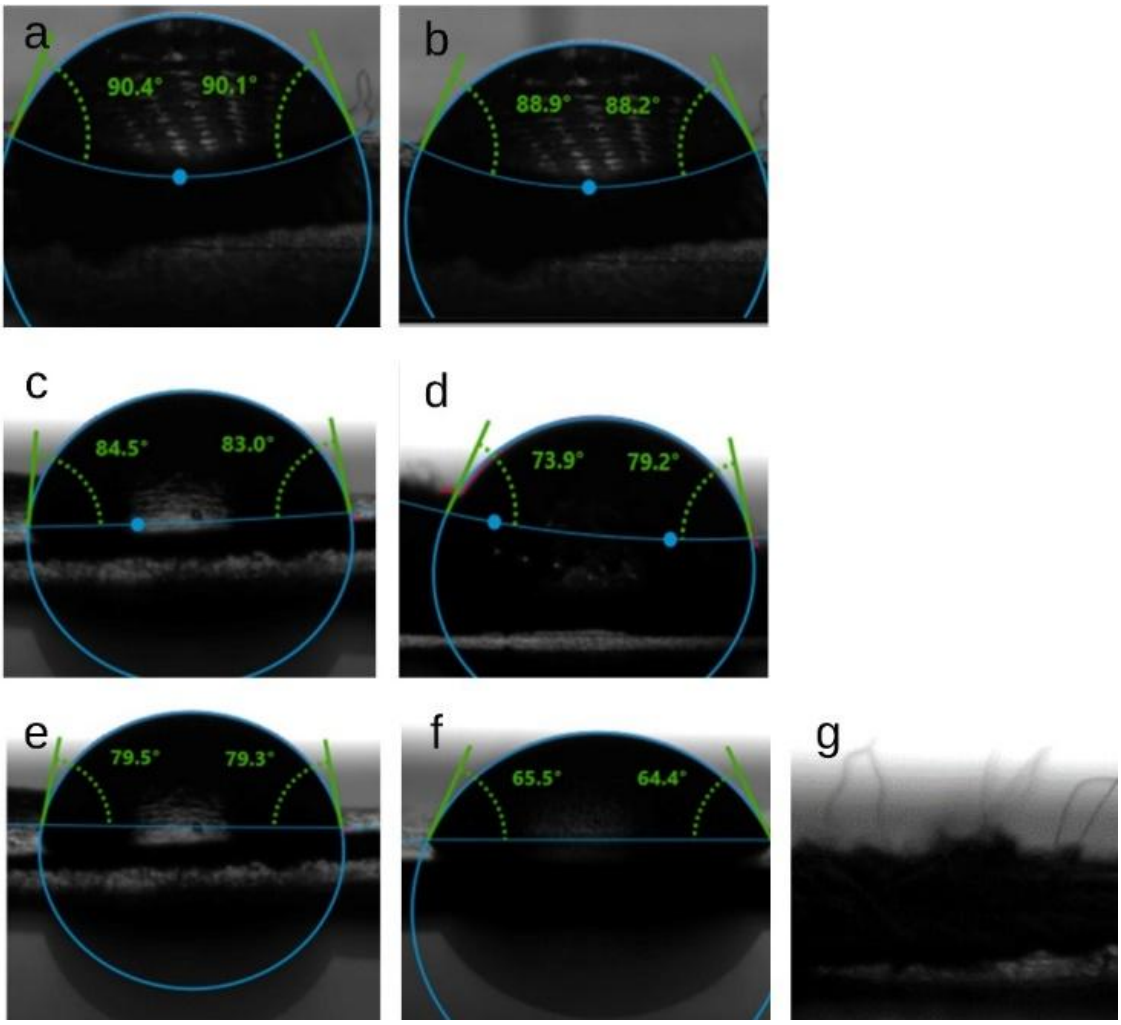

Figure 4.7: Contact angle measurement of a-b) coated and uncoated side of PU1, c-d) coated and uncoated side of PU2, e-f) coated and uncoated side of PU1, g) polyester fabric

Notably, the increasing trend in the hard content (BDO) in all three coatings (PU1-PU3) indicates an increasing level of hydrophobicity across the membranes. However, a crucial observation is the uneven polyol content in the coatings, contributing to an enhanced hydrophobic nature. Specifically, PU3 exhibits the highest polyol content, rendering it more hydrophobic and resulting in a larger contact angle, approximately 90°.

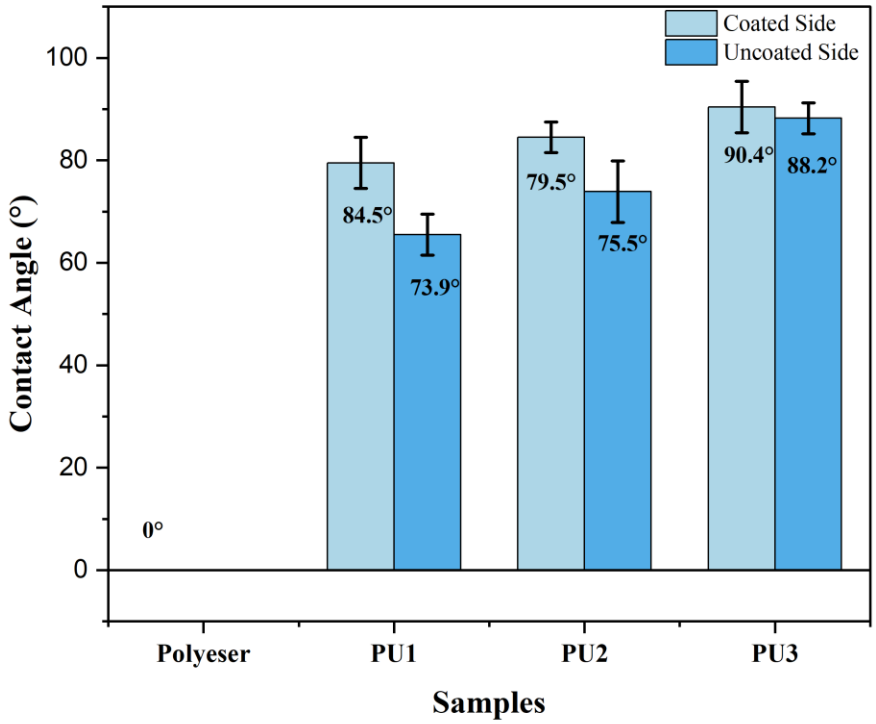

Figure 4.8: Bar Grap representing contact angle analysis in SMPU coating

This trend aligns to tailor coatings for high water vapour barrier properties and effective moisture control. The inherent hydrophobicity observed, particularly in PU3 and the other two coatings, with its significant contact angle, signifies a promising attribute for achieving superior water barrier properties in the coatings. On the other hand, Polyester cloth without any coating does not show any contact angle with water because of the super hydrophilicity of the polyester cloth can be seen in Figure 4.7. Also, the contact angle of the uncoated side is relatively smaller than the coated side observed in all three coatings can be seen in Figure 4.8.

4.7 Differential Scanning Calorimetry (DSC)

The thermal properties of Shape Memory Polyurethanes (SMPUs), denoted as PU1, PU2, and PU3, were investigated using Differential Scanning Calorimetry (DSC). The DSC curve in Figure 4.9 provides a visual representation of the thermal behavior exhibited by all these polyurethane films.

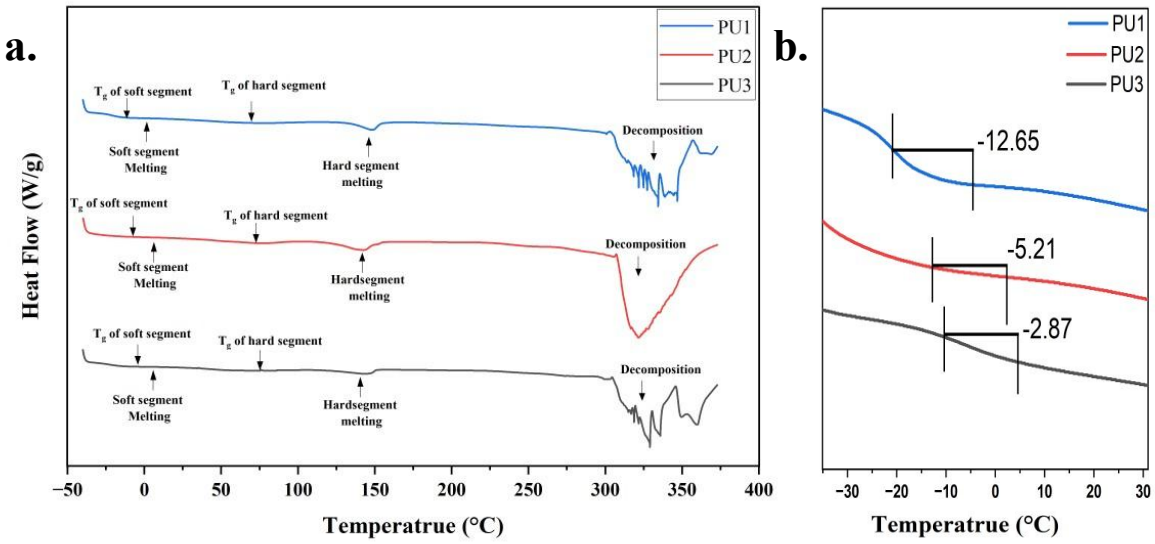

Figure 4.9: DSC analysis of PU1, PU2 and PU3 a. full spectrum and b. enlarged image.

Table 1: Data Analysis of DSC curve represented in Figure 4.9

TAG:HMD/PEG/CO/BDO	Tg,ss (°C)	Tm, ss (°C)	Tg, hs (°C)	Tm, hs (°C)
PU1: 2/0.6/0.4/1	-12.65	1.44	97.64	146.68
PU2: 2/0.5/0.5/1.1	-5.21	5.53	99.84	140.73
PU3: 2/0.4/0.6/1.2	-2.87	6.34	99.41	145.33

The melting temperature (Tm) of the soft segments is documented in Table 4, ranging from 1.44 to 6.34°C. This temperature range signifies the melting of Polyethylene Glycol (PEG) blocks within the soft segment, indicating the presence of a crystalline phase constituted by PEG crystals in the polymer. For the related SMPUs, Tm serves as a transitional temperature (Tg), signifying a shift in the polymer's crystal structure. This parameter has a significant impact on polyurethane film gas permeability and is essential for choosing the right SMPU film composition to produce switched gas permeability at a desired temperature. [76].

The Glass Transition Temperature (Tg) experiences an increase with elevated content of the hard segment and PEG in the polyurethane. This is attributed to increased rigidity arising from a greater number of aliphatic characters in the main chain of the SMPU and the formation of more hydrogen bonds between N-H and C=O groups. The polymer film's intended use in the packaging of fresh fruits and vegetables for crispier results is consistent with the reported Tm. The importance of Tm as a useful parameter in the synthesis of thermosensitive smart packaging films is highlighted by the fact that this temperature range is crucial for the gas permeability of SMPU films, a factor that is further discussed in the sections that follow [66].

Previous research on segmented polyurethane with a crystalline melting transition in the soft segment has supported the use of polyurethane for intelligent food packaging [66]. The hard-segment content, polyol nature, and polymer composition have a significant impact on thermal permeation capabilities. In the context of SMPU films synthesized from PEG 1500, the observed Tm range of 1.66 to 6.34°C makes them viable candidates for the creation of thermo-sensitive smart packaging films. This application is especially useful for managing humidity in the crisper, which addresses the unique requirements of fresh fruit.

4.8 Water Vapour Permeability Test

The films' Water Vapor Permeability (WVP) at 23°C increases with higher Polyethylene Glycol (PEG) content and lower Castor oil (CO) content, especially at a 0.6/0.4 PEG/CO ratio. Higher WVP is also observed with lower melting temperature (Tm) in the films due to the permeability nature of soft domains, which force gases to take a pass through the crystalline–amorphous interface, increasing permeability.

Table 4.1: WVTR and WVP analysis for Prepared SMPU films

Samples	Desiccant Weight Gain (%)	Films	
		WVTR ($g \cdot d^{-1} \cdot m^{-2}$)	WVP ($g.m^{-1}. s^{-1}. Pa$)
PU1	3.98 ± 1.67	394 ± 12.14	1.34E-10±0.78
PU2	4.12 ± 0.61	383 ± 5.68	1.26E-10±1.23
PU3	5.08 ± 0.29	367 ± 9.36	1.18E-10±0.51
Control	12.03 ± 0.83	-	

Taking into account the thermally triggered diffusion of small molecules in polymers, the relationship between WVP and gas diffusion properties is examined. Because PEG crystals melt, PEG1500 films with lower Tm values should have more free volume. Increased CO content, contributing to higher hard segment content, may hinder crystallinity related to PEG, decreasing free volume and contributing to lower WVP in PEG1500-containing films.

Sorption and diffusion mainly occur in amorphous regions, with crystalline regions affecting effective path length and reducing polymer chain mobility, resulting in higher activation energy of diffusion. Films with higher soft segments, such as PU1, show higher diffusivity and increased WVP and WVTR. In summary, WVP in Shape Memory Polyurethane (SMPU) films is primarily influenced by the transitional temperatures of the synthesized polymers [66].

4.9 Moisture Content (MC)

The correlation between Moisture Content (MC) and soft segment content in SMPU films, similar to Water Vapor Permeability (WVP), points to a noteworthy relationship.

This trend is consistently observed across PU1-PU3 films. Specifically, PU1, with higher soft segment content compared to PU3, exhibits the most water absorption.

The phenomenon can be explained by the role of soft domains in influencing the moisture absorption behavior of SMPU films. Soft regions act as channel to the ingress of water molecules, creating a permeable structure. As a result, films with higher soft segment content, such as PU1, demonstrate increased water absorption due to the increased movement of water molecules through the crystalline regions.

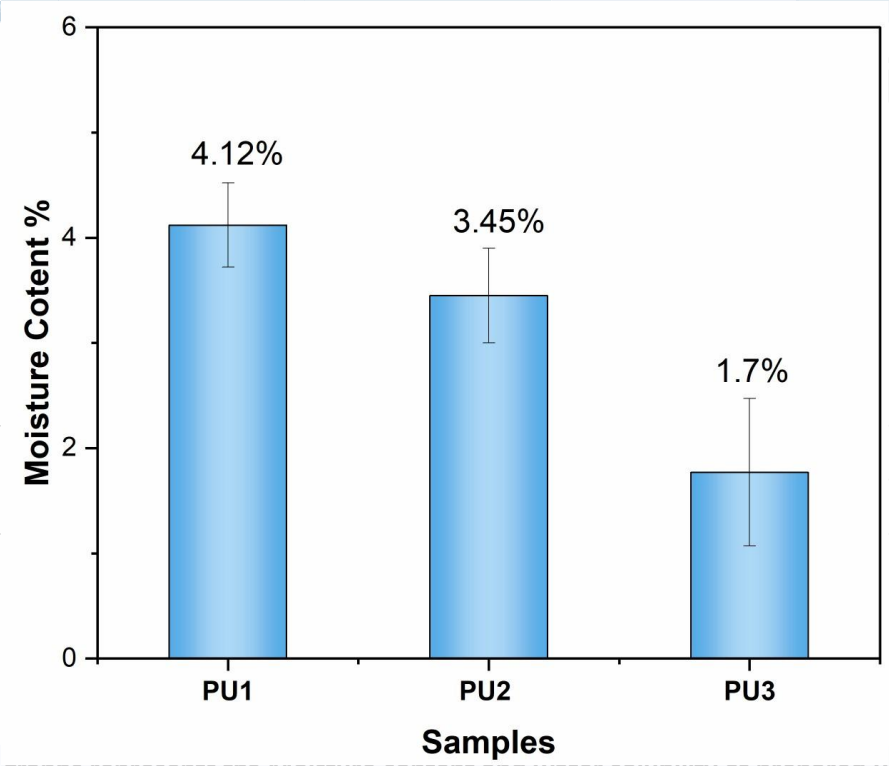

Figure 4.10: Bar graph represents Moisture content for the prepared SMPU films

The relationship between moisture content and soft segments reflects the impact of polymer structure on water absorption characteristics. The increased order and compactness in soft regions increase water molecule permeation, leading to lower moisture content in films with higher CO content in PU3.

4.10 Water Solubility

The observed trend in water solubility, which is closely related to both Moisture Content (MC) and Water Vapor Permeability (WVP), can be elucidated by examining

the impact of soft segment content and transitional temperature on the water interaction behavior of SMPU films.

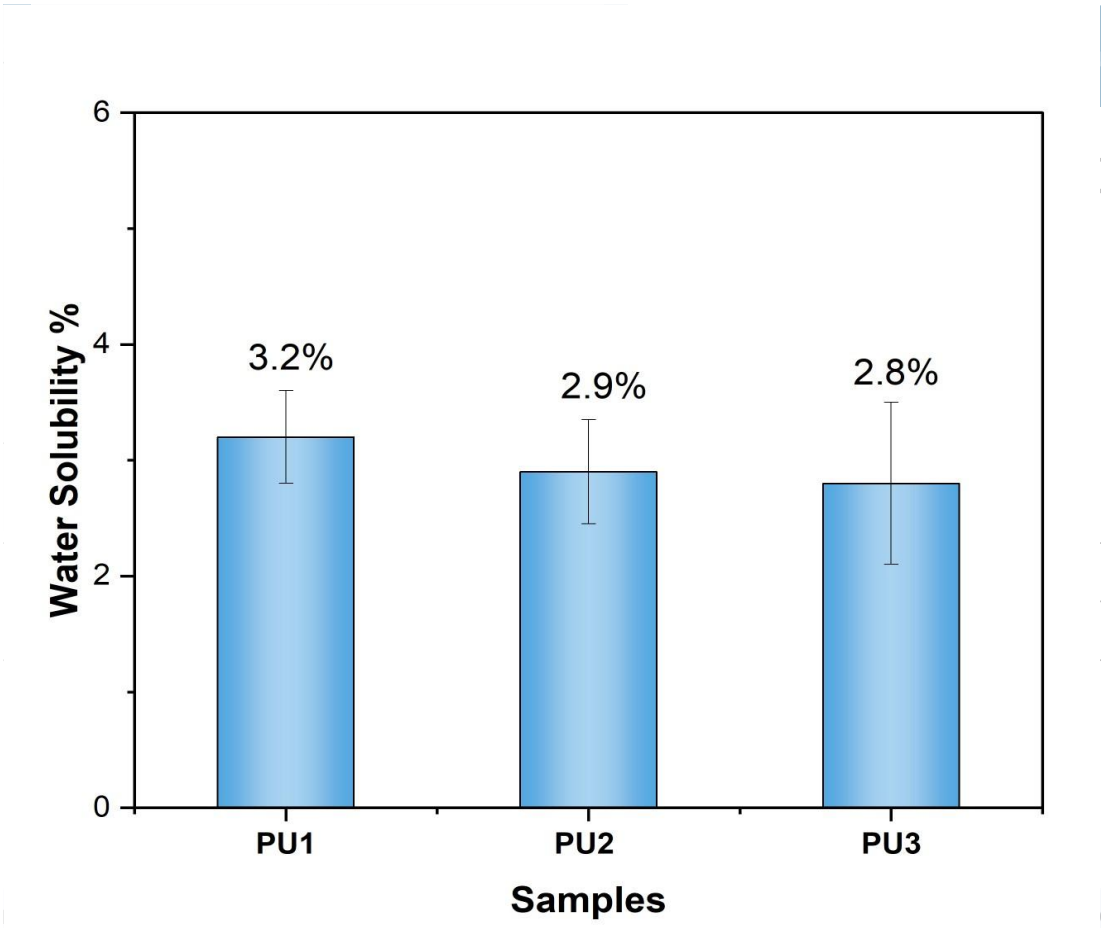

Figure 4.11:Data representing Water solubility percentage of prepared SMPU coating

The PU content regions within SMPU films act as channels that penetration of water molecules. These regions create a permeable structure, increase the movement of water through the material. Films with higher soft segment, exemplified by PU1, exhibit increased water absorption. The greater CO content in PU2-3 inhibits the ingress of water, resulting in lower water absorption. And this trend was recorded same in PU2 and PU3 SMPU films.

So, trend in water absorption aligns with the known influence of soft segment on water interaction in polymers and high transitional temperatures. Higher CO content corresponds to reduced water absorption, a phenomenon attributed to the hindrance posed by hard segment domains to the ingress of water molecules. This understanding

underscores the importance of considering material structure in tailoring water-related properties in SMPU films[77].

4.11 Shape Memory Properties

The shape-memory effect is a crucial feature for smart materials, although not intrinsic to polymeric materials. It's linked to the temperature-sensitive nature of SMPU films, impacting their gas permeability. Investigating shape-memory behavior through bending tests revealed key parameters: Shape Recovery Ratio (Rr) and Shape Fixity Ratio (Rf) are essential indicators of a polymer's temperature-stimulating behavior. These variables show how temperature-sensitive water vapour permeability and shape-memory behavior are related, which is essential for intelligent food packaging.

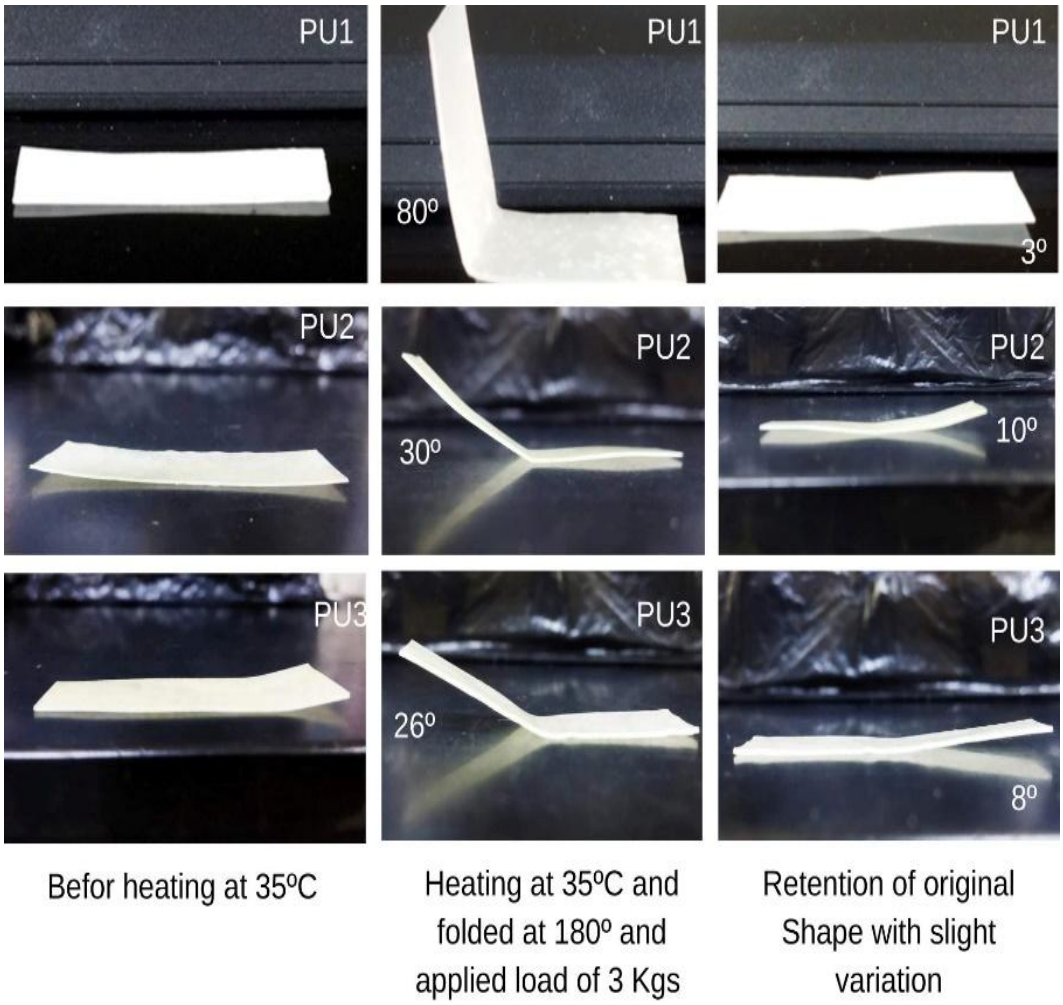

Figure 4.12: indicates the shape memory test of PU1, PU2 and PU3 free-standing SMPU films

Table 2: Shape Fixity and Shape recovery Ratio percentage of free-standing SMPU films

Sample	Shape Fixity Ratio (Rf) %	Shape Recovery Ratio (Rr) %
PU1	44.4	96.2
PU2	16.6	66.6
PU2	14.4	69.2

As PEG content increases, Rr and Rf values rise, indicating enhanced shape-memory properties. Conversely, higher CO/PEG ratio and BDO content led to decreased Rr and Rf values. A notable decrease in Rr and Rf occurs with increased BDO content in PU2 and PU3, suggesting a correlation between hard segment content and shape-memory behavior.

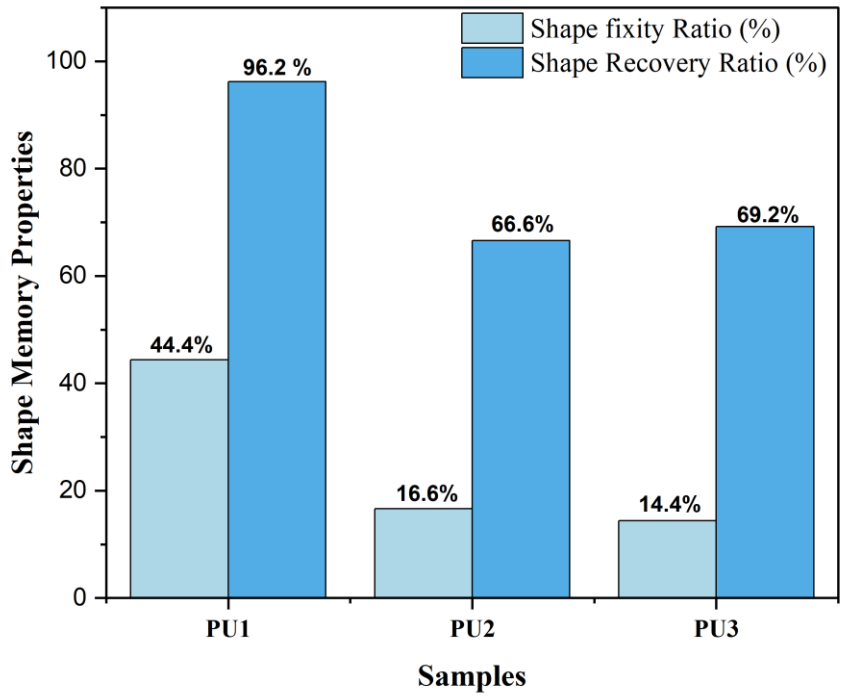

Figure 4.13: Bar graph representation of shape memory properties of PU1, PU2 and PU3

Lower hard segment content exhibits higher Rf due to better crystallinity, as indicated by DSC measurements. The association between soft segment length, hard segment composition, and material properties, influenced by transition temperatures, determines shape-memory behavior. PU1 stands out with excellent shape-memory properties, boasting Rr > 96.2% and Rf > 44.4%.

4.12 Food Packaging Test

The weight loss observed in cabbage samples is attributed to respiration and transpiration phenomena, making them susceptible to water loss during storage. According to the study, every cabbage sample lost weight within the permissible range of 6% (w/w). This limit is commonly set for fresh produce to be considered marketable products [78].

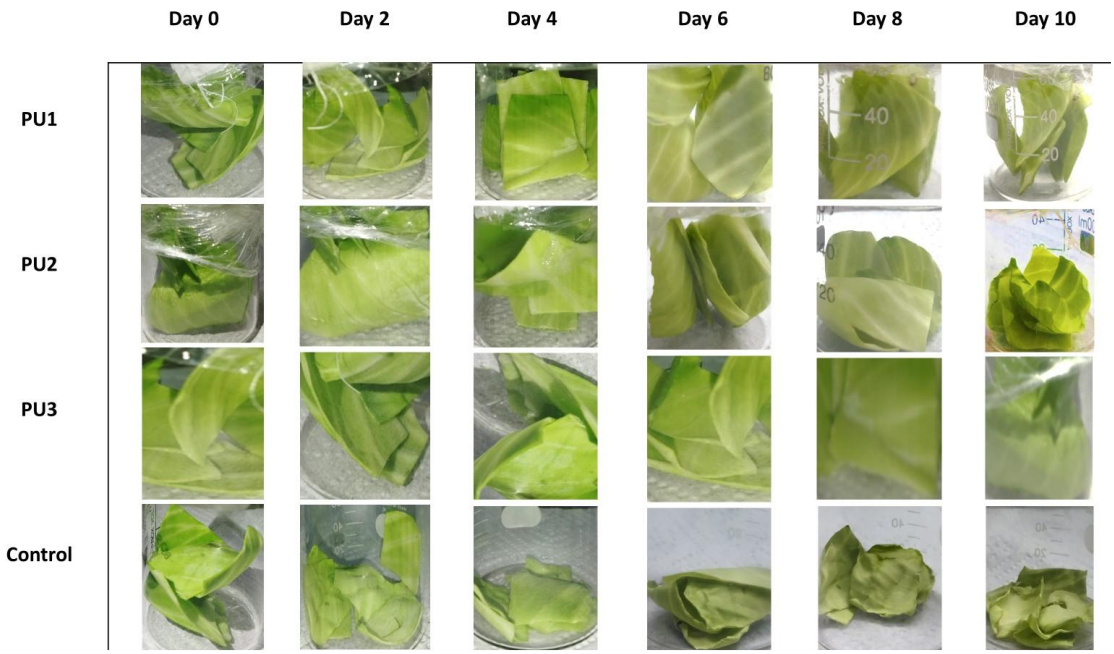

Figure 4.14: Food Packaging test of cabbage leaves for PU1, PU2 and PU3

Weight loss gradually rose in all samples during the storage time, reaching its peak towards the end of the storage period. The increase in weight loss over time could be influenced by various factors such as respiration rates, environmental conditions, and the inherent characteristics of cabbage leaves.

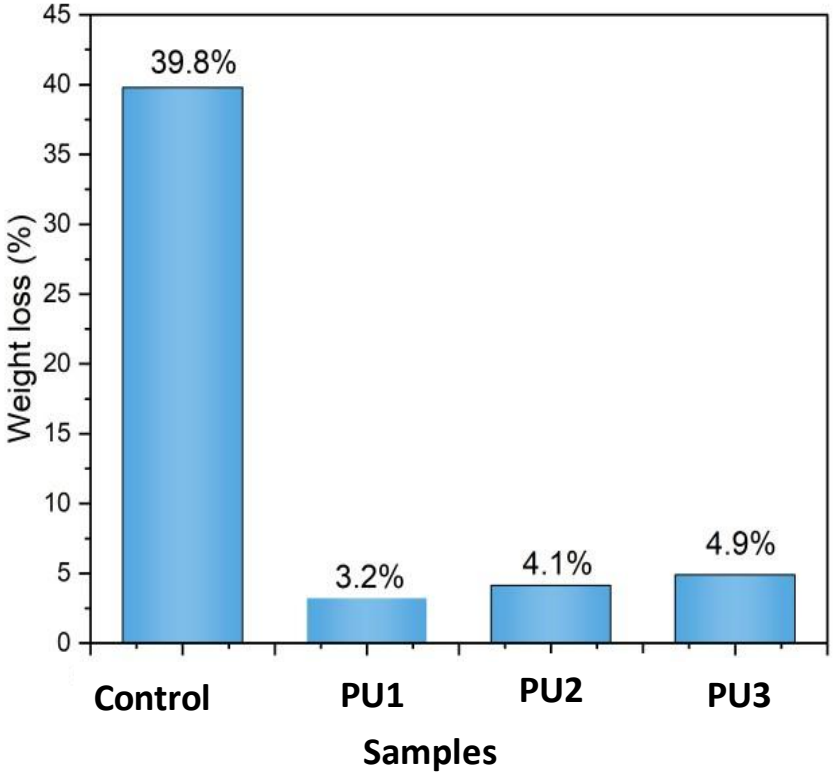

Figure 4.15: Percentage weight loss in food packaging test through PU1, PU2 and PU3

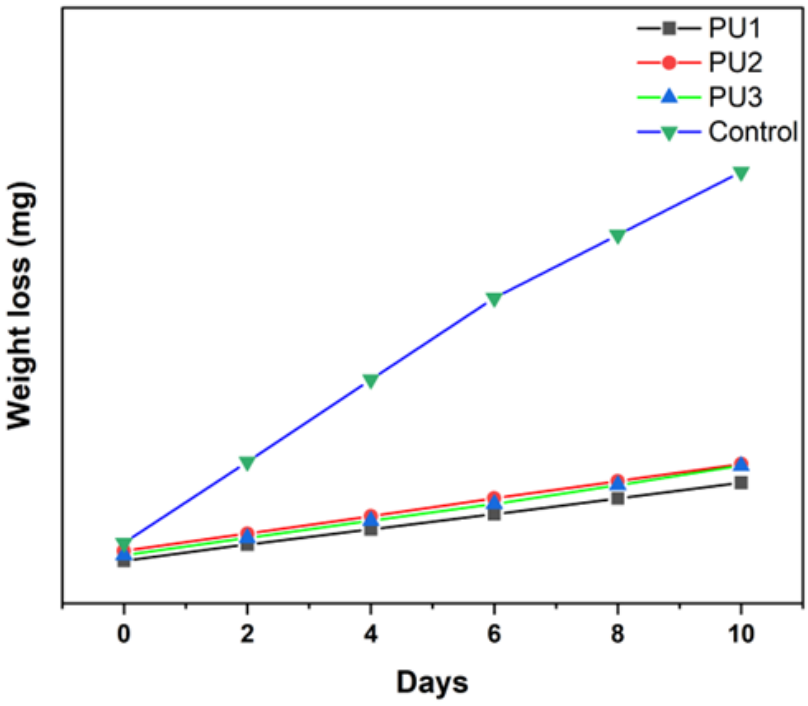

Figure 4.16: Graph representing weight loss of cabbage for the food packaging test.

The occurrence of water loss in cabbage samples is attributed to elevated respiration rates and CO_2 transfer within the vegetable leaves, leading to gradual shrinkage and a decline in overall quality. The study noted that the weight losses at the end of the storage period (10th day) were significantly influenced by the specific Shape Memory Polyurethane (SMPU) films used.

The weight losses observed in this investigation are consistent with those reported by Wenzhong Hu et al. for fresh cabbage held under refrigeration (4-6 °C) for 8-15 days [78]. The differences in weight reduction seen in cabbage sealed with different polymer films were mostly due to changes in water vapour permeability, as stated in the "Water Vapour Permeability" subsection.

CHAPTER 5: CONCLUSIONS

The synthesis of Shape Memory Polyurethane (SMPU) films for intelligent food packaging, particularly in humidity control for fresh produce preservation, is explored through meticulous manipulation of PEG, CO, and BDO content. DSC unravels the intricate interplay of composition on crucial parameters, including melting temperature (Tm) and Glass Transition Temperature (Tg). The gas permeability of SMPU films correlates with PEG content, highlighting their permeability for controlled atmospheres within packaging. Water vapor permeability increases with increased PEG content and Tm, impacting the efficiency of gas barrier properties. The study establishes a correlation between moisture content and soft segments content, crucial for optimal moisture levels in packaged goods.

In real-world applications, SMPU films effectively preserve cabbage samples, with observed weight loss within acceptable limits for marketable fresh produce. This phenomenon is attributed to the influence of SMPU films on water loss due to respiration rates and CO_2 transfer in vegetable tissue. The shape-memory effect is scrutinized through shape recovery ratio (Rr) and shape fixity ratio (Rf), where higher values with increased PEG content signify enhanced temperature-sensitive behavior, essential for maintaining packaging integrity in fluctuating conditions.

This study provides insights into the use of SMPU films in intelligent food packaging, going beyond material science. The interplay of molecular composition, permeability characteristics, and shape-memory behavior positions SMPUs as promising candidates for innovative and functional packaging solutions in the evolving landscape of food preservation.

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LIST OF PUBLICATIONS

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