

Engineered Polysaccharide α -1,3-glucan Thermoplastic Composites

by

Youn Hwan Kim

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EXAMINING COMMITTEE MEMBERSHIP

The following served on the Examining Committee for this thesis. The decision of the Examining Committee is by majority vote.

External Member **Michael Thompson**

Associate Dean and Professor, Department of Chemical Engineering,
McMaster University

Supervisor **Leonardo Simon**

Professor, Department of Chemical Engineering, University of Waterloo

Internal Members **Costas Tzoganakis**

Professor, Department of Chemical Engineering, University of Waterloo

Tizazu Mekonnen

Associate Professor, Department of Chemical Engineering, University of
Waterloo

Internal/External **Jean Duhamel**

Member Professor, Department of Chemistry, University of Waterloo

AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including my required final revisions, as accepted by my examiners.

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ABSTRACT

Thermoplastic materials with biodegradable and sustainable attributes are highly sought after due to the increase in the global plastics waste. Often, filler materials are incorporated into thermoplastics to make them more sustainable and environmentally friendly. Polysaccharides are extensively studied materials as a filler due to their abundance in nature. α -1,3-glucan is a type of polysaccharide that is biodegradable and found in fungi and some bacteria. Aside from its natural origin α -1,3-glucan can also be synthetically produced via enzymatic polymerization which allows for industrial scale production of α -1,3-glucan with controlled structure and molecular weight. It has been reported that α -1,3-glucan shares a few characteristics with cellulose, such as relatively high degree of crystallinity and insolubility in water. Unlike starch and cellulose, which are already commonly used as fillers for thermoplastics, the usage of α -1,3-glucan as a filler in a variety of thermoplastics is lacking. The objective of this research is to investigate the formulation of different thermoplastic composites that utilize α -1,3-glucan.

Three different types of thermoplastics were studied: thermoplastic polyurethane (TPU), poly(butylene adipate-co-terephthalate) (PBAT), and poly(butylene succinate) (PBS). The main goal was to maximize the α -1,3-glucan content in each polymer matrix to fully utilize the sustainability and biodegradability of the α -1,3-glucan. Simultaneously, a wide range of α -1,3-glucan loading levels was tested (ranging from 0 to 80 wt.%) to understand the properties that can be obtained when α -1,3-glucan is used as a filler.

The formulation of the α -1,3-glucan thermoplastic composites involved extrusion, injection moulding, and compression moulding to produce film and bar specimens for analysis. In the case of TPU as the base matrix, different additives such as plasticizers and peroxide were incorporated to investigate their effect on the final properties of the composite samples. With the polyesters, PBAT and PBS, different fillers (cassava starch, microcrystalline cellulose, calcium carbonate) were also used to compare with the α -1,3-glucan counterparts.

Spray drying of the hydrated form of the α -1,3-glucan, known as the wet cake, was investigated with a design of experiment approach to reduce the average particle size. The optimization of the spray drying parameters (sample concentration, feed rate, gas flow rate, drying temperature) was

crucial to minimize the average particle size. The preliminary results demonstrated that the reduction of particle size is achievable by adjusting the spray drying parameters.

α -1,3-glucan is a promising material that showed good compatibility with TPU, PBAT, and PBS, since more than 60 wt.% could be added and processed to make specimens. Additional experimentation involving more additives will further improve the quality of the α -1,3-glucan composites. The preliminary spray drying experiment showed promising results to control the particle size distribution. Continued investigation of the spray dried α -1,3-glucan should be conducted to understand the properties as well as optimize the spray drying process.

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DEDICATION

To my parents, Dong Cheol Kim and Kyoung Ran Lee, and my brother Ihn Hwan Kim.

To my partner, Stefani Starivlah.

To my cats and furry companions, Dubu and BonBon.

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LIST OF ABBREVIATIONS

Å	Angstrom (1 Å = 0.1 nm)
ASTM	American Society for Testing and Materials
ATBC	Acetyl tributyl citrate
CaCO ₃	Calcium carbonate
D05	5-µm grade α-1,3-glucan
D15	15-µm grade α-1,3-glucan
DCP	Dicumyl peroxide
DMSO-d ₆	Deuterated dimethyl sulfoxide
DOE	Design of experiment
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetry
kDa	kilo Dalton (1 kDa = 1.66×10 ⁻²⁴ kg)
LiCl	Lithium chloride
L-N ₂	Liquid nitrogen
MCC	Microcrystalline cellulose
MFI	Melt flow index
NaOH	Sodium hydroxide
NMR	Nuclear magnetic resonance
PBAT	Poly(butylene adipate-co-terephthalate)
PBS	Poly(butylene succinate)
ppm	Parts per million
RH	Relative humidity
rpm	Revolutions per minute
SE	Secondary electron
SEM	Scanning electron microscopy
STP	Standard temperature and pressure (273.15K and 1 bar)
<i>T</i>	Temperature (°C)
TBC	Tributyl citrate

T_c	Peak crystallization temperature (°C)
TEC	Triethyl citrate
T_g	Glass transition temperature (°C)
TGA	Thermogravimetric analysis
T_m	Peak melting temperature (°C)
TMS	Tetramethylsilane
TPU	Thermoplastic polyurethane
Vol. %	Volume percentage
Wt. %	Weight percentage
δ	NMR chemical shift (ppm)
ΔH_c	Enthalpy of crystallization (J/g)
ΔH_m	Enthalpy of melting (J/g)
X_c	Degree of crystallinity (%)

CHAPTER 1:

INTRODUCTION

1.1. Background and motivation

Polymers have been around us throughout the history as essential commodities, such as wool, cotton, and linen for clothing, papyrus or cellulose as paper, and natural rubber in a form of tree sap used for balls and containers. The first chemical modification of natural polymer cellulose was done by Alexander Parkes in 1855, who presented it in 1862 as Parkesine, or celluloid.^[1] It is considered the first “man-made plastic” and it was mostly used as photographic and movie films. The word plastic comes from the Greek *plastikos* meaning capable of being shaped or moulded. The term “plastic” was first coined by Leo Baekeland in 1907, who created the world’s first fully synthetic plastic known as Bakelite.^[2] The word polymer was initially introduced by Jöns Jacob Berzelius in 1833, from the Greek *polus* meaning “many” and *meros* meaning “part”.^[3] The modern concept of polymer being a macromolecule that consists of many repeating lower molecular mass units, known as monomers, was proposed by Hermann Staudinger in 1920.^[4] The improvement in science and technology during the 20th century led to the rapid expansion of plastics synthesis and production. As well, the natural polymers were quickly replaced by synthetic, petroleum-based plastics for mass production, such as poly(vinyl chloride), polystyrene, and polyethylene. Low-cost materials, excellent durability, and lightweight materials were some of the few characteristics of plastics, and it didn’t take long for plastics to replace more traditional materials such as ceramics and glass.

Unfortunately, the environmental impact of these petroleum-based, non-biodegradable plastics during the rapid production throughout the 1900s was not well considered. The estimated global production of plastics is estimated to be close to 400 million metric tons in 2021, which has doubled since the beginning of the 21st century.^[5] The lack of waste management infrastructure has led to an estimate of 30 million metric tons of plastics that have accumulated in the ocean since 1970, while more than 100 million tons have ended up in rivers and lakes.^[6] Since plastic materials are deeply integrated into our society, many researchers are seeking alternatives to address the environmental concerns.

Most plastics have good chemical and thermal resistance; they can remain unchanged for thousands of years. To accelerate the end-of-life of the persistent conventional plastics, biodegradable plastics have been developed, such as poly(butylene adipate-co-terephthalate), poly(butylene succinate), polyhydroxyalkanoates, polylactic acids, thermoplastic starch, and cellulose esters. As well, some petroleum-based plastics are made from renewable and sustainable feedstocks, such as polyethylene derived from bio-ethanol, and poly(ethylene terephthalate) produced by fermentation. The aforementioned plastics and production techniques help relieve the environmental burden but have limitations. Their manufacturing cost is generally higher than the conventional petrochemical plastics, which makes it difficult for the biodegradable plastics to compete in the market. As well, the properties are often not satisfactory, such as low strength and susceptibility to moisture.

There are a few methods to make the biodegradable plastics more competitive. Often, these polymers are blended with other polymers with different properties to compensate the weaknesses. For example, renewable and biodegradable thermoplastic starch can be blended with more durable plastics such as polyethylene and polypropylene. Another approach is to introduce filler materials to bring down the production cost. The fillers can also be reinforcing materials that can boost the strength of the polymer. There are many natural fillers that are used such as polysaccharides, like starch, cellulose, chitin, and alginate. These are abundant, renewable, sustainable, and inexpensive materials that can not only reduce the cost of the plastics but also improve its properties.

Recently, poly- α -1,3-glucan, a type of polysaccharide that can be found in the cell walls of fungi, was synthetically produced using an enzymatic polymerization method.^[7,8] This is achieved by using a culture of *E.coli* that contains the gene for glucosyltransferase enzymes that converts sucrose into unbranched α -1,3-glucan. The enzymatic polymerization technique allows for a controlled synthesis of α -1,3-glucan, keeping the molecular weight and properties between batches consistent.

1.2. Objectives

Much like starch and cellulose, α -1,3-glucan is a bio-based material that can be used as a filler in other polymers to create a thermoplastic blend. The objective of this thesis is to investigate different thermoplastic polymer blends that use α -1,3-glucan as a filler. The goal is to obtain thermoplastic composite materials with improved properties and reduced environmental impact by

incorporating a renewable and sustainable filler. Some of the potential applications of α -1,3-glucan thermoplastic composites could include films and packaging materials.

More specifically, this research aims to find a method to compound various thermoplastic composite materials using extrusion, injection moulding, and compression moulding techniques to produce film samples containing α -1,3-glucan. Three different thermoplastic resins were selected for the study: thermoplastic polyurethane (TPU), poly(butylene adipate-co-terephthalate) (PBAT), and poly(butylene succinate) (PBS). Blends of α -1,3-glucan with these thermoplastics have not been reported yet and their properties are unknown.

1.3. Thesis layout

This thesis consists of nine chapters covering the background, results, and conclusions of this project. Chapter 1 covers the motivation and objectives of the project. Chapter 2 discusses the literature information and research relevant to the project. Chapter 3 and Chapter 4 describe the materials and methods used, and the results and discussion of the TPU- α -1,3-glucan composites study, respectively. Chapter 5 and Chapter 6 discuss the materials and methods used, and the results and discussion of the PBAT- and PBS- α -1,3-glucan composites study, respectively. Chapter 7 and Chapter 8 covers the materials and methods used, and the results and discussion of the spray drying experiments, respectively. Chapter 9 summarizes the conclusions drawn, along with recommendations for future work.

CHAPTER 2:

LITERATURE REVIEW

2.1. Sustainability and Carbon Footprint

The environmental sustainability of plastic materials is becoming one of the important factors driving technology and designing new materials. When selecting materials for manufacturing, the life cycle of the material, product or process can be considered. Therefore, the origin of feedstock and its degradability need to be considered for a more sustainable design. Generally, plastics are categorized into four groups—petroleum-based non-biodegradable, petroleum-based biodegradable, renewable non-biodegradable, and renewable biodegradable plastics. The petroleum-based plastics still account for most of the plastics produced. With the environmental impact of oil extraction and plastic waste becoming more evident there is more incentive to produce renewable and biodegradable materials. Life cycle assessment (LCA) is a method to analyze the environmental impacts that are associated with different stages of the life cycle of a product, process, or service. The purpose of LCA is to consider the impact of a material from its extraction and processing (cradle) to end of its use (grave). Due to the complexity of the material processing and the number of processing steps involved, LCA can be done at different stages, such as cradle-to-cradle, cradle-to-gate, and cradle-to-grave. Through LCA a better understanding of the safety and sustainability of a material can be achieved. Although LCA studies are highly desirable, they are costly and time consuming.

The carbon footprint is one of the metrics used to identify the environmental impact of a material. For a plastic production, it is often reported as emissions (kg CO₂ equivalent) per unit mass produced (kg_{CO₂-eq}/kg_{material}). The greenhouse gas emission (kg CO₂ equivalent) for producing common commercially available materials is summarized in Table 1. By selecting materials that originate from renewable resources and contribute to less greenhouse gas emission during the production stage, it can benefit the environment by reducing the carbon footprint.

Table 1. Carbon footprint of selected materials

Material	Production carbon footprint (kg CO₂-eq per kg material)
High density polyethylene (HDPE) ^[9]	1.8-2.6
Low density polyethylene (LDPE) ^[9]	1.9-3.1
Polypropylene (PP) ^[9]	1.5-3.6
Polyvinyl chloride (PVC) ^[9]	1.5-2.2
Polyurethane (PU) ^[10]	2.7-3.2
Polystyrene (PS) ^[9]	3.2
Polyethylene terephthalate (PET) ^[9]	2.4-5
Bio-Poly(butylene succinate) (Bio-PBS) ^[9]	2.2
Cassava starch ^[11]	0.59
Softwood pulp ^[12]	1.10

2.2. Polysaccharides

Polysaccharides are a type of natural biopolymers that consist of many repeating monosaccharide units. The monosaccharides are the simplest form of a polysaccharide that cannot be further hydrolyzed to smaller units. Typically, they are comprised of carbon, hydrogen, and oxygen, and in some cases, nitrogen. Glucose and glucosamine are examples of the most abundant monosaccharides, and they serve as building blocks to form storage polysaccharides like starch, or structural polysaccharides like cellulose and chitin, respectively. Though there exist many different types of monosaccharides, these molecules share a key characteristic of having hydroxyl (-OH) groups that serve as the primary functional groups. A monosaccharide can react with another monosaccharide via a condensation reaction that occurs between hydroxyl groups, forming a glycosidic linkage. The abundance of hydroxyl groups on monosaccharides also allows for hydrogen bonds to form both within and between the polymer chains. When two monosaccharides form a glycosidic linkage, the resulting molecule is referred to as a disaccharide. An example of a disaccharide is sucrose, which is comprised of two monomers glucose and fructose. As more monosaccharides are added, they form an oligosaccharide, which consists of three to ten monosaccharide units. When more than ten monosaccharide units are connected through glycosidic linkages, they form a polysaccharide. Polysaccharides can be found in many natural

sources such as plants, algae, fungi, bacteria, and even shells of crustaceans. Some examples of sources and applications of different polysaccharides are summarized in Table 2.

Polysaccharides are desirable natural resources that can be utilized as alternatives to the conventional, petroleum-derived plastics to lessen the environmental burden. However, there are several factors that make this process challenging. Starch and cellulose are both abundant polysaccharides found in plants. The extraction, purification, and treatment steps become necessary to obtain starch and cellulose. As well, the structure of starch and cellulose vary depending on the source of which they were extracted from. Since the structure affects the material properties, the variations in molecular weight, degree of branching, and crystallinity can impact the strength and thermal stability of the final extracted product. A key difference between starch and cellulose is their different solubility in water or other solvents, which can be attributed to their crystalline structures.

2.2.1. Starch

Starch is a polysaccharide that is made up of series of α -glucans connected via α -1,4 and α -1,6 glycosidic linkages. It is found as an energy source from plant species such as corn, rice, and potato. Starch consists of two components: a linear polysaccharide amylose and branched polysaccharide amylopectin, as shown in Figure 1. Amylose typically contains branch points less than 20 per molecule, making it mostly linear, while amylopectin has branch points once per 20 glucose units.^[13] It has been reported that a typical amylose chain has a molecular weight of about 100 kDa, whereas amylopectin has a molecular weight in the order of $10^4 - 10^6$ kDa, making it significantly larger than amylose.^[14]

Table 2. Common polysaccharides and their sources and applications

Polysaccharide	Source	Structure	Application
Starch ^[15]	Grain, seeds, roots	α -1,4-glucan α -1,6-glucan	Cosmetics
			Food
			Packaging
			Pharmaceutical
Cellulose ^[16]	Cell walls of plants	β -1,4-glucan	Textiles
			Drug delivery
			Packaging
Chitin ^[17]	Cell walls of fungi Crustacean shells	N-acetylglucosamine	Cosmetics
			Pharmaceutical
Bacterial polysaccharides ^[18]	Microorganisms Various bacteria	α -glucans	Pharmaceutical Food additives
		β -glucans	
		Complex	
		heteropolysaccharides	

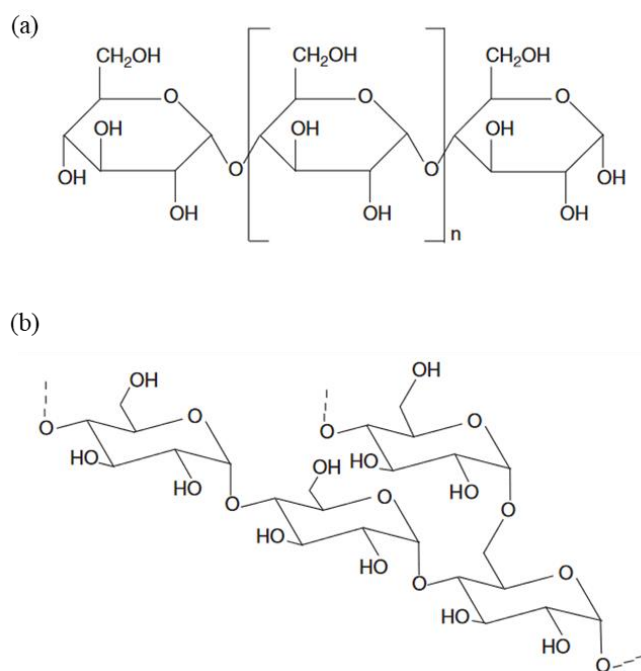


Figure 1. Molecular structure of (a) amylose and (b) amylopectin. Reproduced with permission from John Riley and Sons^[19]

Starch granules have diameters ranging from below 1 μm to over 100 μm depending on the source. The shapes may also vary, where the granules can be regular (round, oval, or angular) or completely irregular.^[15] Within each starch granule, the amorphous and semi-crystalline regions are organized in a concentric alternating fashion.^[13] A schematic representation of the starch granule structure is shown in Figure 2.

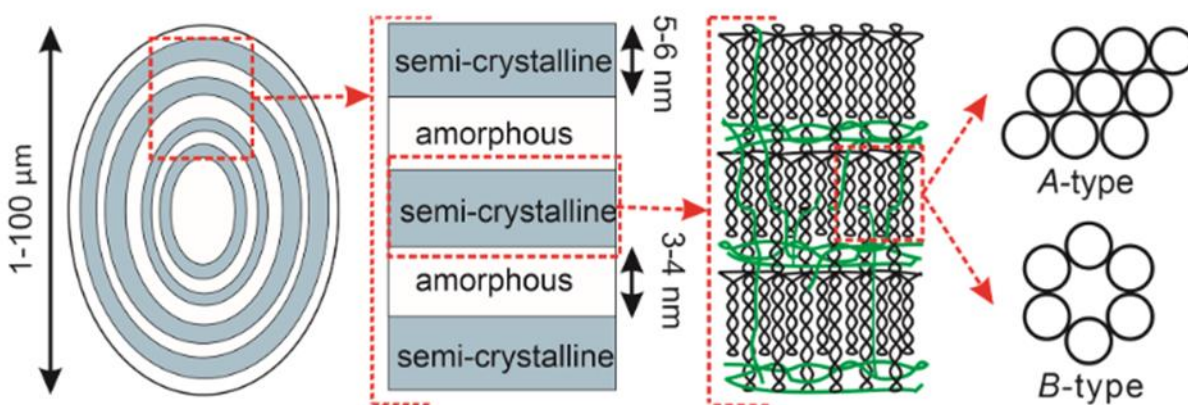


Figure 2. Starch crystalline structure; amylopectin (double helices) in black and amylose (single helices) in green. Reproduced with permission from MDP1^[20]

The morphology, shape, size, degree of crystallinity, amylose and amylopectin content, and the molecular weight all depend on the origin of the starch feedstock.^[20] According to many reports in the literature, the degree of crystallinity of a typical native starch can vary from 14% to 45%, depending on the source.^[21–26] There are variations on the crystalline structure, known as polymorphs, which are commonly referred to as A, B, and C starch types.^[23] The A-type starches are often found in cereal starches, which are starches derived from corn, wheat, rice, etc.^[27] These starches form a densely packed crystalline structure, which causes some hydroxyl groups to be protected, which prevents chemical reactions (like acid hydrolysis) from occurring through reduced reactivity. The B-type starches are typically found in high-amylose starches like fruits and stems (potatoes, bananas, canna, sago, etc.).^[27] Lastly, the C-type starches come from legumes and plant roots, such as pea seeds and cassava roots.^[27] The unit cell dimensions of the A, B, and C starch types have been studied and reported, and the results are summarized in Table 3.

Table 3. Unit cell dimensions of A-, B-, and C-type starches^[28,29]

Starch crystalline structure	Unit cell dimension
A-type	a = 11.90, b = 17.70, c = 10.52 Å $\alpha = \beta = \gamma = 90^\circ$
B-type	a = 18.5, b = 18.5, c = 10.4 Å $\alpha = \beta = 90^\circ, \gamma = 120^\circ$
C-type	a = 18.50, b = 18.50, c = 10.47 Å $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

2.2.2. Cellulose

Cellulose is a linear homopolysaccharide that consists of series of β -glucose monomers connected via β -1,4 glycosidic linkages. The β -configuration of the glucose means that all the hydroxyl groups are positioned in the equatorial position, while the hydrogen atoms are in the axial position. The β -1,4 linkages occur between the two equatorial hydroxyl groups from C-1 and C-4, which causes the molecular chain of cellulose to be linear, as shown in Figure 3. As well, because of the equatorial positions of the hydroxyl groups, they protrude laterally along the cellulose chain. This allows the hydroxyls to be readily available for hydrogen bonding. The abundance of hydrogen bonding causes the cellulose chains to group together tightly in a strong crystalline lattice structure. Since the cellulose is linear, it has a higher degree of crystallinity compared to other polysaccharides. This strong interchain hydrogen bonds in the crystalline regions give cellulose good strength and insolubility in most solvent.^[30]

There are four major types of cellulose allomorphs, denoted as cellulose I, II, III, and IV. Each allomorph has a unique unit cell dimensions and chain configurations that sets them apart, and the differences arise from different hydrogen bonding patterns. The unit cell dimensions for each cellulose allomorph are summarized in Table 4. Depending on the cellulose crystal structure, the hydrogen bonding pattern varies. The morphology of the allomorphs is affected by the hydrogen bonding patterns, which in turn affects the cellulose properties, such as hydroxyl accessibility for chemical reaction, and the rigidity of the fibrils. For example, the relative digestion rate of different cellulose allomorphs by two types of bacteria *Ruminococcus flavefaciens* FD-1 and *Fibrobacter succinogenes* S85 proceeded in the following order: amorphous cellulose > III_I > IV_I > III_{II} > I > II.^[20]

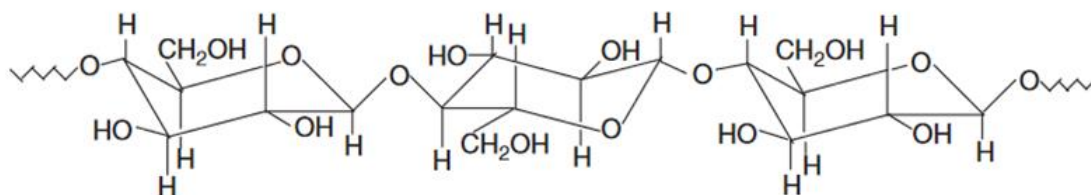


Figure 3. Molecular structure of cellulose. Reproduced with permission from John Wiley and Sons^[19]

The crystalline structure of cellulose has been extensively studied and is well reported. Cellulose I is the natural form of cellulose and is the most abundant type. There are two subcategories of cellulose I, which are referred to as cellulose I_α and I_β. The natural cellulose exists as a composite of the I_α and I_β crystalline forms, and are found as highly crystalline micro-fibril.^[30] Depending on the source of cellulose, the relative quantities of cellulose I_α and I_β may vary; some algae and bacterial cellulose are rich in cellulose I_α, while cotton, wood, and ramie fibres are rich in cellulose I_β and is overall the more common form.^[31] Cellulose I_α can be converted to I_β by high temperature sodium hydroxide (NaOH) treatment.^[30] Cellulose II is prepared from I_β through regeneration or mercerization process. The regeneration process involves full dissolution of cellulose, then coagulation using a poor solvent for cellulose, such as water or alcohol, which is then completely removed for recrystallization to occur. The mercerization process involves soaking the cellulose in an aqueous NaOH solution (typically 17 – 20 wt.%), then washing it with water. The conversion from I_α to I_β and I_β to II are both irreversible processes. Cellulose I_β can be converted to III_I or IV_I by treating with ammonia or ethylenediamine, or glycerol at high temperature, respectively, and both are reversible processes. Similarly, cellulose II can be converted to III_{II} or IV_{II} by ammonia/ethylenediamine or high temperature glycerol treatment, respectively, and both are reversible as well. Cellulose III can be converted to IV using glycerol at a high temperature and is an irreversible process. Cellulose IV_I can be converted to IV_{II} via regeneration or mercerization processes, which are irreversible processes. The overall conversion pathway between the cellulose allomorphs is summarized in Figure 4.

Depending on the cellulose crystal structure, the hydrogen bonding pattern varies. The morphology of the allomorphs is affected by the hydrogen bonding patterns, which in turn affects the cellulose properties, such as hydroxyl accessibility for chemical reaction, and the rigidity of the fibrils. For example, the relative digestion rate of different cellulose allomorphs by two types

of bacteria *Ruminococcus flavefaciens* FD-1 and *Fibrobacter succinogenes* S85 proceeded in the following order: amorphous cellulose > III_I > IV_I > III_{II} > I > II.^[32]

Table 4. Unit cell dimensions of cellulose allomorphs^[33–38]

Cellulose crystalline structure	Unit cell dimension
I _α	a = 6.74, b = 5.93, c = 10.36 Å (fibre axis) α = 117°, β = 113°, γ = 81°
I _β	a = 8.01, b = 8.17, c = 10.36 Å (fibre axis) α = 90°, β = 90°, γ = 97°
II	a = 8.10, b = 9.04, c = 10.36 Å γ = 117°
III _I	a = 4.45, b = 7.85, c = 10.33 Å γ = 105.1°
III _{II}	a = 4.45, b = 7.64, c = 10.36 Å γ = 106.96°
IV	a = 8.03, b = 8.13, c = 10.34 Å

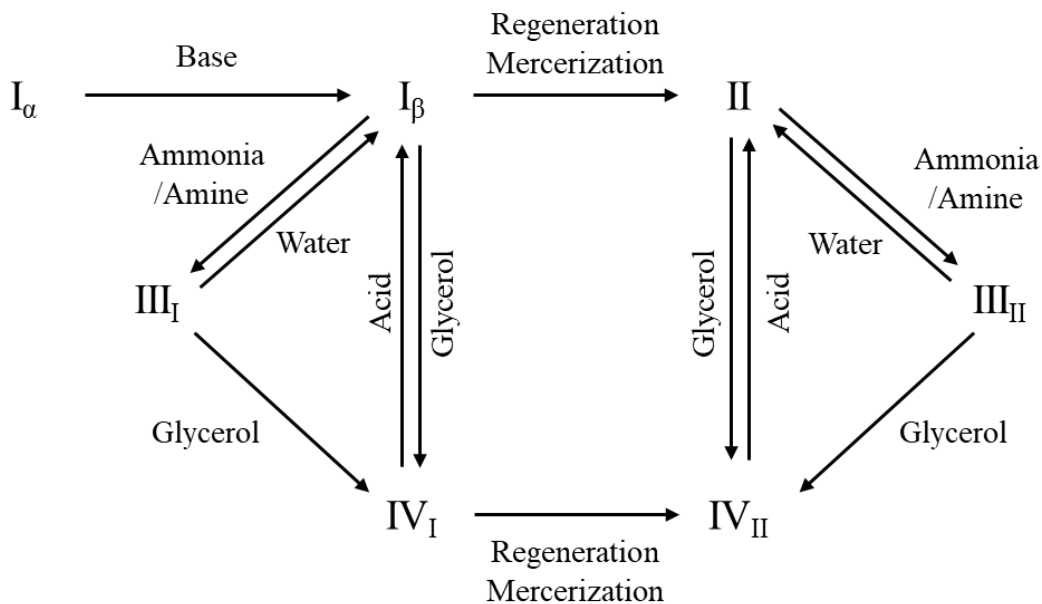


Figure 4. Conversion between cellulose allomorphs, adapted from ^[30]

The different structures of cellulose allomorphs influence their applications. Cellulose I is widely available, as it exists in almost all plants. It has many advantages such as low cost, high toughness, reduced tool wear, and reduced dermal and respiratory irritation, and therefore commonly used in fibres, foods, and pharmaceuticals industries.^[30] Cellulose II has a much lower degree of polymerization and crystallinity than cellulose I due to the mercerization and regeneration processes. Reduced crystallinity means that it has higher water absorption and accessibility, hence it is utilized as films, fibres, foods, and cosmetics.^[30] Cellulose III has reduced crystallinity and higher cellulose accessibility due to the ammonia or amine treatment. This leads to increase in reactivity, and thus commonly used for derivatization for different applications.^[39,40]

2.3. α -1,3-glucan

2.3.1. Structure

α -1,3-glucan is another type of polysaccharide that has been gaining more interest recently as a composite filler, hydrogel, and immunological material. Similar to starch and cellulose, α -1,3-glucan is formed by a large number of glucose units connected via α -1,3 glycosidic linkages. The molecular structure of α -1,3-glucan is shown in Figure 5. α -1,3-glucan forms a linear polysaccharide chain, which leads to a tighter chain packing and increased crystallinity. The hydrogen bonding occurs at regular intervals along the backbone of the polysaccharide chain, which contributes to an increase in crystallinity.

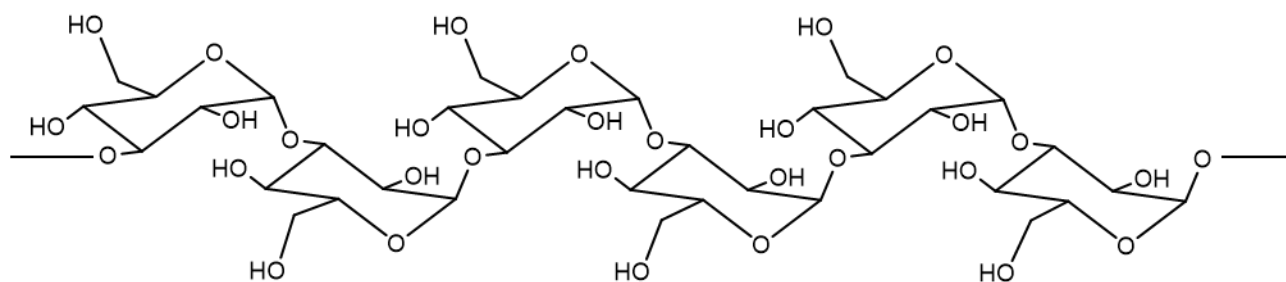


Figure 5. Molecular structure of α -1,3-glucan

Much like cellulose, α -1,3-glucan is a polymorphic material that has different crystalline structures. There are four α -1,3-glucan polymorphs that have been reported in the literature, and they have been referred to as polymorphs I, II, III, and IV.^[41–46] Polymorph I is the metastable

native form that can be found in native tissue of fungus species, such as *Laetiporus sulphureus* and *Piptoporus betulinus*.^[42] Polymorph II is obtained by dissolving the native α -1,3-glucan in alkaline solution then precipitating it in a poor solvent like water.^[41,42] In order to extract α -1,3-glucan from its source, dissolution and precipitation is almost always required, which makes it difficult to analyze the structure of polymorph I in its native state. Polymorph II is also referred to as the hydrated form. Polymorph III is the dehydrated form of polymorph I and II. The dehydration process from polymorph II to III is a reversible step, but dehydration from I to III is not reversible.^[43] Polymorph IV is obtained from polymorph II through an acetylation and deacetylation process, and is referred to as the regenerated form.^[44] The conversion pathway between α -1,3-glucan polymorphs is summarized in Figure 6. The unit cell dimensions of different polymorphs are given in Table 5.

Table 5. Unit cell dimensions of α -1,3-glucan polymorphs^[43–45]

α -1,3-glucan crystalline structure	Unit cell dimension
I	Unknown
II	a = 10.04, b = 9.63, c = 8.35 Å (fibre axis)
III	a = 9.14, b = 8.65, c = 8.35 Å (fibre axis)
IV	a = 16.46, b = 9.55, c = 8.44 Å (fibre axis)

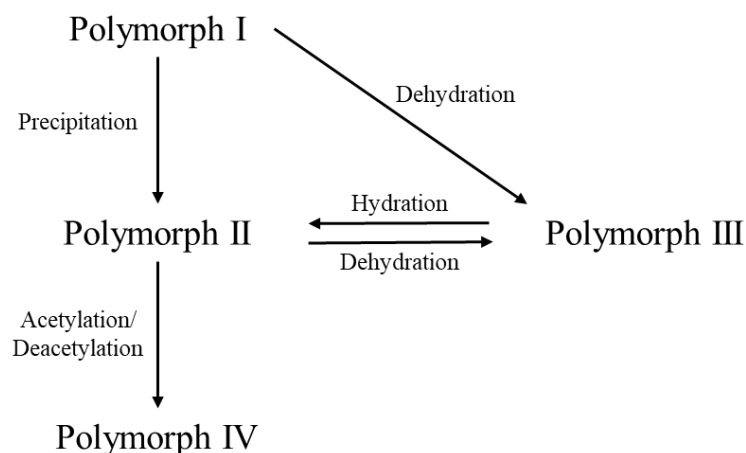


Figure 6. Conversion between α -1,3-glucan polymorphs

Kobayashi et al. investigated the aggregate morphology of α -1,3-glucan synthesized *in vitro* by the recombinant enzyme of glucosyltransferase (GtfJ) using transmission electron microscopy (TEM), X-ray diffraction (XRD), and solid-state ^{13}C nuclear magnetic resonance (NMR) analysis.^[45] The synthetic α -1,3-glucan that had been produced using the GtfJ enzyme is entirely linear without any branching.^[47] These glucans have two unique morphologies: a wavy fibril-like crystals that contain α -1,3-glucan chains that are folded over each other, and a thin lamellae structure at the edge of the α -1,3-glucan crystal structure.^[45] The wavy fibril-like crystals were the most dominant structure that aggregated into plates. The width and thickness of these fibrils were measured using the TEM images, which revealed to be approximately 13 and 20 nm, respectively. The length, however, was difficult to measure due to difficulties in locating the edges of the aggregated fibrils, but it was estimated to be between 200 nm and 1 μm .^[45] The thin lamellae arrangement is considered a secondary form since there were very few of them and their molecular weights were significantly lower than that of the fibrils. The dimensions of the thin lamellae were reported to be 30 to 40 nm in width, 100 to 500 nm in length, and about 5 nm in thickness.^[45] The two morphologies of the synthetic α -1,3-glucan are shown in Figure 7.

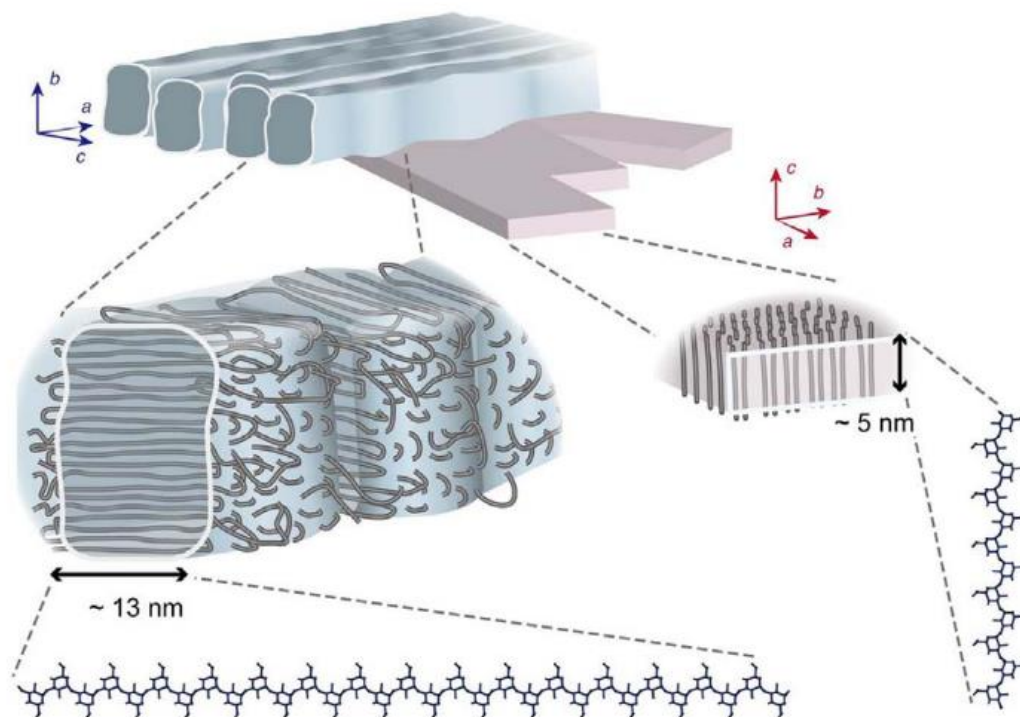


Figure 7. Morphology of α -1,3-glucan; wavy fibril-like crystals (left, blue), and thin lamellae crystals (right, pink). Reproduced with permission from Elsevier^[45]

2.3.2. Sources

α -1,3-glucan is found in the cell walls of several fungi, such as *Piptoporus*, *Shizophyllum*, *Penicillium*, and *Aspergillus*.^[48–51] Fungi have been used as edible and medicinal resources, especially in the East Asian countries.^[52] A variety of α - and β -glucans that are present in these fungi have been recognized to have antitumor and immunomodulating properties.^[52] There are extensive studies on β -glucans, but α -glucan has not been investigated thoroughly due to their insolubility in water. However, more research has been performed to better understand the structure, properties, and functions of these α -glucan polymers. As a result, several applications of α -1,3-glucans have been reported in the medical field as a mutanase inducer, support for lipase immobilization, prebiotic, and heavy metal sorbent.^[53–60] α -1,3-glucan is also found in yeast and bacteria.^[7] It is a known major component of dental plaque extracellularly synthesized from sucrose by *Streptococcus* in the human oral cavity.^[61]

2.3.3. Extraction and purification

Polysaccharides are rarely found as pure materials in nature; they are mixed with other polysaccharides, carbohydrates, proteins, and other impurities. As such, a successful extraction of

α -1,3-glucan from natural sources involves purification steps to remove impurities that had been extracted along with α -1,3-glucan. There are several extraction methods, including the solvent extraction, microwave assisted extraction (MAE), ultrasound assisted extraction (UAE), and enzyme assisted extraction (EAE) methods.

The conventional solvent extraction method is one of the popular methods of extracting polysaccharides due to the simple equipment set-up, low energy cost, and low toxicity of the solvents used, which include hot water, alkali solution, and poly(ethylene glycol).^[62]

The MAE method is used alongside the conventional solvent extraction method. The microwave radiation improves the process efficiency by reducing the amounts of solvent required and the extraction time needed.^[62] This method is commonly used for thermally unstable, bioactive materials. There are several parameters that affect the efficiency of the process: polarity and volume of extracting solvent, dielectric constants of the sample, ratio between solvent and sample, and microwave power.^[63]

The UAE method utilizes the cavitation that forms in the solvent as the ultrasonic wave propagates in alternating high- and low-pressure cycles.^[62] This is another inexpensive method of extraction that can expedite the extraction process and improve the extraction rate. The cavitation bubbles cause the necessary disruption and disintegration of cells in plant material. The efficiency of the UAE method depends on factors such as ultrasonic power, frequency, and intensity, as well as solvent-to-sample ratio.^[63,64]

The EAE method is another alternative to the conventional solvent extraction method due to the selectivity of enzymes, which increases the yield and efficiency of the extraction process. EAE methods have been proven to provide high yield for compounds such as oil, natural pigments, medicinal compounds, and polysaccharides.^[62] During the EAE process, the enzyme hydrolyzes the cell wall by forming an enzyme-substrate binding complex.^[65] This leads to the release of desired compounds from the cell and cell wall. The commonly used enzymes include cellulases, hemicellulases, and pectinases, which are derived from bacteria and fungi.^[65] Depending on the composition of the cell wall, a mixture of different enzymes is used. The factors that affect the extraction efficiency are related to the enzyme activity, thus conditions such as temperature, pH, and enzyme concentration are important.

Polysaccharide extraction may happen in multiple stages, utilizing different extraction techniques if necessary. Once extracted, the solids are typically dissolved in either water or other aqueous systems and need to be purified. The purification step is necessary due to a mixture of materials that get extracted simultaneously, such as macromolecules like protein, and smaller molecules like monosaccharides, amino acids, and phenolic compounds.^[62]

The isolation of the desired substance may require multiple purification steps. Typical purification steps involve chemical, chromatographic, or membrane filtration methods.

There are several methods to perform the chemical purification method: distribution precipitation method, salting out method, quaternary ammonium salt precipitation, Sevag method, and enzymatic method.^[62] In the distribution precipitation method, miscible solvents such as methanol or ethanol are added to precipitate proteins or other polysaccharides. The salting out method uses neutral salt like ammonium sulfate, which increases the interaction between the proteins, causing them to aggregate and eventually precipitate. The quaternary ammonium salt precipitation method is essentially the salting out method, except that it uses a much bigger salt such as hexadecyltrimethylammonium bromide and cetylpyridinium chloride.^[62] In the Sevag method, a mixture of chloroform, *n*-butanol, and trifluoroacetic acid is used. This mixture is capable of denaturing the proteins, which are then precipitated out using ethanol. The enzymatic method is similar to the Sevag method but instead uses a protease enzyme to break down the protein.

The column chromatography method uses the different adsorption behaviour of the substances to separate and purify individual compounds from the mixture. In short, a mobile phase (eluent) passes through the stationary phase (column) while carrying the compounds with it. Typically, the eluent moves down the column by gravity, but a faster flow rate can be achieved if a pump or compressed gas is used. The stationary phase is strategically selected such that it will have different interaction with the compounds. If the column exhibits polar behaviour, then the compounds that are more polar will take longer to exit the column, leading to a longer retention time. Conversely, compounds that are non-polar or have lower polarity will have minimal interaction with the column, thus leaving the column first. The eluent is collected at different times to separate the compounds.

The membrane filtration method uses a selectively permeable membrane that lets through molecules based on their size. Larger molecules remain in the original solution while the smaller molecules pass through the membrane. Multiple membranes may be installed to perform multiple filtration steps. Depending on the size of the molecules to be filtered, filtration membranes are classified as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis membrane.^[66]

2.3.4. Enzymatic synthesis

In recent years, α -1,3-glucan has been synthetically produced in a controlled environment using enzymatic polymerization.^[7,8,47,67,68] This process eliminates the need to extract and purify the polysaccharide from the natural source. The heart of this enzymatic polymerization is the GH70 class of glucosyltransferase (GTF) enzymes, which are used as biocatalyst to convert sucrose into α -1,3-glucan polysaccharide. Fructose is generated as a by-product, which is washed away while the water insoluble α -1,3-glucan is precipitated. α -1,3-glucan produced through the enzymatic polymerization is unbranched with controlled chain length and can be manufactured at an industrial scale.^[8,67,68] This enzymatically produced α -1,3-glucan has a typical degree of polymerization of 800 glucose repeat units with a polydispersity index in the range of 1.7 to 2.0.^[69] Depending on the application, a higher molecular weight α -1,3-glucan can be produced based on the processing conditions. The α -1,3-glucan is then separated from the reaction vessel and dried, and the resulting dry powder has been reported to have a crystallinity index of 50%.^[70] Much like other long chain polysaccharides, α -1,3-glucan has a melting point that exceeds the degradation temperature. As a result, α -1,3-glucan does not exhibit any melting behaviour up to 300°C and begins to decompose beyond that temperature.

2.4. Thermoplastics

2.4.1. Thermoplastic polyurethane

Thermoplastic polyurethane (TPU) is a special type of polyurethane that is soft, flexible, and recyclable.^[71] TPU is a multiphase block copolymer that consists of hard and soft segments in the polymer chain. The hard segment is immobile and stiff, which provides strength, while the soft segment has some mobility, thus giving flexibility to the polymer. There are several routes to producing polyurethane, but the most common method is the reaction between a diisocyanate and polyol. Depending on the required properties, chain extenders (low molecular weight polyols) may also be incorporated. A typical structure of polyurethane is shown in Figure 8.

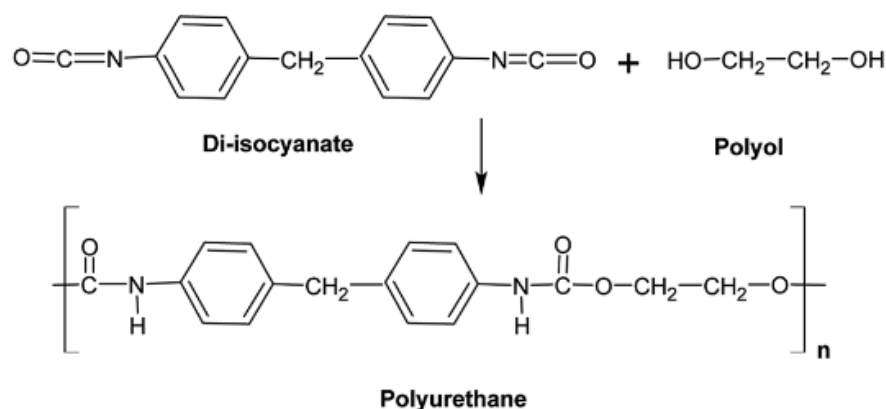


Figure 8. Molecular structure of polyurethane. Reproduced with permission from Royal Society of Chemistry^[72]

The isocyanate component of the polyurethane is categorized as difunctional or heterofunctional and aromatic or aliphatic.^[72] The most commonly used ones are methylene diphenyl diisocyanate (MDI) and toluene diisocyanate, which have a strong aromatic nature. The isocyanate can react with the hydroxyl from polyols to form a urethane linkage. The hard segment of the TPU is formed from the isocyanate and chain extenders. Chain extenders are low molecular weight compounds with two functional groups ($f = 2$) and are usually hydroxyl terminated. Due to the urethane groups, the hard segment is rich of potential hydrogen bonding sites, forming the hard domain.^[73] The hard domains are below the glass transition temperature (T_g), and are responsible for hysteresis, plastic deformation, high modulus, and tensile strength.^[73]

The polyol can be categorized into polyether or polyester types. The polyether polyols are prepared from the reaction between epoxide and active hydrogen-containing compounds. The polyester polyols are produced from the polycondensation reaction between monomers with hydroxyls and carboxylic acids.^[72] The molecular weight of the polyols depends on their use. The low molecular weight polyols are used to produce more rigid polyurethanes, while the high molecular weight polyols produce more flexible polyurethanes.^[74] The soft segment of the TPU is formed by polyols. The soft domains have a T_g below room temperature and exhibit a rubber-like behaviour.

Polyurethanes have wide range of applications; they can be rigid for insulating materials or flexible for cushion, packaging, and biomedicine applications. In the case of TPUs, common applications include automotive, footwear, and construction.^[72] The versatility of polyurethanes

comes from the wide variety of properties that can be obtained by changing the type and molecular weight of the hard and soft segments, their ratios, and addition of additives like catalysts, plasticizers, cross-linkers, surfactants, and flame retardants.^[72,73] However, there are some limitations of TPU such as poor thermal stability, low mechanical strength, and poor aging characteristics.^[71]

TPU is often reinforced with other polymers or fillers to create composites to improve its properties. Several filler materials to produce TPU composites have been reported, such as carbon fibres and nanotubes, graphene, glass fibre, natural fibres, cellulose nanocrystals, chitin, and clay.^[75–82] The selection of filler the material depends on many factors like cost, compositions, morphology, aspect ratio, and optical properties.^[71] Recently, more eco-friendly and renewable filler materials have been gaining attraction for environmental sustainability. Fillers like polysaccharides are a good example of natural, renewable, and sustainable materials that help overcome the environmental concerns while improving the mechanical properties.

2.4.2. Poly(butylene adipate-co-terephthalate)

Poly(butylene adipate-co-terephthalate) (PBAT) is a synthetic, random copolymer that is biodegradable and flexible.^[83] It is synthesized by a polycondensation reaction between 1,4-butanediol and a mixture that consists of adipic acid and dimethyl terephthalate.^[84] In short, the synthesis of PBAT begins with the preparation of two separate polyesters. The first kind is poly(butylene adipate), which is formed by reacting 1,4-butanediol and adipic acid. The second is poly(butylene terephthalate) formed by the reaction between 1,4-butanediol and dimethyl terephthalate. Then, the two polyesters are combined with a catalyst, such as tetrabutoxytitanium, that aids the transesterification reaction. There is no selectivity between the two polyesters, thus a random PBAT copolymer is formed. The random structure of PBAT leads to lower crystallinity, which translates to lower modulus and stiffness when compared to other homopolymers. The generic structure of PBAT is illustrated in Figure 9.

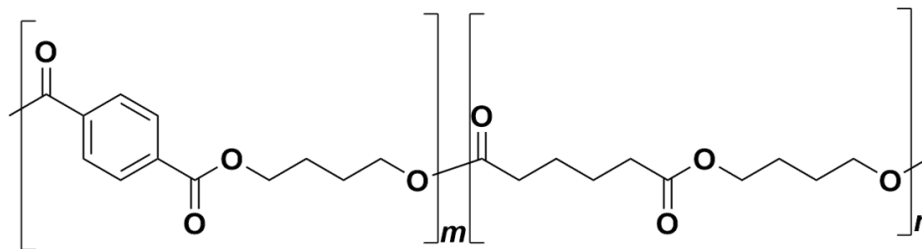


Figure 9. Molecular structure of PBAT

PBAT is used in several applications, such as packaging, hygiene products, biomedical fields, industrial composting, and agricultural films.^[85–88] The properties of PBAT can be tailored based on the application and its end-use purposes by controlling the monomers stoichiometry and reactor conditions, such as temperature and pressure, to control the molecular weight. For example, the modulus increases with the concentration of the terephthalate units but decreases the elongation. The increase in the molecular weight has shown to improve the tensile strength as well.^[89]

The biodegradability and good flexibility of PBAT is certainly appealing for many applications, but the high production costs, and low thermo-physical and mechanical resistance, when compared with conventional plastics, hinders its growth in the market.^[90] To overcome the aforementioned challenges, low-cost materials, such as natural fibres and cellulosic materials, are commonly added to improve the mechanical properties and reduce the cost while keeping the polymer biodegradable. However, challenges remain concerning a good dispersion of the filler materials and interaction between the filler and matrix due to the inherent incompatibility between the hydrophobic PBAT and hydrophilic natural fillers. To increase the compatibility, compatibilizers such as maleic anhydride are added, or a filler is functionalized to be more hydrophobic.^[83,91]

2.4.3. Poly(butylene succinate)

Poly(butylene succinate) is a synthetic, aliphatic polyester that has a good chemical and thermal resistance, strength, and biodegradability.^[92–94] The synthesis of PBS is divided into two steps. The first step involves the esterification reaction between succinic acid and 1,4-butanediol or transesterification of dimethyl succinate and 1,4-butanediol to produce oligomers. The second step involves the removal of the 1,4-butanediol group via a polycondensation reaction to form a high-molecular weight PBS.^[93] The polycondensation step is often carried out with catalysts, such as titanium (IV) isopropoxide, titanium (IV) isobutoxide, titanium (IV) *n*-butoxide, tin (II) chloride,

p-toluenesulfonic acid, and tetrabutyl titanate, to name but a few.^[93,95–99] The structure of PBS is illustrated in Figure 10.

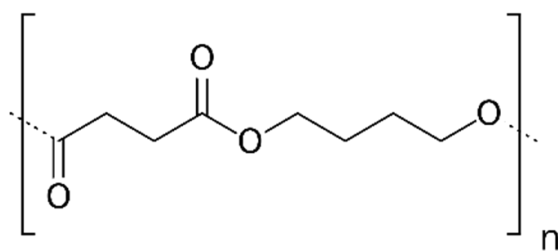


Figure 10. Molecular structure of PBS

PBS is used in many applications such as food packages, bottles, grocery bags, mulch films, and compost bags.^[93,100] The physical properties and biodegradability of PBS can be adjusted by selecting different types and contents of comonomers used for the synthesis. The different types of comonomers that can be used include adipic acid, terephthalic acid, and ethylene glycol.^[92] As well, the catalyst type and concentration, along with the reaction conditions can be changed to control the molecular weight of the resulting PBS.^[99]

Similar to PBAT resins, PBS has drawbacks due to its high production cost. PBS also demonstrates a moderate level of stiffness and relatively low ductility.^[92,94] PBS is blended with other biodegradable polyesters with higher flexibility, such as PBAT, or incorporated with fillers to improve its mechanical properties. Natural fillers such as starch and cellulose are hydrophilic, making them incompatible with hydrophobic PBS. The incompatibility issue is often resolved by the addition of compatibilizers or surface modification on either of the polymers.^[84,96,101]

2.5. Applications

This synthetic α -1,3-glucan has not been commercialized yet—it is in its pre-commercialization stages. As such, this research work presented in this thesis is an effort to understand its properties for applications in combination with thermoplastics. A potential application of an α -1,3-glucan composite material is short-term packaging for situations when recycling is not easy. Examples are single-use plastics such as cutlery and disposable cups, and food packaging materials such as meat trays and clamshell containers. Currently, petroleum-based polymers, such as polyethylene and polypropylene, are commonly used for packaging, which are both non-renewable and non-

biodegradable. With the consumers need for a more sustainable alternative, as well as changes in government legislations regarding the use of plastic packaging materials, the demand for a more sustainable and biodegradable packaging material has grown over the years. In the case of the United States, many cities have already banned or began charging additional fees for plastic bags.^[102]

Table 6. Status of plastic bag legislation (Adapted from ^[102])

States/Territories	Plastic bag ban	Plastic bag fee
Alaska ^a	2009 (Bethel)	2009 (Fairbanks)
Arizona ^a	2013 (Bisbee)	--
Arkansas	--	2013 (Little Rock)
California ^a	2007 (San Francisco)	--
Colorado ^a	2010 (Telluride)	--
Connecticut ^a	2008 (Westport)	--
Hawaii ^a	2008 (Maui County)	2009 (Kauai County)
Illinois ^a	2014 (Chicago)	--
Iowa ^a	2009 (Marshall County)	--
Maine ^a	--	2014 (Portland)
Maryland ^a	2012 (Chestertown)	2011 (Montgomery County)
Massachusetts ^a	2012 (Brookline)	--
New Mexico ^a	2013 (Santa Fe)	--
New York ^a	2011 (East Hampton)	--
North Carolina ^a	2009 (Hyde, Currituck, and Dare)	--
Oregon ^a	2010 (Portland)	2012 (Corvallis) 2013 (Eugene)
Rhode Island ^a	2009 (Barrington)	--
Texas ^a	2010 (Fort Stockton)	--
Washington ^a	2009 (Edmonds)	--
American Samoa	2011 (Territory)	--
District of Columbia	--	2009 (Washington)

^a State, of which one or more cities/counties approved plastic bag ban or fee.

Another potential application for α -1,3-glucan is packaging for food or convenience meals. Typical thermoplastic materials that are used are summarized in Table 7. Most food packaging materials are also non-renewable and non-biodegradable. In the past decade, many biopolymers that are obtained from renewable sources and are compostable have been introduced. These materials include many polyester-based polymers and starch-based polymers.^[103] Although the biopolymers were able to address the environmental issues, they still have limitations when it comes to thermal resistance, barrier properties, mechanical performance, and cost of production.

Table 7. Food packaging application from thermoplastics. Reproduced with permission from MDPI^[104]

Thermoplastic Material	Abbreviation	Packaging Application
Polyethylene terephthalate	PET	Water/juice/soft drink bottles
		Food jars
		Microwavable containers
		Plastic films
Polypropylene	PP	Drinking bottles
		Bottles for milk
		Food containers
Polyvinyl chloride	PVC	Plastic bags
		Frozen foods stretch films
		Container lids
Polystyrene	PS	Take away clamshells
		Meat trays
		Bottle caps
		Straws
Low density polyethylene	LDPE	Disposal cups
		Plates
		Spoons
		Bread bags
High density polyethylene	HDPE	Custom packages
		Grocery bags
		Water/milk/juice containers
		Cereal and snack liners

CHAPTER 3:

MATERIALS AND METHODS –

TPU AND α -1,3-GLUCAN COMPOSITES

This chapter contains the methodology for the research presented in Chapter 4-6. The common goal for those chapters is to explore the use of α -1,3-glucan as a filler in thermoplastic composites.

3.1. Materials

The α -1,3-glucan powder was provided by International Flavours & Fragrances (IFF). Two different types of α -1,3-glucan powders with different average particle diameters were received. The “D05” type had an average particle diameter of 5 μ m and “D15” type had an average particle diameter of 15 μ m. These powders were supplied in plastic bags with low moisture content (<12%). The thermoplastic polyurethane (TPU) (Zythane® 4070A) was purchased from Alliance Polymers & Services and received as pellets 5 mm in length. Triethyl citrate (TEC, 99%) was purchased from Alfa Aesar. Tributyl citrate (TBC, $\geq 97.0\%$), acetyl tributyl citrate (ATBC, 98%), dicumyl peroxide (DCP, 98%), deuterated dimethyl sulfoxide (DMSO-d₆, 99.8% with 0.03% tetramethylsilane), and acetone (99%) were purchased from Sigma Aldrich.

3.2. Methods

3.2.1. Sample preparation

The α -1,3-glucan and TPU were dried in a Forced Air Oven (VWR International) at 70°C overnight prior to the compounding process. The TPU pellets were ground using the ZM 200 Ultra Centrifugal Mill (Retsch GmbH) and liquid nitrogen (L-N₂) into a finer powder. The resulting TPU pellets had a particle size of less than 1.0 mm. This step was necessary to improve the mixing with the α -1,3-glucan powder before feeding the mixture into the extruder.

The first study investigated the effect of TEC as a plasticizer on the mechanical properties of the TPU- α -1,3-glucan composites. A design of experiment (DOE) (2² factorial design with centre point replicates) approach was used to analyze the effect of the TPU and TEC concentrations (Table 8). The second study investigated the effect of different citrate-based plasticizers, specifically TEC, TBC, and ATBC, on the mechanical properties of the TPU- α -1,3-glucan composites with a fixed α -1,3-glucan content. The third study investigated the effect of the DCP

as a compatibilizer in the TPU- α -1,3-glucan composites. The compositions of the samples for the first, second, and third studies is tabulated in Tables 9, 10, and 11, respectively.

The sample preparation for the first and second studies started with the extrusion process using the Haake MiniLab II Micro Compounder (Thermo Fisher Scientific Inc.), with the processing conditions of 175°C and 75 screw rpm. The extrudate was then pelletized using the Thomas Wiley Mill (Thomas Scientific), and then injection moulded using the Test Sample Injection Moulding Press (Ray-Ran Test Equipment Ltd.) with the barrel temperature of 195-205°C and mould temperature of 60-80°C. A total of twelve replicates of rectangular IZOD bars and six replicates of dog-bone bars were produced per sample for different mechanical tests.

The samples for the third study were prepared by extrusion at 190°C and 50 screw rpm. Prior to the extrusion, the DCP was first dissolved in acetone, then sprayed onto the ground TPU. Once the acetone had fully evaporated, the α -1,3-glucan was added to the mixture, then fed into the extruder. The extrudate was ground using the Thomas Wiley Mill, and then compression moulded using the Carver Bench Top Heated Press (Carver, Inc.) at 180°C and 7 metric tonnes of force to produce film specimens with average thickness of 0.2 mm. The films were cut into dog-bone shapes using a cutter dye that conforms to the ASTM standards for the tensile test. A total of six replicates per sample was produced.

Table 8. ²² factorial design parameters for the α -1,3-glucan-TPU-TEC study

Factor	Lower Bound (-)	Centre Point (0)	Upper Bound (+)
α -1,3-glucan:TPU (A)	60:40	70:30	80:20
α -1,3-glucan:TEC (B)	80:20	90:10	100:0

Table 9. Overall composition of the α -1,3-glucan-TPU-TEC composites

Sample ^a	Ratio		Overall wt. % ^b		
	α -1,3-glucan:TPU	α -1,3-glucan:TEC	α -1,3-glucan	TPU	TEC
0/0	70:30	90:10	64.9	27.8	7.2
-/-	60:40	80:20	52.2	34.8	13.0
+/-	80:20	80:20	66.7	16.7	16.7
+/+	80:20	100:0	80.0	20.0	0
-/+	60:40	100:0	60.0	40.0	0
0/0*	70:30	90:10	64.9	27.8	7.2

^a A level / B level; e.g., -/+ indicates lower bound for A and upper bound for B; 0/0* is a replicate of sample 0/0.

^b The composition calculated as volume fraction (vol.%) is listed in Appendix A

Table 10. Citrate-based plasticizer content in α -1,3-glucan-TPU composites with fixed ratio of 80:20 α -1,3-glucan:TPU

Sample ^a	Plasticizer Type	α -1,3-glucan:Plasticizer
No Plasticizer	None	100:0
TEC10	TEC	90:10
TEC20		80:20
ATBC10	ATBC	90:10
ATBC20		80:20
TBC10	TBC	90:10
TBC20		80:20

^a “10” and “20” in sample names represent 90:10 and 80:20 α -1,3-glucan:plasticizer ratios, respectively.

Table 11. Overall composition of the α -1,3-glucan-TPU-DCP formulations

α -1,3-glucan (wt.%)	TPU (wt.%)	DCP (wt.%)	DCP in TPU (wt.%)
0	100	0	0
	99.9	0.1	0.1
	99.5	0.5	0.5
	99	1	1
	98	2	2
20	80	0	0
	79.92	0.08	0.1
	79.6	0.4	0.5
	79.2	0.8	1
	78.4	1.6	2
50	50	0	0
	49.95	0.05	0.1
	49.75	0.25	0.5
	49.5	0.5	1
	49	1	2
80	20	0	0
	19.98	0.02	0.1
	19.9	0.1	0.5
	19.8	0.2	1
	19.6	0.4	2

3.2.2. Specimen characterization

Flexural testing. The flexural test was conducted using the Universal Testing Machine (TestResources, Inc.) in accordance with ASTM D790. All specimens (dog-bone and rectangular IZOD bars) were conditioned in a controlled chamber with 50% relative humidity (RH) for at least 40 hours prior to the testing. A three-point bending test was conducted to measure the material's ability to resist bending, or flexural deformation.

Tensile testing. The tensile test was conducted in accordance with ASTM D638 using the Universal Testing Machine. All specimens were conditioned in a controlled chamber with 50% RH for at least 40 hours prior to the testing. A test specimen undergoes uniaxial deformation while the load cell monitors the stress. The toughness of the specimens was calculated by integrating the stress-strain curve.

Impact testing. The impact test was conducted in accordance with ASTM D256 using the Monitor Impact Tester (Testing Machines Inc.). Prior to the impact test, the specimens were notched using the Specimen Notch Cutter (Chengde Jinjian Testing Instrument Co., Ltd.). All specimens were conditioned in a controlled chamber with 50% RH for at least 40 hours prior to the testing. The IZOD impact test was conducted, where a pendulum of known weight strikes the specimen.

Thermogravimetric analysis (TGA). The thermal degradation pattern was analyzed using the TGA Q500 (TA Instruments, Inc.) under a constant nitrogen flow using approximately 10-20 mg of sample. The heating rate for the tests was 20°C/min until 800°C was reached. The TGA curves, as well as the derivative thermogravimetry (DTG) curves were generated for the analysis.

Differential scanning calorimetry (DSC). The DSC Q2000 (TA Instruments, Inc.) was used to analyze the melting and crystallizing behaviour. The DSC sequence was 30°C/min to 200°C from room temperature, 10°C/min to 25°C, then 10°C/min to 200°C. Approximately 5-10 mg of sample was used for analysis.

Scanning electron microscopy (SEM). The SEM technique was used to analyze the fracture surface of the specimens from the first and second studies using the Quanta FEG-250 SEM (FEI Company). The specimens were first cryo-fractured using the L-N₂, then coated with a thin layer of gold using the Magnetron Sputter Coater (Vac Coat Ltd.) before the SEM analysis. The SEM images for the analysis were taken at 1000× magnification using the secondary electron (SE) detector. The acceleration voltage of 15 kV was used for SEM scanning.

Water absorption. The water absorption test was conducted for the third study to investigate the water retention of the TPU- α -1,3-glucan composite films. The test was performed in accordance with ASTM D570 and was conducted in triplicates per specimen. The curve fitting was done using the equation:

$$M = A + B \cdot \exp(-C \cdot \sqrt{t}) \quad (1)$$

Nuclear magnetic resonance (NMR). The proton NMR (¹H NMR) analysis was performed using the Bruker Avance 300 MHz (Bruker Corporation) spectrometer at room temperature and 32 scans. The samples were prepared by dissolving them in 3% lithium chloride (LiCl) in DMSO-d₆ solution. The tetramethylsilane (TMS) was used to calibrate the ¹H NMR spectra at a chemical shift (δ) of 0 ppm.

Batch mixing experiment. Haake PolyLab QC (Thermo Fisher Scientific, Inc.) was used with processing conditions of 190°C and 50 rpm. The torque and internal temperature were recorded for the analysis.

CHAPTER 4:

RESULTS AND DISCUSSIONS –

TPU AND α -1,3-GLUCAN COMPOSITES

4.1. Highly filled TPU- α -1,3-glucan composites

The objective of the first study was to investigate the properties of the highly filled TPU- α -1,3-glucan composite systems with TEC as the plasticizer. The plasticizer was included in the system as they serve an important role in polymer processing. Plasticizers are commonly used in numerous applications to not only improve the flow of the polymer during processing, but also to improve a wide variety of properties such as glass transition temperature, mechanical properties, rheological behaviours, and chemical reactivity.^[105] In this section, TEC was selected as an external plasticizer to aid with processibility of the composite during the extrusion process since it has a low vapour pressure, and it is an inert, and environmentally friendly material.

To maintain a high level of biodegradable content, a lower limit of 60:40 and upper limit of 80:20 α -1,3-glucan to TPU ratio was selected. The α -1,3-glucan level beyond 80% prevented any melt-flow behaviour during the extrusion, and therefore 80:20 ratio was selected as the upper limit for the α -1,3-glucan:TPU ratio. The lower and upper limit of the α -1,3-glucan:TEC ratio was selected as 80:20 and 100:0, respectively. The addition of more TEC than the 80:20 α -1,3-glucan:TEC ratio reduced the composite viscosity excessively during the extrusion, making it undesirable from a processing perspective. A successful extrusion does not require the addition of the TEC, and therefore 100:0 α -1,3-glucan:TEC ratio was selected as the upper limit.

4.1.1. Mechanical properties

The purpose of this analysis was to understand the change in composite behaviour from flexible to brittle with varying amounts of filler and plasticizer. The flexural, tensile, and impact test results for the factorial design samples are tabulated in Tables 12 and 13. The difference between the two grades of the α -1,3-glucan (i.e., D05 and D15) are minimal based on the analysis of variance. The contour plots for the mechanical properties are presented in Figures 11-17.

The contour plots for the flexural properties are shown in Figures 11 and 12. The flexural strength and modulus improved with the amount of the α -1,3-glucan, with the maximum strength

and modulus occurring when the amounts of the TPU and TEC were minimum, regardless of the grade of the α -1,3-glucan. This increase in strength and modulus with the α -1,3-glucan demonstrates the reinforcing effect of the α -1,3-glucan on the TPU composite system. Similar trends of increase in stiffness and modulus have been observed in the literature for TPU systems with the addition of fillers.^[71,106,107] Hosur et al. reported the effect of wood flour as a filler in a TPU foam system, and observed that the wood flour stiffened the polymer and therefore increased the flexural strength and modulus. The inclusion of the wood flour reduced the TPU foam cell size, which led to the restriction in the polymer chain movement and thus produced a stiffer composite material.^[106] El-Shekeil et al. studied the effect of kenaf fibre on the TPU, and observed a similar behaviour where the increase in the fibre loading increased the flexural properties.^[107] The addition of the TEC decreased the strength and modulus since the plasticizer increases the flexibility of the composite by making it softer and more flexible.

Table 12. Flexural and impact test results for 2² factorial design

Sample	Flexural Strength (MPa)		Flexural Modulus – Secant at 1% (MPa)		Impact Strength (J/m)	
	D05	D15	D05	D15	D05	D15
0/0	3.53 ± 0.11 ^a	3.21 ± 0.29 ^a	84.78 ± 4.53 ^a	84.00 ± 6.42 ^a	101.19 ± 6.90 ^a	107.18 ± 3.05 ^a
-/-	1.40 ± 0.11 ^a	1.32 ± 0.03 ^a	38.37 ± 5.24 ^a	32.49 ± 2.38 ^b	154.44 ± 9.47 ^a	163.81 ± 3.61 ^a
+/-	1.67 ± 0.07 ^a	1.34 ± 0.16 ^b	44.70 ± 4.35 ^a	37.17 ± 5.35 ^a	91.18 ± 6.70 ^a	82.24 ± 2.37 ^a
+/+	19.83 ± 0.72 ^a	17.83 ± 0.70 ^b	713.66 ± 52.29 ^a	643.13 ± 59.28 ^a	54.45 ± 2.55 ^a	57.95 ± 2.66 ^a
-/+	4.85 ± 0.24 ^a	5.09 ± 0.17 ^a	129.36 ± 9.01 ^a	126.13 ± 5.37 ^a	117.61 ± 10.32 ^a	112.90 ± 2.25 ^a
0/0*	3.65 ± 0.15 ^a	3.53 ± 0.10 ^a	95.91 ± 3.81 ^a	93.59 ± 2.73 ^a	93.13 ± 11.49 ^a	108.46 ± 5.84 ^b

Note: Different letters in the same row for each mechanical property represent significant difference ($p < 0.05$) between means through the analysis of variance

0/0 is a replicate of sample 0/0.*

Table 13. Tensile test results for 2² factorial design

Sample	Tensile Strength (MPa)		Tensile Modulus – Tangent (MPa)		Elongation at Break (%)		Toughness (MPa)	
	D05	D15	D05	D15	D05	D15	D05	D15
0/0	6.05 ± 0.20 ^a	4.82 ± 0.16 ^b	40.45 ± 0.91 ^a	38.24 ± 1.87 ^b	24.66 ± 1.10 ^a	19.39 ± 1.60 ^b	0.95 ± 0.08 ^a	0.62 ± 0.04 ^b
-/-	3.60 ± 0.43 ^a	3.19 ± 0.23 ^a	15.45 ± 0.76 ^a	17.86 ± 0.63 ^b	46.59 ± 6.87 ^a	36.19 ± 5.53 ^b	1.17 ± 0.32 ^a	0.80 ± 0.19 ^b
+/-	1.73 ± 0.69 ^a	2.15 ± 0.33 ^a	20.66 ± 1.67 ^a	17.69 ± 1.10 ^b	10.42 ± 4.27 ^a	15.92 ± 2.08 ^b	0.11 ± 0.08 ^a	0.20 ± 0.06 ^a
+/+	13.32 ± 0.60 ^a	11.03 ± 0.84 ^b	112.10 ± 19.17 ^a	129.87 ± 12.20 ^a	15.21 ± 1.14 ^a	18.33 ± 4.39 ^a	1.36 ± 0.26 ^a	1.52 ± 0.30 ^a
-/+	7.82 ± 0.50 ^a	6.60 ± 0.59 ^b	52.84 ± 1.06 ^a	57.64 ± 3.94 ^b	27.87 ± 4.88 ^a	31.66 ± 6.48 ^a	1.51 ± 0.42 ^a	1.35 ± 0.12 ^a
0/0*	6.97 ± 0.26 ^a	6.04 ± 0.08 ^b	49.52 ± 3.68 ^a	50.92 ± 2.69 ^a	24.66 ± 1.20 ^a	23.58 ± 1.64 ^a	1.10 ± 0.11 ^a	0.98 ± 0.09 ^a

Note: Different letters in the same row for each mechanical property represent significant difference ($p < 0.05$) between means through the analysis of variance

0/0* is a replicate of sample 0/0.

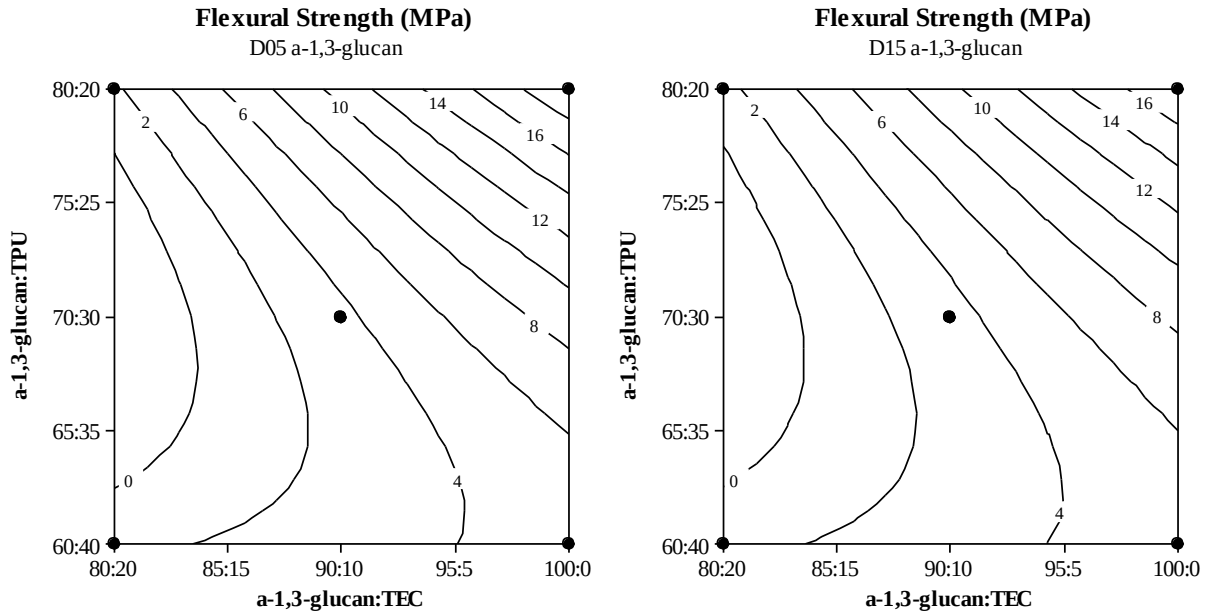


Figure 11. Flexural strength contour plots for D05 composites (left) and D15 composites (right)

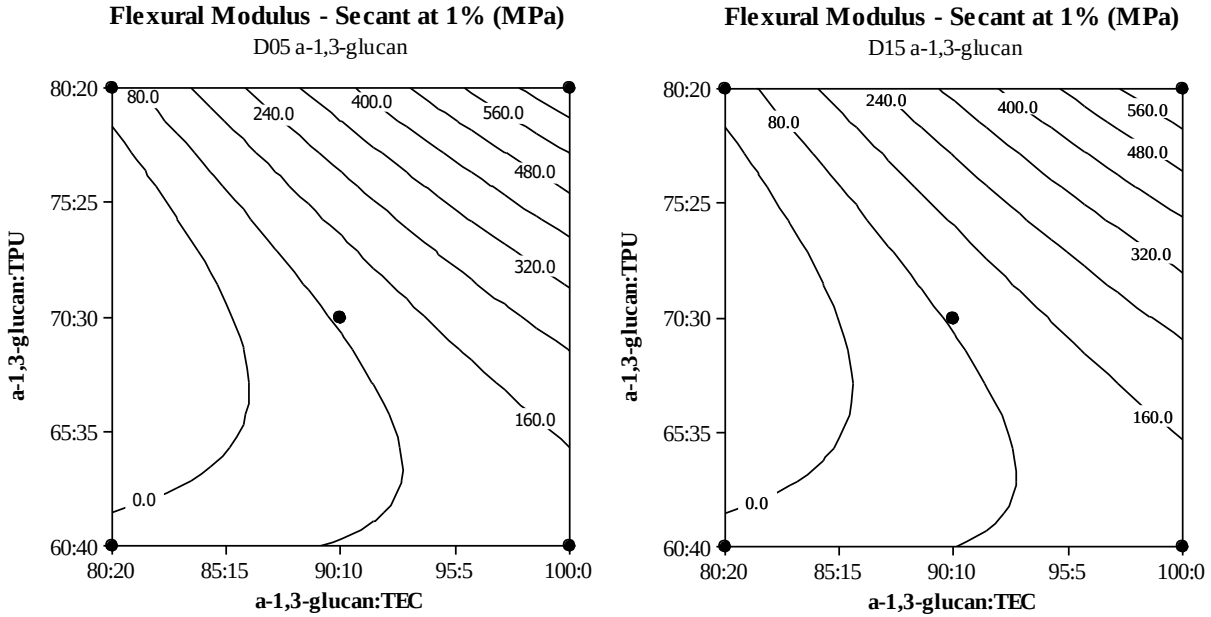


Figure 12. Flexural modulus contour plots for D05 composites (left) and D15 composites (right)

The contour plots for the tensile properties are shown in Figures 13-16. Similar to the flexural properties, an improvement in tensile strength and modulus was observed with the addition of the α -1,3-glucan due to its reinforcing effect when comparing the 60 wt.% to 80 wt.% α -1,3-glucan composite samples. The addition of the TEC plasticizer reduced the strength and modulus by making the composites soft and flexible. The elongation at break showed higher dependence on the TPU concentration. TPU is an elastomer which displays high elongation at break characteristic, therefore higher elongation was observed when higher concentration of the TPU was present in the composite system. The decrease in the elongation at break as the filler content increases is commonly observed in composite systems.^[71,108,109] Chen et al. investigated a cellulose and TPU blend and observed that the tensile strength and modulus both increased with the amount of cellulose, while the elongation at break decreased at higher loadings of cellulose.^[108] In a different study by Pursula et al., incorporation of nanocellulose improved the tensile strength and modulus of TPU, but reduced the elongation at break due to stiffening.^[110]

The toughness of the composites was calculated by integrating the stress-strain curve, and it showed improvement when the TPU concentration increased while reducing the TEC concentration. This is because the toughness requires a balance of strength and elongation, and the strength increases by reducing the TEC while the elongation increases by increasing the TPU concentration.

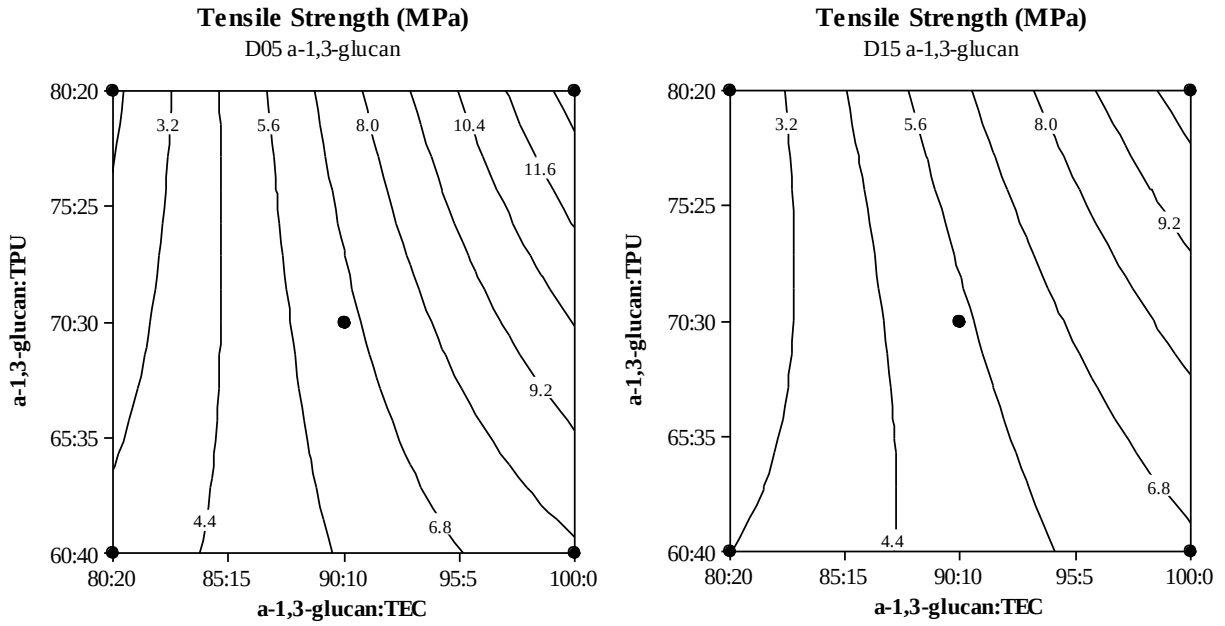


Figure 13. Tensile strength contour plots for D05 composites (left) and D15 composites (right)

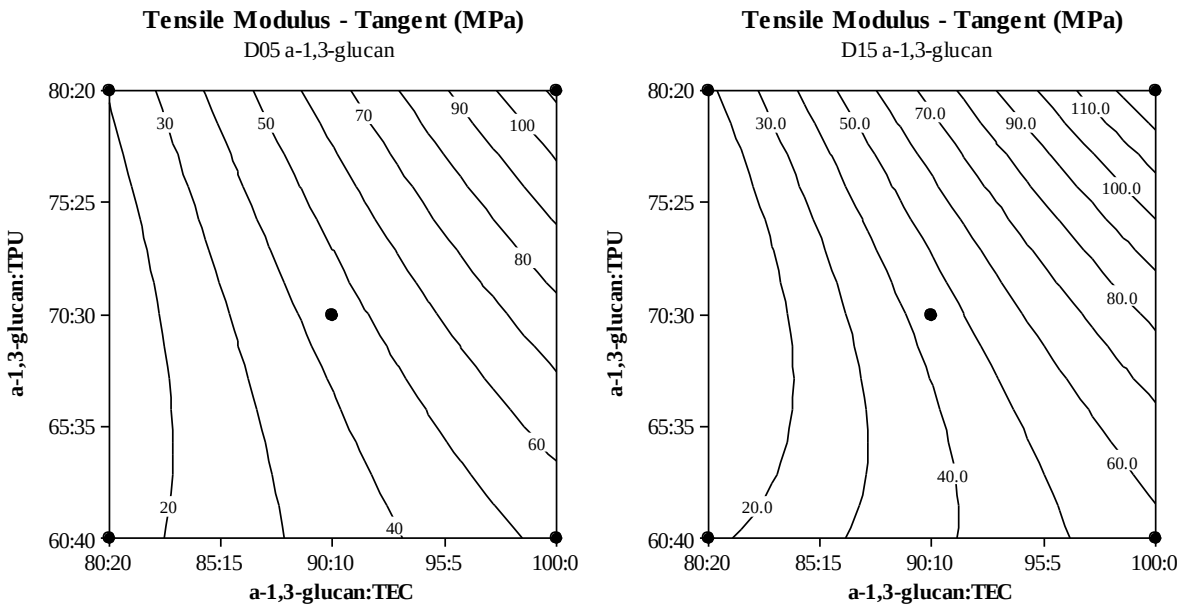


Figure 14. Tensile modulus contour plots for D05 composites (left) and D15 composites (right)

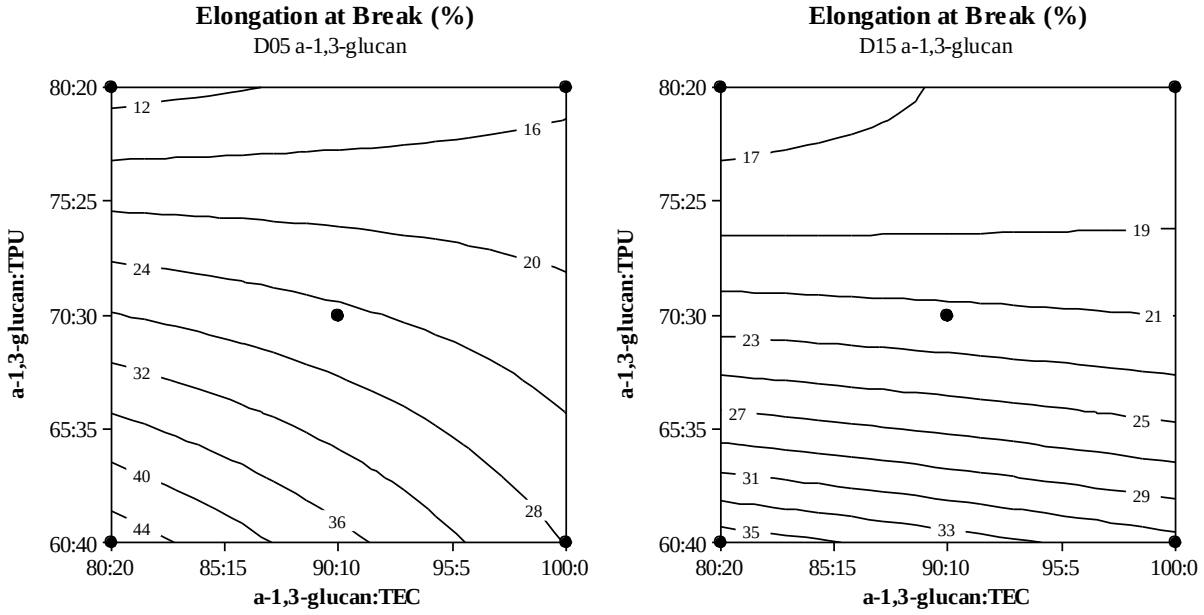


Figure 15. Elongation at break contour plots for D05 composites (left) and D15 composites (right)

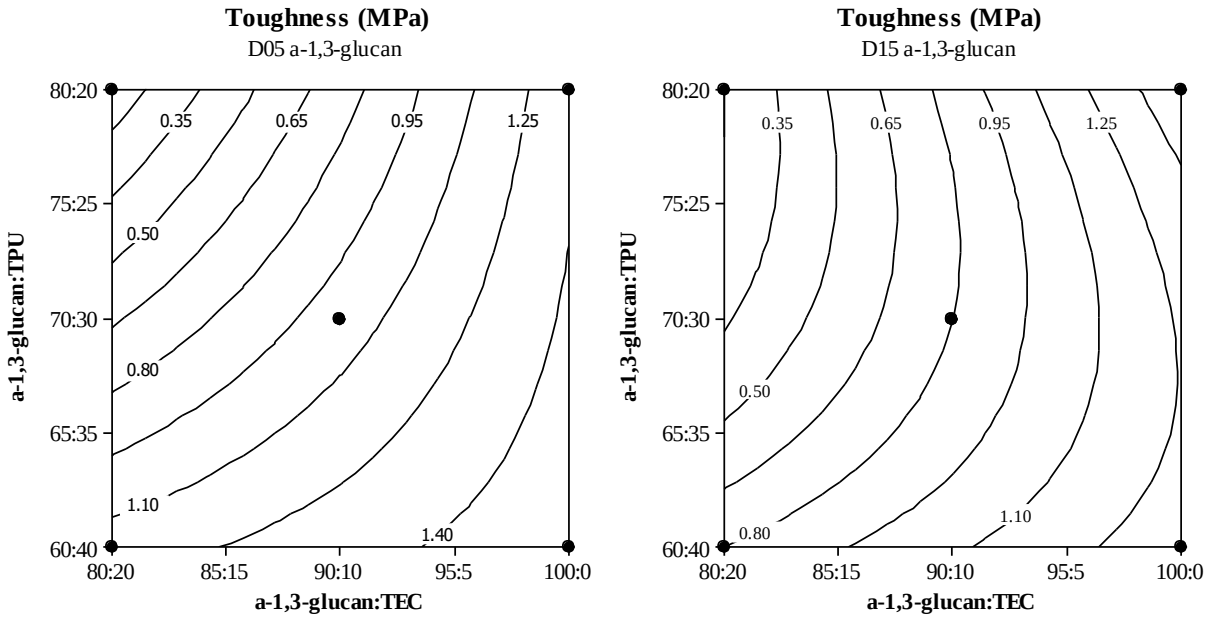


Figure 16. Toughness contour plots for D05 composites (left) and D15 composites (right)

The contour plots for the impact strength are shown in Figure 17. A reduction in the impact strength was observed at a high level of the α -1,3-glucan. This was due to a brittle behaviour of the composites as the concentration of the α -1,3-glucan increased; the composite system was not able to absorb the energy efficiently which resulted in easier crack propagation, and thereby

reducing the impact strength. Like the flexural properties, the impact strength was improved with the addition of the plasticizer molecule TEC, or by reducing the amount of the α -1,3-glucan.

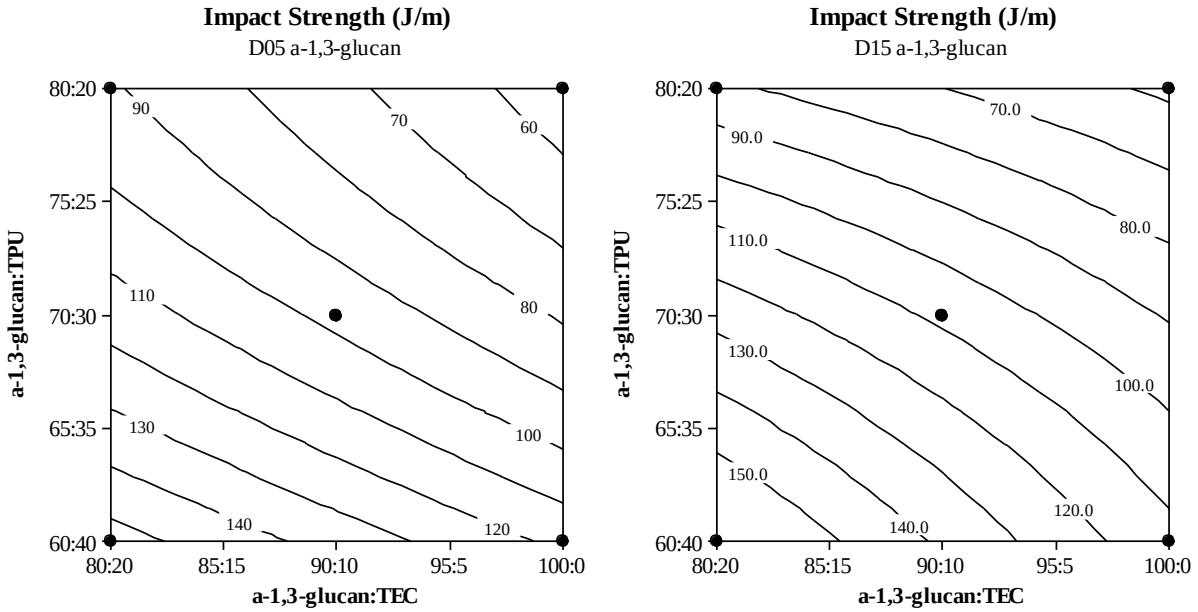


Figure 17. Impact strength contour plots for D05 composites (left) and D15 composites (right)

The effect of factors α -1,3-glucan:TPU (A), α -1,3-glucan:TEC (B), interaction (A $\times$ B), and adjusted R^2 are tabulated in Tables 14-17.

Table 14. Coded regression coefficients, standard error coefficient, and p -values for selected properties (D05 α -1,3-glucan)

Term	Flexural Strength (MPa)			Flexural Modulus (MPa)			Impact Strength (J/m)		
	Coeff.	SE Coeff.	p	Coeff.	SE Coeff.	p	Coeff.	SE Coeff.	p
Constant	5.82	1.12	0.035	184.5	47.11	0.059	102.00	2.93	0.001
A	3.81	1.37	0.108	147.7	57.70	0.125	-31.60	3.58	0.013
B	5.40	1.37	0.058	190.0	57.70	0.081	-18.39	3.58	0.036
A $\times$ B	3.68	1.37	0.115	144.5	57.70	0.129	0.02	3.58	0.995
Adj. R^2	0.85			0.81			0.98		

Table 15. Coded regression coefficients, standard error coefficient, and p -values for selected properties (D05 α -1,3-glucan)

Term	Tensile Strength (MPa)			Tensile Modulus (MPa)			Elongation at Break (%)			Toughness (MPa)		
	Coeff.	SE Coeff.	p	Coeff.	SE Coeff.	p	Coeff.	SE Coeff.	p	Coeff.	SE Coeff.	p
Constant	6.58	0.19	0.001	48.50	2.55	0.003	24.90	0.12	0.000	1.03	0.03	0.001
A	0.91	0.23	0.061	16.12	3.13	0.036	-12.21	0.15	0.000	-0.30	0.04	0.015
B	3.95	0.23	0.003	32.21	3.13	0.009	-3.48	0.15	0.002	0.40	0.04	0.009
A $\times$ B	1.84	0.23	0.016	13.51	3.13	0.050	5.88	0.15	0.001	0.23	0.04	0.027
Adj. R^2	0.99			0.97			0.99			0.98		

Table 16. Coded regression coefficients, standard error coefficient, and p-values for selected properties (D15 α -1,3-glucan)

Term	Flexural Strength (MPa)			Flexural Modulus (MPa)			Impact Strength (J/m)		
	Coeff.	SE Coeff.	p	Coeff.	SE Coeff.	p	Coeff.	SE Coeff.	p
Constant	5.39	1.01	0.033	169.4	40.36	0.052	105.42	1.23	0.000
A	3.19	1.24	0.123	130.4	49.43	0.119	-34.13	1.50	0.002
B	5.07	1.24	0.055	174.9	49.43	0.071	-18.80	1.50	0.006
A×B	3.18	1.24	0.124	128.1	49.43	0.122	6.66	1.50	0.047
Adj. R ²	0.84			0.82			0.99		

Table 17. Coded regression coefficients, standard error coefficient, and p-values for selected properties (D15 α -1,3-glucan)

Term	Tensile Strength (MPa)			Tensile Modulus (MPa)			Elongation at Break (%)			Toughness (MPa)		
	Coeff.	SE Coeff.	p	Coeff.	SE Coeff.	p	Coeff.	SE Coeff.	p	Coeff.	SE Coeff.	p
Constant	5.64	0.27	0.002	52.04	4.54	0.008	24.18	1.60	0.004	0.91	0.09	0.010
A	0.85	0.33	0.124	18.02	5.56	0.083	-8.40	1.95	0.050	-0.11	0.11	0.442
B	3.07	0.33	0.011	37.99	5.56	0.021	-0.53	1.95	0.812	0.47	0.11	0.054
A×B	1.37	0.33	0.054	18.10	5.56	0.083	1.74	1.95	0.468	0.19	0.11	0.231
Adj. R ²	0.96			0.93			0.77			0.78		

4.1.2. Thermal properties

The TGA was used to analyze the thermal stability and degradation pattern of the composites at an elevated temperature. The thermal degradation behaviour of the D05 α -1,3-glucan composites is summarized in Figure 18. The degradation pattern was mostly similar between the samples produced from the factorial study. The key difference was an earlier onset of degradation for the samples that contain the TEC, due to its evaporation point lying below the onset of degradation for the α -1,3-glucan and the TPU. From the DTG curves, it was observed that the peak degradation of the α -1,3-glucan was below that of the TPU, where the α -1,3-glucan degradation rate peaked at around 350°C while the TPU peaked at around 420°C. The thermal degradation pattern appeared similar for both the D05 and D15 grades of the α -1,3-glucan. The TGA and DTG curves for the D15 α -1,3-glucan composites are summarized in Figure 19. The plots reveal that the degradation pattern of the D15 α -1,3-glucan composites is similar to the D05 composites.

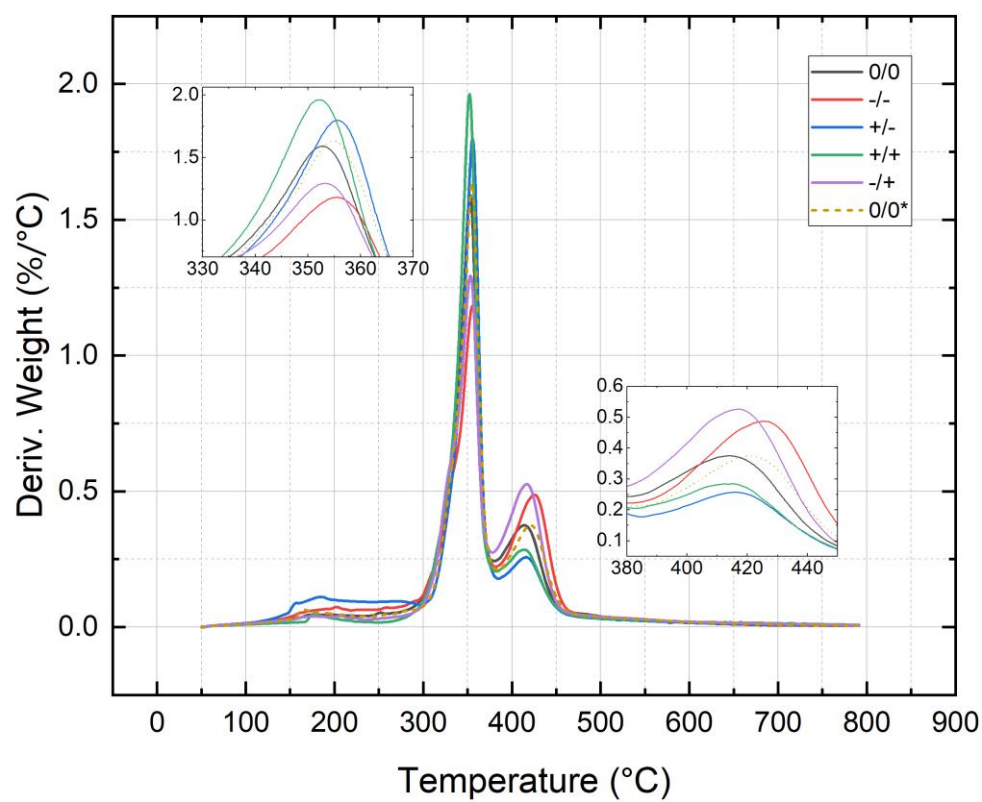
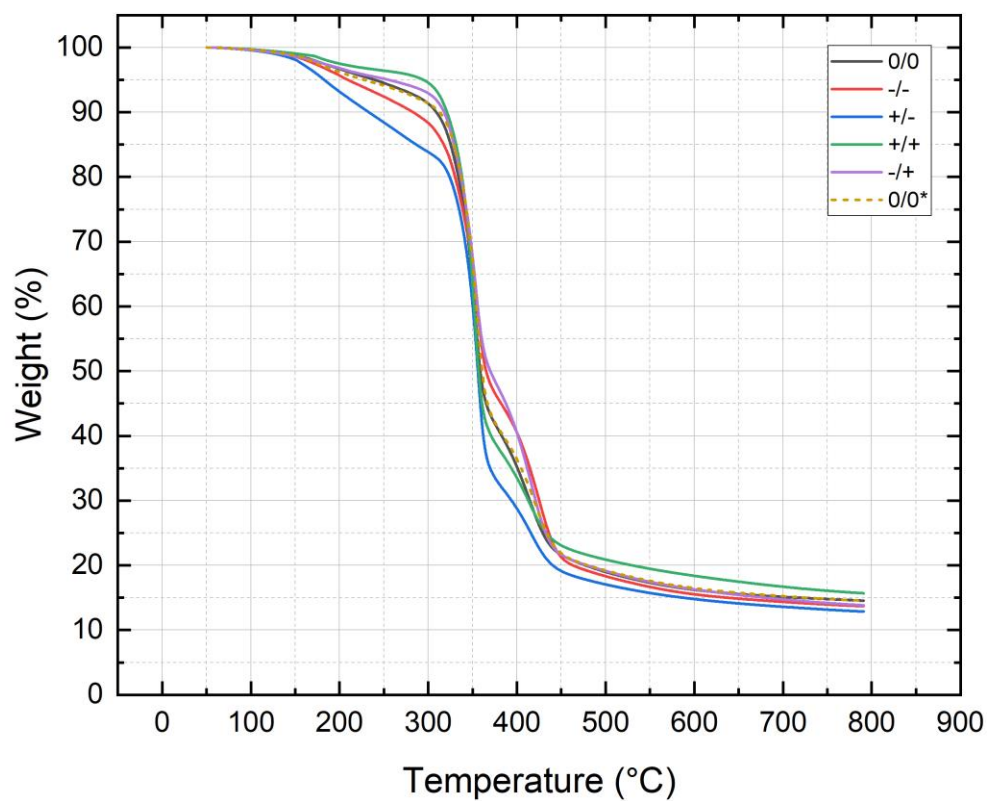


Figure 18. TGA (top) and DTG (bottom) curves for D05 composites

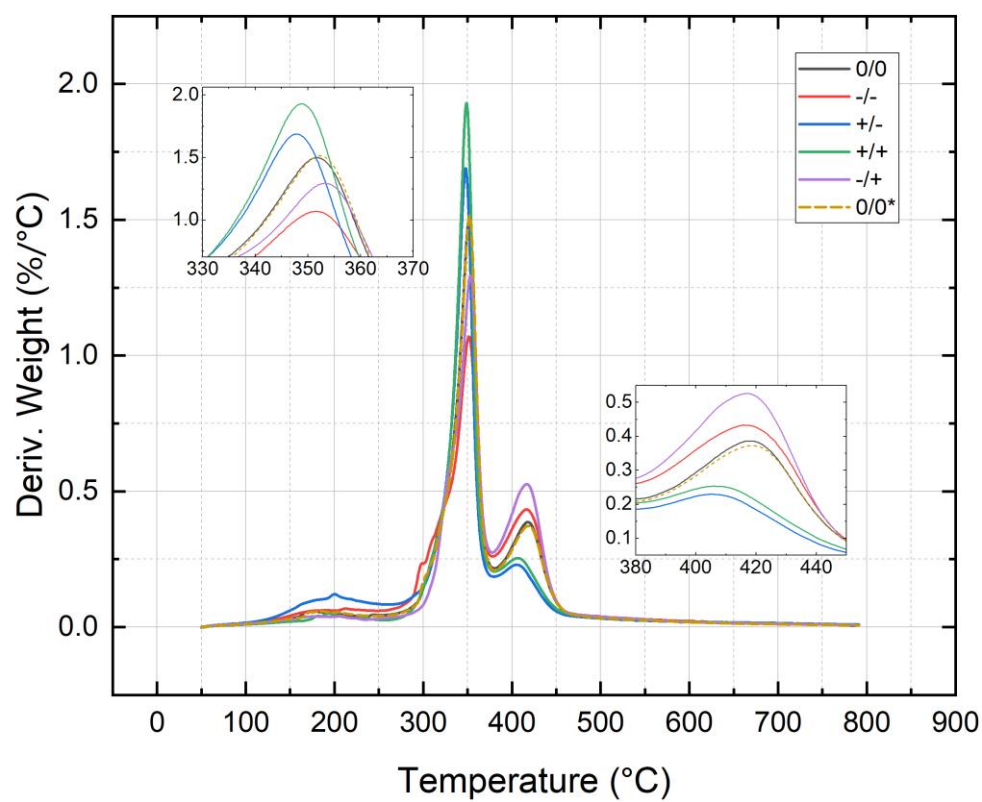
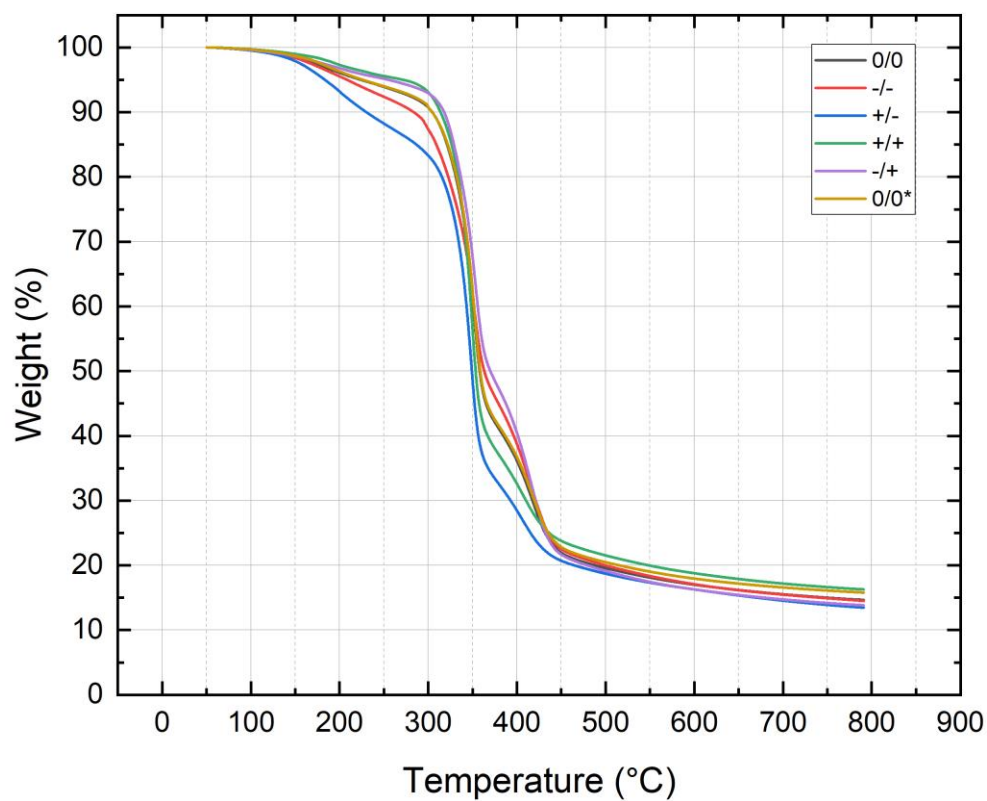


Figure 19. TGA (top) and DTG (bottom) curves for D15 composites

4.2. The effect of citrate-based plasticizers

Understanding the effect of plasticizer on the composite system is important since it can be used to tailor the properties such as flexibility and the processability. The type of plasticizer can be categorized into internal and external plasticizers.^[111] The internal plasticizers are a part of a polymer which are grafted or reacted onto the polymer chain or have high solubility with the polymer. This prevents the polymer chain from packing too closely and therefore allows it to be less ordered, and thus reduces the glass transition temperature. Since the reaction or solubilization between the polymer and the plasticizers is required, the internal plasticizers are often added during the polymerization steps. The external plasticizers are more forgiving since the plasticizer molecules are not required to react with the polymer. In commercial applications, external plasticizers are more favourable since they allow the manufacturers to be more flexible with formulations. The external plasticizers are molecules of low vapour pressure, are inert, and can interact with the polymer through swelling.

There are several theories that have been proposed to understand the plasticization mechanism. The most popular and well accepted theories are the lubricity theory, gel theory, and free volume theory.^[105] In the lubricity theory, the plasticizer reduces the intermolecular friction between the polymer molecules, allowing them to slip past each other, which lowers the deformation. The gel theory extends the lubricity model and describes the solvation-desolvation and aggregation-deaggregation equilibria between the polymer and the plasticizer molecules. The flexibility of the polymer chain is increased by the reduction of the polymer gel structure. In the free volume theory, the free volume is defined as the difference in volume when the polymer is at absolute zero temperature and at a selected temperature.^[105] Within the internal free volume, the polymer chain is able to freely move. The plasticizer molecules are able to expand the free volume and help the system to maintain the increased free volume post processing, as well as lower the glass transition temperature.

The citrate-based plasticizers have been reported in the literature as external plasticizers in cellulosic systems such as cellulose acetate.^[112,113] This is relevant to α -1,3-glucan since the solubilization behaviour of cellulose and α -1,3-glucan are similar.^[7] Zepnik et al. have reported that an increase in triethyl citrate in cellulose acetate resulted in a lowering of the glass transition temperature and increased flexibility.^[113] As well, the citrate-based plasticizers are promising

molecules for polysaccharide systems as these molecules are non-toxic and are fully bio-based plasticizers.

In this section, different citrate-based plasticizers were investigated with a fixed α -1,3-glucan:TPU ratio. More specifically, TEC, TBC, and ATBC were compared to see the effect on different properties of the composites.

4.2.1. Mechanical properties

The mechanical properties of the 80:20 α -1,3-glucan:TPU composites with different types and amounts of plasticizer are tabulated in Tables 18 and 19. The flexural strength and modulus decreased with the addition of the plasticizer, which aligns with the results from the factorial study in section 4.1.1. The analysis of variance showed that the nature of the plasticizer did not affect the properties, but rather the concentration. The most significant change was observed between the samples with no plasticizer and 90:10 α -1,3-glucan:plasticizer ratio. The decrease in the flexural properties is attributed to the increase in flexibility due to the plasticizer molecules reducing the friction between the polymeric chains.

The increase in flexibility of the composites affected the impact strength. With the addition of the plasticizer, the impact strength was improved, meaning the samples were able to absorb more energy and prevent crack propagation. It should be noted that using the TBC as the plasticizer had the most significant improvement in the impact strength.

Table 18. Flexural and impact test results for 80:20 α -1,3-glucan:TPU composites with different plasticizers

	Flexural Strength (MPa)	Flexural Modulus – Secant at 1% (MPa)	Impact Strength (J/m)
No plasticizer	17.83 $\pm$ 0.70	643.13 $\pm$ 59.28	57.95 $\pm$ 2.66
TEC10	3.15 $\pm$ 0.10 ^a	86.88 $\pm$ 5.70 ^a	53.40 $\pm$ 5.81 ^a
ATBC10	3.25 $\pm$ 0.18 ^a	96.03 $\pm$ 7.10 ^a	75.07 $\pm$ 2.50 ^b
TBC10	3.08 $\pm$ 0.16 ^a	89.74 $\pm$ 8.43 ^a	89.81 $\pm$ 2.58 ^c
TEC20	1.34 $\pm$ 0.16 ^a	37.17 $\pm$ 5.35 ^a	82.24 $\pm$ 2.37 ^a
ATBC20	1.25 $\pm$ 0.03 ^a	37.29 $\pm$ 2.84 ^a	59.72 $\pm$ 2.56 ^b
TBC20	0.95 $\pm$ 0.07 ^b	28.43 $\pm$ 3.08 ^b	91.53 $\pm$ 1.78 ^c

Note: Different letters in the same column represent significant difference ($p < 0.05$) between means through analysis of variance

The tensile results are tabulated in Table 19. The stress-strain curves from the tensile tests are shown in Figure 20. The addition of the plasticizer reduced the tensile strength and modulus because the samples became softer and more flexible. Like in the case with the flexural properties, the analysis of variance showed that the type of the plasticizer used had a little effect on the properties. The most significant reduction in strength and modulus was observed between the samples without any plasticizer and 90:10 α -1,3-glucan:plasticizer ratio. Further significant decrease in the modulus was observed when more plasticizer was added.

The elongation at break was not significantly influenced by the plasticizer since this property is more dependent on the TPU concentration. The toughness requires a balance between the strength and elongation, and since the strength decreased with the addition of the plasticizer, so did the toughness.

Table 19. Tensile test results for 80:20 α -1,3-glucan:TPU composites with different plasticizers

	Tensile Strength (MPa)	Tensile Modulus – Tangent (MPa)	Elongation at Break (%)	Toughness (MPa)
No plasticizer	11.36 $\pm$ 1.28	458.58 $\pm$ 42.16	17.84 $\pm$ 2.07	1.52 $\pm$ 0.30
TEC10	3.49 $\pm$ 0.27 ^a	114.12 $\pm$ 13.67 ^a	10.51 $\pm$ 1.34 ^a	0.21 $\pm$ 0.04 ^a
ATBC10	4.48 $\pm$ 0.82 ^b	226.85 $\pm$ 31.57 ^b	9.19 $\pm$ 0.99 ^a	0.25 $\pm$ 0.06 ^a
TBC10	3.60 $\pm$ 0.21 ^a	91.05 $\pm$ 16.30 ^a	10.68 $\pm$ 0.78 ^a	0.22 $\pm$ 0.03 ^a
TEC20	2.15 $\pm$ 0.33 ^a	25.32 $\pm$ 3.76 ^a	15.91 $\pm$ 2.09 ^a	0.20 $\pm$ 0.06 ^a
ATBC20	1.69 $\pm$ 0.17 ^b	46.05 $\pm$ 11.83 ^b	12.24 $\pm$ 1.01 ^b	0.13 $\pm$ 0.01 ^b
TBC20	2.18 $\pm$ 0.37 ^a	42.35 $\pm$ 20.80 ^b	19.07 $\pm$ 2.82 ^a	0.25 $\pm$ 0.07 ^a

Note: Different letters in the same column represent significant difference ($p < 0.05$) between means through analysis of variance

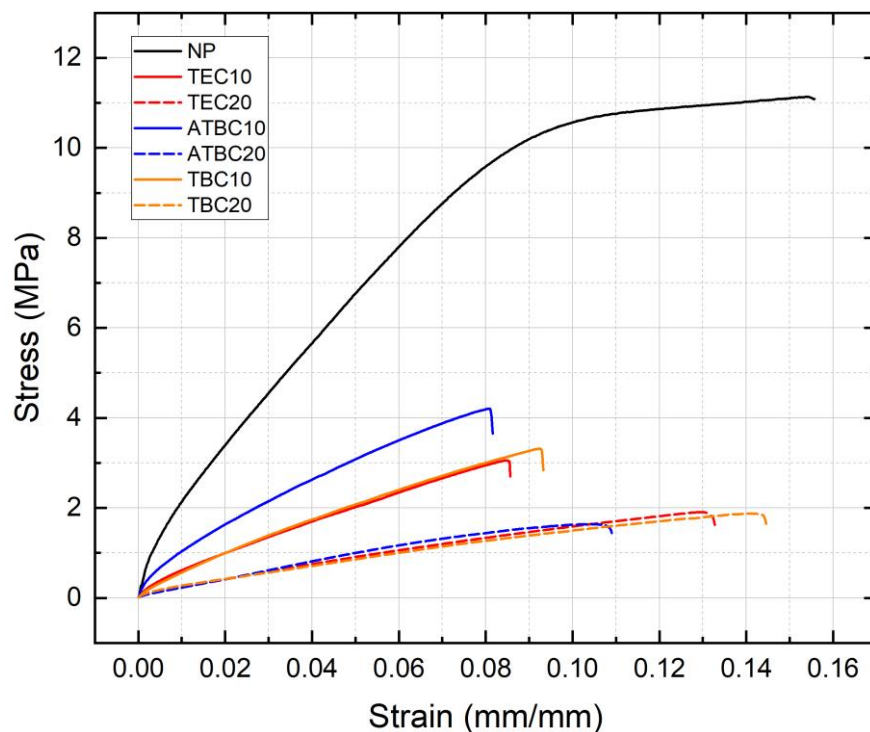


Figure 20. Stress-strain curves for 80:20 α -1,3-glucan:TPU composites with different plasticizers; NP: no plasticizer

4.2.2. Thermal stability

The TGA and DTG curves are summarized in Figure 21. The TGA is a great tool for analyzing the change in the composite degradation behaviour when a plasticizer is added. The overall degradation pattern remained unchanged, with only some slight change with the initial onset of degradation when the plasticizer was added. This was due to the evaporation of the plasticizers that occurs before the degradation of the α -1,3-glucan and TPU. Similar thermal stability studies on PVC with plasticizer using TGA have been reported in literature. Beltran and Marcilla concluded that the evaporation of a plasticizer is typically the first step of thermal degradation during the TGA studies.^[114] In a different study with polystyrene (PS), the TGA technique was used to analyze the amount of migrated plasticizer. The different weight loss steps corresponded to the plasticizer release, followed by the PS degradation, and the magnitude of each step was used to quantify the amount of plasticizer migration.^[105] Once the plasticizers had evaporated, the remaining degradation pattern was similar for all the samples, where the peak degradation of the α -1,3-glucan and TPU was observed at around 350 and 400°C, respectively.

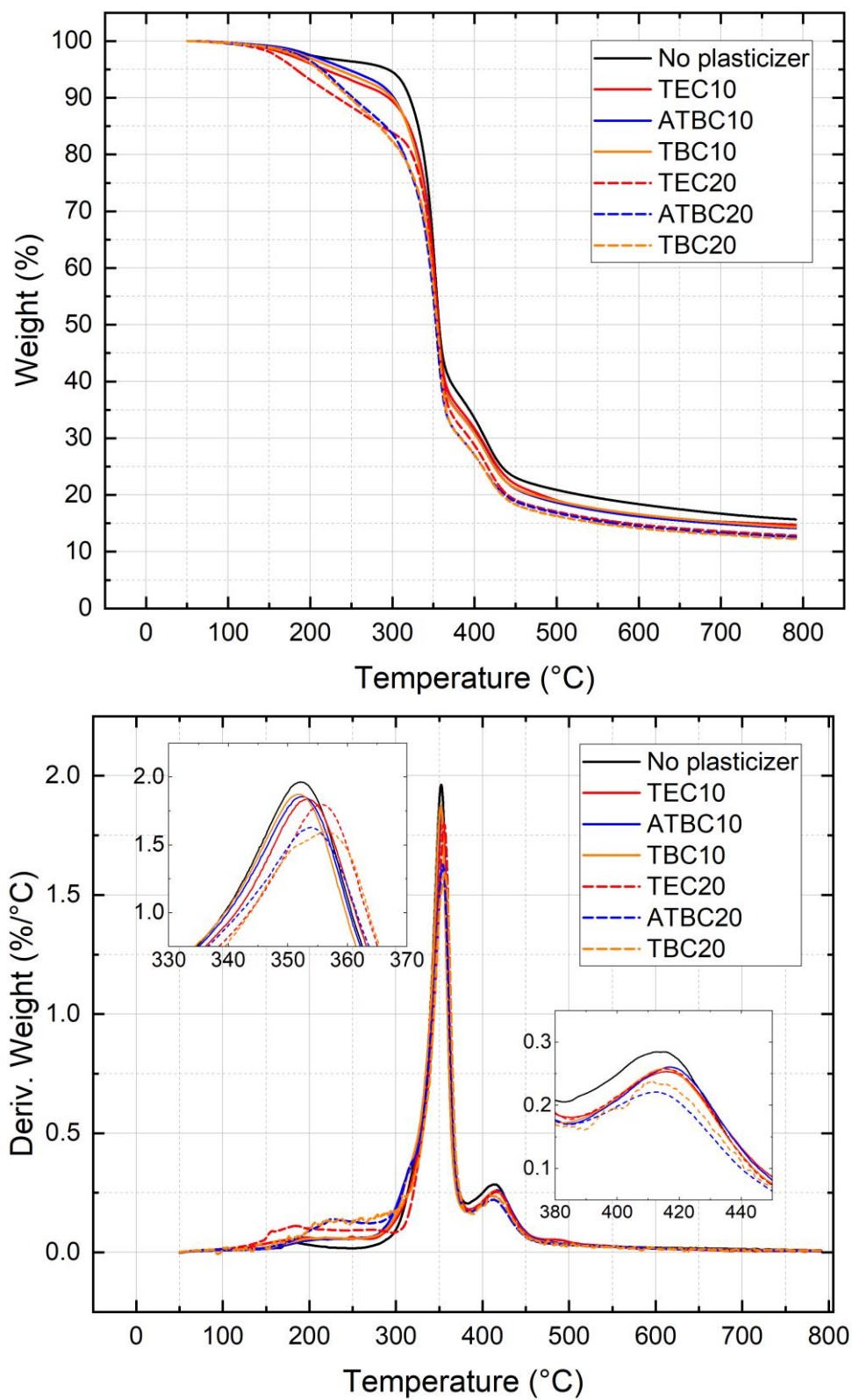


Figure 21. TGA (top) and DTG (bottom) curves for 80:20 α -1,3-glucan:TPU composites with different plasticizers

4.2.3. Scanning electron microscopy

The SEM images of the film cross-sectional area are summarized in Figure 22. The α -1,3-glucan particles appear as rigid particles and no sign of size reduction was observed when compared to the SEM image of the α -1,3-glucan powder as received. The shear and temperature from the extruder were not sufficient to reduce the particle size, even when the citrate-based plasticizer was added. This is an indication that the citrate-based chemicals were acting as an external lubricant, and to achieve size reduction, an internal plasticization or chemical modification of the α -1,3-glucan is required. As an external plasticizer, the citrate-based chemicals were able to provide a smoother surface and filled the gaps that are present between the α -1,3-glucan and the TPU matrix. The smoother surface was a sign that there was a good compatibility between the plasticizer and the composite system. At such high levels of the α -1,3-glucan, the TPU was functioning as a binder that provided adhesion and mechanical integrity of the composite.

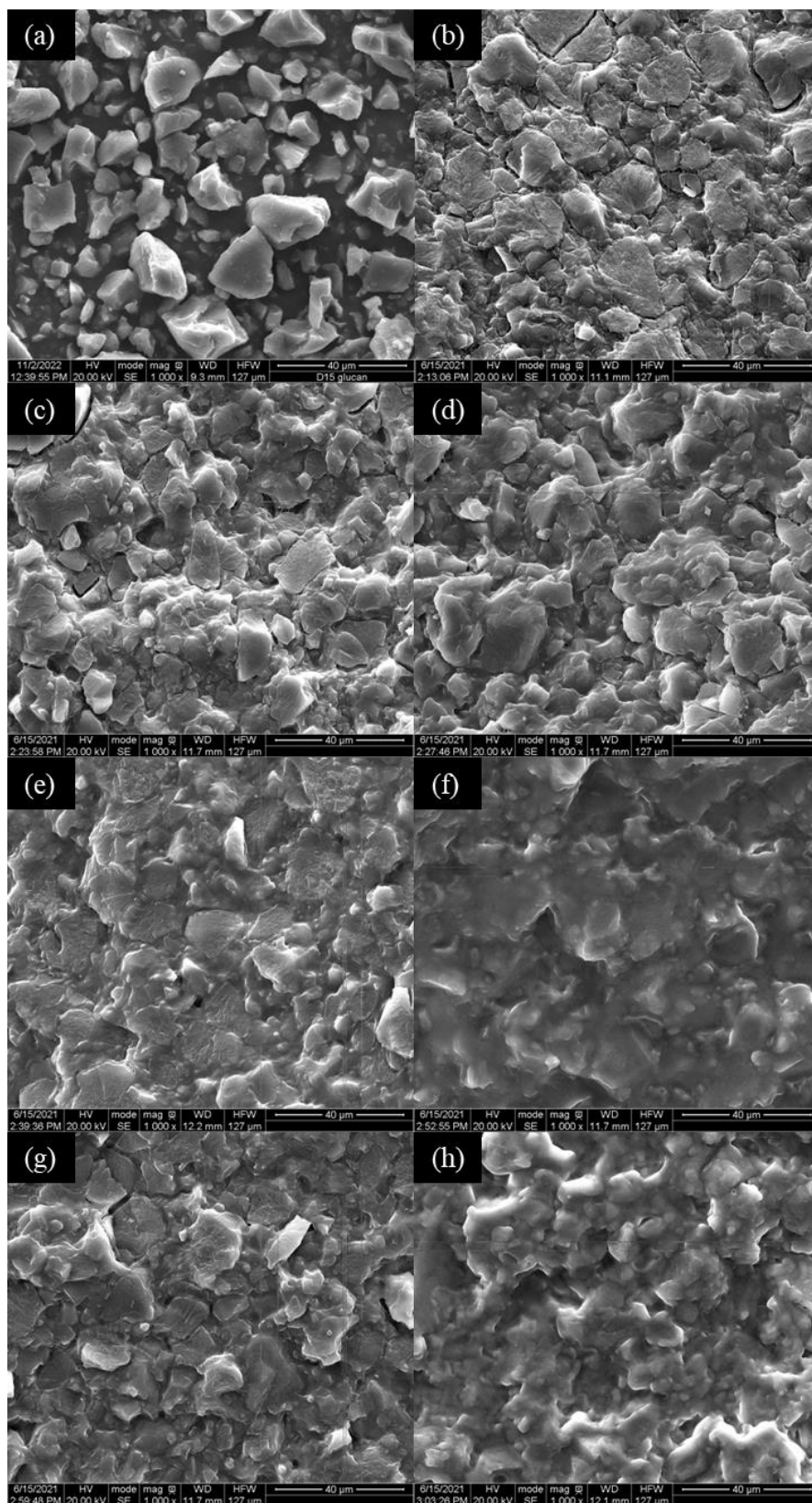


Figure 22. SEM images of (a) pristine D15 glucan; 80:20 α -1,3-glucan:TPU with (b) no plasticizer, (c) 10% TEC, (d) 20% TEC, (e) 10% ATBC, (f) 20% ATBC, and (g) 10% TBC

4.3. DCP as a compatibilizer

In the third study, the DCP was added to the TPU- α -1,3-glucan composite system to investigate the improvement in the compatibility between the TPU and α -1,3-glucan. The question is whether DCP can provide chemical changes to the structure of either phase in order to improve the properties. The DCP is used in TPU systems to achieve crosslinking reactions by forming radical initiators. The images of the films are shown in Figure 23. The direction of the arrow indicates the increase in DCP concentration in the composite system, and the formulations are provided in Table 11. As the α -1,3-glucan was added, the colour of the resulting films turned slightly brown. It was hypothesized that the colour comes from the degradation of low molecular weight polysaccharide impurities, such as sucrose (starting material for the α -1,3-glucan enzymatic polymerization) and fructose (by-product of the enzymatic polymerization), that caused the discolouration of the samples.

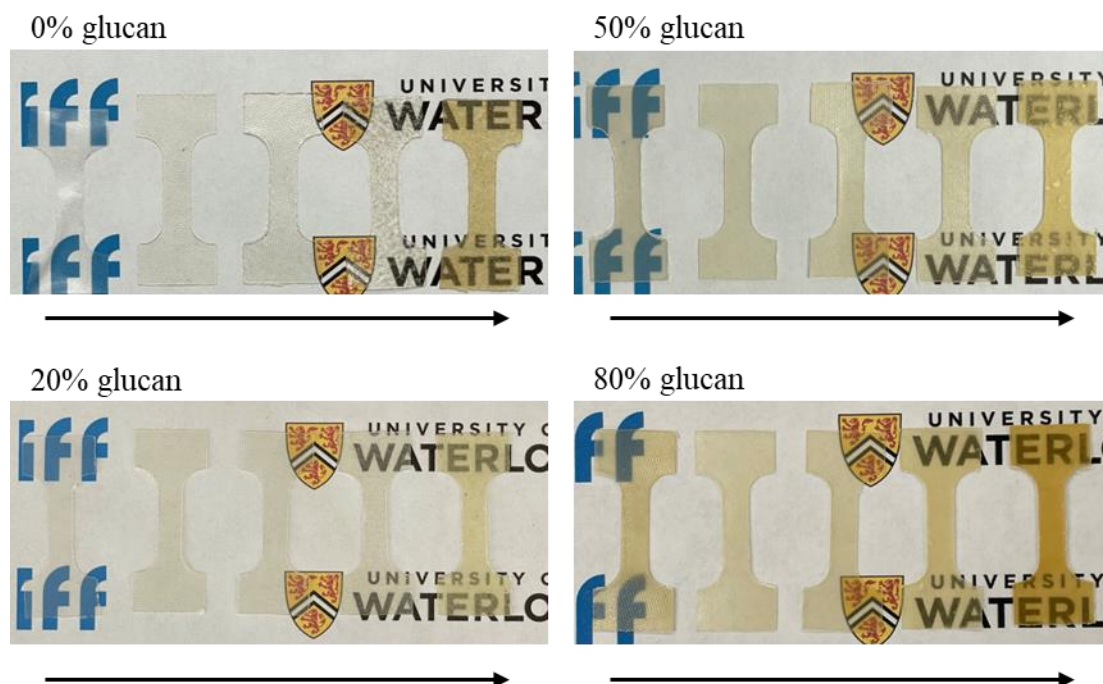


Figure 23. Tensile test specimens with different levels of α -1,3-glucan and DCP (the arrow direction represents increasing level of DCP: 0, 0.1, 0.5, 1, and 2 wt.%)

4.3.1. Batch mixer

The batch mixer was used to investigate the change in TPU melt behaviour when DCP was added. The torque and temperature of the batch mixer as a function of time are shown in Figures 24 and 25, respectively. In the first 2 minutes of the mixing, a peak in torque was observed, which

corresponds to when the samples were charged into the mixing chamber. For the samples that did not contain any or a low concentration of DCP, the torque level stabilized after the 2-minute mark. However, the samples containing higher levels of DCP showed a second peak, which was an indication of DCP activity. As well, a higher value of the slope was observed at high concentration of DCP since higher concentration of free radicals were formed. Once the reaction had ended, the torque began to decrease and stabilize at a much higher torque level compared to the pristine TPU or TPU with low concentration of DCP. This increase in the torque at equilibrium is an indication of increase in the melt viscosity due to some cross-linking that may have occurred. On the other hand, the decrease in torque followed by a peak is also an indication that mechanical degradation may have occurred. For example, the TPU containing 0.5% DCP had a peak torque value of 60 N m during the DCP reaction phase, but afterwards, the torque gradually decreased to about 18 N m, which is an about 70% decrease. Likewise, the TPU with 1% showed an about 40% decrease in torque after the initial increase in torque due to the DCP activity. The degradation was a result of the mechanical shear since the torque increased significantly. The sign of degradation can be observed by the colour of the specimens as shown in Figure 23. The specimens without any α -1,3-glucan show that the addition of 2% DCP caused the browning of the TPU. The high level of DCP caused a mechanical degradation to occur by high level of shear.

The two-stage torque behaviour in the batch mixer when DCP was incorporated was reported in a literature.^[115] Céspedes et al. observed that not only did the addition of DCP to the thermoplastic vulcanizates increase the torque for the second time, but also saw that the higher concentration of DCP led to a sharper increase in torque. As well, when relatively high contents of DCP were incorporated, the torque started to decrease with time as a result of molecular scission. The decrease in torque was also due to the significant increase in the internal temperature as shown in Figure 25. The high temperature led to a decrease in the viscosity, which subsequently decreased the torque.

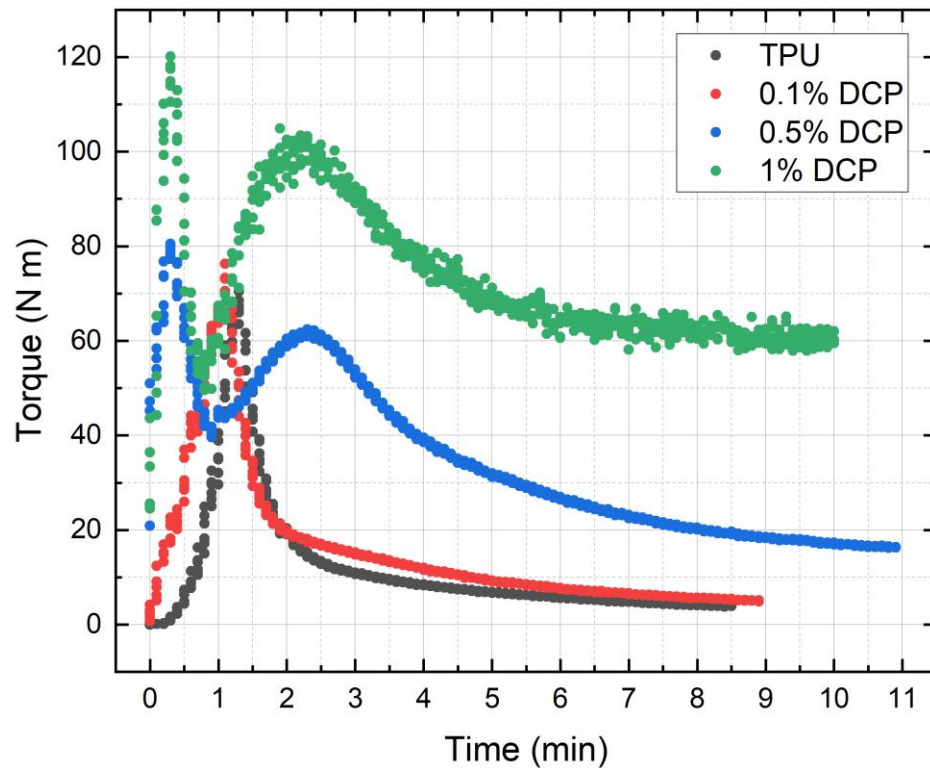


Figure 24. Torque vs. time for TPU with different levels of DCP

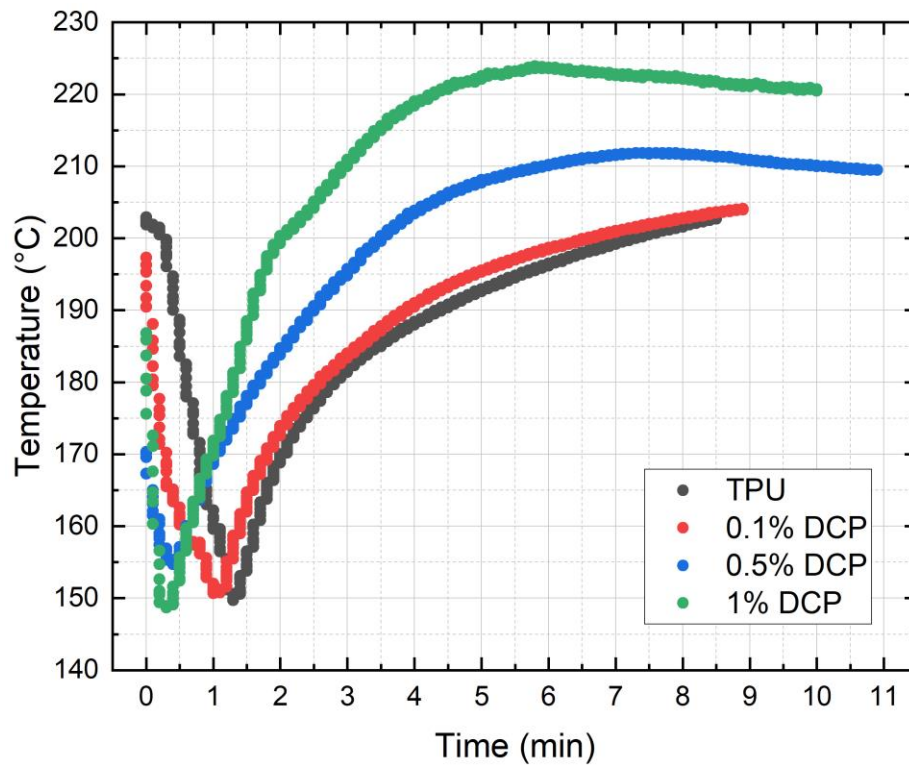


Figure 25. Temperature vs. time for TPU with different levels of DCP

4.3.2. Chemical analysis

The NMR analysis was conducted to investigate the effect of DCP on TPU and α -1,3-glucan. The ^1H NMR plots for pristine TPU and α -1,3-glucan are shown in Figures 26 and 27. Based on the NMR analysis, it was determined that the TPU used for this study was of aromatic and ester kind, and the corresponding chemical structure with peak assignments are shown in Figure 26.

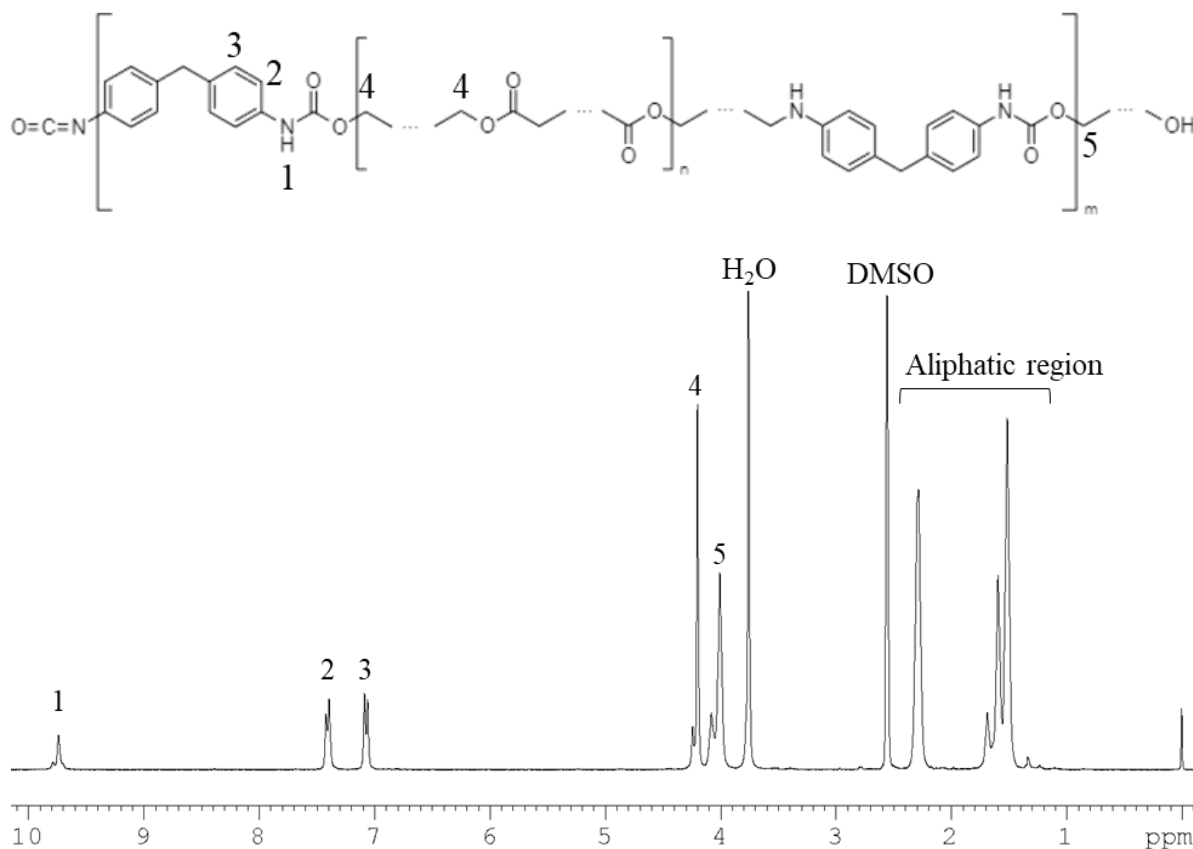


Figure 26. Pristine TPU chemical structure and ^1H -NMR plot

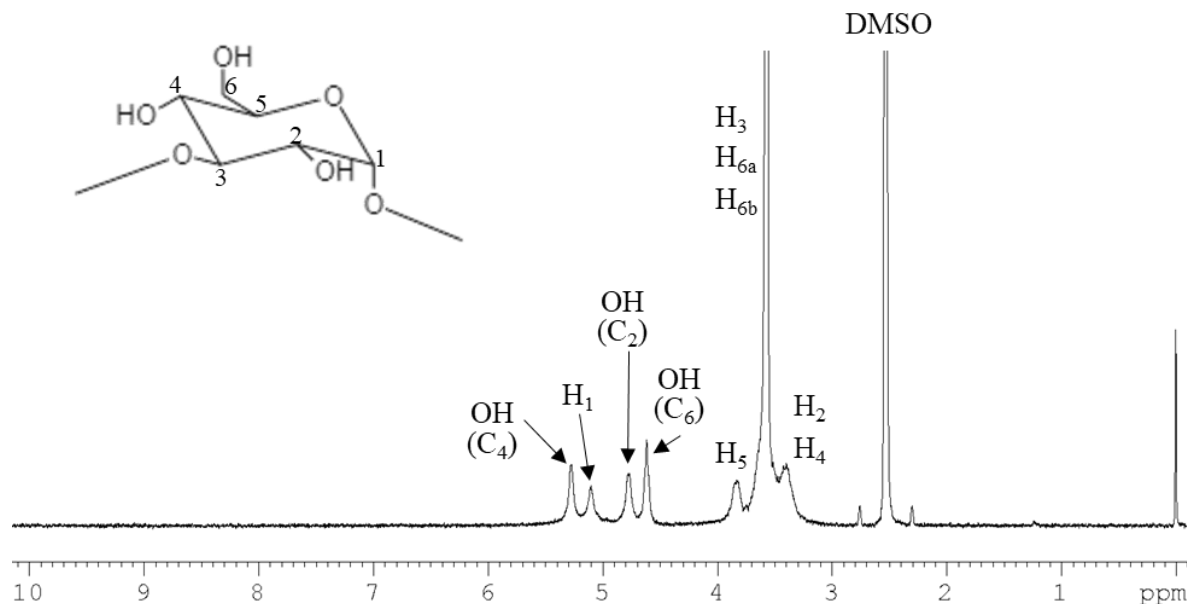


Figure 27. Pristine α -1,3-glucan chemical structure and ^1H -NMR plot; subscripts correspond to the carbon number (e.g., H_1 is hydrogen in carbon 1 and $\text{OH}(\text{C}_2)$ is hydroxyl hydrogen in carbon 2)

The effect of DCP on the TPU is shown in Figure 28, where the ^1H NMR plots of the pristine TPU and TPU with 0.5% DCP was compared. The signal obtained were mostly identical with some key changes between 4.3 and 3.8 ppm. The peak corresponding to the urethane linkage at 4.2 ppm showed a decrease in intensity when DCP was added. The urethane linkage exists in the soft segment of the polyurethane, and hence is an indication that the DCP prefers to react with the soft segment. A similar behaviour was observed when α -1,3-glucan was added to the composite, as shown in Figures 29-31, where the intensity of the urethane peak changed when DCP was added. When 80% of α -1,3-glucan was added, the signal intensity corresponding to the hydroxyl groups of the glucan molecule (5.4 – 4.5 ppm) showed a slight decrease. Although the DCP prefers to react with TPU over α -1,3-glucan, when the system is comprised of a majority of α -1,3-glucan, the DCP prefers to react with the free hydroxyls of the glucan. Wei et al. conducted a study on grafting polyhydroxybutyrate (PHB) onto cellulose by using DCP. Their analysis showed that the cellulose radicals were formed by DCP attacking the free hydroxyls of cellulose.^[116]

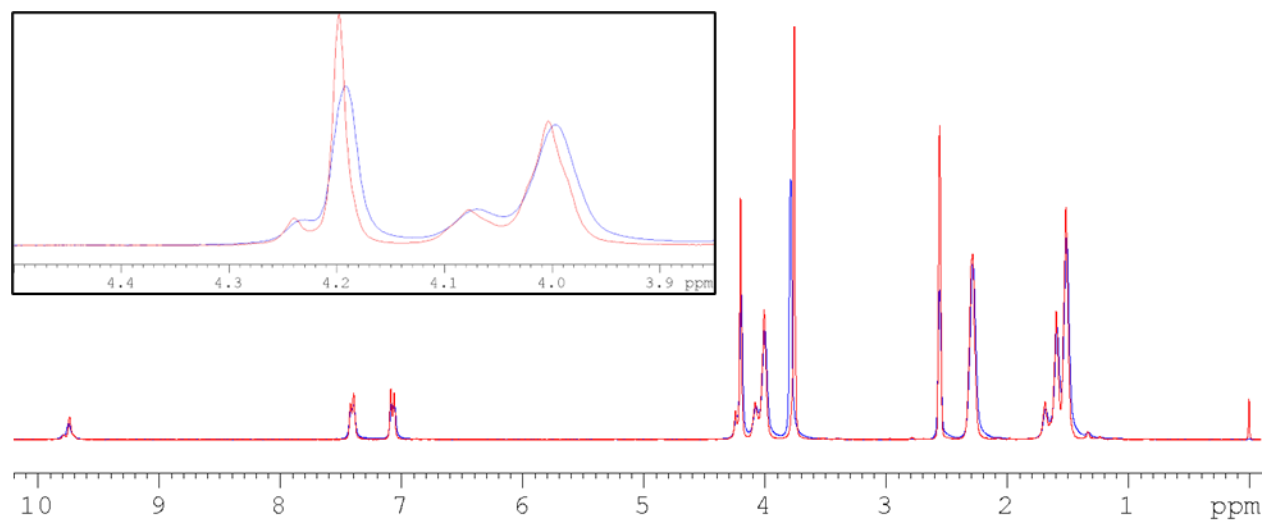


Figure 28. Pristine TPU (red) and TPU with 0.5% DCP (blue) NMR plot

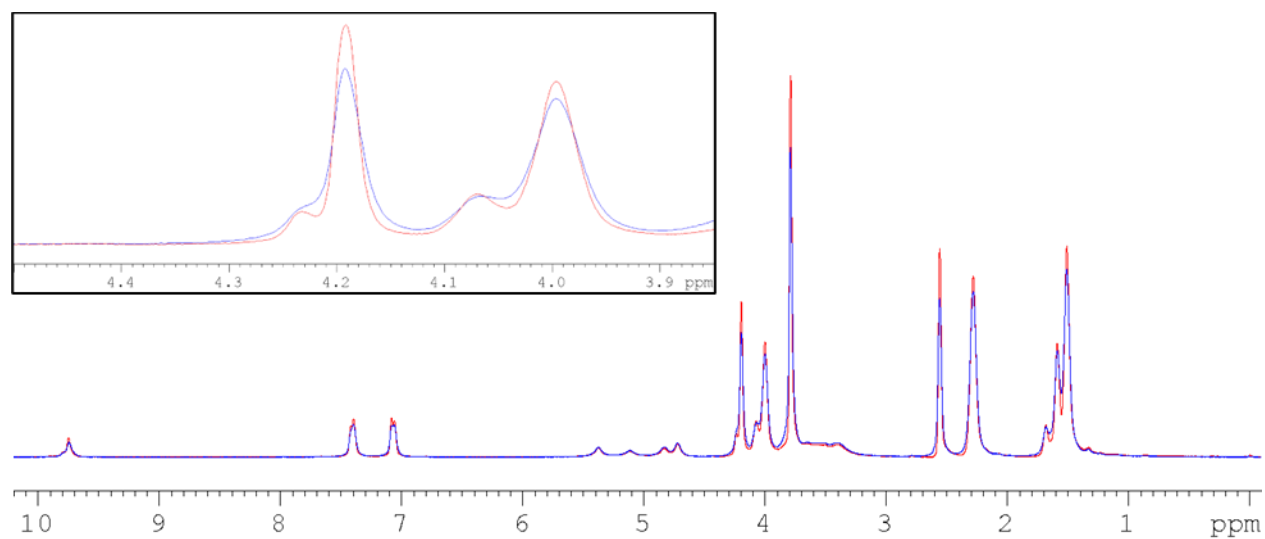


Figure 29. 20% α -1,3-glucan TPU composite (red) and 20% α -1,3-glucan TPU composite with 0.5% DCP (blue) NMR plots

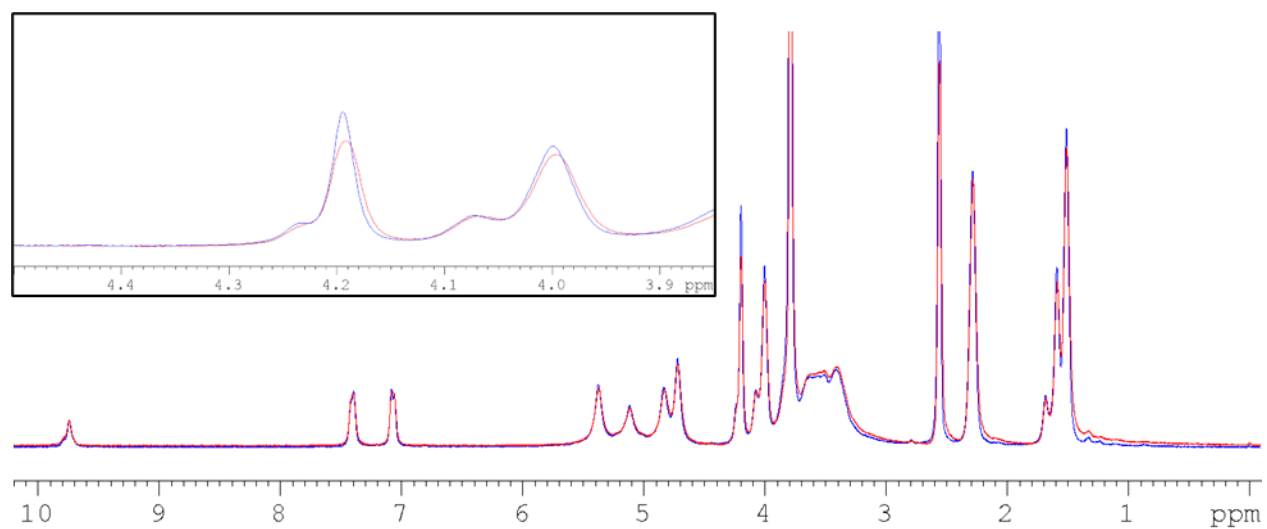


Figure 30. 50% α -1,3-glucan TPU composite (red) and 50% α -1,3-glucan TPU composite with 0.5% DCP (blue) NMR plots

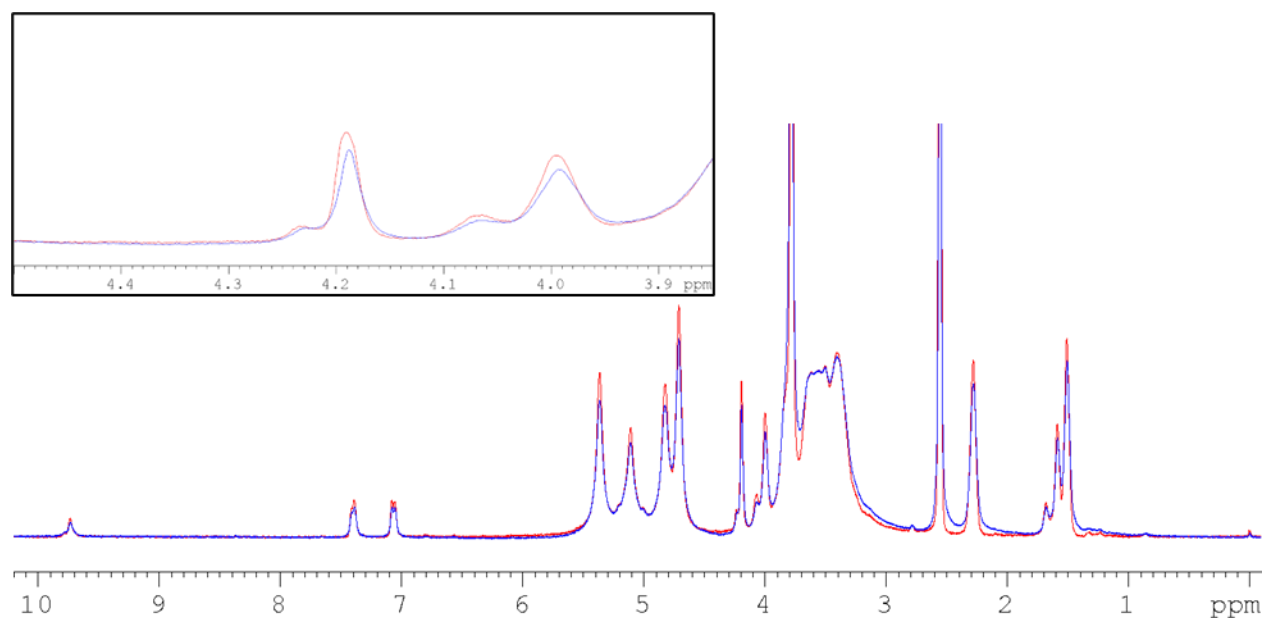


Figure 31. 80% α -1,3-glucan TPU composite (red) and 80% α -1,3-glucan TPU composite with 0.5% DCP (blue) NMR plots

4.3.3. Thermal properties

The TGA and DTG curves for TPU- α -1,3-glucan composites with different levels of DCP are summarized in Figures 32-35. The polyurethane is comprised of hard and soft segments. The hard segment has a lower thermal stability than the soft segment, with their degradation peak occurring at around 335 and 390°C, respectively.^[117] With the addition of the DCP, the intensity of the soft segment degradation decreases since the soft segment is more readily available for reaction with the DCP, as shown from ¹H-NMR results. However, at a higher concentration of DCP, a significant decrease in the soft segment is no longer observed. This is because when a high level of DCP is incorporated, the melt viscosity increases significantly during the extrusion process, which prevents the movement of the DCP. The increase in the melt viscosity was observed during the batch mixer experiment, where high concentration of DCP resulted in much higher and sudden increase in torque. When the α -1,3-glucan was added to the system, the change in degradation peak locations for the TPU was not significant. Regardless of the level of DCP, the onset of degradation and the degradation peak locations for both the α -1,3-glucan and TPU were similar to one another.

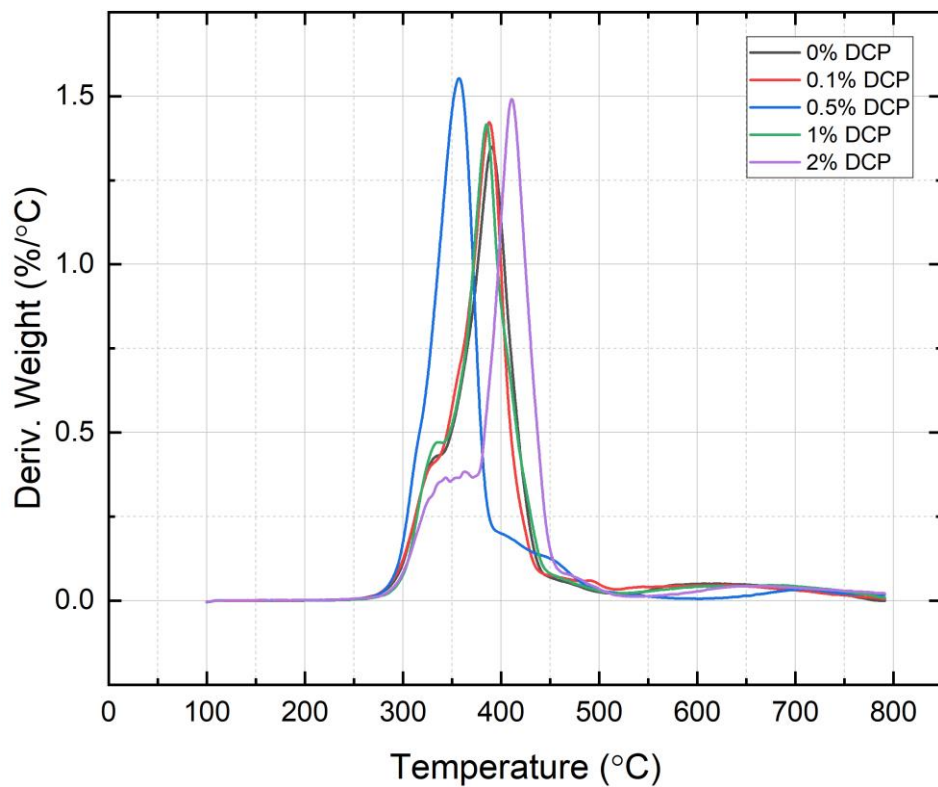
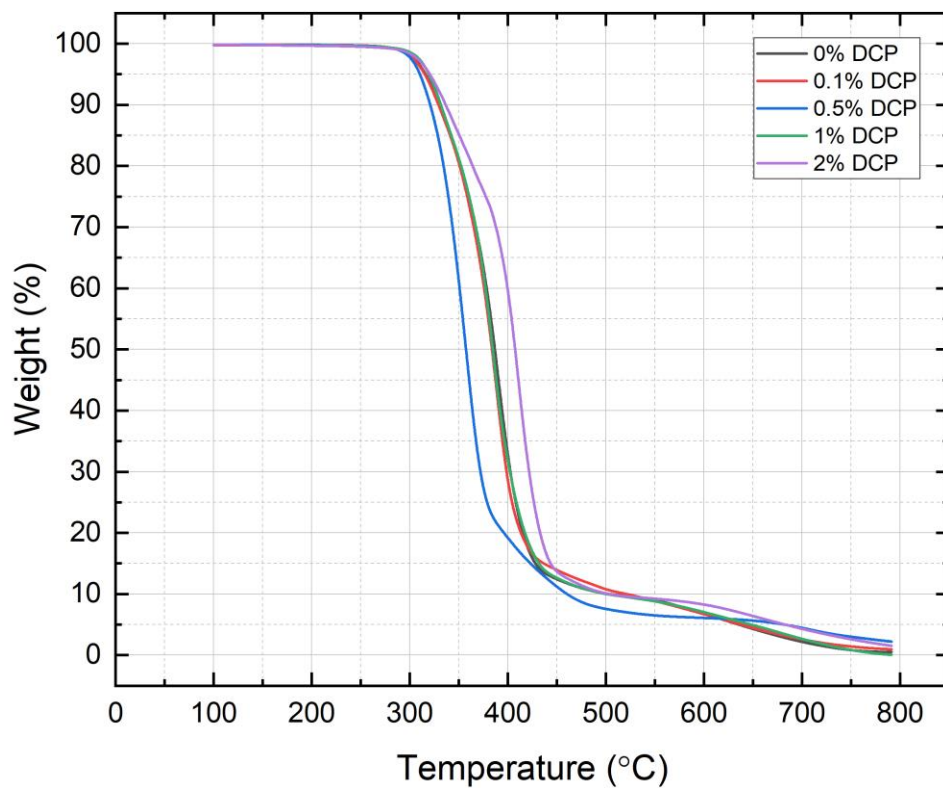


Figure 32. TGA (top) and DTG (bottom) curves for TPU with different levels of DCP

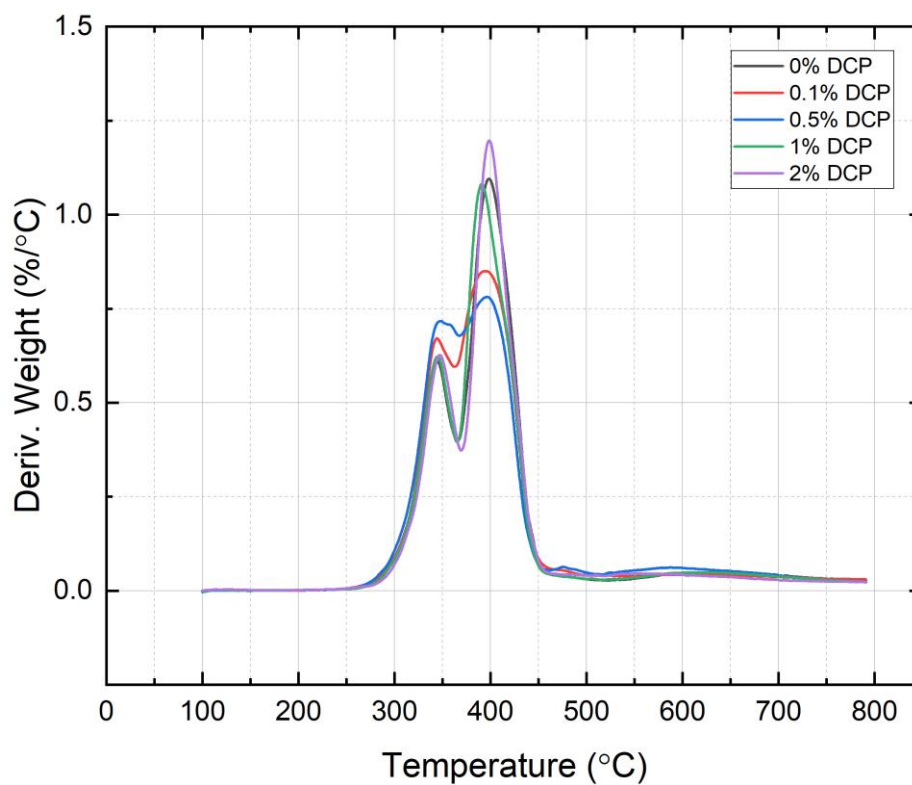
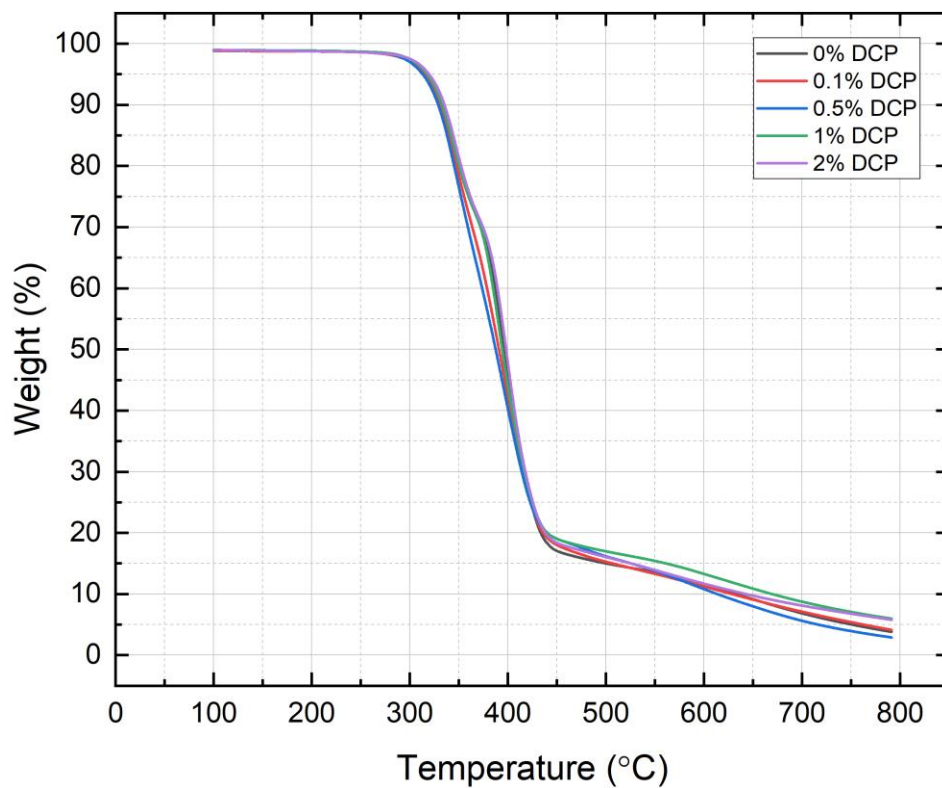


Figure 33. TGA (top) and DTG (bottom) curves for 20% α -1,3-glucan TPU composites with different levels of DCP

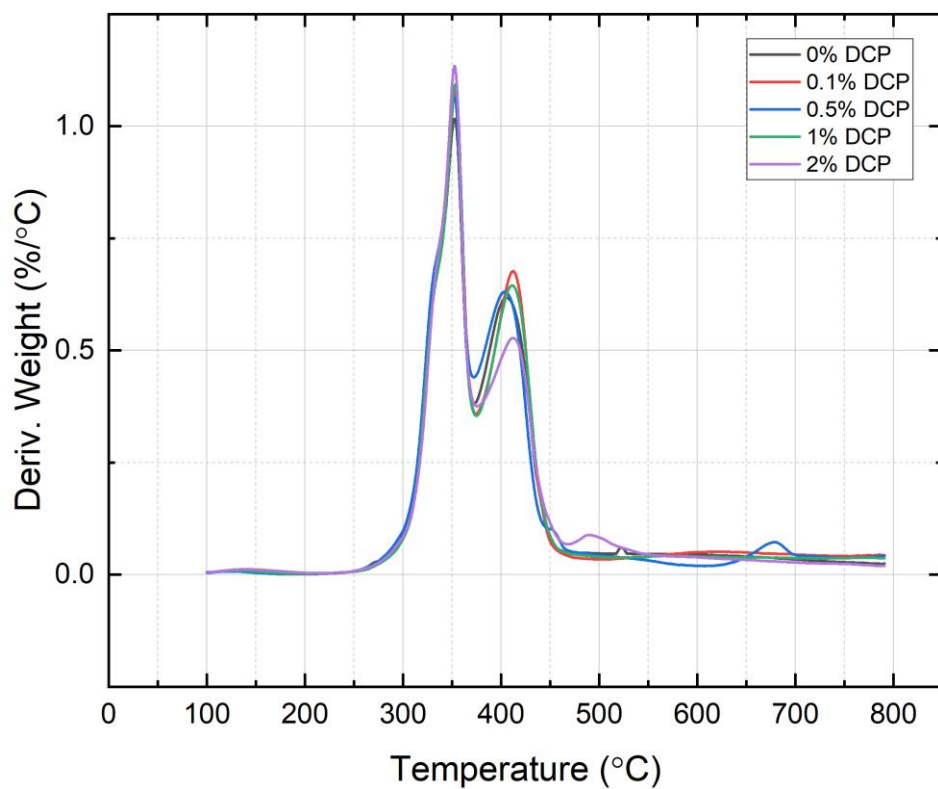
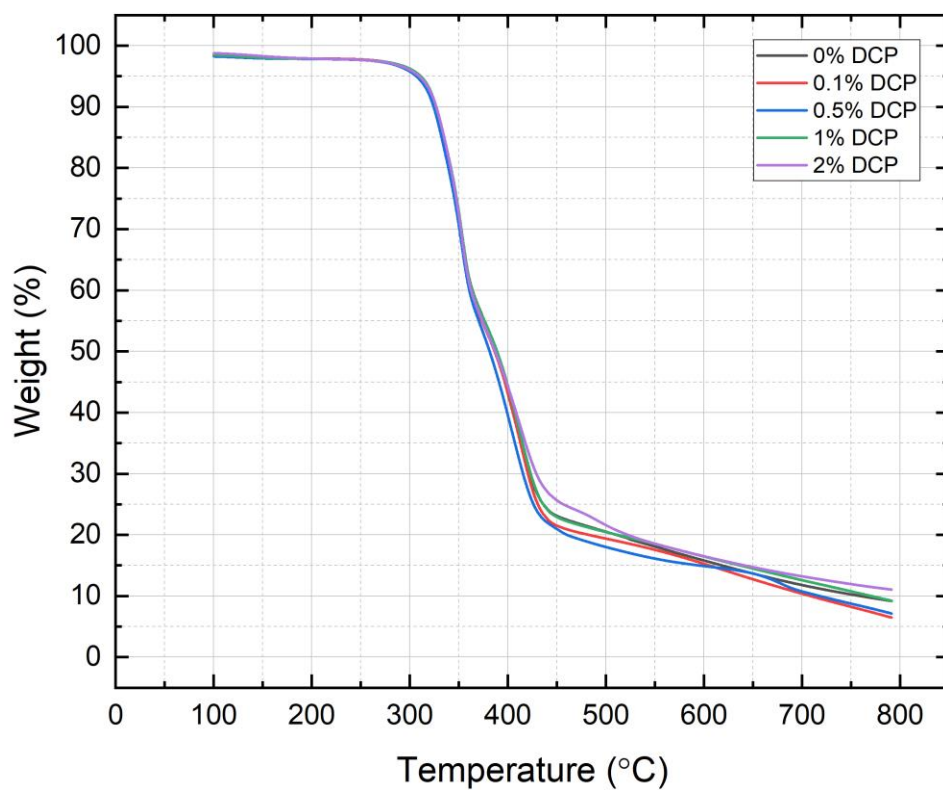


Figure 34. TGA (top) and DTG (bottom) curves for 50% α -1,3-glucan TPU composites with different levels of DCP

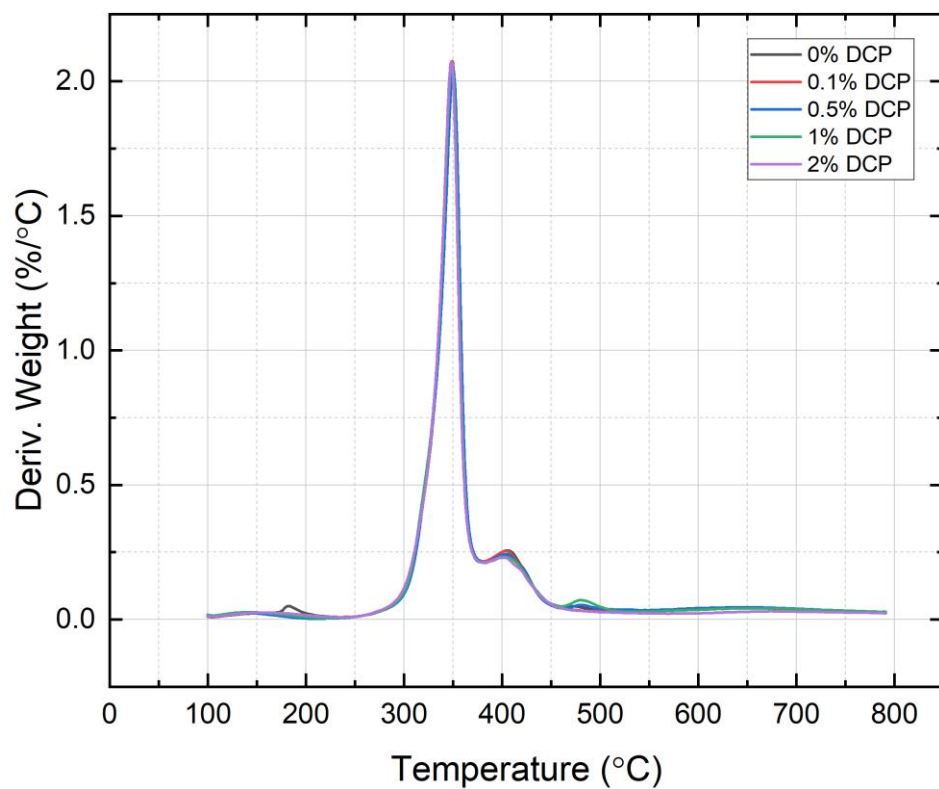
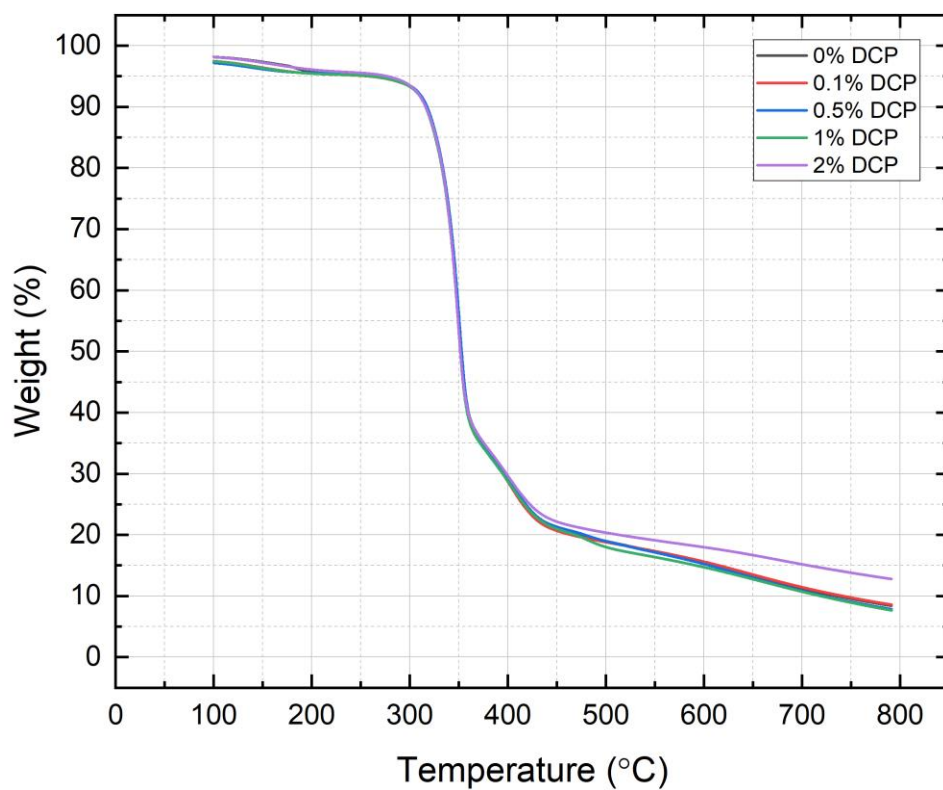


Figure 35. TGA (top) and DTG (bottom) curves for 80% α -1,3-glucan TPU composites with different levels of DCP

The DSC plots for the TPU- α -1,3-glucan composites with different levels of DCP are summarized in Figures 36-39. The change in crystallization and melting temperatures with the addition of α -1,3-glucan and DCP is summarized in Figure 40. It was observed that the crystallization temperature increased with the α -1,3-glucan content.

As DCP is added to the system, the crystallization temperature showed a decreasing trend. This may be attributed to the change in the TPU polymer chain due to the free radicals from the DCP. The change in torque with different levels of DCP from section 4.3.1. revealed that crosslinking reactions occur as well as mechanical degradation of the polymer chain due to increased viscosity and temperature. As well, the NMR analysis from section 4.3.2. showed evidence of reaction occurring at the urethane linkage, further supporting the presence of chemical changes that led to the change in the TPU polymer chain. A slight decrease in the melting temperature was observed with the addition of DCP but was mostly similar regardless of the α -1,3-glucan or DCP content. The signal intensity of the melting and crystallization peaks decreased as the α -1,3-glucan content increased. Since the α -1,3-glucan does not exhibit any melting or crystallization behaviour, the decrease in signal intensity was a result of low concentration of TPU in the composite system. Regardless, the peak locations are relatively similar for all the composite samples, which is an indication that the processing condition, specifically the temperature, is not significantly affected by the DCP or the α -1,3-glucan content.

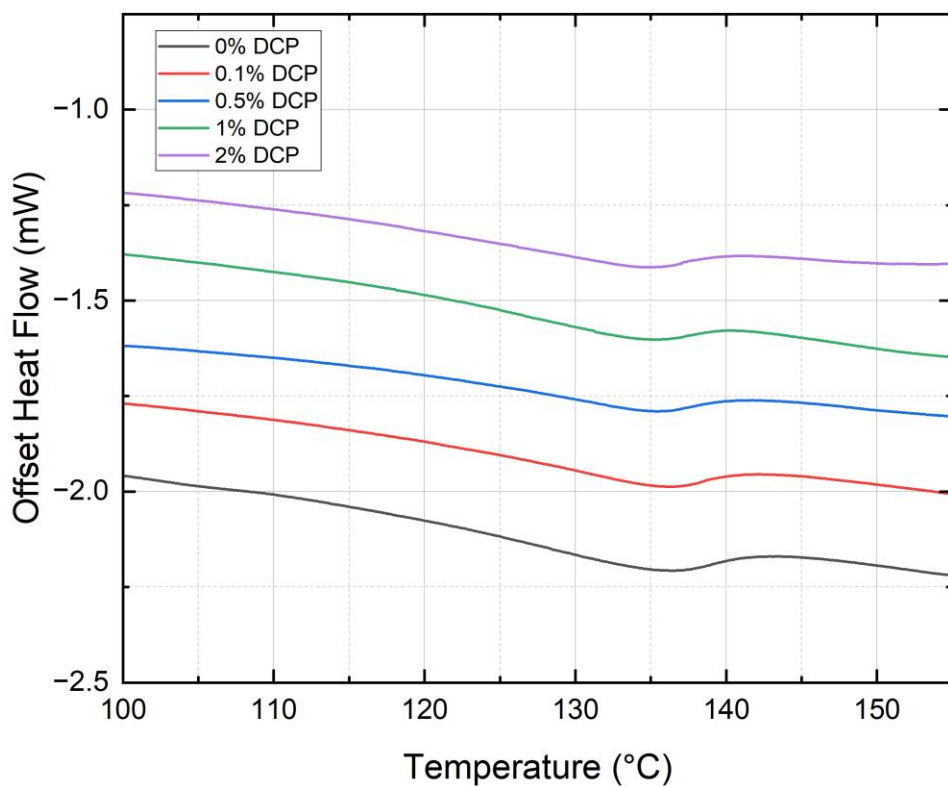
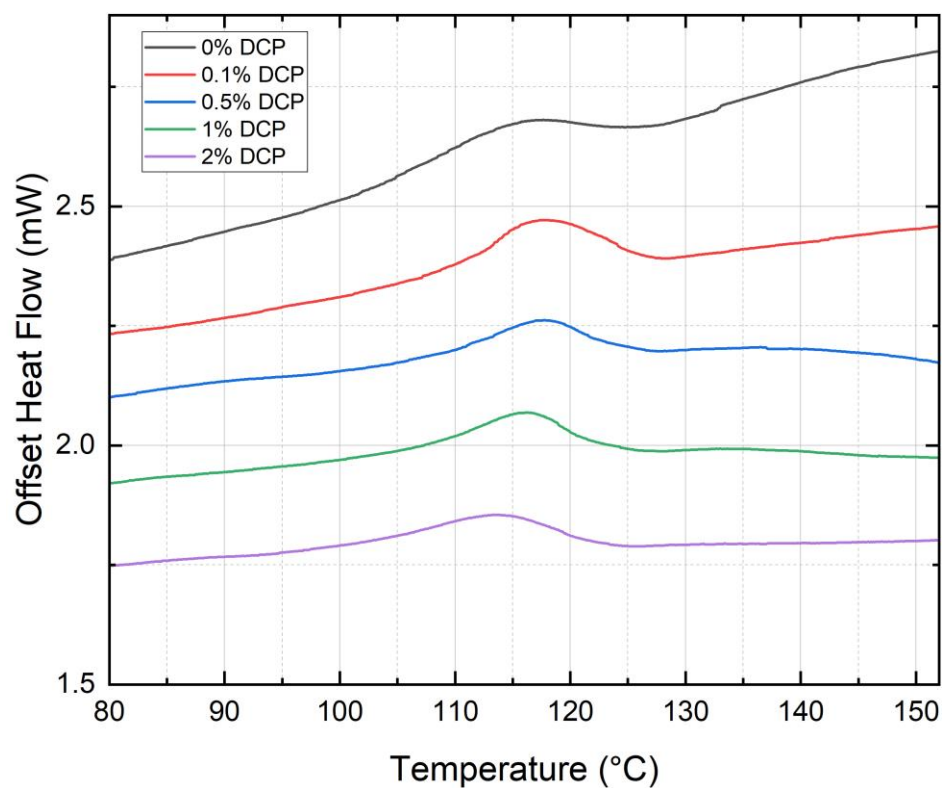


Figure 36. DSC curves for TPU with different levels of DCP; first cooling (top) and second heating (bottom) cycle

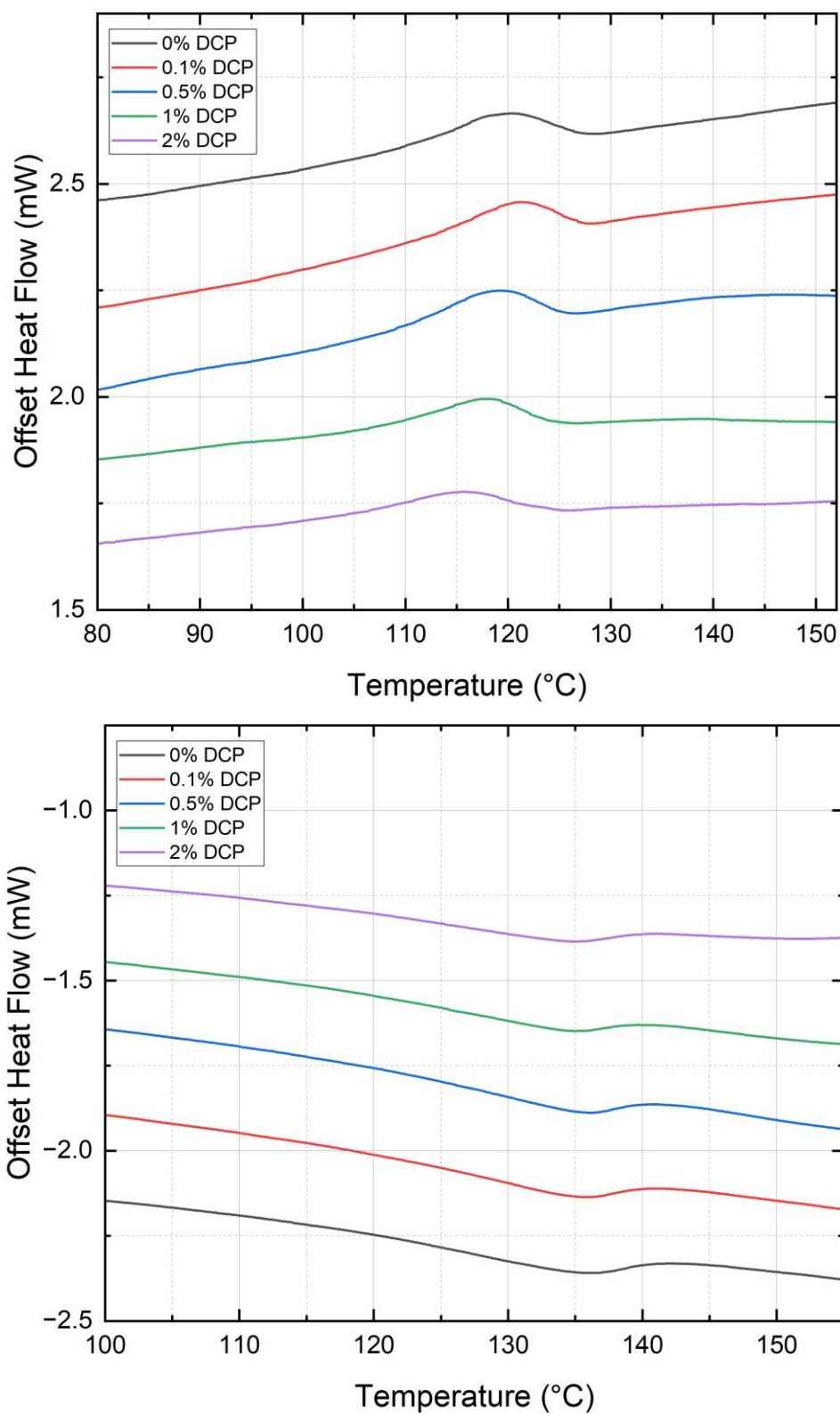


Figure 37. DSC curves for 20% α -1,3-glucan TPU composites with different levels of DCP; first cooling (top) and second heating (bottom) cycle

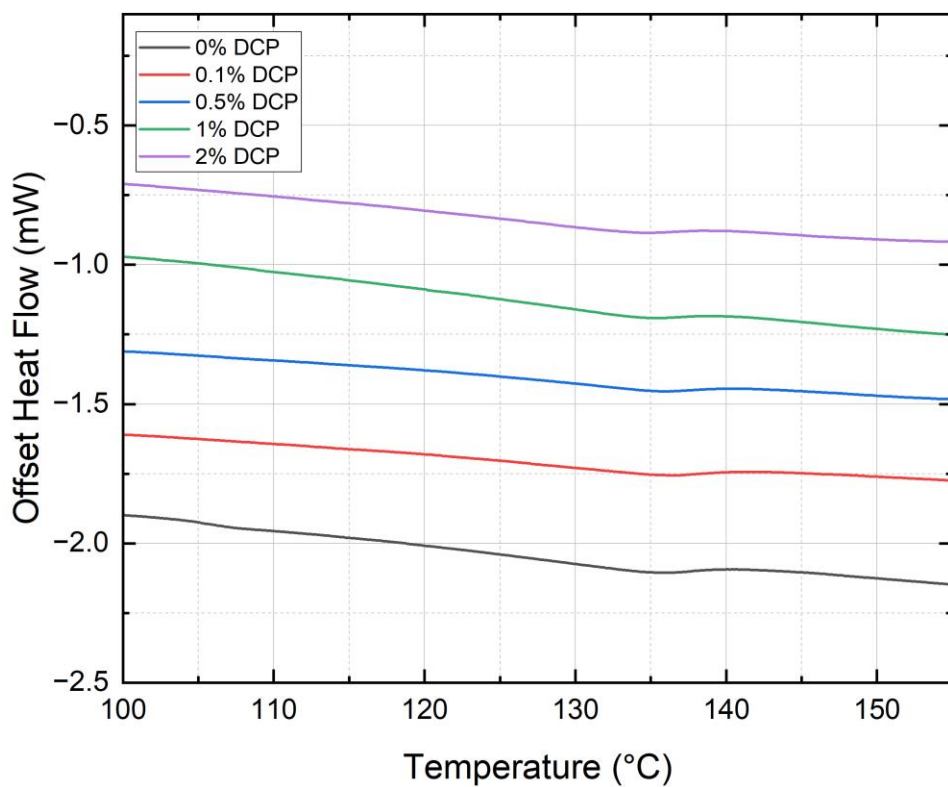
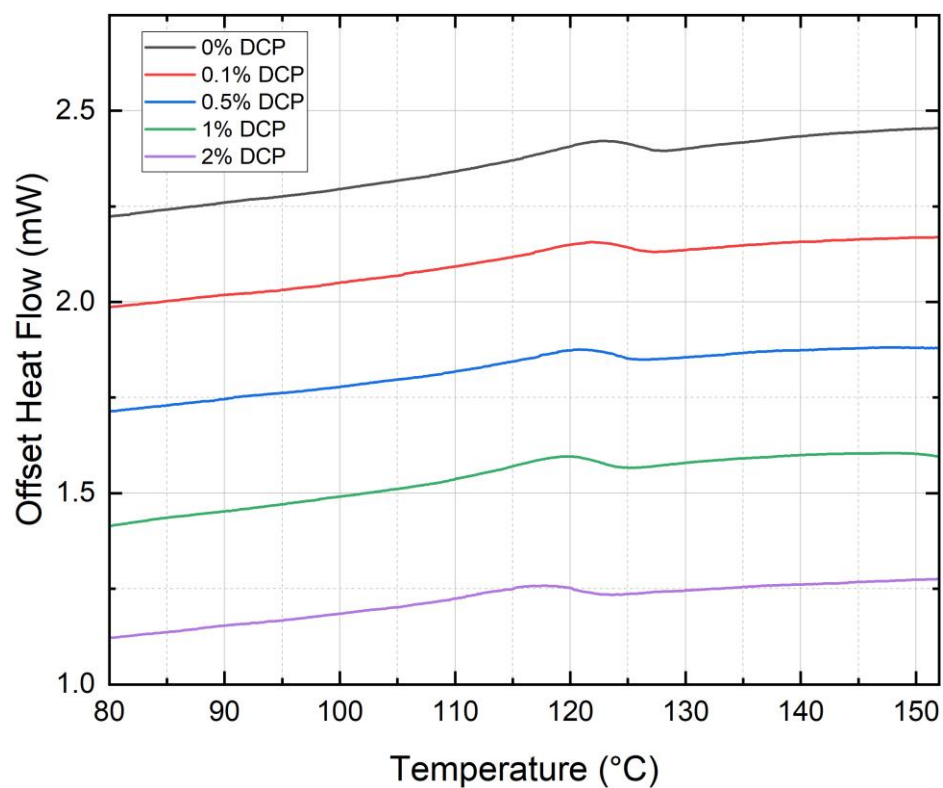


Figure 38. DSC curves for 50% α -1,3-glucan TPU composites with different levels of DCP; first cooling (top) and second heating (bottom) cycle

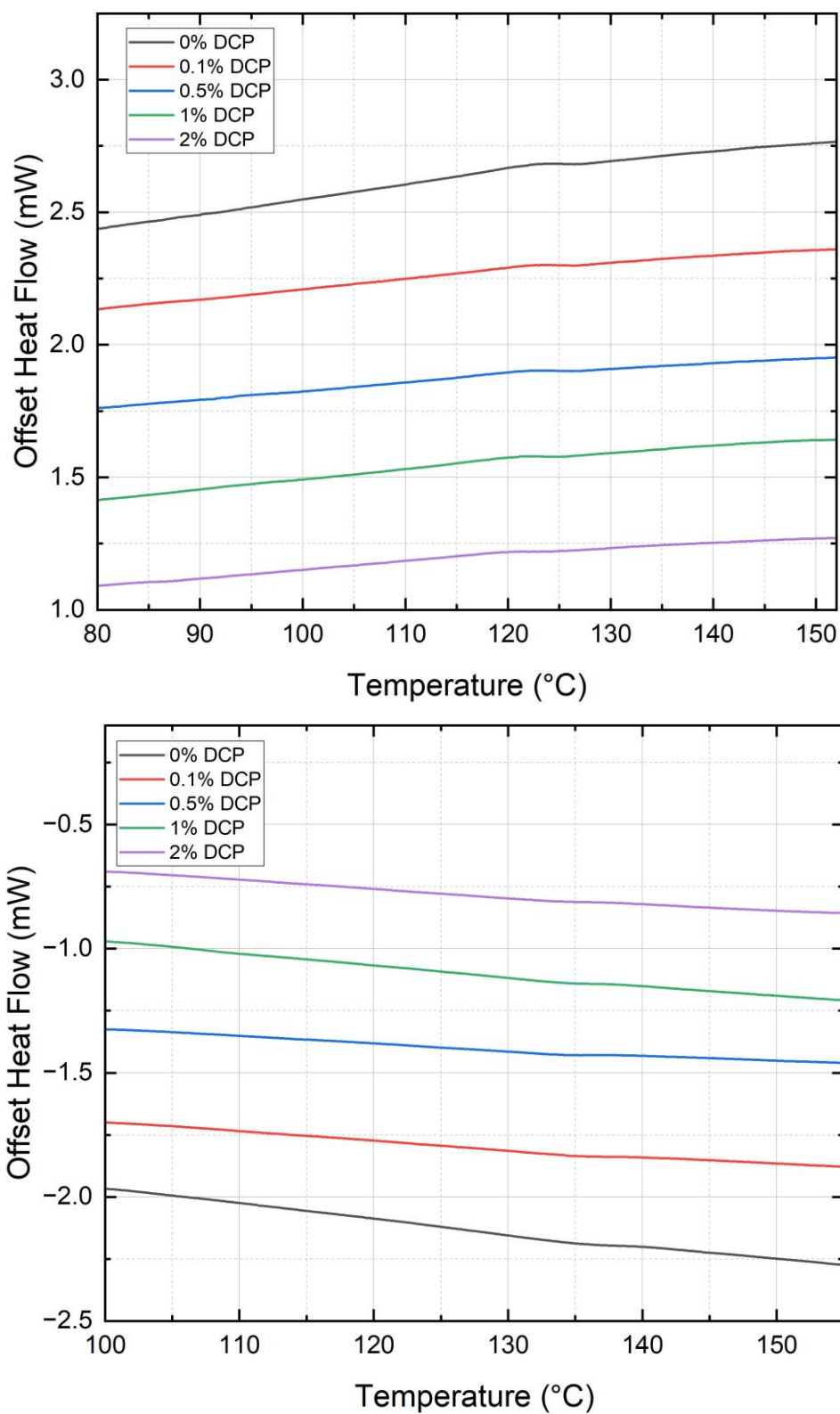


Figure 39. DSC curves for 80% α -1,3-glucan TPU composites with different levels of DCP; first cooling (top) and second heating (bottom) cycle

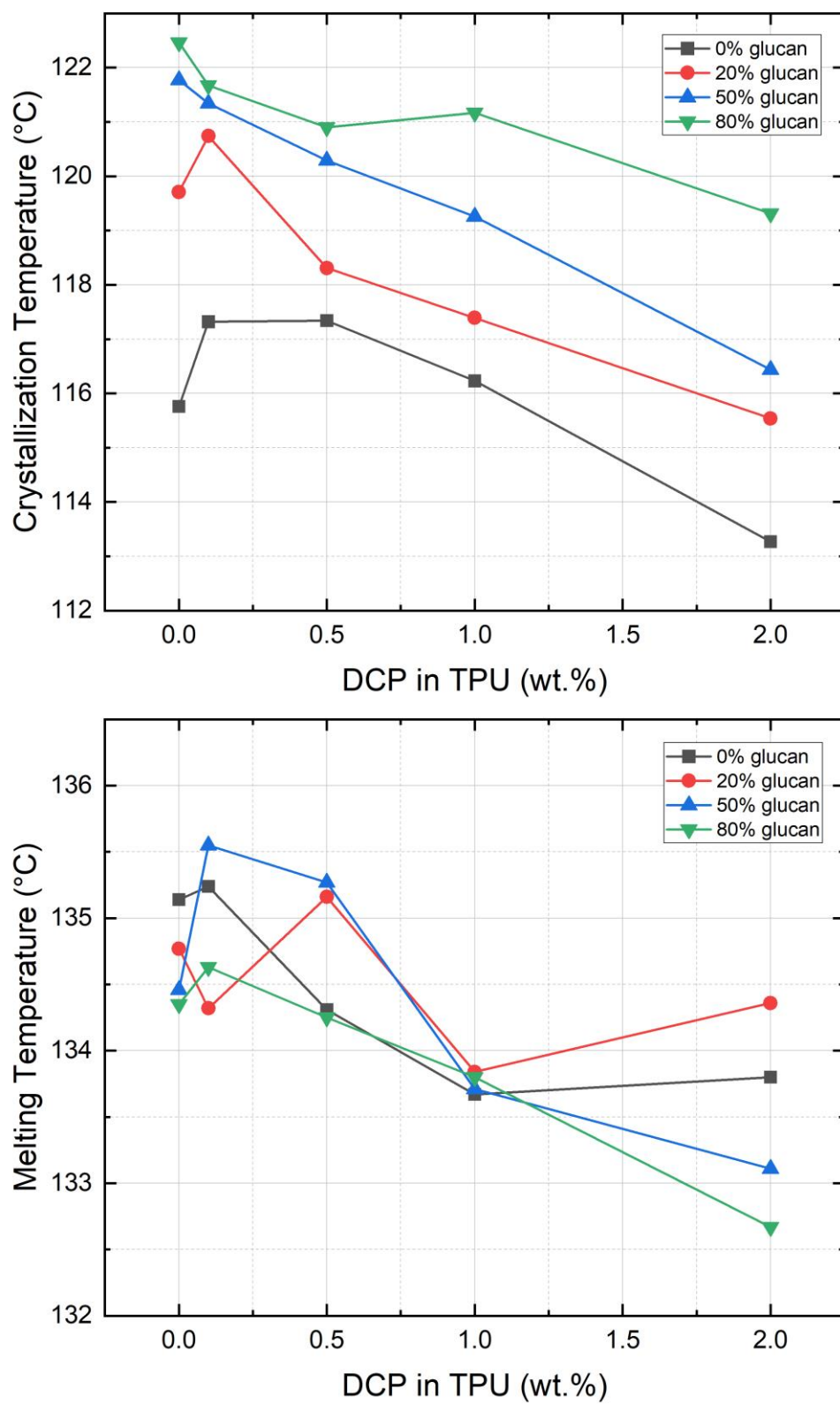


Figure 40. Crystallization (top) and melting (bottom) temperatures of TPU- α -1,3-glucan composites with different levels of DCP

4.3.4. Mechanical properties

The mechanical properties, specifically the tensile properties, are summarized in Figures 41-44. Without the presence of the DCP, the change in the tensile modulus, elongation at break, and toughness align with the trend observed from sections 4.1.1. and 4.2.1. A significant improvement in the modulus was observed with the increasing level of the α -1,3-glucan due to its reinforcing effect, while decreasing the elongation at break and toughness because the composites became more brittle.

The tensile strength, shown in Figure 42, demonstrated an interesting result as the amount of the α -1,3-glucan increased. A steady decrease in the tensile strength was observed until 50% α -1,3-glucan content then a slight increase up to 80% α -1,3-glucan content. This is because the pristine TPU displays a strain-hardening behaviour during the plastic deformation phase as the strain increases. The strain-hardening characteristic allows the ultimate tensile strength of the TPU to be higher than the stress at yield point. As more α -1,3-glucan is incorporated into the TPU, there is less fraction of TPU that can undergo large elongation, which reduces the effect of strain-hardening behaviour. With the reduced contribution of the strain-hardening, the tensile strength decreases. However, the α -1,3-glucan acts as a reinforcing filler, so it increases the stiffness and modulus of the composites, which ultimately increases the yield strength. Since the composite with high level of the α -1,3-glucan undergoes minimal elongation, the yield strength equals the tensile strength, and therefore an increase in tensile strength is observed. The stress-strain curve for the TPU- α -1,3-glucan composites without DCP is shown in Figure 45.

When DCP is added to the system, a slight decrease in tensile modulus was observed (Figure 41). It has been reported that the decrease in the modulus as a function of DCP content may be associated with a change in crystallizing and melting processes.^[115] The tensile strength showed improvement with the addition of DCP (Figure 42). This improvement demonstrates that the α -1,3-glucan and TPU interacted more strongly. However, adding 1 wt.% or more of DCP negatively impacted the strength, which is an indication that a high level of DCP might induce chain scission and degradation. The change in colour of the films as shown in Figure 23 as the level of DCP increases is another sign of degradation.

The evidence of chain scission was more evident in the elongation at break (Figure 43). The elongation remained mostly unchanged with the addition of DCP, but beyond 1 wt.% of DCP, a

significant decrease was observed. The reduction of the chain length due to the DCP activity reduced the chain sliding and therefore reduced the strain of the material. Conversely, a slight increase in the elongation at break for composites with 80% α -1,3-glucan was observed. This may be a result of the TPU acting as a binder between the α -1,3-glucan particles since the concentration is very low. Combined with an increase in the compatibility between the two phases, the void and crack formation between the α -1,3-glucan may have been delayed, resulting in a slight increase in the elongation. It is also worth noting that since the 80% α -1,3-glucan samples are quite brittle, hence the slight increase in elongation at break from ~5% to ~10% may not be significant.

The toughness of the composites (Figure 44) also showed a decreasing pattern due to the significant decrease in elongation and tensile strength as the level of DCP increased.

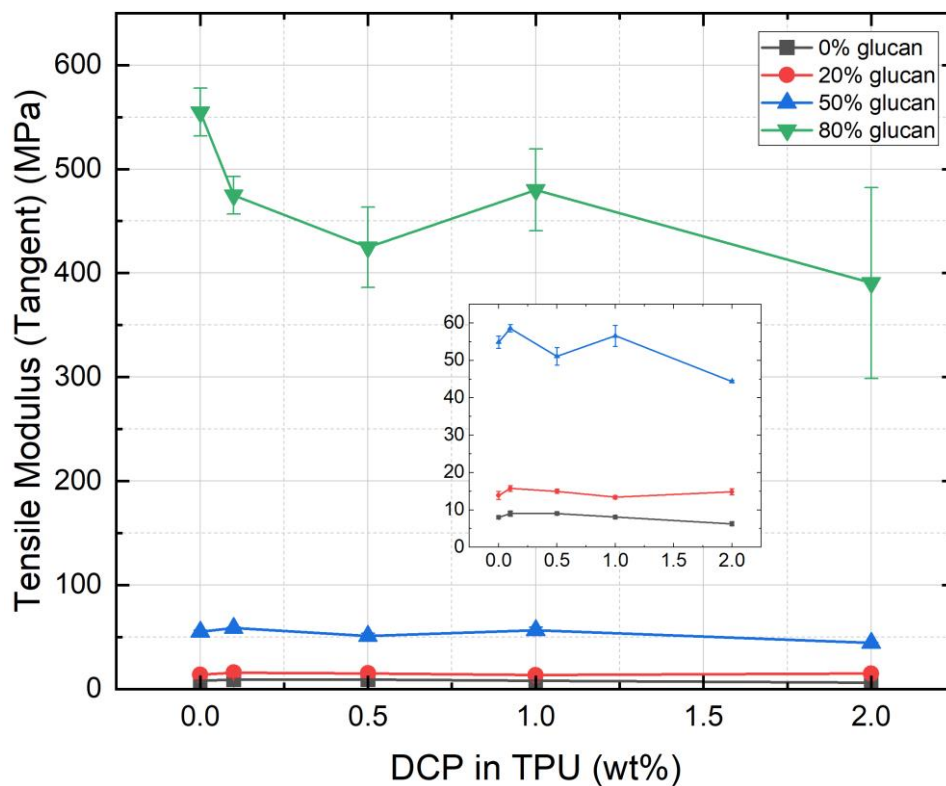


Figure 41. Tensile tangent modulus of α -1,3-glucan-TPU-DCP composites

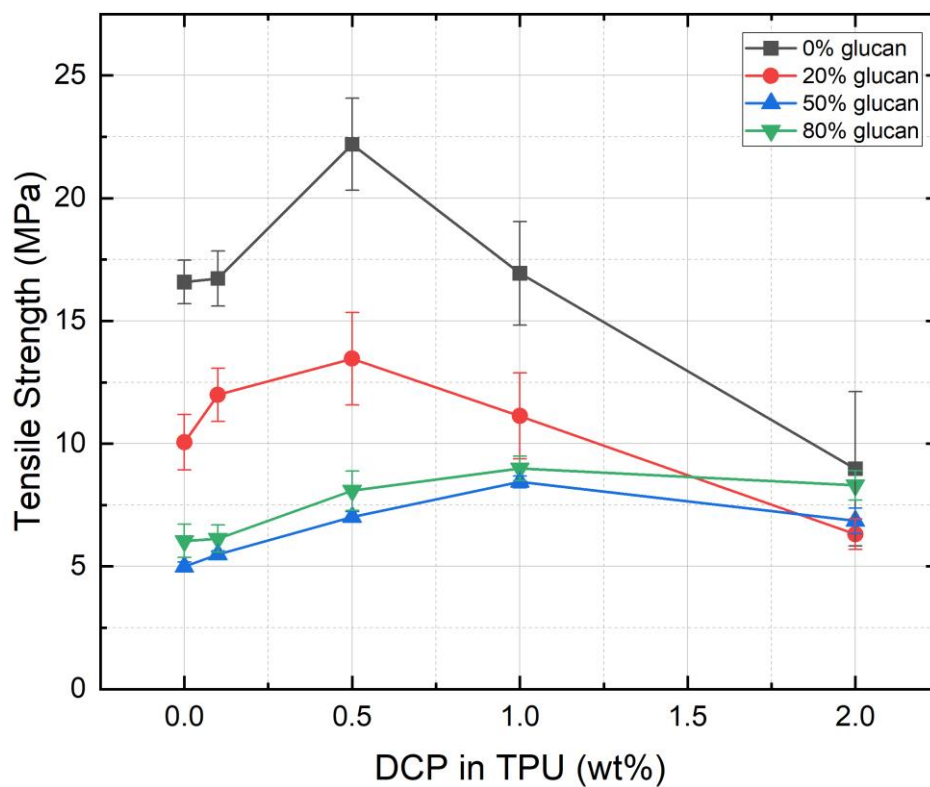


Figure 42. Tensile strength of α -1,3-glucan-TPU-DCP composites

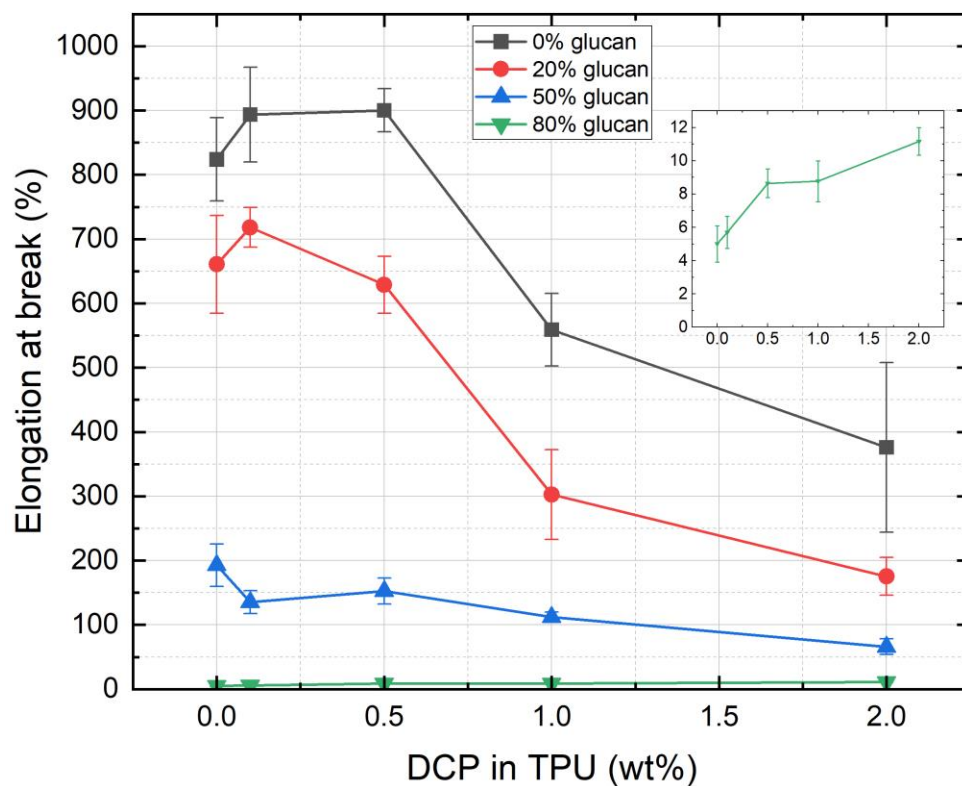


Figure 43. Elongation at break of α -1,3-glucan-TPU-DCP composites

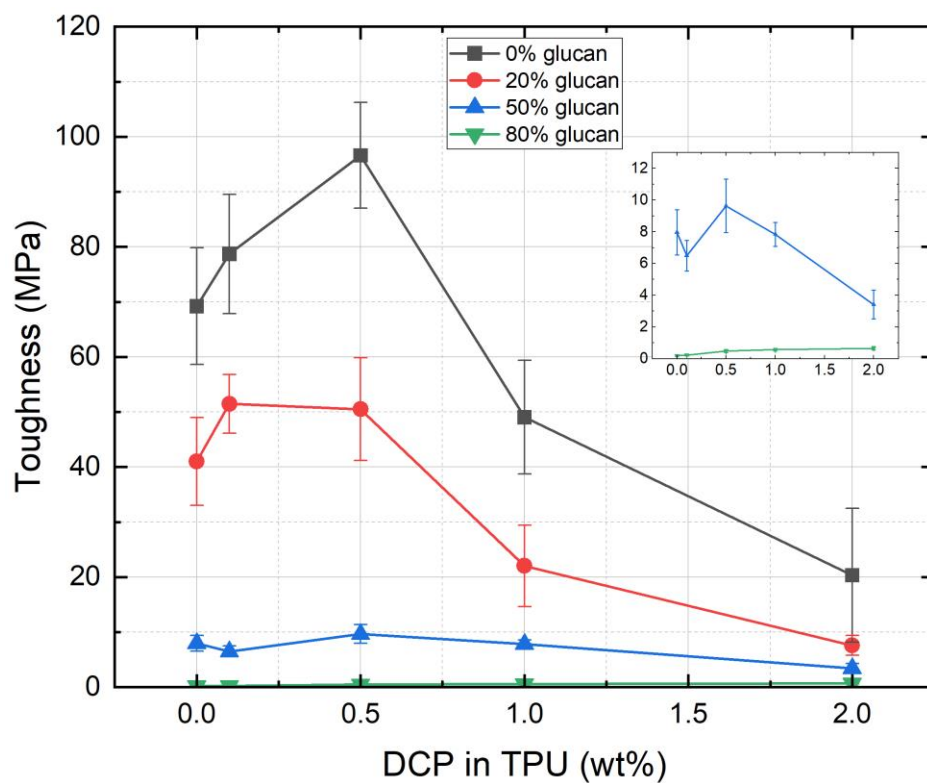


Figure 44. Toughness of α -1,3-glucan-TPU-DCP composites

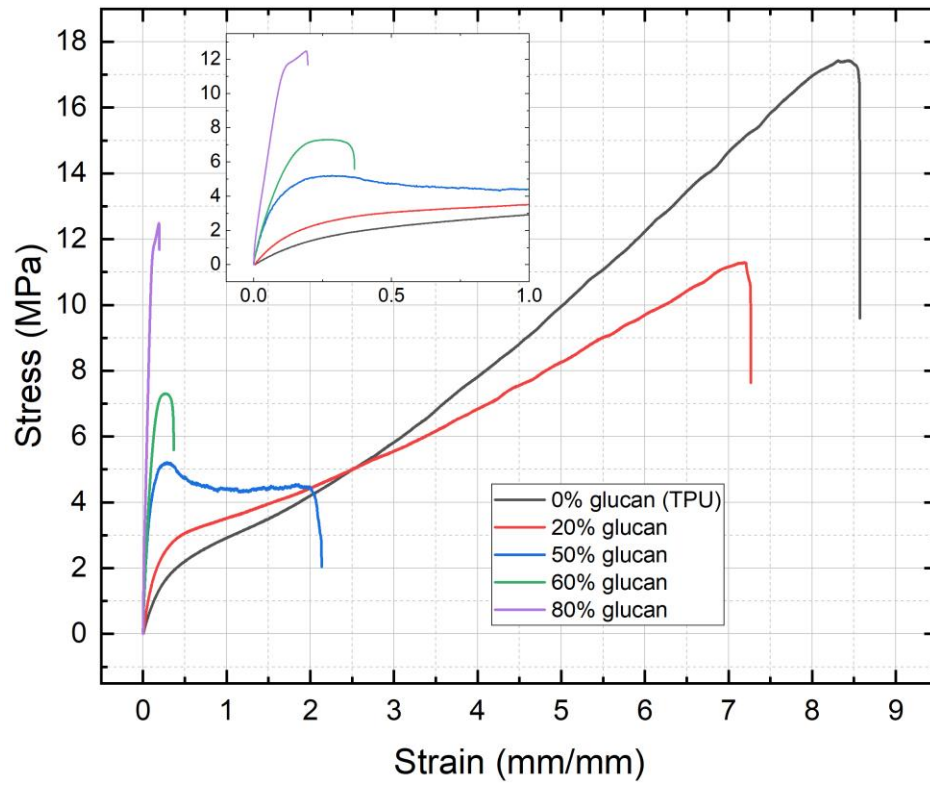


Figure 45. Stress-strain curve for TPU- α -1,3-glucan composites without DCP

The mechanical properties were also constructed as a 3D surface plot in Figures 46-49 which is useful for observing the overall effect and trend when the concentration of the α -1,3-glucan and DCP was varied.

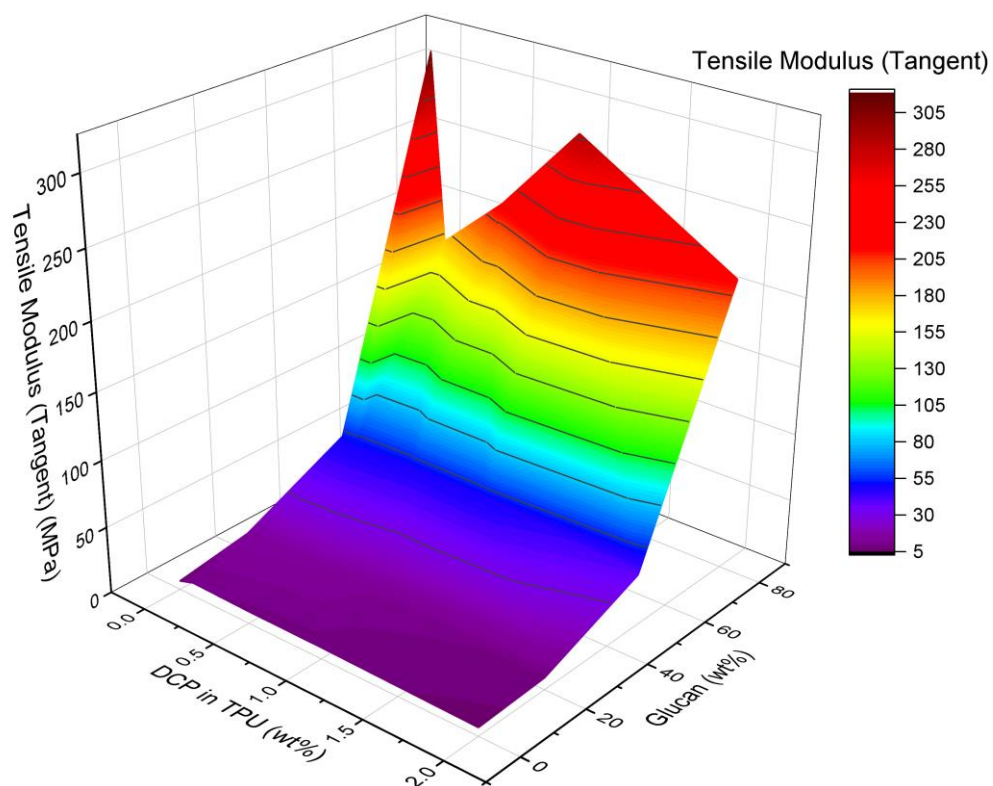


Figure 46. 3D surface plot for tensile tangent modulus of α -1,3-glucan-TPU-DCP composites

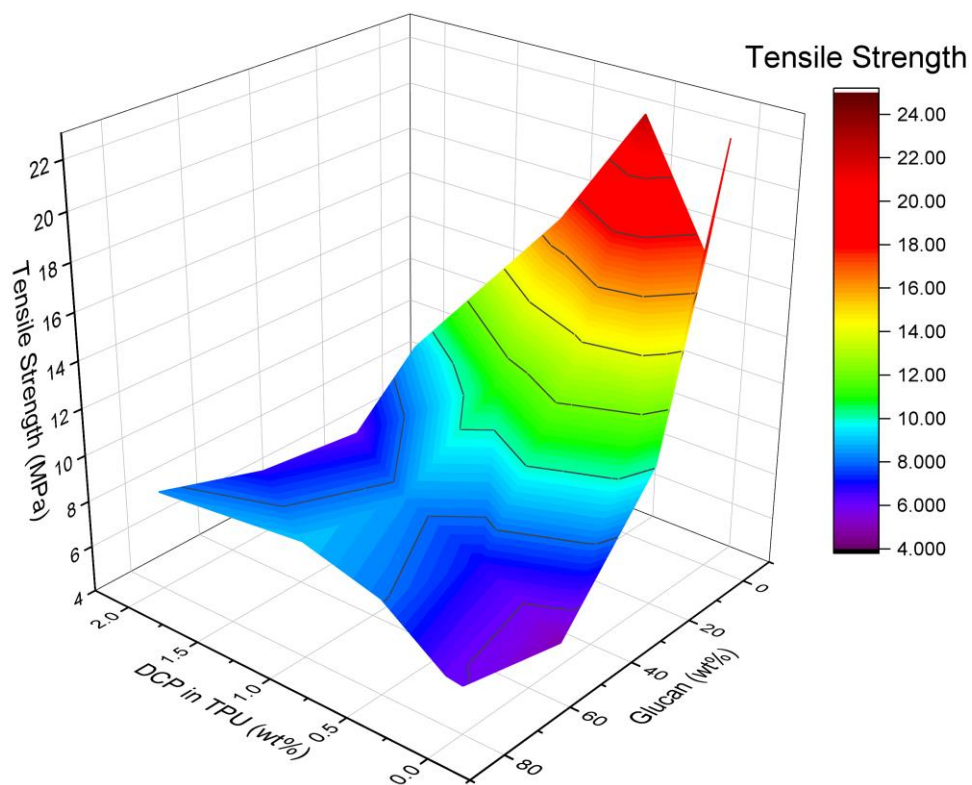


Figure 47. 3D surface plot for tensile strength of α -1,3-glucan-TPU-DCP composites

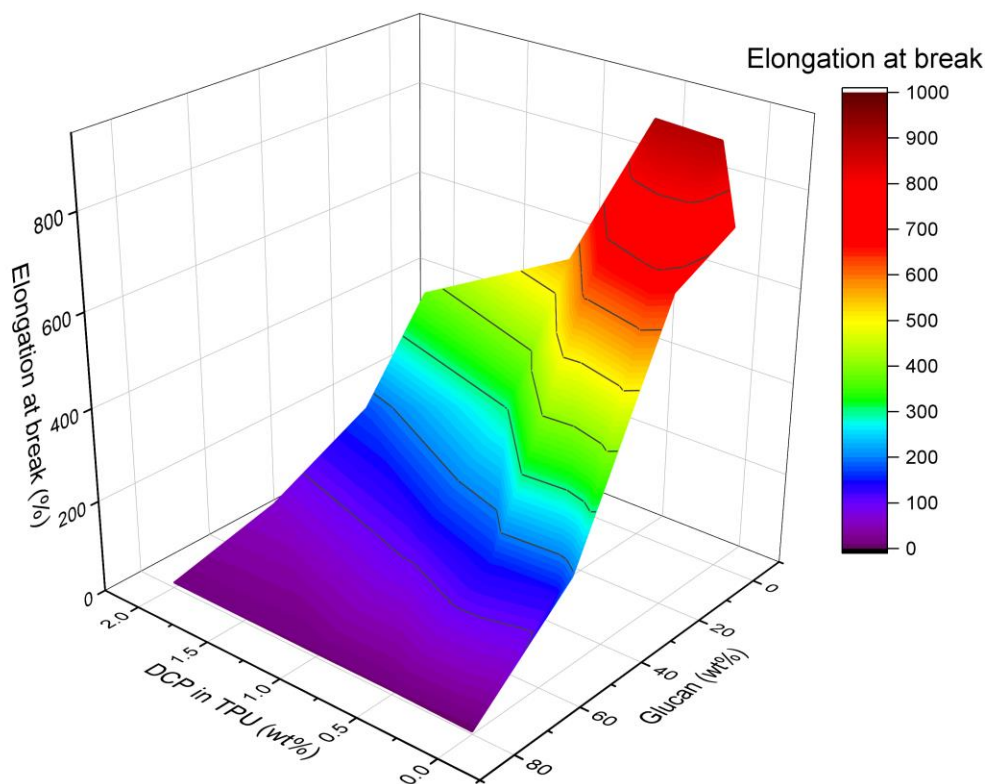


Figure 48. 3D surface plot for elongation at break of α -1,3-glucan-TPU-DCP composites

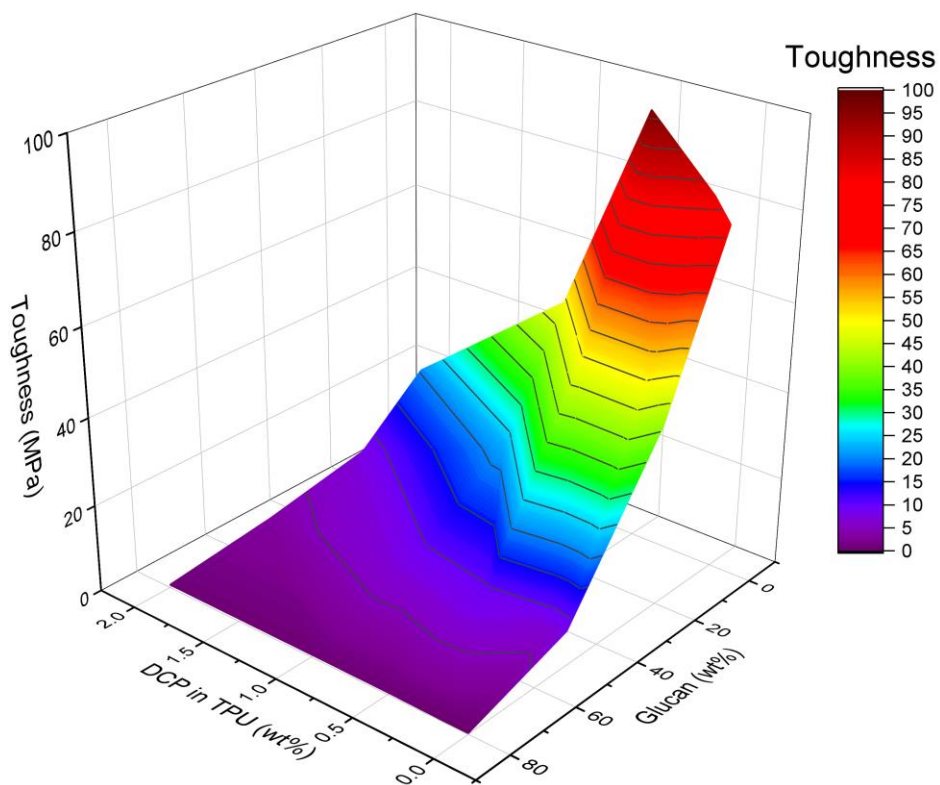


Figure 49. 3D surface plot for toughness of α -1,3-glucan-TPU-DCP composites

4.3.5. Water absorption

The water absorption results are summarized in Figures 50-54. Since the α -1,3-glucan is hydrophilic, the amount of water absorbed by the composite increased as the α -1,3-glucan content increased. The pristine TPU showed a weight increase of about 1.25% at saturation. Since the fraction of α -1,3-glucan is known for each composite, the amount of water absorbed by α -1,3-glucan can be calculated, which was about 44%. Figure 54 shows the total amount of water absorbed by the composites at saturation. An initial reduction of the total water uptake at saturation was observed as the DCP content increased up to 0.5%. This was due to the crosslinking of TPU, as seen from the batch mixer experiment in section 4.3.1., which reduced the water diffusion process. However, at a higher level of DCP, the water uptake amount increased. Since the chain scission and mechanical degradation was more prominent at a high level of DCP, the effect of crosslinking was reduced, which resulted in the total amount of water uptake to increase again.

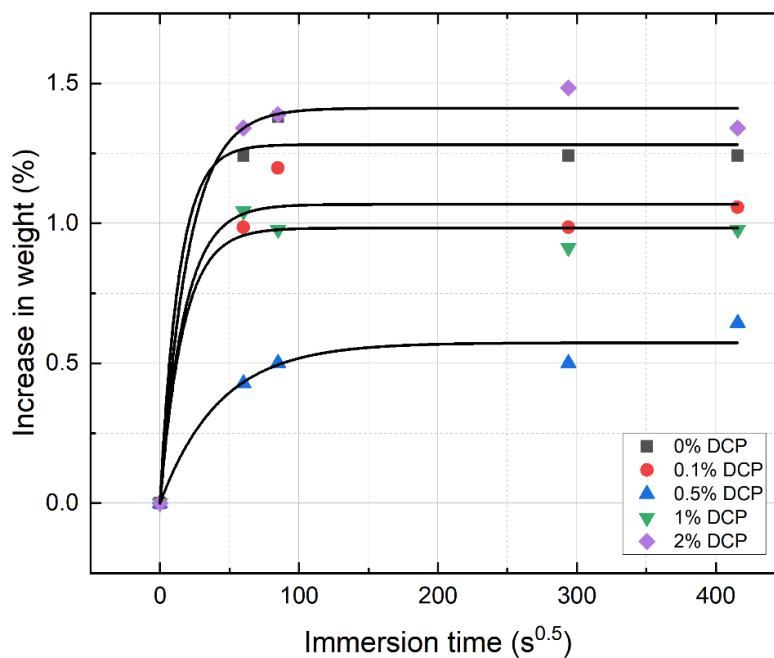


Figure 50. Amount of water absorbed at different times by TPU with different levels of DCP

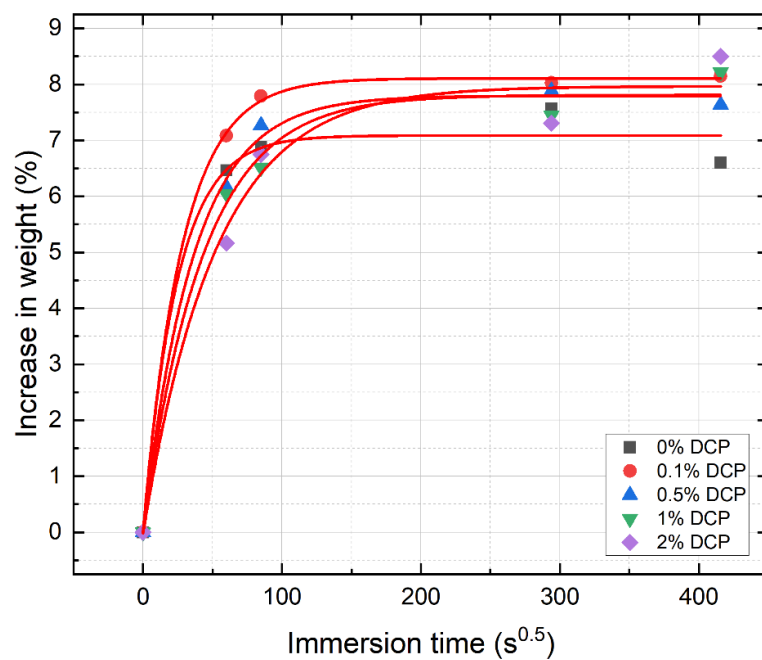


Figure 51. Amount of water absorbed at different times by 20% α -1,3-glucan TPU composites with different levels of DCP

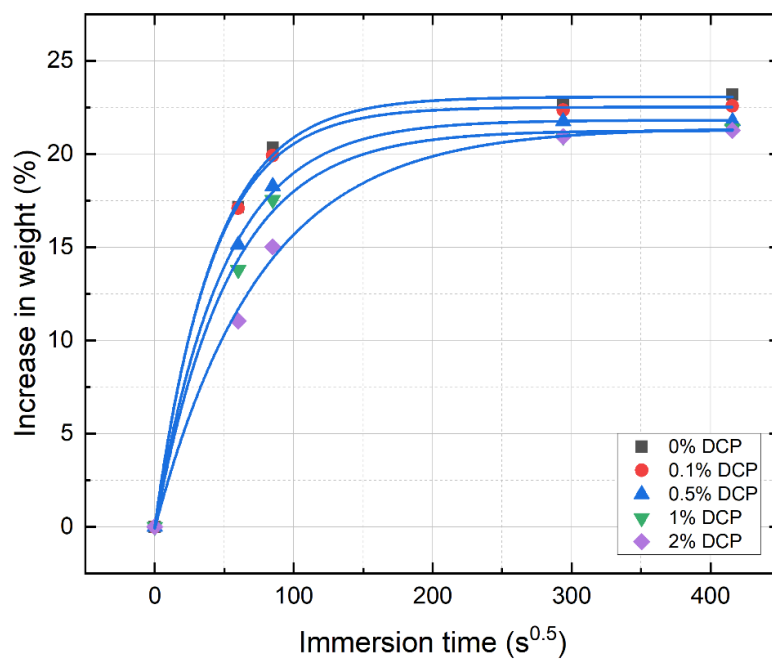


Figure 52. Amount of water absorbed at different times by 50% α -1,3-glucan TPU composites with different levels of DCP

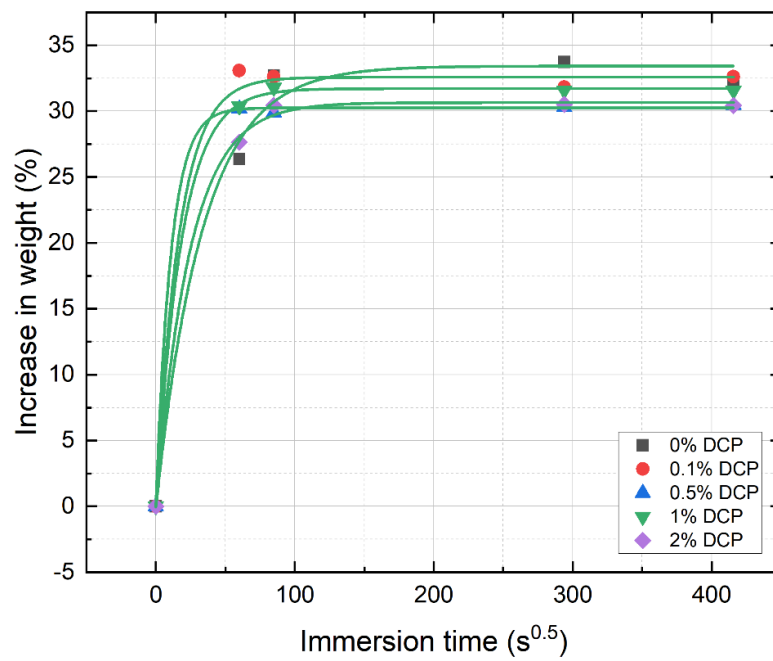


Figure 53. Amount of water absorbed at different times by 80% α -1,3-glucan TPU composites with different levels of DCP

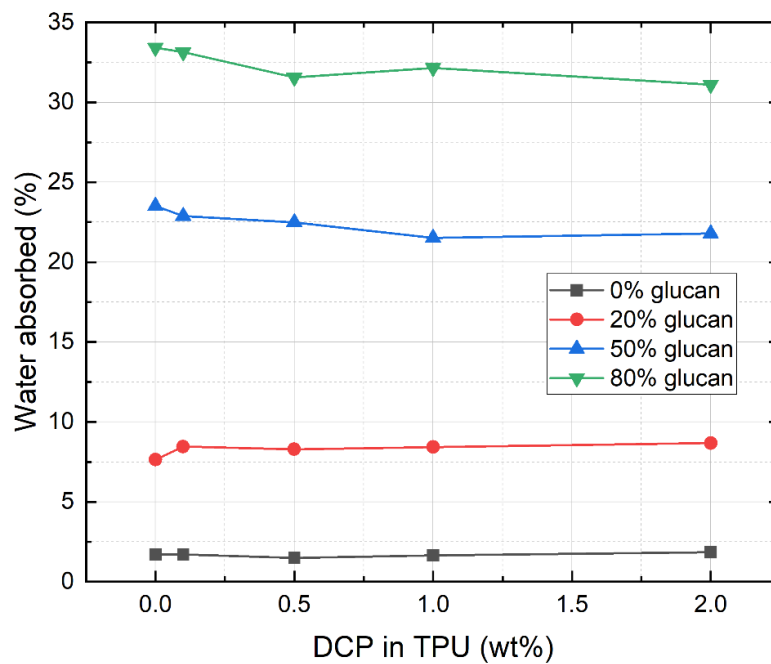


Figure 54. Total amount of water absorbed by composites with different levels of α -1,3-glucan and DCP

4.4. Conclusions

In this chapter, the α -1,3-glucan was used as a filler in a TPU matrix. The α -1,3-glucan showed good compatibility with TPU, allowing up to 80 wt.% to be incorporated, which led to significant improvement in strength and modulus. The addition of citrate-based plasticizers (TEC, ATBC, and TBC), helped with processibility and flexibility of the TPU- α -1,3-glucan composites. The addition of DCP enhanced the compatibility between the α -1,3-glucan and TPU, but when the amount of DCP exceeded 1%, it led to undesirable mechanical degradation of the TPU which reduced the properties such as tensile strength. Chemical analysis did not reveal any information regarding covalent bonds forming between the α -1,3-glucan and TPU. Since many hydrogen bonds can be formed between the α -1,3-glucan and TPU, a model (Figure 55) is proposed below that depicts the potential interactions between the two phases.

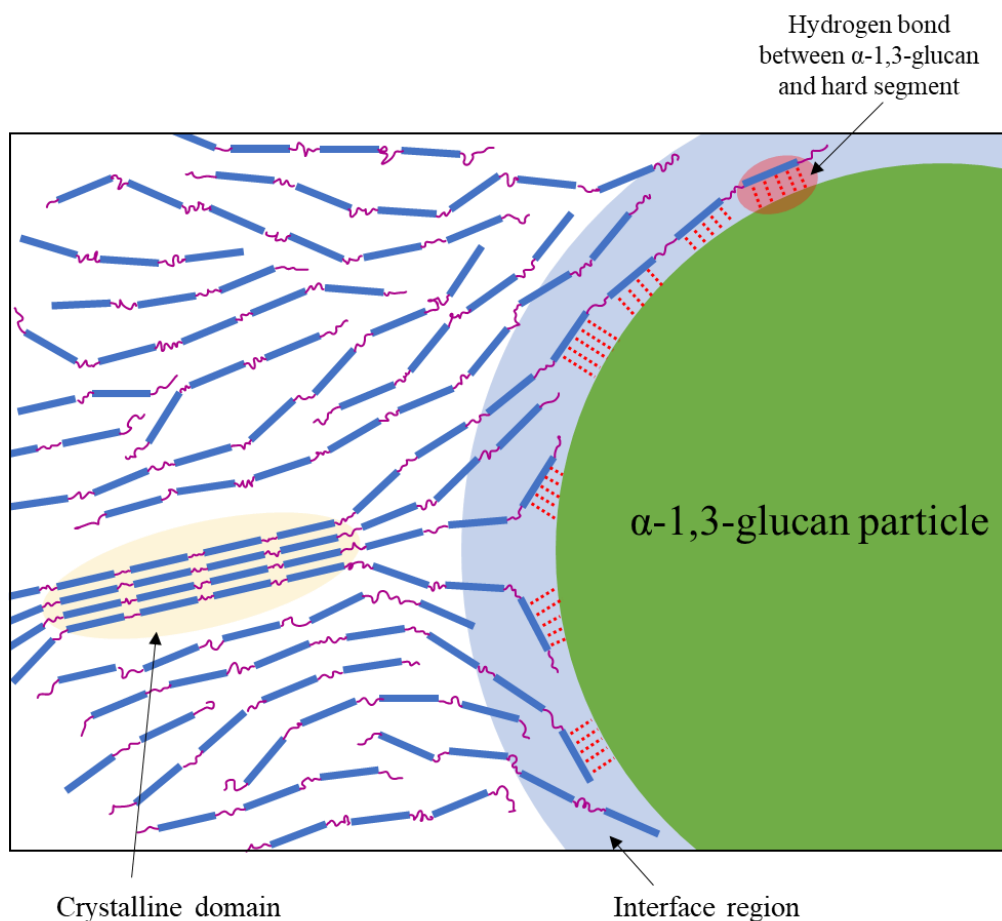


Figure 55. α -1,3-glucan and TPU interactions

CHAPTER 5:

MATERIALS AND METHODS –

POLYESTER AND α -1,3-GLUCAN COMPOSITES

5.1. Materials

The D15 α -1,3-glucan with 15 μ m average particle diameter was provided by IFF. The poly(butylene adipate-co-terephthalate) (PBAT) (ecoflex® F Blend C1200) was purchased from BASF. The poly(butylene succinate) (PBS) (BioPBS™ FD92PM) was purchased from PTT MCC Biochem Company. The cassava starch was purchased from Bahiamido. The microcrystalline cellulose (MCC) was purchased from Sigma Aldrich. The calcium carbonate (CaCO_3) was purchased from Fisher Scientific.

5.2. Methods

5.2.1. Sample preparation

The PBAT and PBS pellets were ground into a finer powder using the ZM 200 Ultra Centrifugal Mill and L-N_2 . The grinding was necessary to improve the mixing between the PBAT or PBS and filler materials.

The first study investigated the properties of PBS- and PBAT- α -1,3-glucan composite films with varying levels of the α -1,3-glucan, ranging from 0 to 70 wt.%.

The second study investigated the difference between the filler materials, specifically the difference between the α -1,3-glucan, cassava starch, MCC, and CaCO_3 , when incorporated into PBAT and PBS. The filler comparison was conducted at two levels: 10 and 30 wt.%.

The first step to producing the samples was the extrusion compounding step using the Haake MiniLab II Micro Compounder, with processing conditions of 130°C and 60 rpm. Prior to the extrusion, all the materials were dried at 70°C in a Forced Air Oven overnight. The extrudate was pelletized using the ZM 200 Ultra Centrifugal Mill. After milling, the samples were compression moulded using the Carver Bench Top Heated Press at 140°C and 5 metric tonnes of force to produce films with average thickness of 0.2 mm.

5.2.2. Specimen characterization

Mechanical testing. Film tensile test was performed in accordance with ASTM D638 using the Universal Testing Machine. All test specimens were conditioned in a controlled chamber with 50% RH for at least 40 hours. Six replicates for each sample were tested.

Thermogravimetric analysis. The thermal degradation pattern was analyzed using the TGA Q500 equipment under a constant nitrogen flow. Approximately 10-20 mg of sample was used, with heating rate of 20°C/min until 800°C was reached.

Differential scanning calorimetry. The melting and crystallizing behaviour of the composite films were analyzed using the DSC Q2000. The DSC sequence was comprised of three steps. The first heating step was 30°C/min to 200°C from room temperature, and the purpose was to remove the previous thermal history. The next step was the first cooling step, going from 200°C to -50°C at 10°C/min. The last step was the second heating step, going from -50°C to 200°C at 10°C/min. The first cooling and second heating steps were reported. Approximately 5-10 mg of sample was used per formulation.

Melt flow index analysis (MFI). The rheological property was measured using the Melt Flow Indexer (Dynisco) in accordance with ASTM D1238. The test was conducted at 190°C with a 2.16 kg weight.

Water absorption test. The water absorption test was conducted in accordance with ASTM D570 to determine the total amount of water absorbed by the films. The test was conducted in triplicates.

Water vapour permeability test. The water vapour transmission test was performed in accordance with ASTM E96. The test was conducted in triplicates.

Scanning electron microscopy. The cross-section of the selected films was analyzed with the Quanta FEG-250 SEM. The samples were cryo-fractured then coated with gold with the Magnetron Sputter Coater prior to the scanning.

CHAPTER 6:

RESULTS AND DISCUSSIONS –

POLYESTER AND α -1,3-GLUCAN COMPOSITES

In this chapter, α -1,3-glucan was incorporated into two different polyesters, namely PBAT and PBS. Unlike the TPU system that was studied in the previous chapters, PBAT and PBS are both recognized biodegradable polymers that are commercially available. As well, for PBS, the monomers can be sourced from sustainable materials, making the polymer both biodegradable and sustainable. There are several reports in the literature where polysaccharides such as starch and cellulose are used as filler materials, but to the best of the author's knowledge, there is no example in the literature dealing with mixtures of α -1,3-glucan with PBAT or PBS. Since both PBAT and PBS are considered specialty polymers, the cost of manufacturing and production can be alleviated by incorporating filler material like α -1,3-glucan. Thus, the properties of PBAT- and PBS- α -1,3-glucan composites were studied.

6.1. PBAT- and PBS- α -1,3-glucan composite films

In this study, the effect of α -1,3-glucan on the PBAT and PBS composites was explored. The images of the films are shown in Figure 56. The amount of α -1,3-glucan in each polymer matrix ranged from 0 to 70 wt.% with 10% increments.

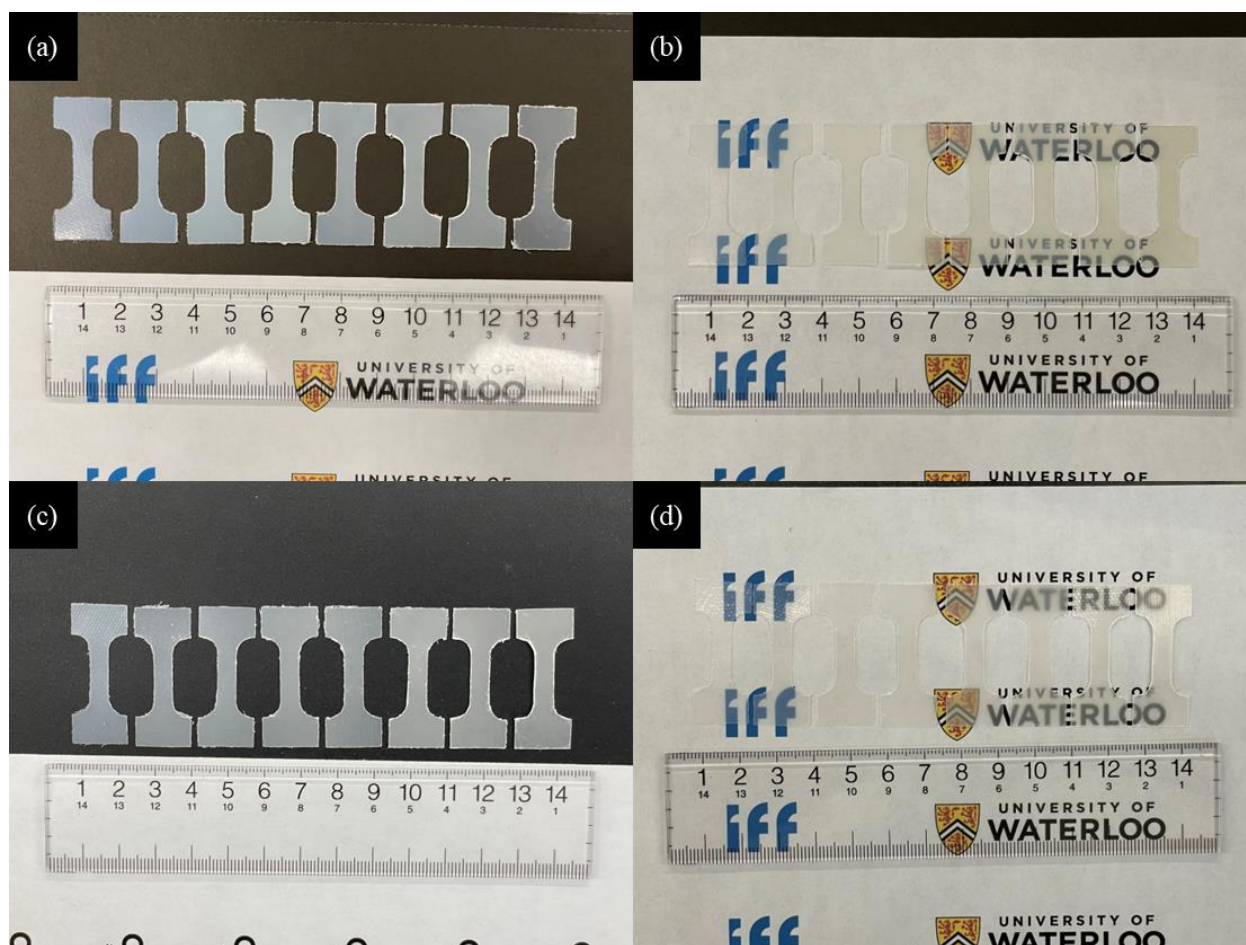


Figure 56. Tensile test specimens for (a, b) PBAT composites and (c, d) PBS composites; increasing levels of α -1,3-glucan from left to right in each image (0, 10, 20, 30, 40, 50, 60, 70 wt.% α -1,3-glucan)

6.1.1. Thermal properties

The TGA and DTG plots for PBAT- and PBS- α -1,3-glucan composites are summarized in Figures 57 and 58, respectively. The onset of degradation of the α -1,3-glucan was lower than both PBAT and PBS. The peak degradation for α -1,3-glucan occurred at around 330°C, whereas it was around 400°C for PBAT and PBS. The intensity of the degradation peak as shown on the DTG plots is associated with the α -1,3-glucan fraction in the composite. When α -1,3-glucan is added to the composite, an initial weight loss ranging from 2-5% before 200°C was observed. This is due to the moisture absorbed by the α -1,3-glucan. As the concentration of the α -1,3-glucan increased, the initial weight loss before 200°C increased as well. All the samples showed good thermal stability up to 250°C, which is above most typically processing conditions.

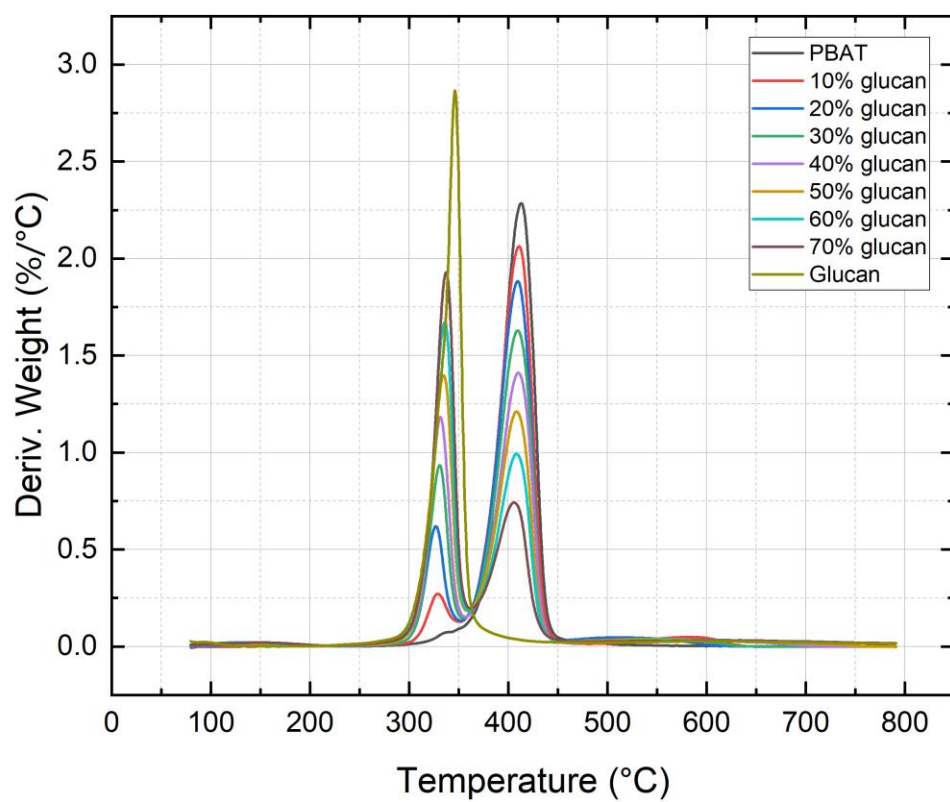
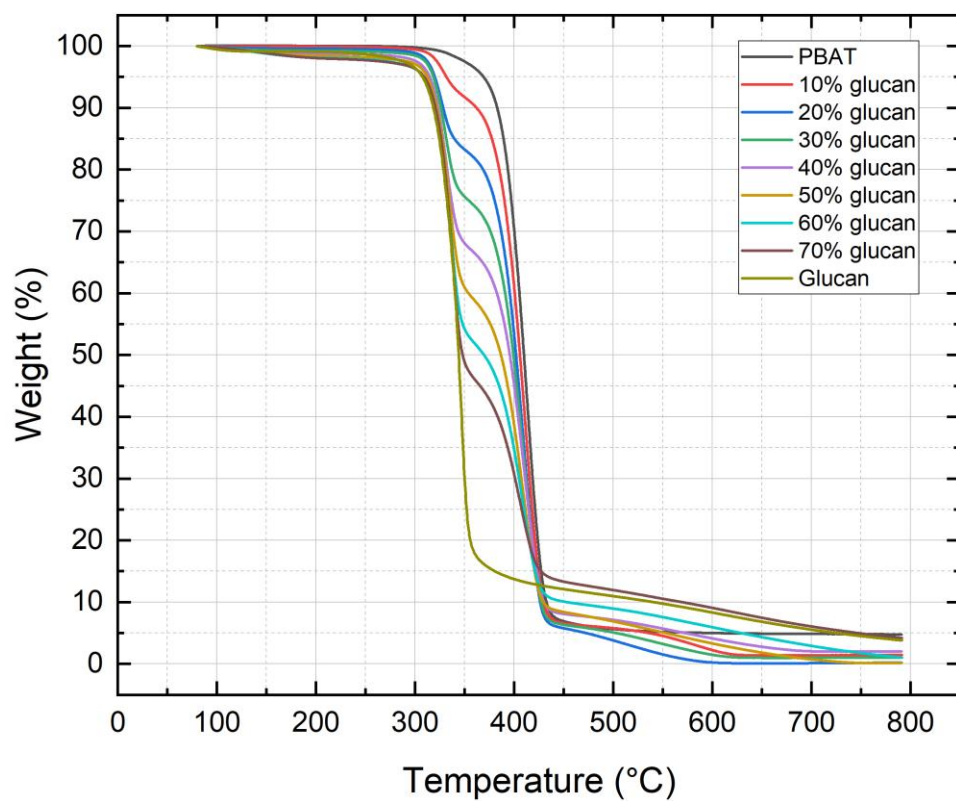


Figure 57. TGA (top) and DTG (bottom) curves for PBAT- α -1,3-glucan composites

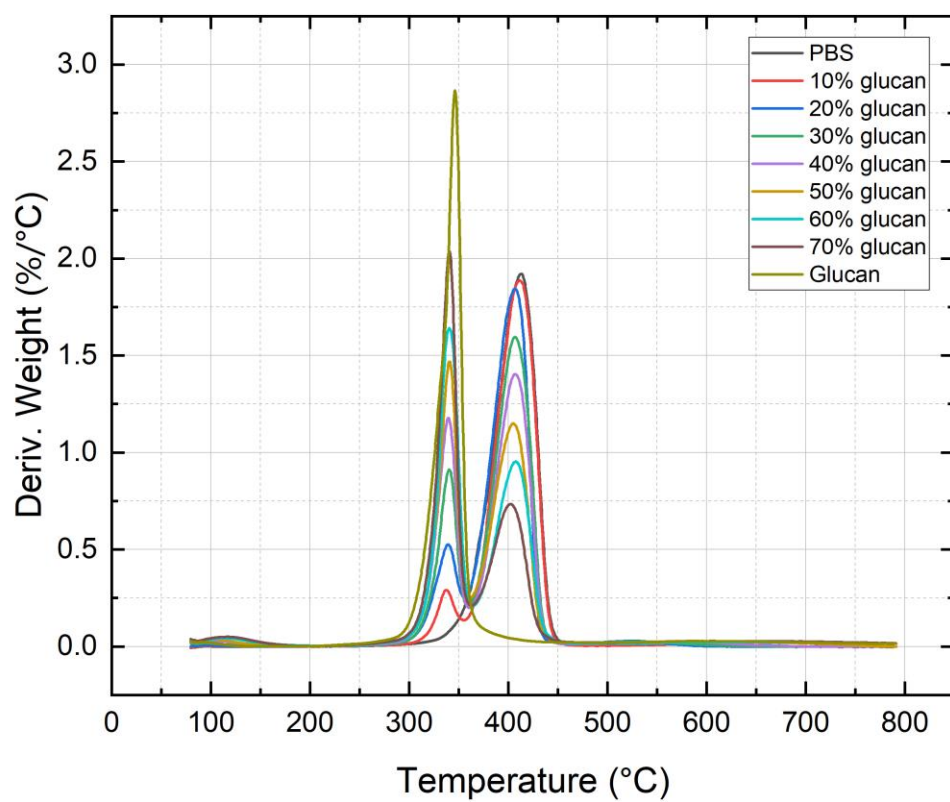
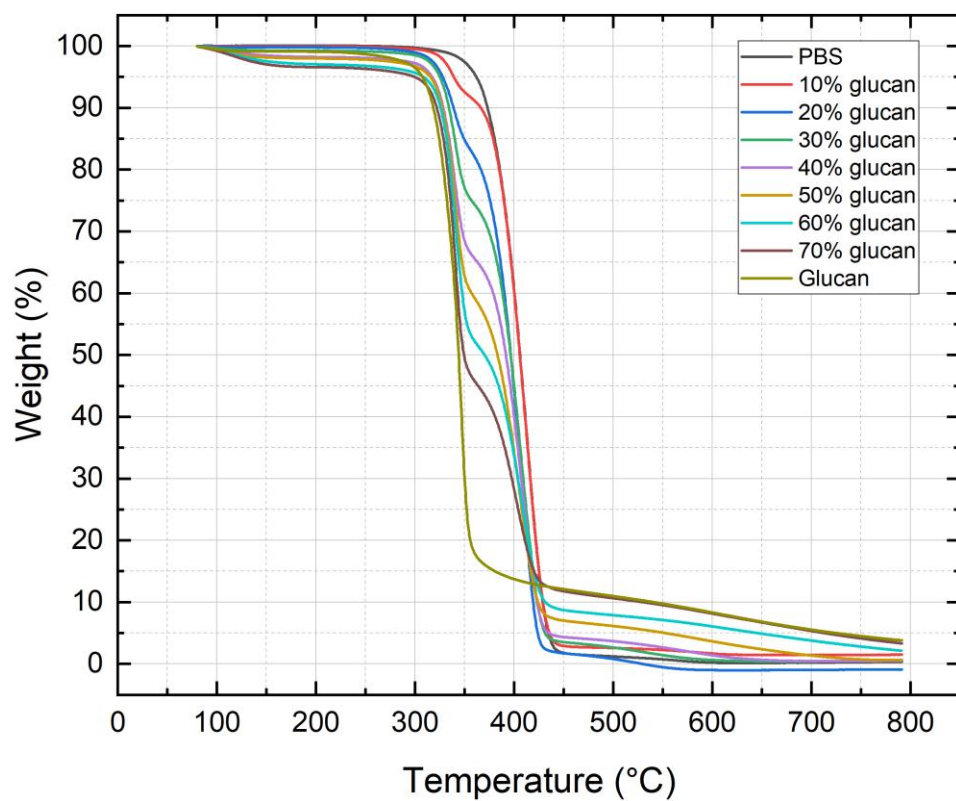


Figure 58. TGA (top) and DTG (bottom) curves for PBS- α -1,3-glucan composites

The DSC plots for PBAT- and PBS- α -1,3-glucan composites are summarized in Figures 59 and 60, respectively. The analysis results are tabulated in Table 20 for the PBAT- α -1,3-glucan composites and Table 21 for PBS- α -1,3-glucan composites. The crystallization temperature increased when α -1,3-glucan was incorporated for both polyesters. This is a similar behaviour from section 4.3.3., where the α -1,3-glucan increased the crystallization temperature. The melting temperatures were similar regardless of the α -1,3-glucan level. The crystallization and melting peaks were integrated to calculate the enthalpy of crystallization and melting and are tabulated in Tables 20 and 21. The degree of crystallinity (X_c) was calculated by using the equation:

$$X_c = \frac{\Delta H_m}{\Delta H_0(1 - W_f)} \times 100(\%) \quad (2)$$

where ΔH_0 is the enthalpy of 100% crystalline PBAT (114 J/g) or PBS (200 J/g) and W_f is the filler (α -1,3-glucan) weight fraction.^[118,119] The degree of crystallinity of the PBS composites remained consistent regardless of the content of α -1,3-glucan. However, the degree of crystallinity of the PBAT composites decreased as a function of α -1,3-glucan content. Kargarzadeh et al. also reported a decrease in crystallinity when lignin filler was added to PBAT.^[120] This apparent reduction in crystallinity was due to cold crystallization, which appears as a slight exothermal anomaly right before the melting occurs. For PBS composites, an initial drop in crystallinity is observed due to the cold crystallization, but as the α -1,3-glucan content increased, the effect of cold crystallization diminished, hence the crystallinity became similar to the neat PBS.

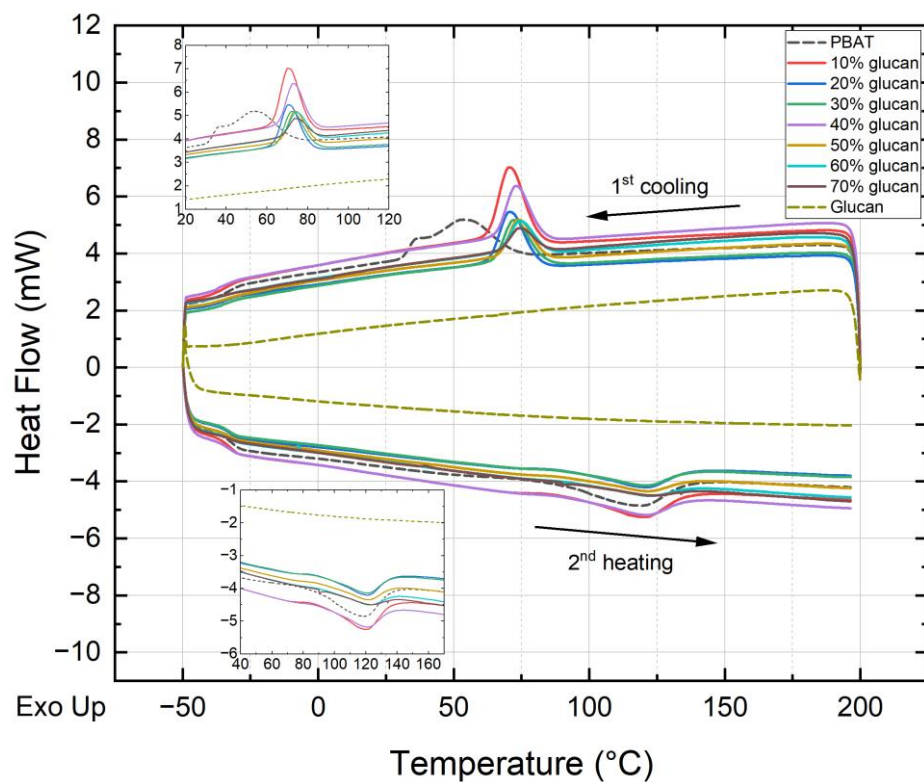


Figure 59. DSC curves for PBAT- α -1,3-glucan composites

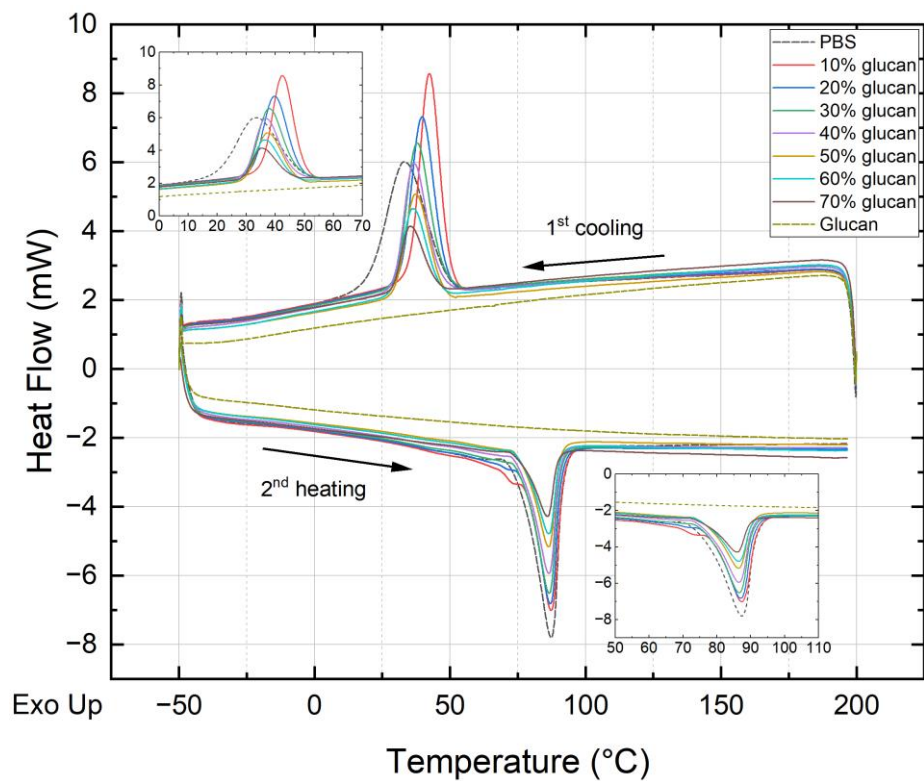


Figure 60. DSC curves for PBS- α -1,3-glucan composites

Table 20. DSC analysis results for PBAT- α -1,3-glucan composites

α -1,3-glucan (wt. %)	ΔH_c (J/g)	T_c (°C)	ΔH_m (J/g)	T_m (°C)	T_g (°C)	X_c (%)
0	18.77	54.5	14.30	118.9	-31.7	11.4
10	14.48	70.5	9.55	120.2	-31.9	9.3
20	12.88	70.7	8.47	120.7	-31.6	9.3
30	10.56	72.2	7.66	120.6	-32.2	9.6
40	9.61	72.8	6.77	120.6	-32.0	9.9
50	7.69	73.8	5.58	120.8	-32.2	9.8
60	5.89	74.3	4.35	121.7	-33.7	9.5
70	4.50	74.1	2.56	122.6	-34.0	7.5

Table 21. DSC analysis results for PBS- α -1,3-glucan composites

α -1,3-glucan (wt. %)	ΔH_c (J/g)	T_c (°C)	ΔH_m (J/g)	T_m (°C)	X_c (%)
0	40.95	32.8	31.48	87.5	17.3
10	36.52	42.4	26.62	87.4	14.8
20	31.92	39.7	23.87	87.1	14.9
30	28.88	37.9	22.10	86.7	15.8
40	24.53	36.7	18.39	86.6	15.3
50	20.10	37.2	15.55	86.5	15.6
60	15.98	36.2	12.55	86.4	15.7
70	12.35	35.2	9.94	85.9	16.6

6.1.2. Melt flow index

The MFI was plotted as a function of the α -1,3-glucan in Figure 61. The addition of α -1,3-glucan increased the melt viscosity of the PBAT and PBS because the rigid α -1,3-glucan hindered the polymer chain movement, making it more viscous. In the case of PBS composites, an initial increase in MFI was observed when a low level of α -1,3-glucan was added. The pristine PBS had an MFI value of 4 g/10 min and it was observed experimentally that the addition of 10% α -1,3-glucan increased the MFI value to about 5.4 g/10 min. Such increase of the MFI has not been reported for composites that incorporate rigid fillers like the α -1,3-glucan. It is postulated that because the pristine PBS is tacky in the molten state and has the tendency to stick to the walls of the indexer tube, it had lower MFI value than the 10% α -1,3-glucan composite counterpart, which

reduced the tackiness of the PBS and allowed the mixture to flow through the indexer more. The reduction in the MFI as the filler amount increases has been observed by several authors. Yokesahachart et al. investigated the effect of jute fiber on the thermoplastic starch/polylactic acid (PLA)/PBAT blend, while Cui et al. studied the effect of acetylated cellulose nanocrystals on PBAT.^[121,122] In both cases, a significant reduction in MFI was observed as a result of reduced mobility of the polymer chains. Similarly, Park et al. studied wood flour and PBS composite and Gaidukova et al. used coffee waste as a filler in PBS, and both groups observed a decrease in MFI as the filler content increased.^[123,124]

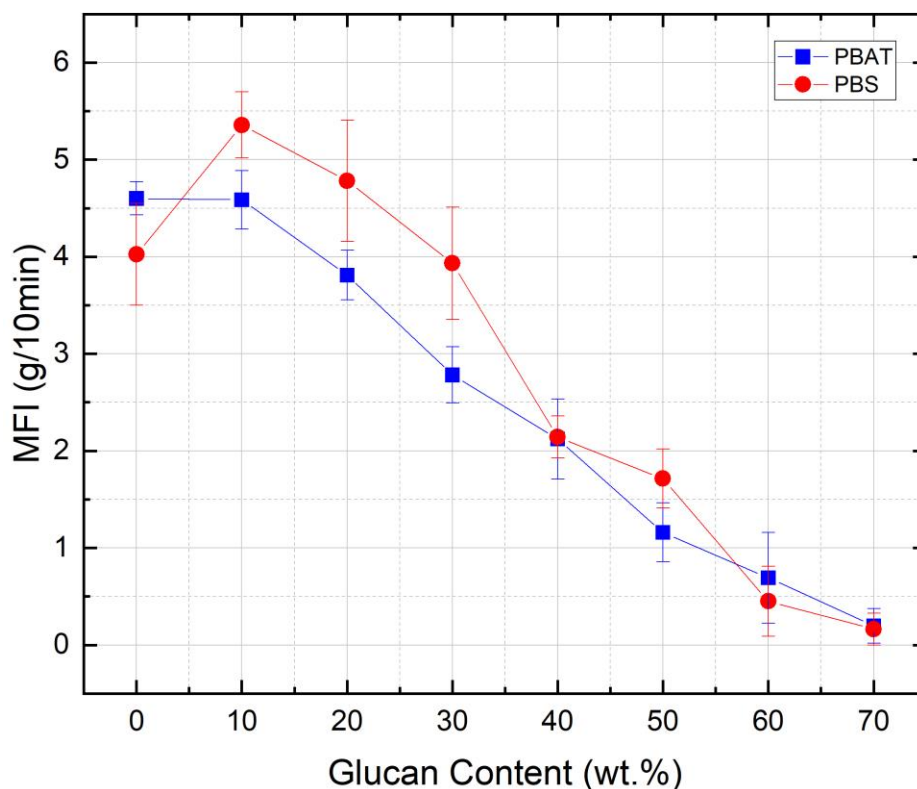


Figure 61. MFI results for PBAT- and PBS- α -1,3-glucan composites

6.1.3. Water absorption

The water absorption plots are summarized in Figures 62-64. As the amount of α -1,3-glucan in the composite increased, the amount of water uptake increased. The increase in water absorption as more α -1,3-glucan is added is not a surprising result. α -1,3-glucan is a hydrophilic polysaccharide that can absorb moisture. As the α -1,3-glucan content increased, it became easier for the water molecules to diffuse through due to their proximity to each other, thus the rate of diffusivity increased. Dammak et al. reported a similar behaviour when investigating a starch and

PBAT composite system.^[125] Due to the hydrophilic nature of the starch, more water was absorbed as the starch content increased. At a high concentration of starch, the continuity of the starch phase allowed the water to be completely accessible. The increase in water uptake when a hydrophilic filler is incorporated is quite common. Phiriyawirut et al. addressed the high water uptake of starch in PBS blends and investigated a crosslinking strategy to mitigate the high water absorption of starch.^[126]

The PBS composites reached the equilibrium water absorption at around 8 hours, whereas the PBAT composites took longer to stabilize, reaching the equilibrium at around 24 hours. The total amount of water absorbed by the composites are summarized in Figure 64. Overall, the composites with PBAT as the base matrix absorbed more water than the PBS. The difference in water absorption between PBAT and PBS may be attributed to the difference in their crystallinity, as shown from the DSC results. The PBS samples have higher crystallinity than the PBAT counterpart, hence less prone to water absorption. Similar behaviour was observed when Yap et al. prepared PBAT and PBS composites with rice husk, where the water absorption was higher when the crystallinity was lower.^[101]

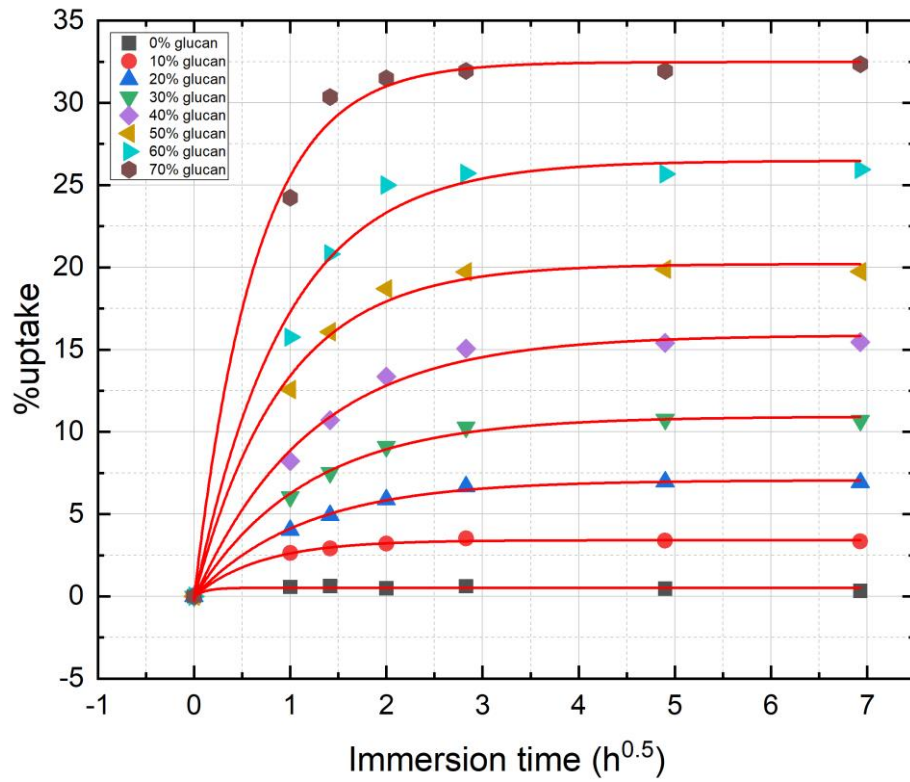


Figure 62. Amount of water absorbed by the PBAT- α -1,3-glucan composites at different times

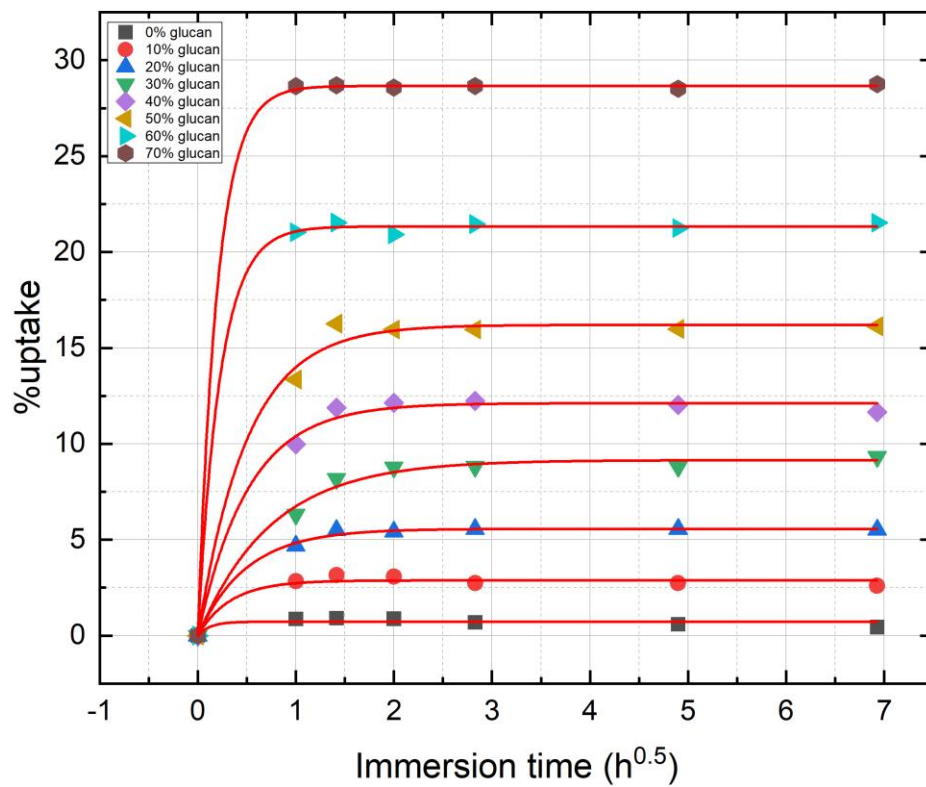


Figure 63. Amount of water absorbed by the PBS- α -1,3-glucan composites at different times

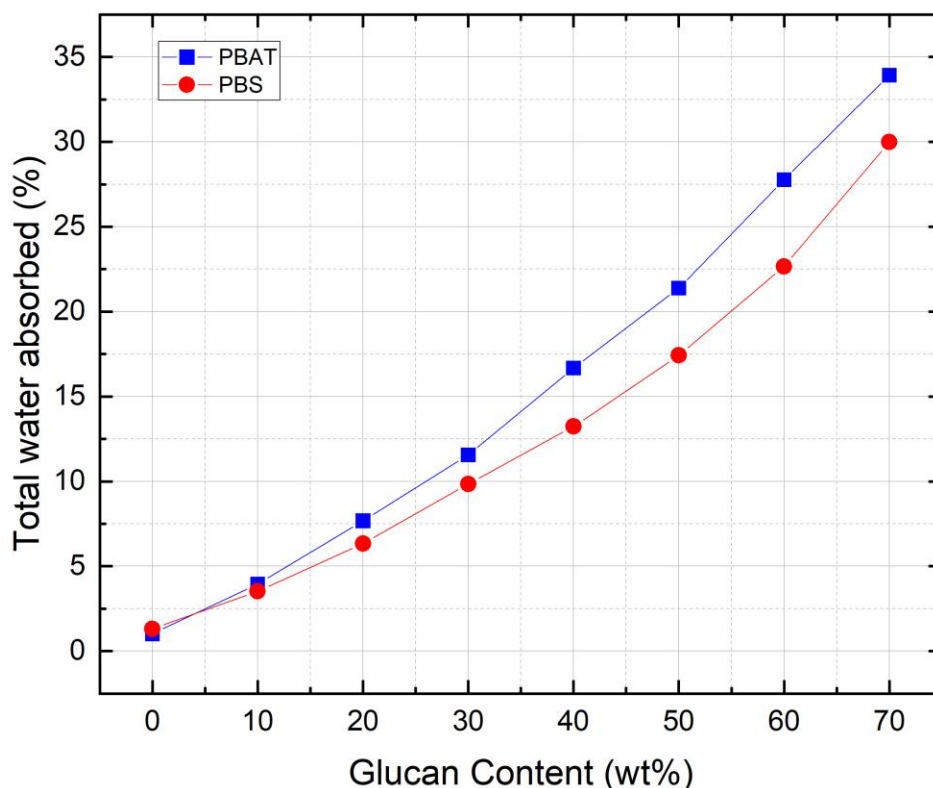


Figure 64. Total amount of water absorbed by the PBAT- and PBS- α -1,3-glucan composites

6.1.4. Mechanical properties

The tensile properties of the PBAT- and PBS- α -1,3-glucan composites are summarized in Figures 65-68. The same trend was observed for both composite systems; as the level of the α -1,3-glucan increased, the modulus increased, while the strength, elongation at break, and toughness decreased.

The increase in the modulus is due to the reinforcing effect of the α -1,3-glucan, making the composites stiffer as more α -1,3-glucan was added. Generally, PBS exhibited higher stiffness than PBAT, thus higher moduli were observed for the PBS composites. The modulus is measured at a low deformation stage, so it is only moderately affected by polymer-particle interactions, since the separation between the matrix and the particles generally does not occur.^[127,128] Therefore the increase in modulus as the α -1,3-glucan content increases demonstrates that the α -1,3-glucan particles are intrinsically stiffer compared to PBAT and PBS. A similar observation was made when grape stalks were used as a reinforcing filler in the PBS matrix.^[129] The decrease in the strength may be attributed to the inability of the fillers to support the stress that had been transferred from the polymer matrix. Since the α -1,3-glucan exists as rigid particles, it is difficult

to efficiently transfer the stress. As well, voids may form between the particles and the polymer matrix, allowing the crack to propagate more easily, resulting in lower tensile strength. Alghamdi reported a similar behaviour when using polypropylene and polycarbonate with halloysite nanotubes, with a reduction in strength as more fillers were added.^[130]

The elongation at break decreased because in a typical composite system, the elongation comes from the base polymer since the fillers are often rigid in comparison. Since increasing the α -1,3-glucan content decreases the amount of polymer available for elongation, the elongation at break decreased. The toughness is calculated by integrating the stress-strain curve, which means that it requires a balance of both strength and elongation. Since both the tensile strength and elongation at break decrease as a function of the α -1,3-glucan content, the toughness decreased as well.

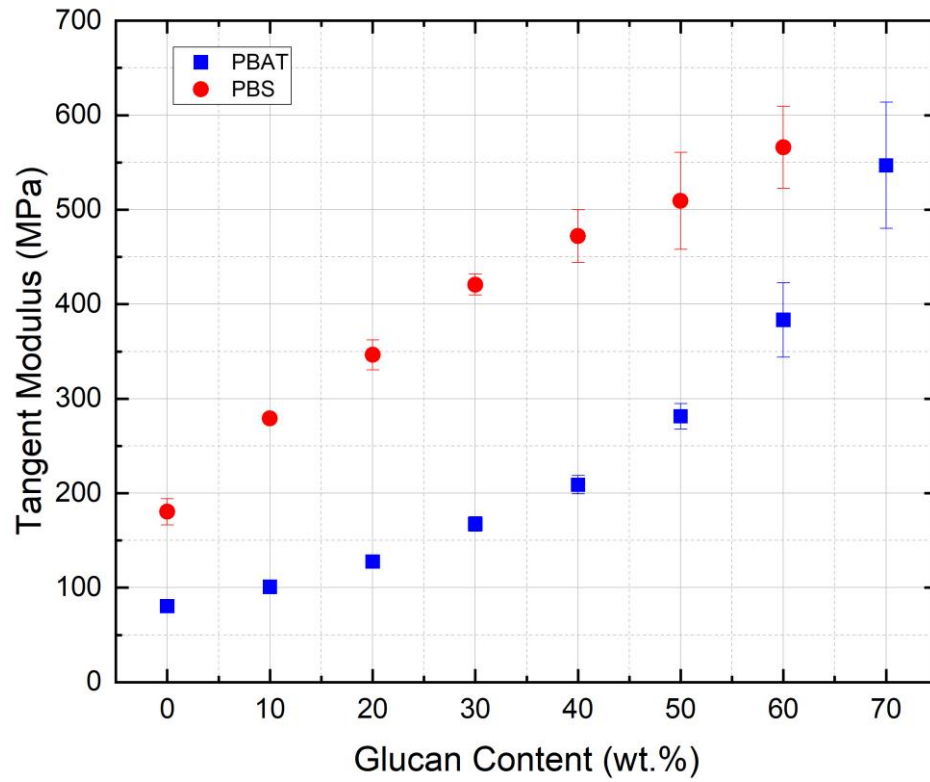


Figure 65. Tensile tangent modulus of PBAT- and PBS- α -1,3-glucan composites

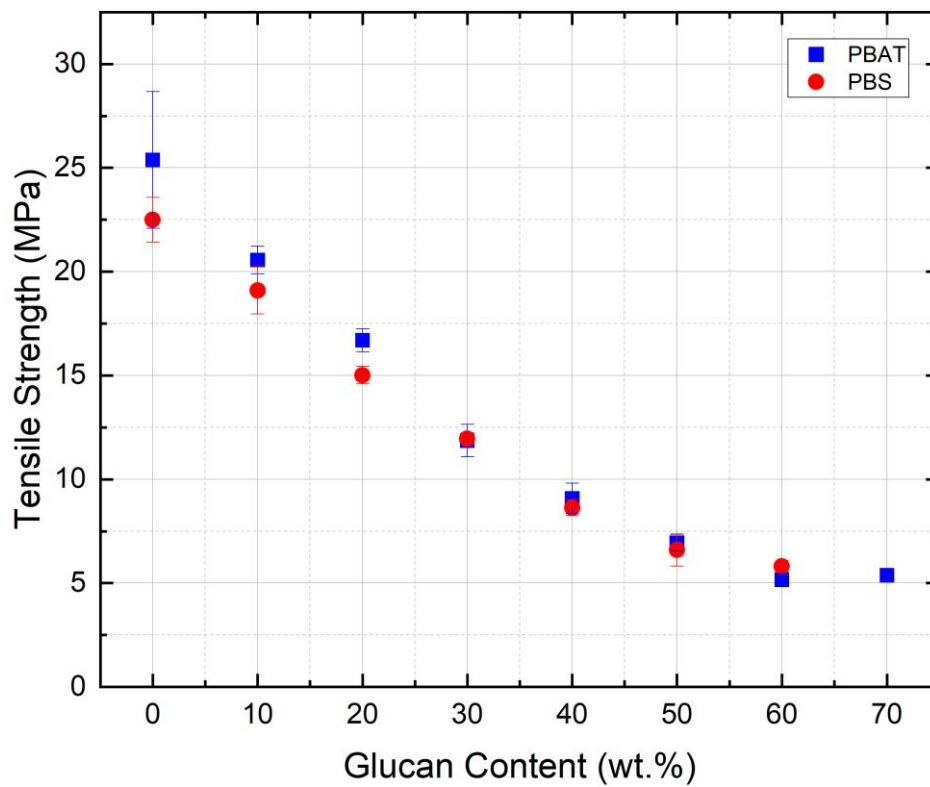


Figure 66. Tensile strength of PBAT- and PBS- α -1,3-glucan composites

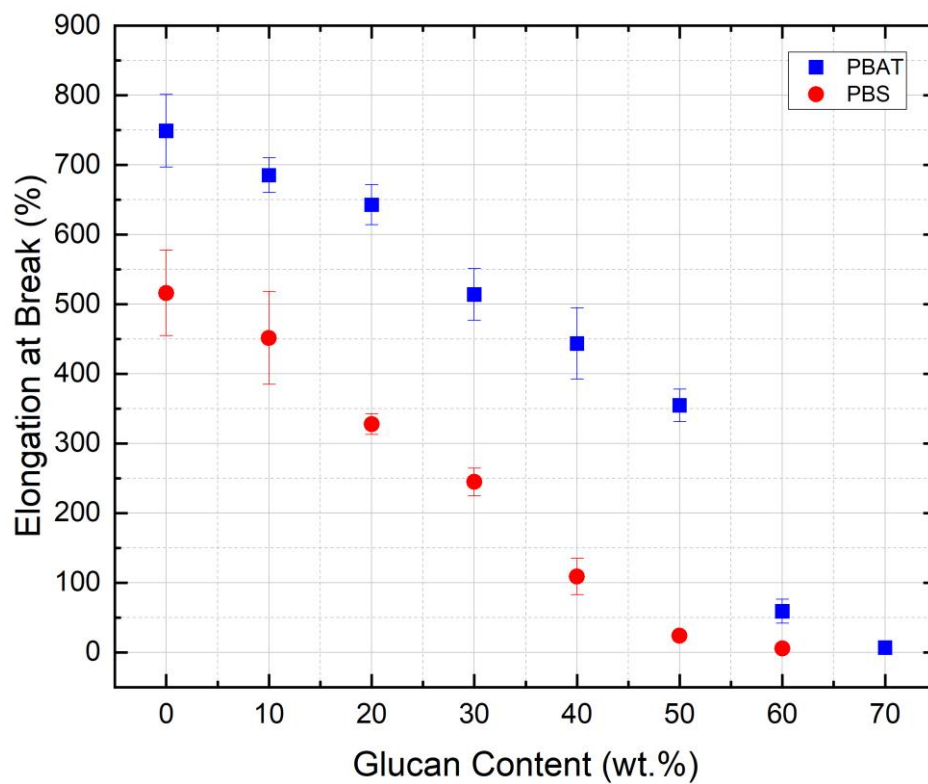


Figure 67. Elongation at break of PBAT- and PBS- α -1,3-glucan composites

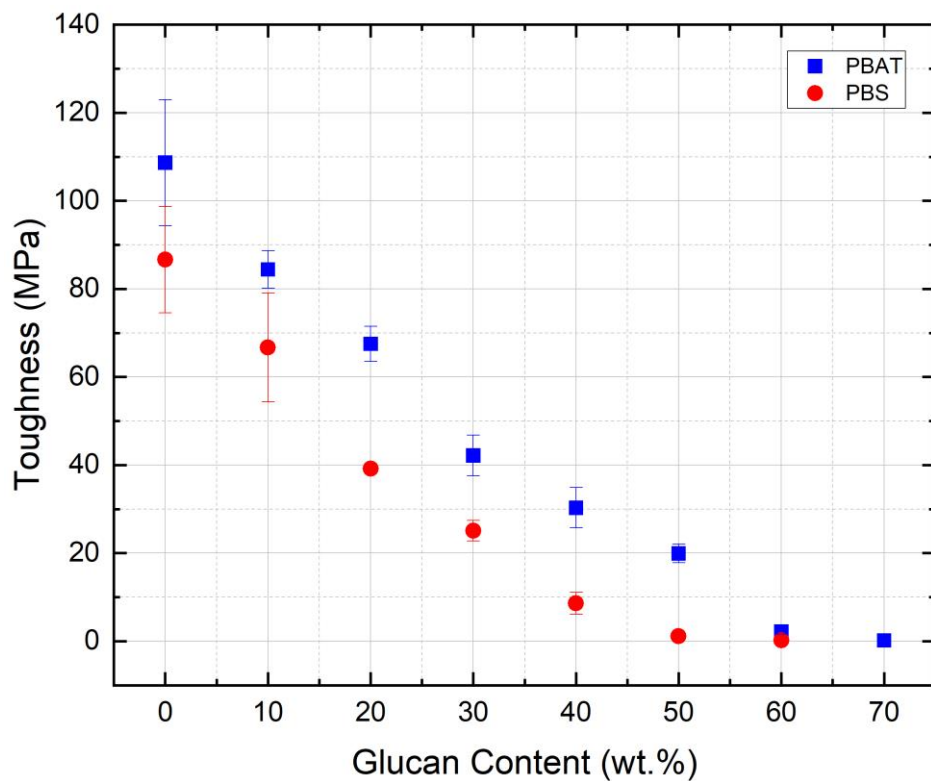


Figure 68. Toughness of PBAT- and PBS- α -1,3-glucan composites

6.1.5. Water vapour permeability

The water vapour transmission test results are summarized in Figures 69-72. When the change in mass of the test set-up stabilized, which was indicated by a straight line, the water vapour transmission (WVT) rate could be calculated using:

$$WVT = (G/t)/A \quad (3)$$

where G/t is the slope of the straight line from Figures 69 and 70, and A is the test area (cup mouth area). Once the WVT rate was determined, the water vapour permeability (WVP) was calculated using:

$$WVP = WVT \cdot \frac{l}{\Delta p} \quad (4)$$

where l is the thickness of the film, and Δp is the water vapour pressure difference. Both the WVT and WVP increased as the α -1,3-glucan content increased (Figure 72), for both PBAT- and PBS- α -1,3-glucan composites. The increase in the permeability was due to the hydrophilic nature of the α -1,3-glucan. As more α -1,3-glucan particles were in the system, they created a permeable route for the water vapour to travel through. The order of magnitude of the water vapour permeability is similar to the work by Zhai et al, where they investigated the PBAT and starch composite films.^[131] In Figure 72, the rate at which the permeability increased was non-linear. When there are large number of α -1,3-glucan particles present in the system, it is more likely for the particles to be in contact or near each other, allowing the water vapour to be transported at a faster rate. The increase in the permeability as the fillers has been reported in literature due to the hydrophilic nature of the filler materials.^[132,133]

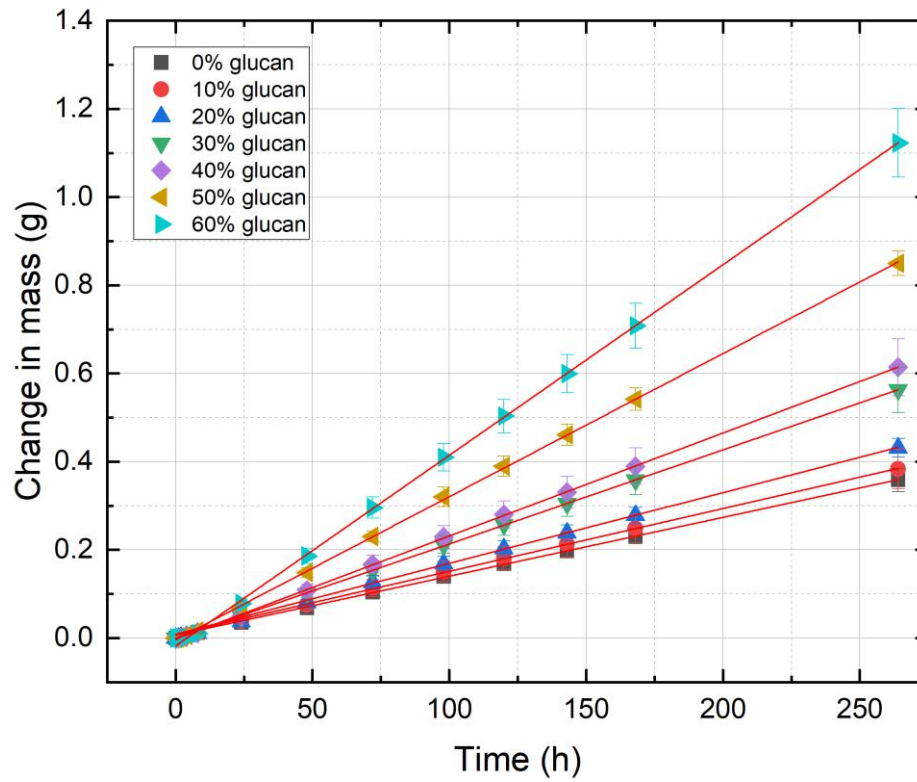


Figure 69. Amount of water lost through the PBAT- α -1,3-glucan composite films at different times

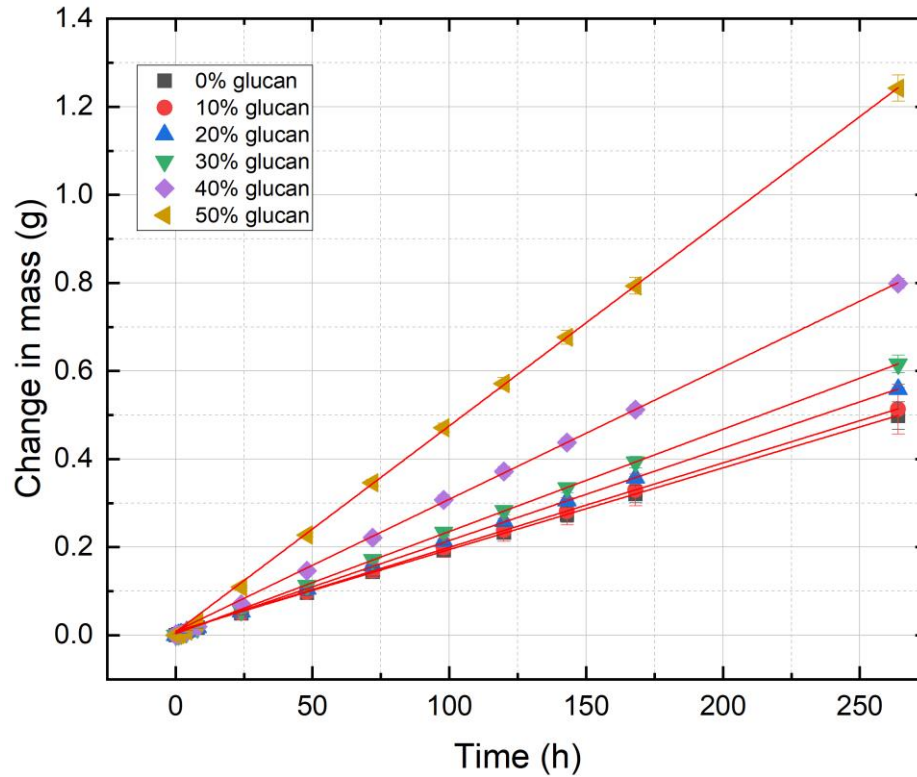


Figure 70. Amount of water lost through the PBS- α -1,3-glucan composite films at different times

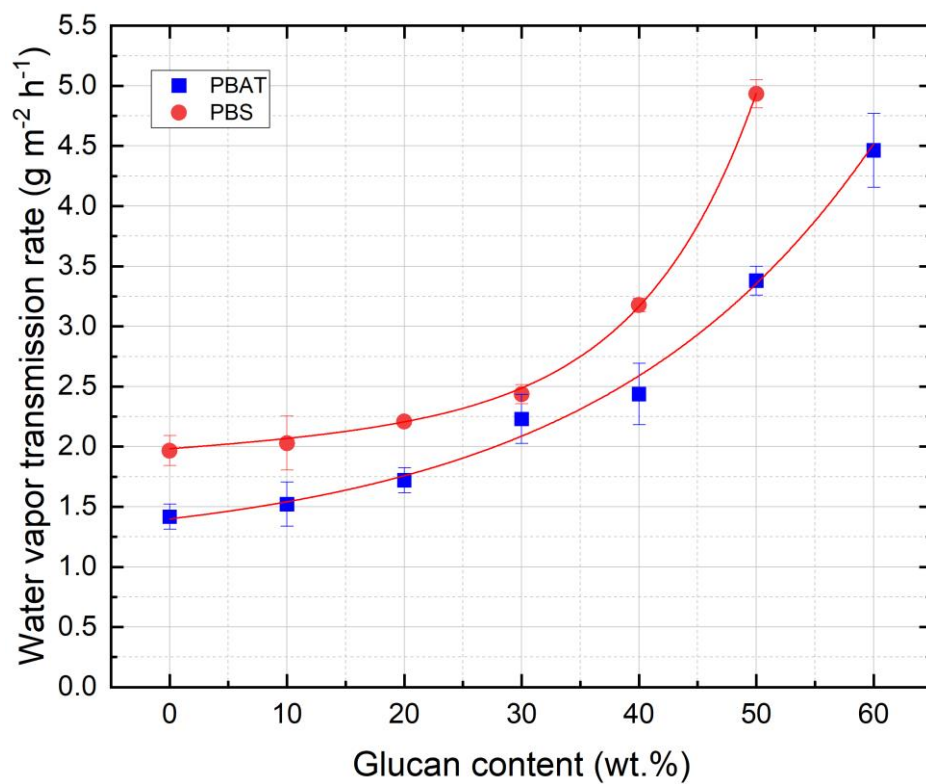


Figure 71. Water vapour transmission rate of PBAT- and PBS- α -1,3-glucan composite films

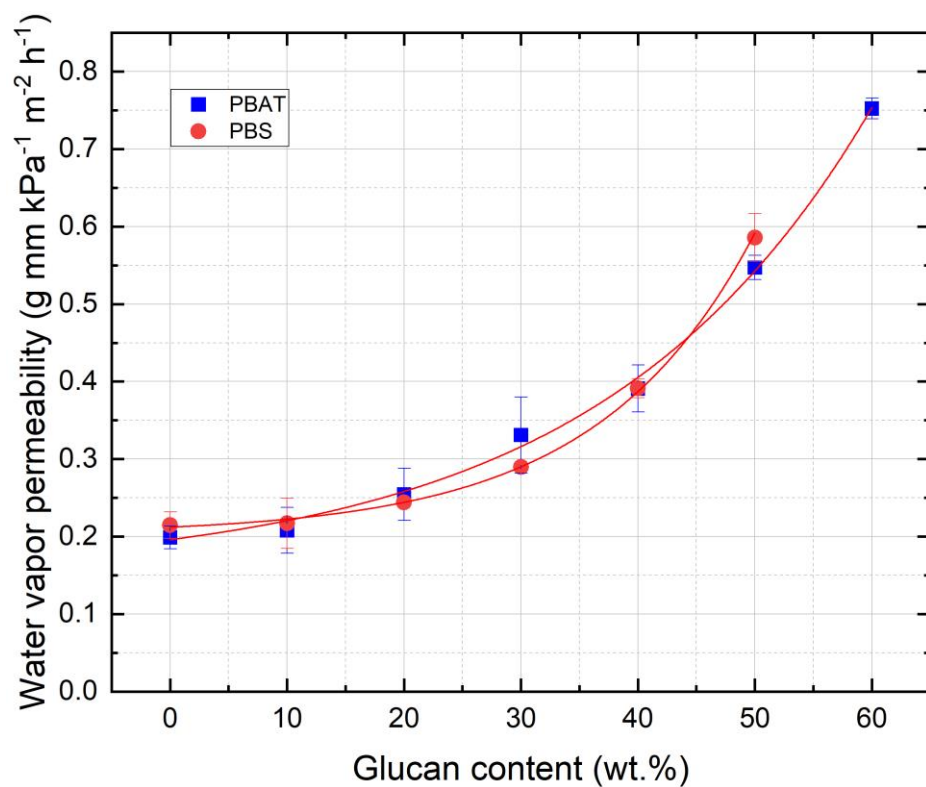


Figure 72. Water vapour permeability of PBAT- and PBS- α -1,3-glucan composite films

6.2. Effect of different fillers in PBAT and PBS

In the previous section, the properties of PBAT and PBS composites containing α -1,3-glucan was established. In this section, different commonly used fillers (starch, cellulose, and CaCO_3) were investigated to compare the performance difference with the α -1,3-glucan counterpart. For simplicity, two levels of filler loading were selected at 10 and 30 wt.%. This will help understand the performance of α -1,3-glucan in comparison. The SEM images of the different fillers used for this study are shown in Figure 73. The films made from different fillers and polymer matrix are shown in Figure 74.

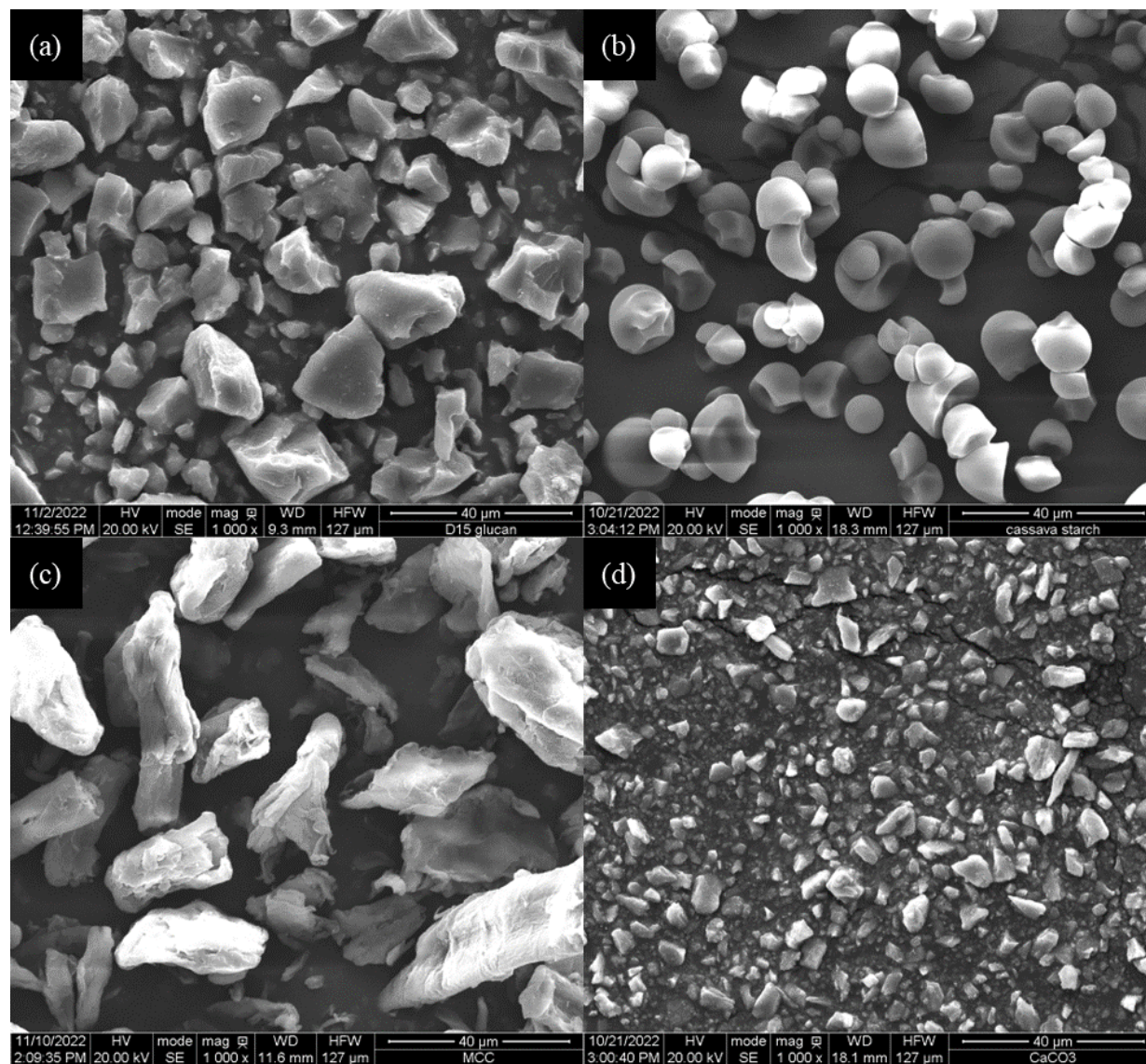


Figure 73. SEM images of (a) D15 α -1,3-glucan, (b) cassava starch, (c) MCC, and (d) CaCO_3



Figure 74. (a) PBAT composites and (b) PBS composites with different fillers

6.2.1. Tensile properties

The tensile properties of the PBAT and PBS composites with different fillers are summarized in Figures 75-78. The overall trend observed was similar to the results from section 6.1.4. For the modulus, the MCC had the highest improvement, whereas the CaCO_3 had the lowest improvement, while the starch and α -1,3-glucan were in between the two aforementioned fillers. The MCC offers the highest amount of crystallinity amongst the polysaccharides and combined with its abundance of hydroxyl groups that can form hydrogen bonds, led to the highest level of reinforcement in the system. An extensive XRD work by Rowe et al. on different brands of MCC showed that the crystallinity of MCC ranges from 61.8-65.0%.^[134] In a different study by Gomand et al. the cassava starch was reported to have a crystallinity in the range of 40%.^[135] According to the material data from IFF, the α -1,3-glucan has a crystallinity of about 50%, which is right between the MCC and starch.^[70]

As well, it has been reported that bigger particles increase the modulus, and since the MCC has relatively bigger size distribution, a higher increase in modulus was observed.^[136–138] Additionally, the rod-like shape of the MCC provides higher aspect ratio than the other more spherical particles. Botta et al. investigated the PBAT and MCC system with different aspect ratios and concluded that the higher aspect ratio resulted in higher reinforcing action, and therefore increased the modulus.^[139] The polysaccharides MCC, starch, and α -1,3-glucan also have an abundance of hydroxyl groups that can form hydrogen bonds with the polyesters, but starch and α -1,3-glucan have lower crystallinity compared to the MCC, and therefore a slightly less reinforcing effect than the MCC was observed. But overall, all the filler materials were capable of making the composite films stiffer.

The tensile strength showed a decreasing trend regardless of the filler type. When polysaccharides (i.e., starch, α -1,3-glucan, and MCC) were used, the tensile strength was similar and decreased at a similar rate. However, the composites containing the CaCO_3 showed significantly different decreasing trend. This may be attributed to the different particle size. As shown in Figure 73, the average particle size of the CaCO_3 is significantly smaller than the other polysaccharides, with some particles in the nano-range. The near nano distribution of the CaCO_3 particles increases the contact surface area with the base polymer matrix, which allows for a more efficient distribution of stress when applied to the system.

The elongation at break decreased as the filler amount increased regardless of the type of filler. Since the ductility mainly comes from the base polymer matrix, the reduction of the available base polymer as a result of the increase in filler content leads to a decrease in elongation. The particle size had a slight effect on the elongation, where the bigger particles led to a higher decrease. This may be attributed to the ability of smaller particles to distribute more homogeneously in the base polymer matrix. The toughness showed a decreasing trend as the filler concentration increased, since both the strength and elongation decreased with the filler content.

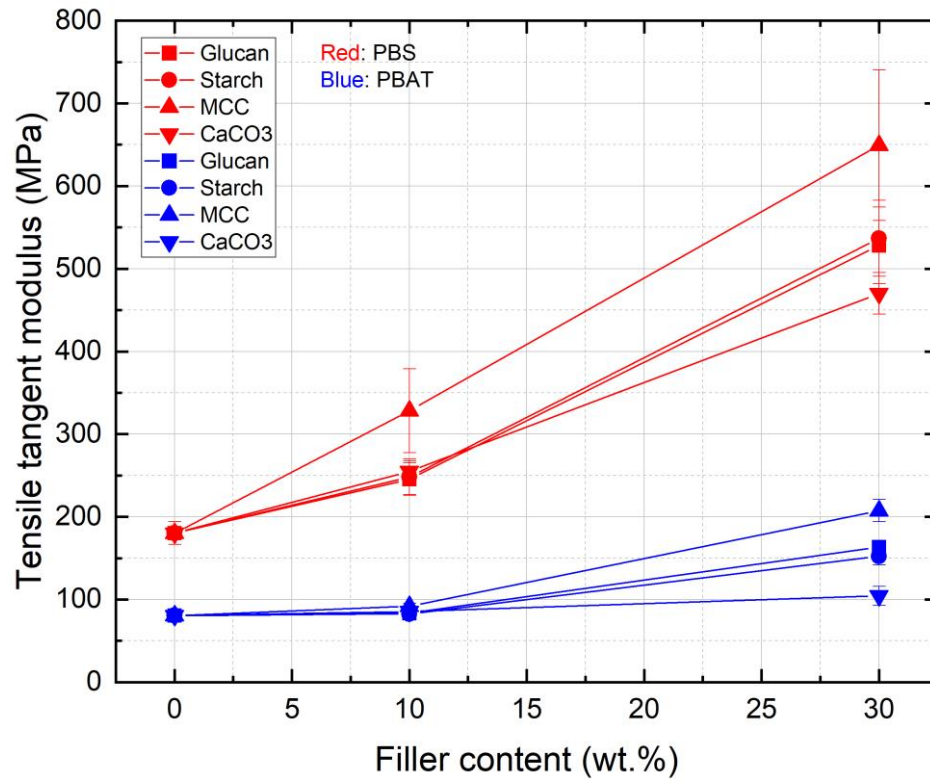


Figure 75. Tensile tangent modulus of PBAT and PBS composites with different fillers

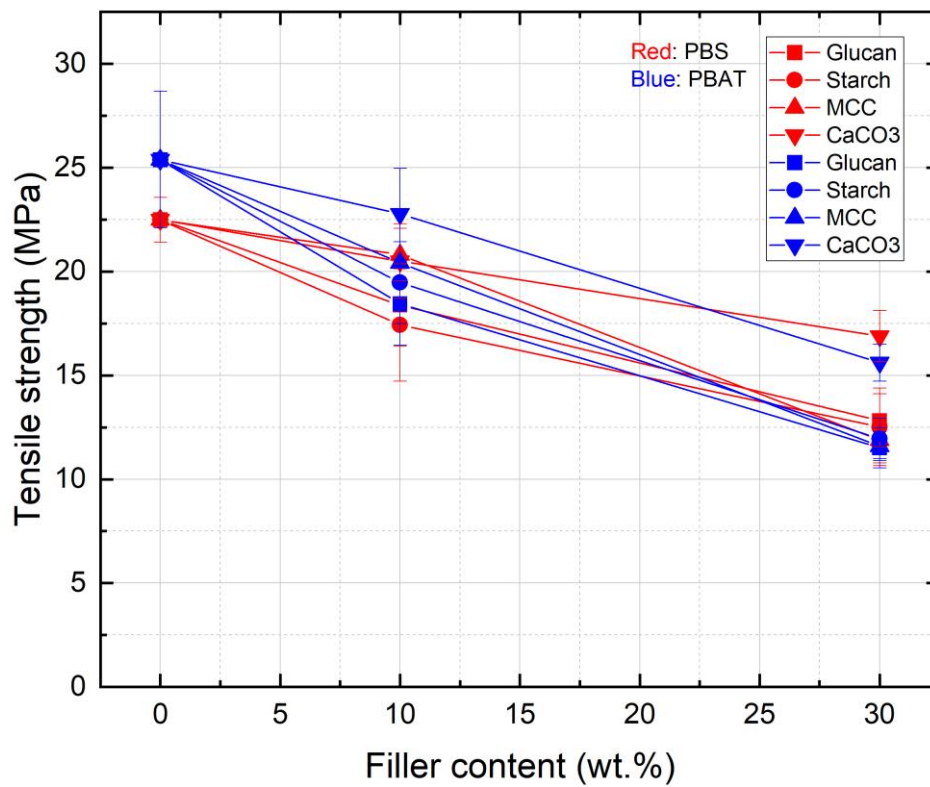


Figure 76. Tensile strength of PBAT and PBS composites with different fillers

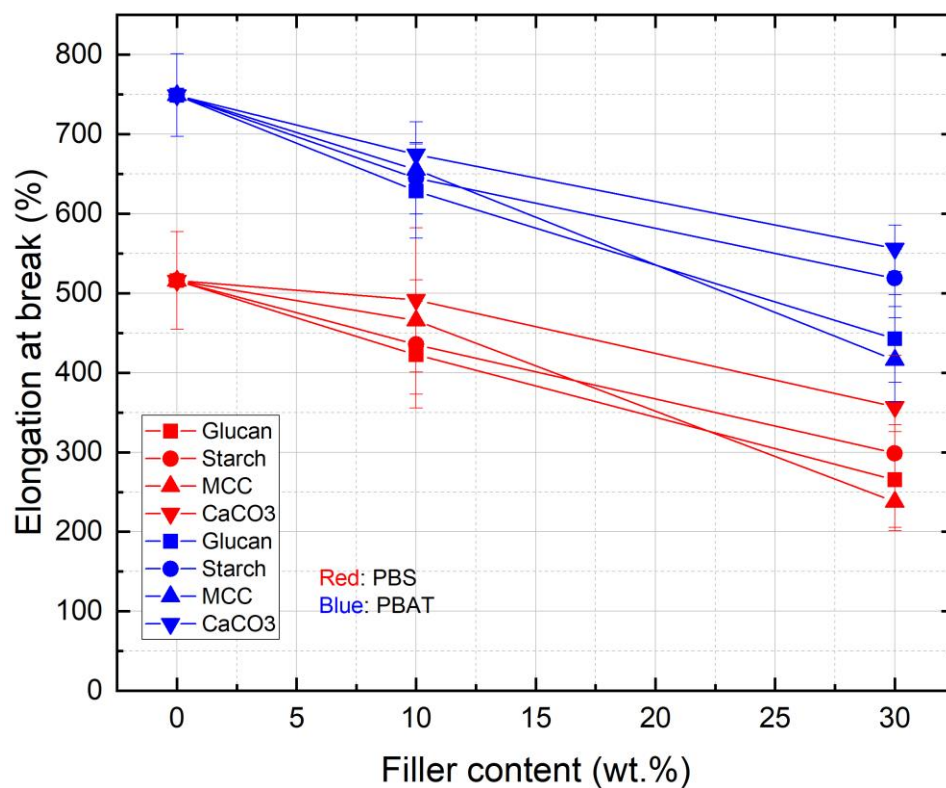


Figure 77. Elongation at break of PBAT and PBS composites with different fillers

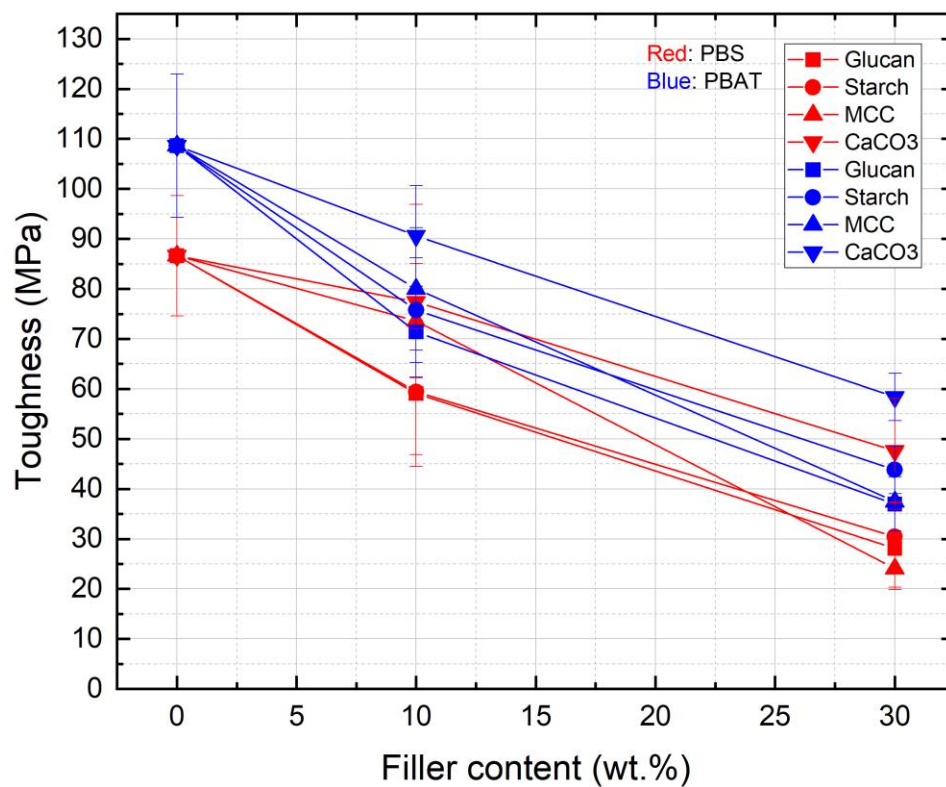


Figure 78. Toughness of PBAT and PBS composites with different fillers

6.2.2. Water absorption

The water absorption plots for PBAT and PBS composites are summarized in Figures 79 and 80, respectively. When polysaccharides were used as a filler, the amount of water absorbed by the composite increased with the filler content. It was observed that the α -1,3-glucan composites absorbed the most amount of water, followed by the starch, then MCC. The samples containing MCC tend to absorb less water than the other polysaccharides due to the high crystallinity of cellulose.^[140] Generally, the crystalline domain is not capable of absorbing water. Instead, the water diffuses into the amorphous region, as well as the in the interface between the polymer and the filler. α -1,3-glucan forms irregular rough particles, which increases the surface area that is in contact with the polymer, as opposed to the spherical starch. Garcia de Rodriguez and Dufresne reported that in a composite system, the water diffuses into the particle-polymer interface, as well as the amorphous domain.^[140] In contrast, the addition of CaCO_3 as a filler slightly reduced the amount of water absorbed by the composite. This may be attributed to the difference in the particle size. The CaCO_3 particles have near nano-size distribution and hence can be more homogeneously dispersed in the polymer matrix. These nanofillers create a tortuous pathway, making it difficult for the water molecules to diffuse through the composite system. Nano-size fillers have been reported to reduce the water absorption.^[132,141,142]

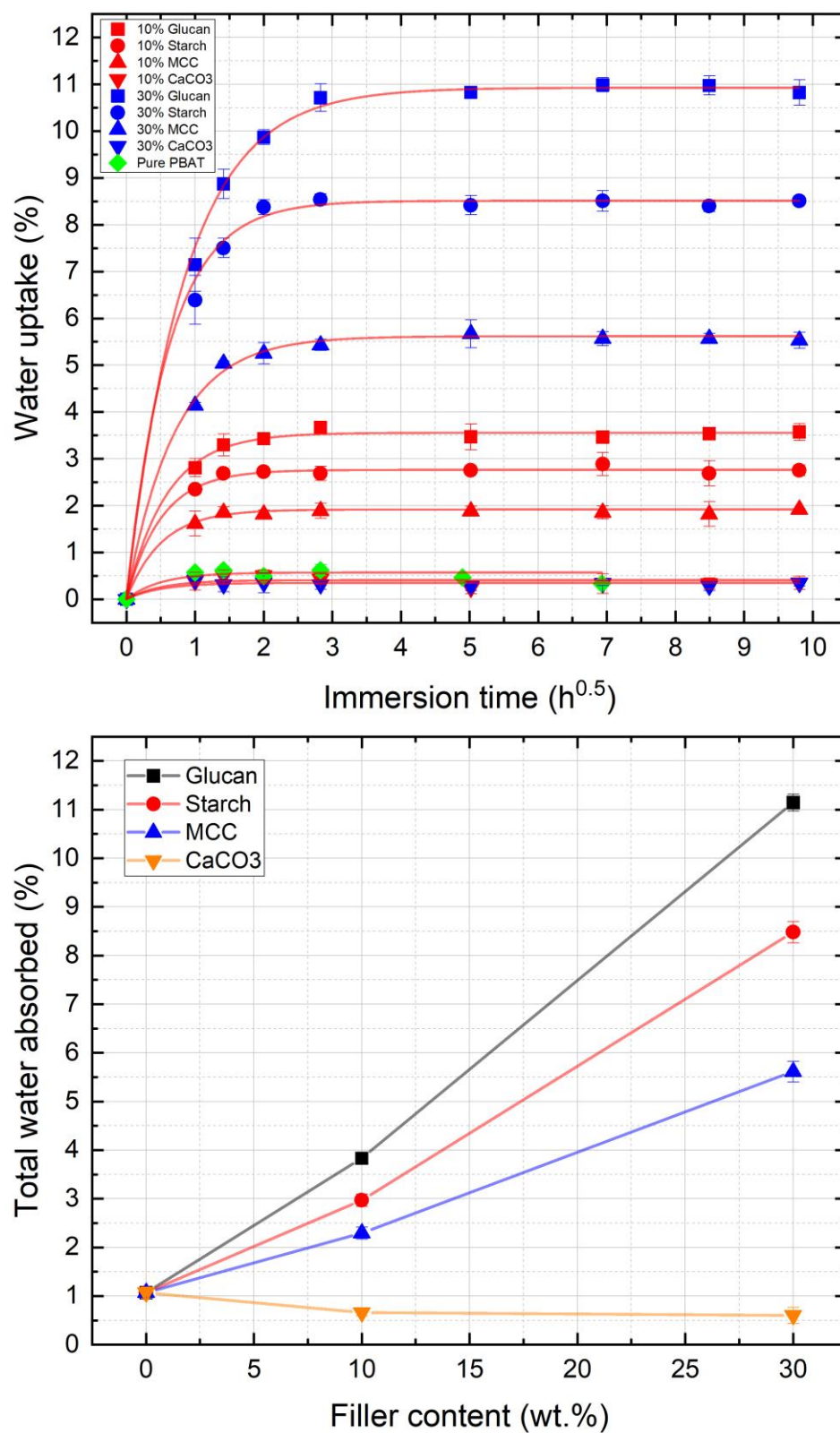


Figure 79. Amount of water absorbed at different times (top) and total amount of water absorbed (bottom) by PBAT composites with different fillers

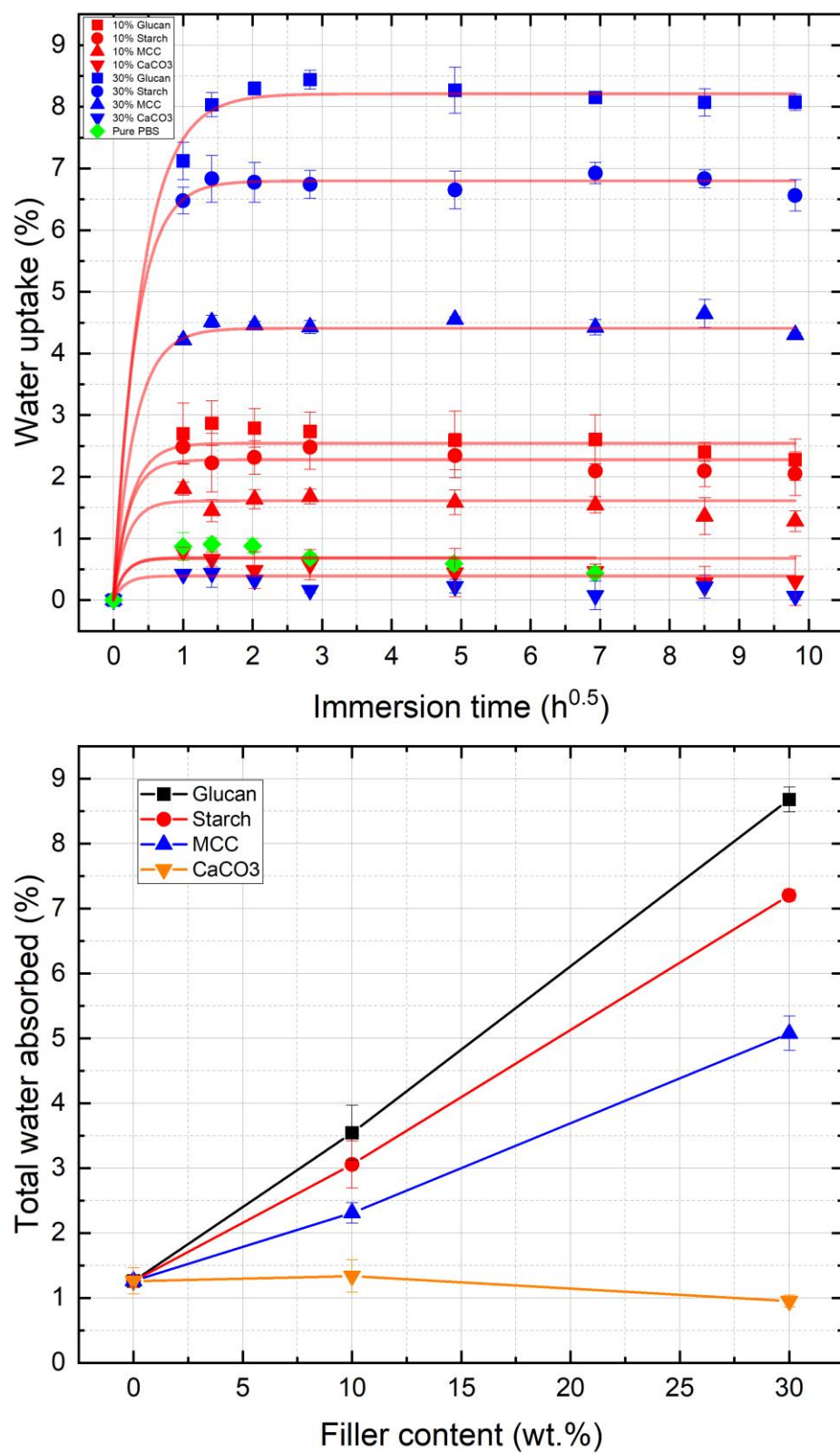


Figure 80. Amount of water absorbed at different times (top) and total amount of water absorbed (bottom) by PBS composites with different fillers

6.2.3. Thermal properties

The TGA and DTG curves for the PBAT and PBS composites with different fillers are shown in Figures 81 and 82, respectively. The polysaccharides showed an earlier onset of degradation in comparison to the PBAT and PBS. The starch showed the lowest onset of degradation and peak degradation temperature, while the α -1,3-glucan and MCC had a similar onset of degradation temperature. The composites with the MCC had a slightly higher peak degradation temperature than the α -1,3-glucan counterpart. The thermal degradation pattern for different filler materials obtained from this research are similar to what is reported in the literature. Spada et al. investigated thermal stability of cassava starch and reported that the degradation of starch peaked at close to 300°C.^[143] A report by Izzati et al. shows that depending on the brand of MCC, the degradation peak can be anywhere from 300 to 360°C, which aligns with the results obtained in this section.^[144] Qi et al. tested PBAT films that contain calcium carbonate and noted that the degradation continued beyond 500°C when CaCO₃ was present.^[145]

The difference in the onset of degradation temperature between the polysaccharides may be attributed to the different levels of crystallinity. The starch typically has the lowest crystallinity while the MCC has the highest, and the α -1,3-glucan somewhere between the starch and MCC. The inorganic filler CaCO₃ showed significantly higher degradation temperature than the base polymer, therefore no early onset of degradation before the PBAT was observed. The different levels of fillers in the composites were reflected by the degradation peak intensities in the DTG plot.

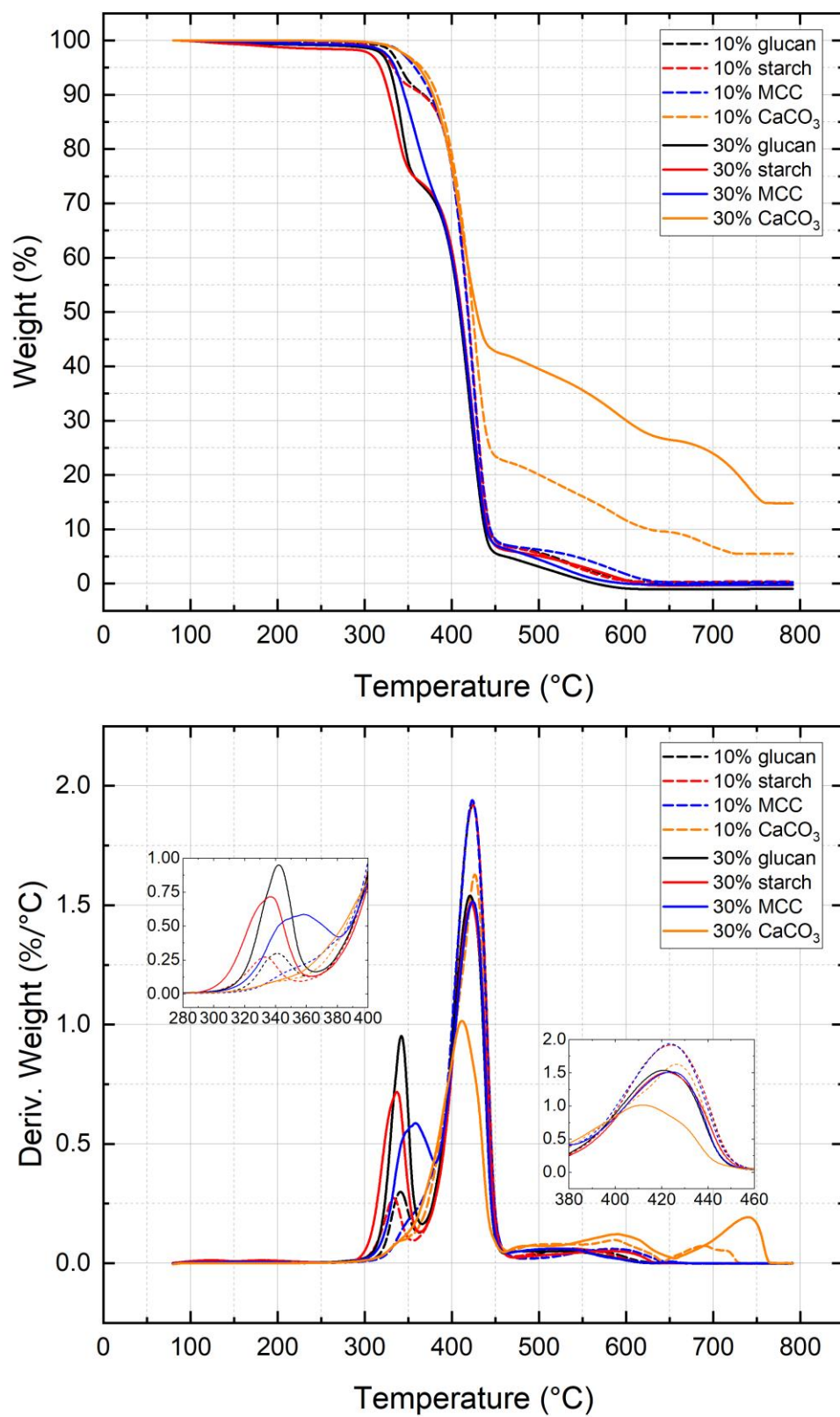


Figure 81. TGA (top) and DTG (bottom) curves for PBAT composites with different fillers

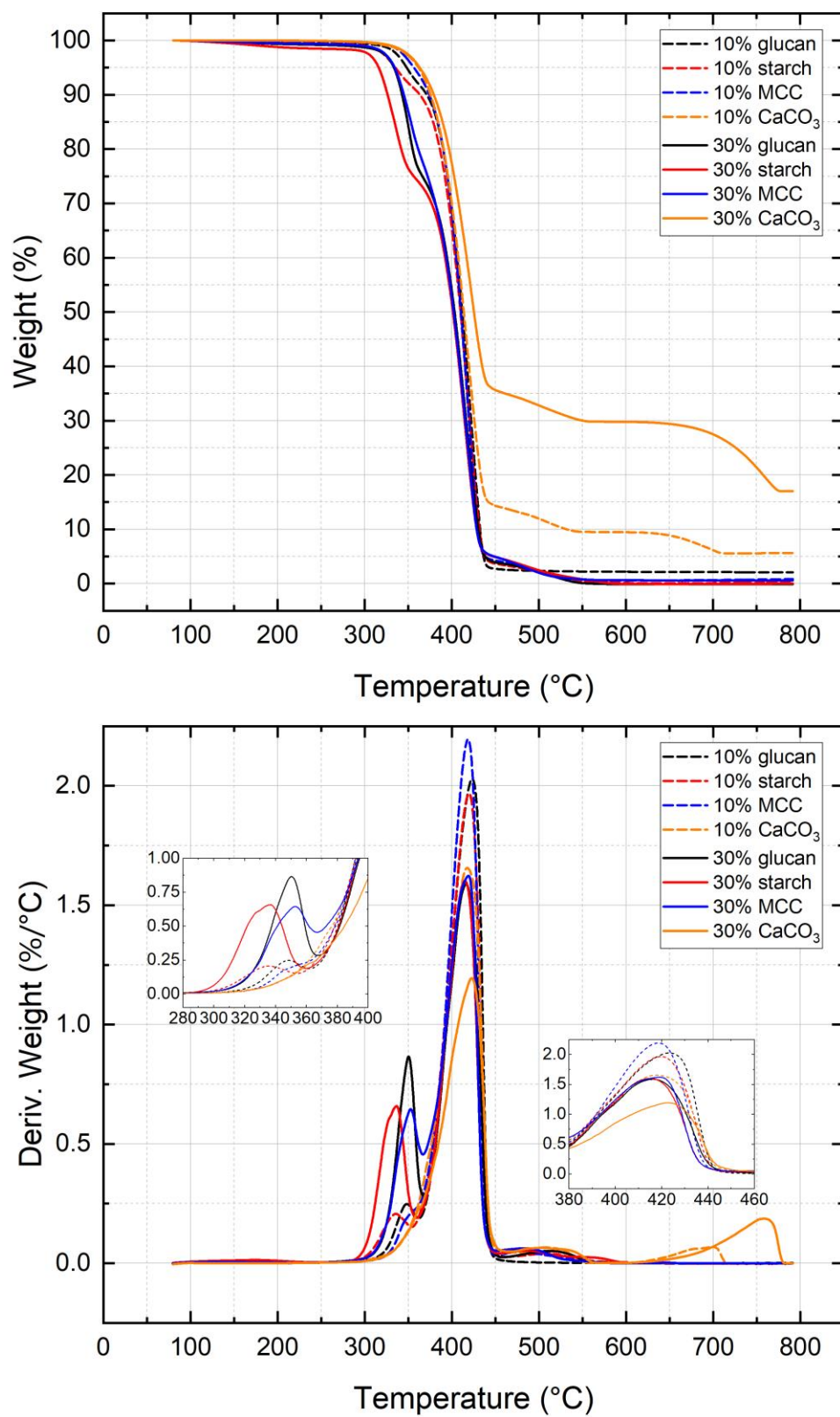


Figure 82. TGA (top) and DTG (bottom) curves for PBS composites with different fillers

The DSC curves for PBAT and PBS composites are summarized in Figures 83 and 84, respectively. As seen from sections 4.3.3. and 6.1.1., it was observed that the fillers shifted the crystallization temperature higher. Increasing the filler concentration from 10 to 30 wt.% did not significantly change the crystallization temperature. The melting temperature remained mainly unchanged as the filler type and concentration changed in both PBAT and PBS composites. The change in crystallization and melting temperatures are tabulated in Table 22 for the PBAT composites and Table 23 for the PBS composites.

Table 22. DSC analysis results for PBAT composites with different fillers

Filler (wt.%)	Filler type	T _c (°C)	T _m (°C)	X _c (%)
0	N/A	54.5	118.9	11.4
10	α -1,3-glucan	71.3	120.1	10.0
	Cassava starch	68.2	120.1	10.5
	MCC	72.4	120.7	10.0
	CaCO ₃	72.1	120.1	10.2
30	α -1,3-glucan	73.4	120.5	10.1
	Cassava starch	66.9	120.3	11.7
	MCC	77.3	121.8	8.7
	CaCO ₃	73.1	120.2	10.5

Table 23. DSC analysis results for PBS composites with different fillers

Filler (wt.%)	Filler type	T _c (°C)	T _m (°C)	X _c (%)
0	N/A	32.8	87.5	17.3
10	α -1,3-glucan	46.0	86.3	18.5
	Cassava starch	45.8	86.2	18.0
	MCC	48.3	86.3	18.1
	CaCO ₃	48.5	86.4	19.1
30	α -1,3-glucan	42.5	86.0	20.1
	Cassava starch	41.6	85.6	19.0
	MCC	46.5	86.2	20.2
	CaCO ₃	44.7	86.6	19.0

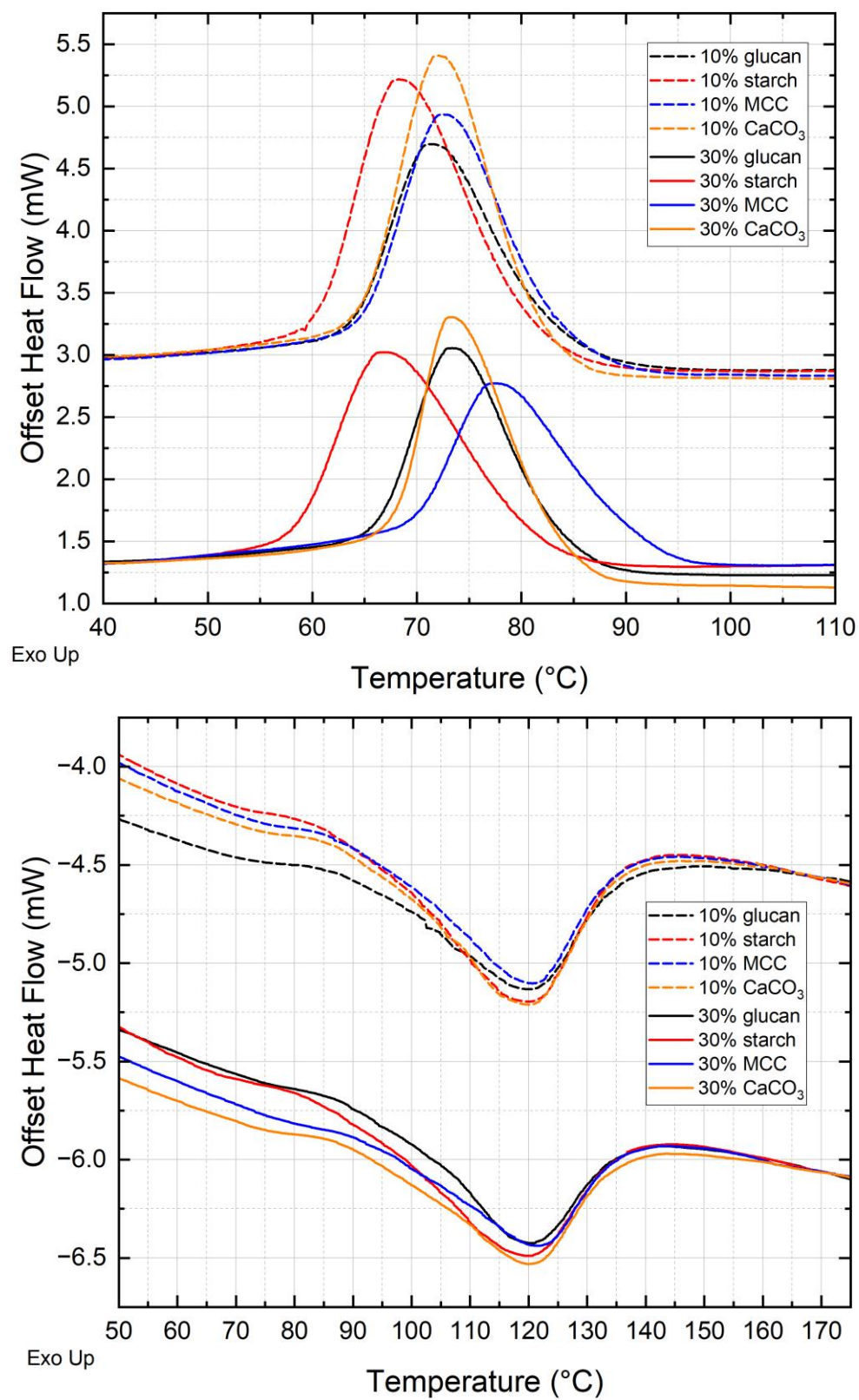


Figure 83. First cooling cycle (top) and second heating cycle (bottom) for PBAT composites with different fillers

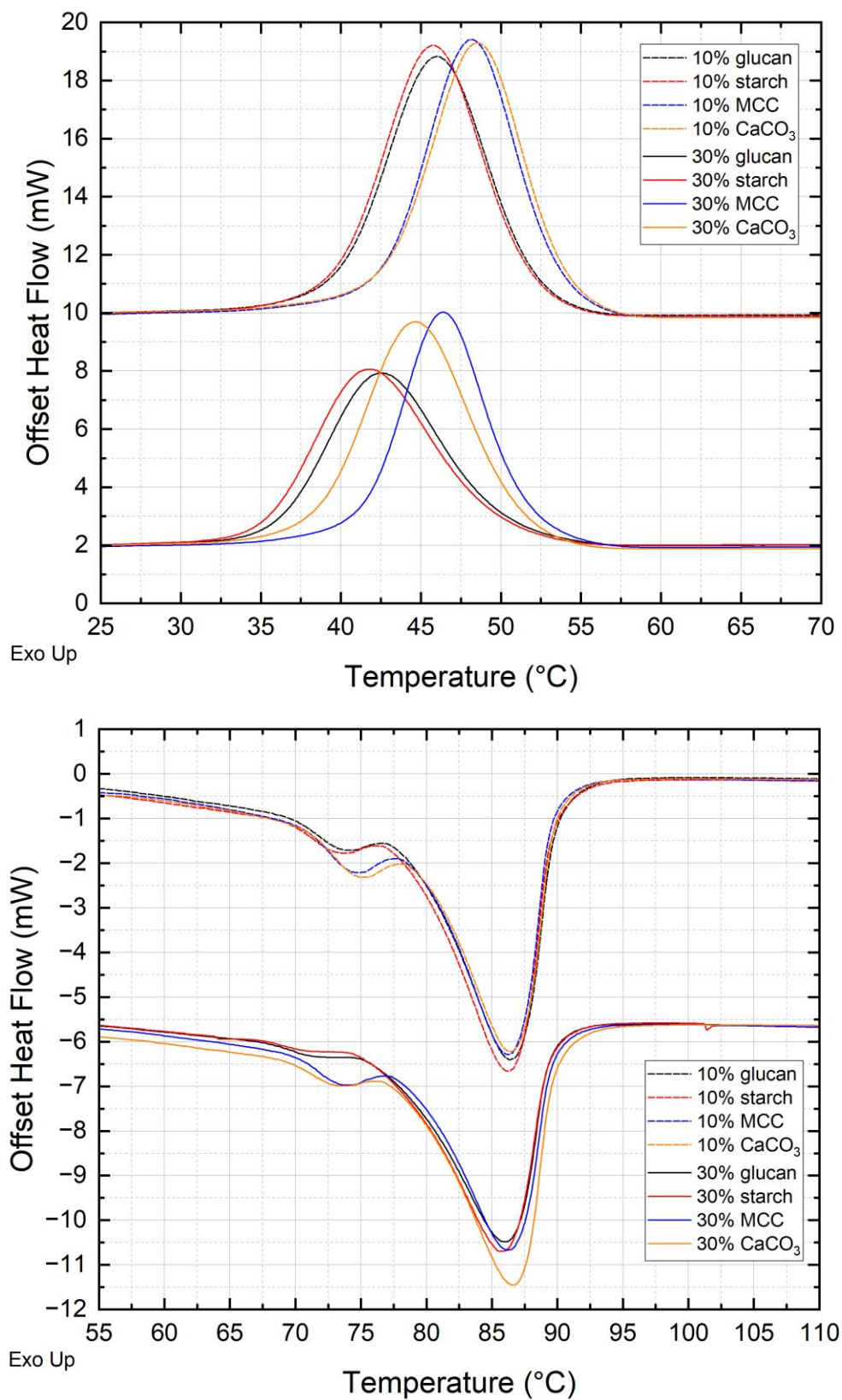


Figure 84. First cooling cycle (top) and second heating cycle (bottom) for PBS composites with different fillers

6.3. Conclusions

In this chapter, the use of α -1,3-glucan as a filler material for PBAT and PBS thermoplastics was investigated. A high filler loading of 70 wt.% was achieved for both the PBAT and PBS systems using the extrusion method. Much like what was observed from the previous chapters with TPU experiments, the addition of α -1,3-glucan led to improvements in strength and modulus of the PBAT and PBS systems. The hydrophilic nature of α -1,3-glucan increased the composites affinity towards water as expected. This can be an advantage in an application where quick and timely biodegradation of the composite material is desired since the water can easily diffuse into the composite system and eventually lead to degradation. Other conventional fillers, specifically starch, microcrystalline cellulose, and calcium carbonate, were compared to the α -1,3-glucan. The results demonstrate that the α -1,3-glucan is competitive as a filler compared with the other fillers.

CHAPTER 7:

MATERIALS AND METHODS –

SPRAY DRYING

7.1. Materials

An α -1,3-glucan with 43 wt.% solids content, also referred to as wet cake, was provided by IFF. The wet cake was stored in the refrigerator at 4°C. The difference between the α -1,3-glucan powder used in the previous chapters and the wet cake is that the wet cake is the final product of the enzymatic polymerization of α -1,3-glucan. Further drying, milling, and filtration of the wet cake eventually leads to the dry powder form of α -1,3-glucan (such as the D05 and D15 grades) that was used in the previous chapters.

7.2. Methods

7.2.1. Sample preparation

The wet cake was added to deionized water such that 10 wt.% overall solids content was achieved. The mixture was then homogenized using the Fisherbrand™ 850 Homogenizer (Thermo Fisher Scientific) to create a stable dispersion, denoted as a slurry. The wet cake and deionized water mixture was homogenized for 10 minutes at 10 000 rpm with 1 minute pause for every 2 minutes of homogenizing to prevent overheating. When preparing slurries with concentration of less than 10 wt.%, the 10 wt.% slurry that had been homogenized was diluted by adding prescribed amounts of deionized water to achieve the desired dilution level. The diluted samples were further homogenized for an additional 5 minutes to ensure adequate dispersion of the α -1,3-glucan solids in water were achieved.

7.2.2. Spray drying

The spray drying was conducted using the B-290 Mini Spray Dryer (BÜCHI Corporation) with a nozzle tip diameter of 0.7 mm and a standard cyclone vessel. The schematic diagram of the spray dryer is shown in Figure 85. The main parameters to adjust were slurry concentration, sample feed pump rate, gas flow rotameter height, and drying temperature. The levels of each parameter are listed in Table 24. The principal fraction of the half-factorial design with four parameters ($\frac{1}{2} 2^4$

design) and 3 centre point replicates was used to study the effects (Table 25) of drying conditions on the particle size distribution.

Table 24. Half 2^4 factorial design factors for the spray drying experiment

Factor		-	0	+
A	Slurry concentration (wt.%)	1	5.5	10
B	Pump rate ^a (%)	10	20	30
C	Rotameter height ^b (mm)	30	42.5	55
D	Temperature (°C)	180	195	210

^a 10%, 20%, 30% correspond to 3.0, 5.9, 9.0 mL/min, respectively.

^b 30, 42.5, 55 mm correspond to 357, 505, 670 L/h, respectively.

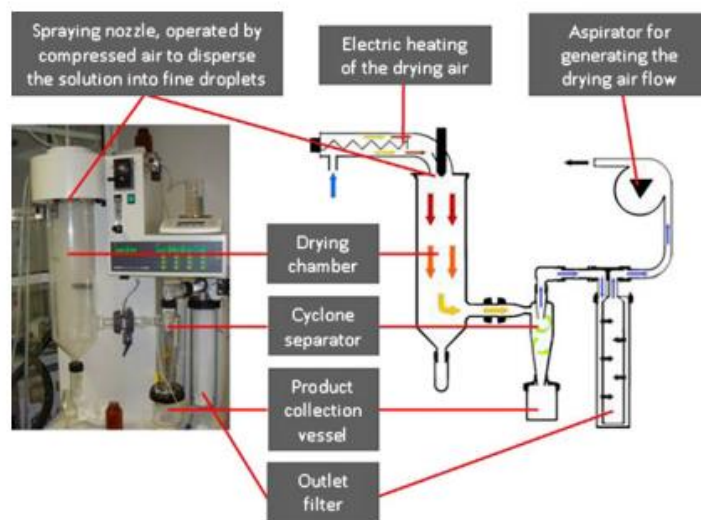


Figure 85. Schematic representation of the spray-drying process. Reproduced with permission from Springer Nature^[146]

Table 25. The principal fraction of the half 2^4 factorial design with three centre point replicates

Standard Order	Factor A	Factor B	Factor C	Factor D
1	-	-	-	-
2	+	-	-	+
3	-	+	-	+
4	+	+	-	-
5	-	-	+	+
6	+	-	+	-
7	-	+	+	-
8	+	+	+	+
9	0	0	0	0
10	0	0	0	0
11	0	0	0	0

The conversion from the rotameter height to the gas flow rate and pressure drop is tabulated in Table 26. Boyle's law was used to calculate the actual gas flow rate at standard temperature and pressure (STP; 273.15 K and 1 bar).

$$P_1 V_1 = P_2 V_2$$

$$(P_2 + \Delta P) V_1 = P_2 V_2$$

$$V_2 = \frac{(P_2 + \Delta P) V_1}{P_2}$$

At STP and using Q as the volumetric flow rate, the equation simplifies to:

$$\text{Actual flow rate } (Q_2) = (1 + \Delta P) Q_1 \quad (5)$$

Table 26. Conversion table for rotameter height and the gas flow rate

Height (mm)	Gas flow (L/hr)	Pressure drop (bar)	Actual flow at STP (L/hr)
5	84		
10	138		
15	192		
20	246	0.15	283
25	301	0.18	355
30	357	0.23	439
35	414	0.3	538
40	473	0.41	667
45	536	0.55	831
50	601	0.75	1052
55	670	1.05	1374
60	742	1.35	1744
65	819	1.8	2293

The relationship between the feed flow rate and the pump rate is shown in Figure 86.

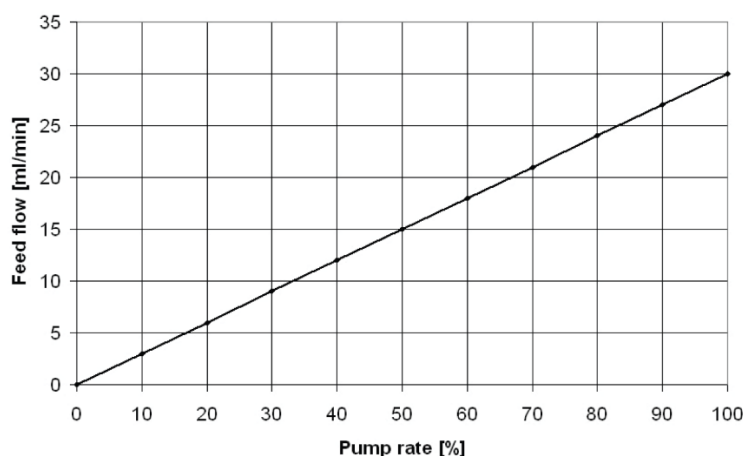


Figure 86. Sample feed flow rate vs. pump rate conversion

7.2.3. Scanning electron microscopy

The SEM technique was used to analyze the particle size using the Quanta FEG-250 SEM. The specimens were coated with a thin layer of gold using the Magnetron Sputter Coater before the SEM analysis. The SEM images for the analysis were taken at 500x magnification using the SE detector. The acceleration voltage of 15 kV was used for SEM scanning.

7.2.4. Particle size analysis

The SEM images were analyzed using the open-source Fiji software.^[147] An example of analyzing the particle size is shown in Figure 87.

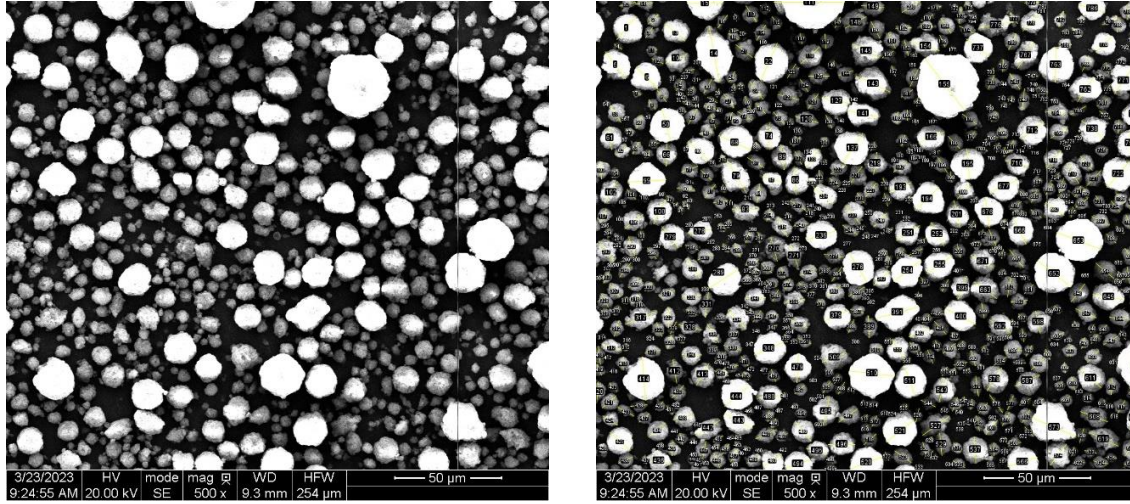


Figure 87. SEM image of the α -1,3-glucan particles before the image analysis (left), and after the image analysis (right)

The number average diameter was calculated using:

$$d_N = \frac{\sum_{i=1}^n d_i}{n} \quad (6)$$

The yield was analyzed by calculating the difference between the actual amount of the sample collected versus the initial amount of solids in the slurry.

CHAPTER 8:

RESULTS AND DISCUSSIONS –

SPRAY DRYING

In this chapter, the spray drying technique was investigated to prepare a powder with smaller α -1,3-glucan particles. The wet cake is α -1,3-glucan that has not been dried yet, with moisture content of about 53 wt.%. The D05 and D15 α -1,3-glucan powders used in previous chapters are obtained by drying the wet cake in the oven. The dried wet cake aggregates into large particles as the moisture is removed, thus mechanical grinding and sieving is necessary to obtain α -1,3-glucan particles with specific average particle size. In this approach, the α -1,3-glucan is strategically prepared before the processing step such that the smaller particle size is achieved. The spray drying method is commonly used to prepare starch, cellulose and protein samples, but there are currently no literature that discuss spray drying for α -1,3-glucan particles.^[146,148–153] Amaro et al. and Bilancetti et al. investigated methods to optimize the spray drying process to reduce the processing time and the particle size of sugar and starch samples.^[146,149] Since spray drying is one of the faster drying methods, investigating ways to prepare α -1,3-glucan via spray drying will provide insight on different particle size that can be obtained. The reduction of particle size is desirable to produce thin films that can be used for packaging applications.

8.1. Particle Size Distribution

The particle size distribution was measured using image analysis. The SEM images of the particles from the half-factorial design are shown in Figure 88. Each SEM image was processed using the Fiji software to measure the individual particle diameter.

The number average particle size was calculated using the Equation (6). The size distribution, as well as the cumulative frequency was plotted on a log-scale, as shown in Figure 89. The data were well fitted with a log-normal distribution curve, represented as the solid red curve in Figure 89. The particle size distribution results are summarized in Table 27. The d_{10} , d_{50} , and d_{90} corresponds to the number average particle diameter that represents the first 10%, 50%, and 90% of the sample population, respectively.

Table 27. Particle size analysis result for the half 2^4 factorial design

StdOrder	A	B	C	D	d_{10}^a (μm)	d_{50}^b (μm)	d_{90}^c (μm)	d_N^d (μm)	σ^e (μm)
1	-	-	-	-	1.18	2.81	6.66	3.44	2.34
2	+	-	-	+	2.36	5.29	11.88	6.29	3.92
3	-	+	-	+	2.10	4.15	8.20	4.75	2.60
4	+	+	-	-	2.42	5.42	12.10	6.51	4.14
5	-	-	+	+	0.85	1.85	4.02	2.26	1.65
6	+	-	+	-	1.34	3.04	6.86	3.68	2.44
7	-	+	+	-	1.02	2.21	4.78	2.68	1.88
8	+	+	+	+	1.35	3.10	7.11	3.78	2.54
9	0	0	0	0	1.27	2.95	6.85	3.65	2.50
10	0	0	0	0	1.28	2.89	6.55	3.53	2.38
11	0	0	0	0	1.40	3.00	6.40	3.54	2.19
D05	N/A				1.93	3.80	7.53	4.29	2.20
D15					3.21	7.01	15.35	8.53	5.73

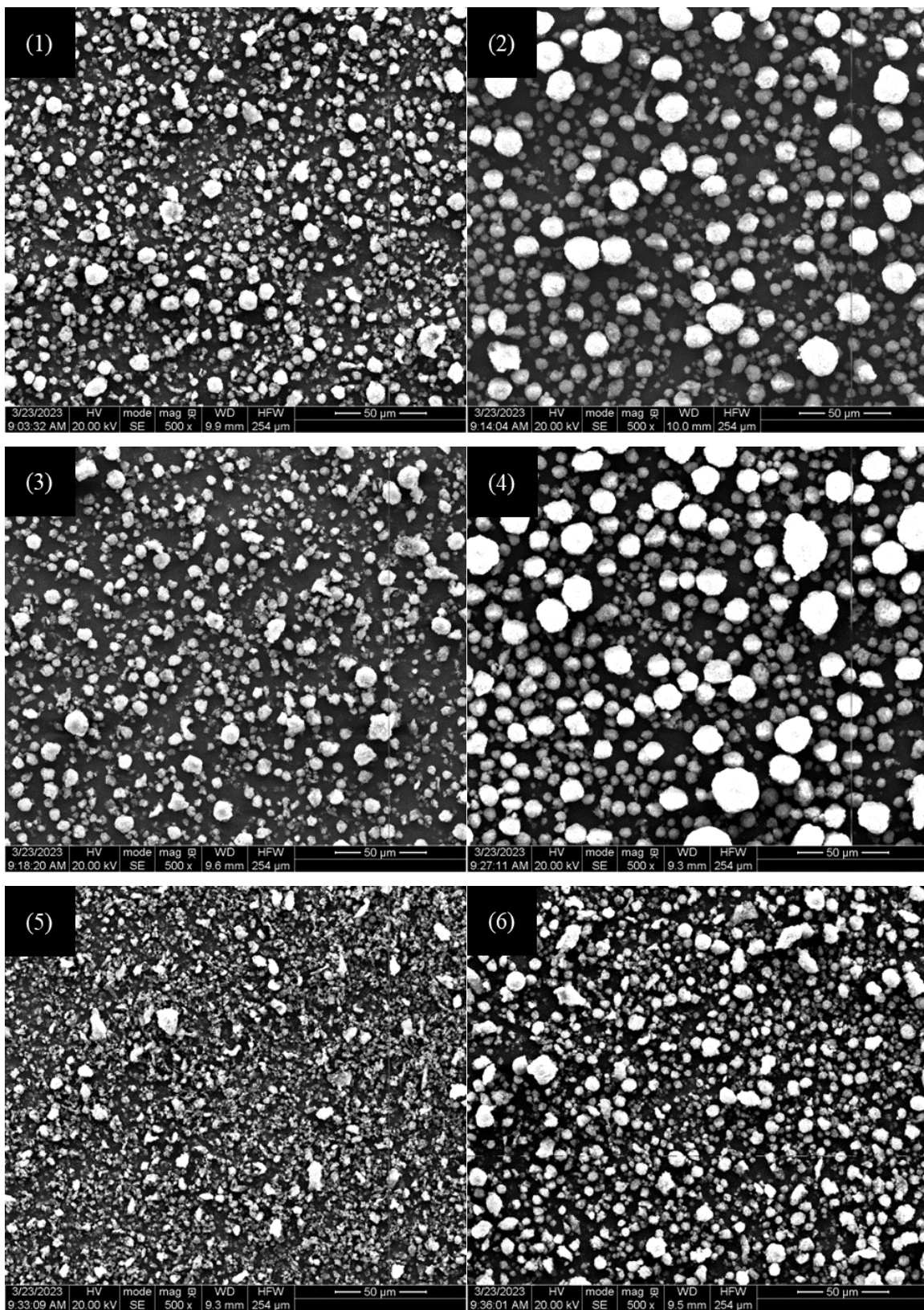
^a Number average particle diameter that represents the first 10%

^b Number average particle diameter that represents the first 50%

^c Number average particle diameter that represents the first 90%

^d Number average particle diameter

^e Standard deviation



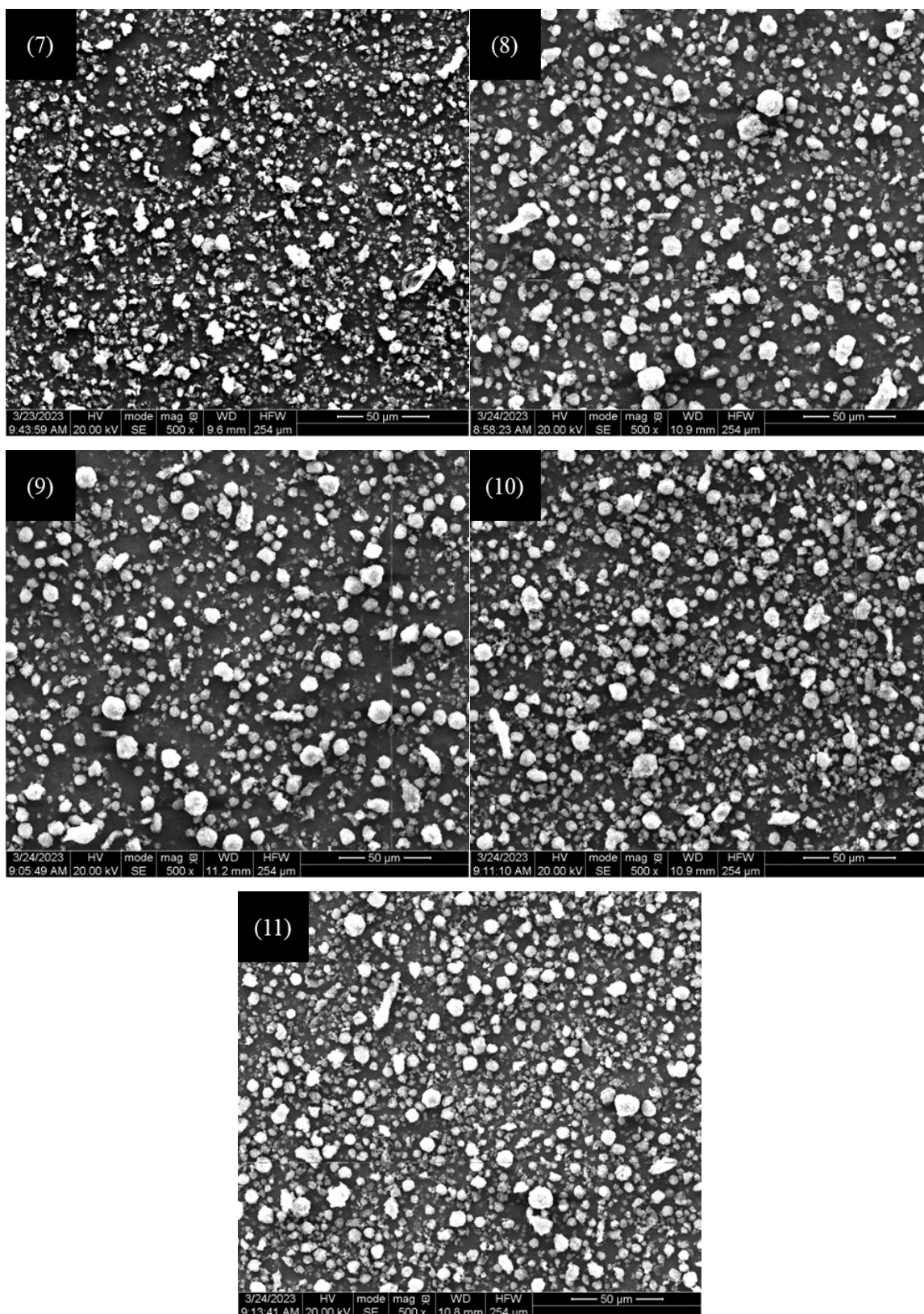
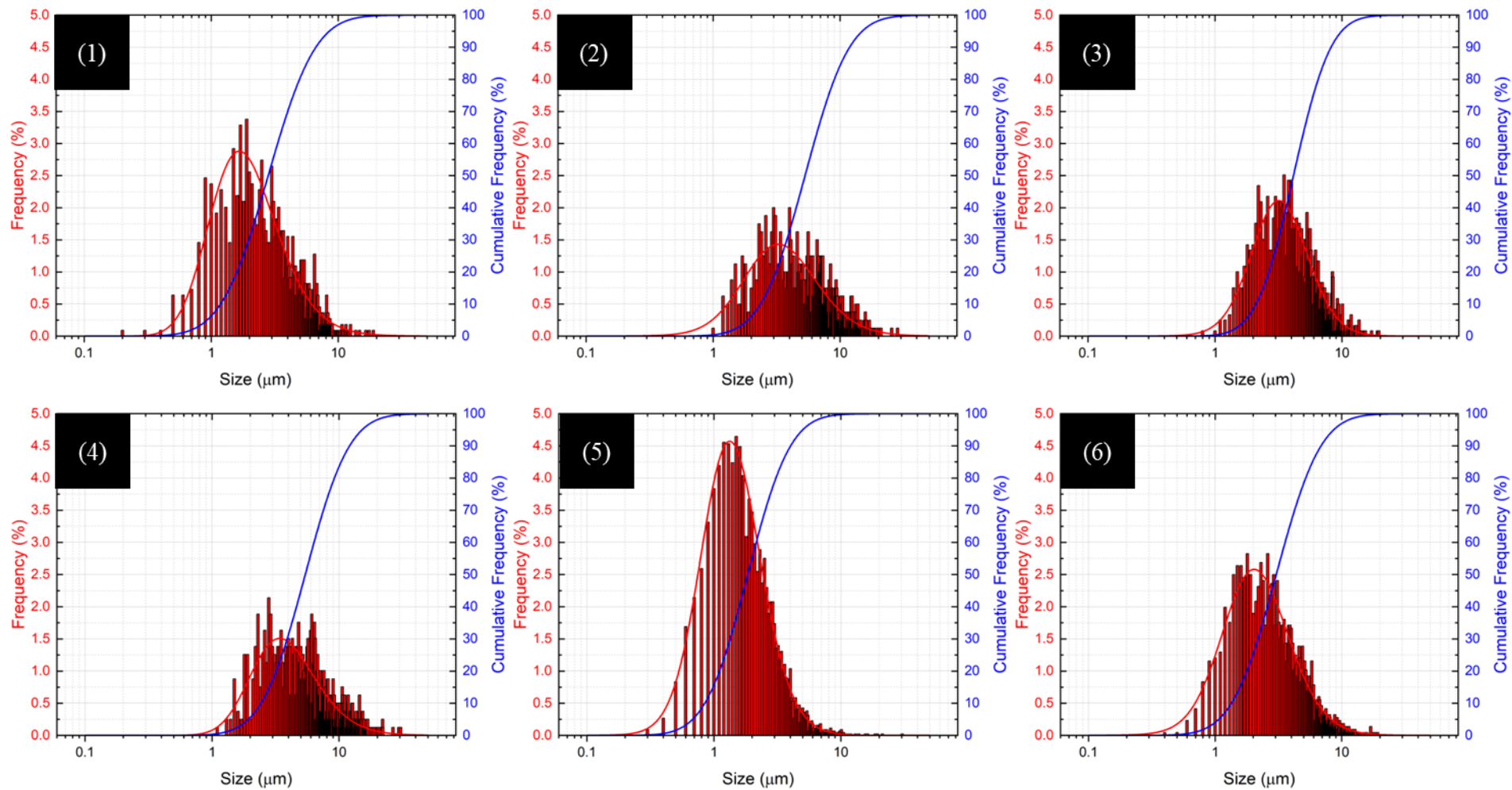


Figure 88. SEM images of the spray dried α -1,3-glucan particles; the number in the top left corner corresponds to the standard order of the principal fraction from Table 25



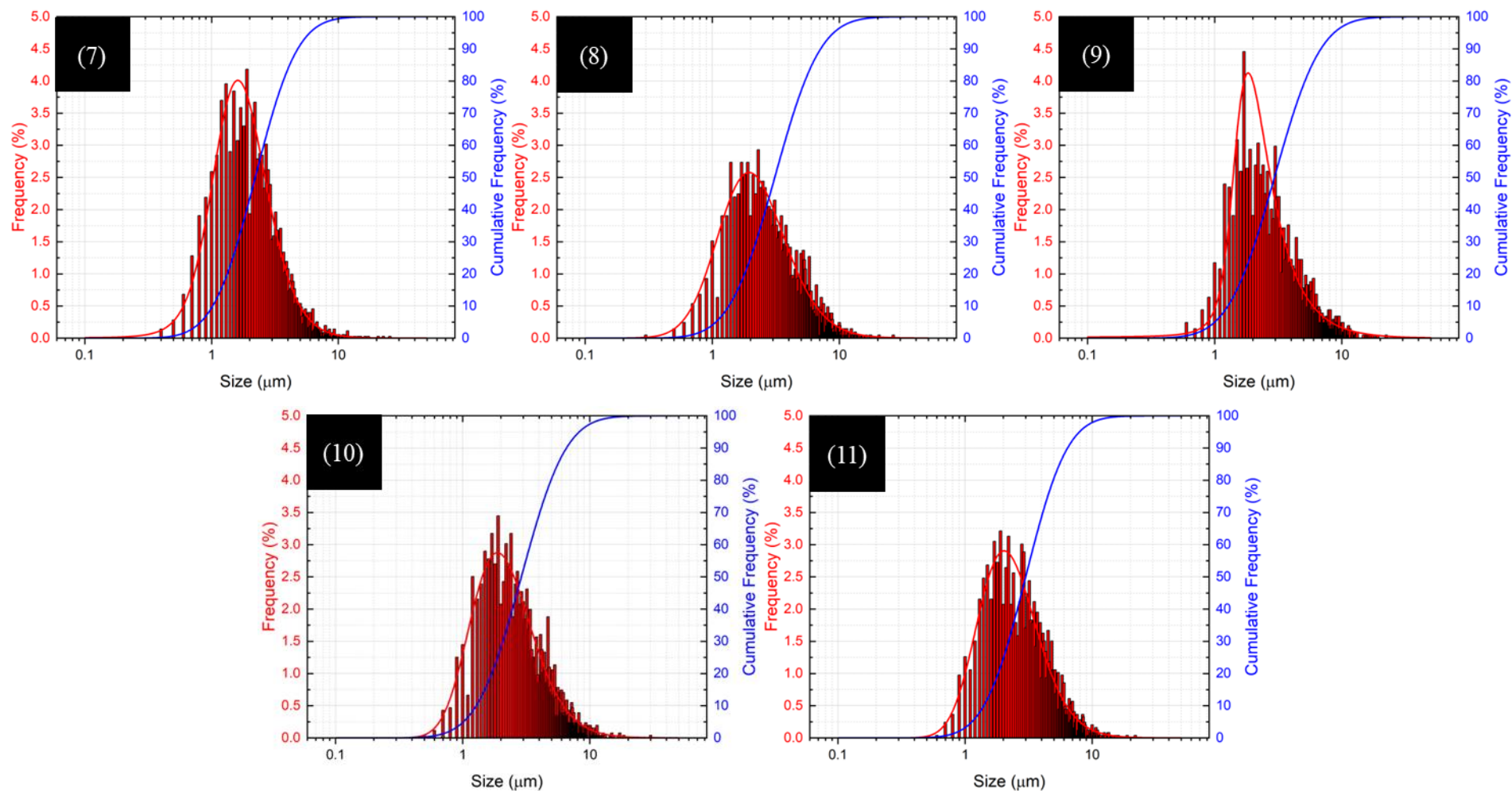


Figure 89. Particle size distribution and cumulative number frequency of the spray dried α -1,3-glucan particles; the number in the top left corner corresponds to the standard order of the principal fraction from Table 25

To compare the spray drying results, the size distribution of the particles of the D05 and D15 α -1,3-glucan samples was also measure and calculated. These two samples were dry powders provided by IFF. The distribution plot is shown in Figure 90, and the values are tabulated on the bottom rows of Table 27.

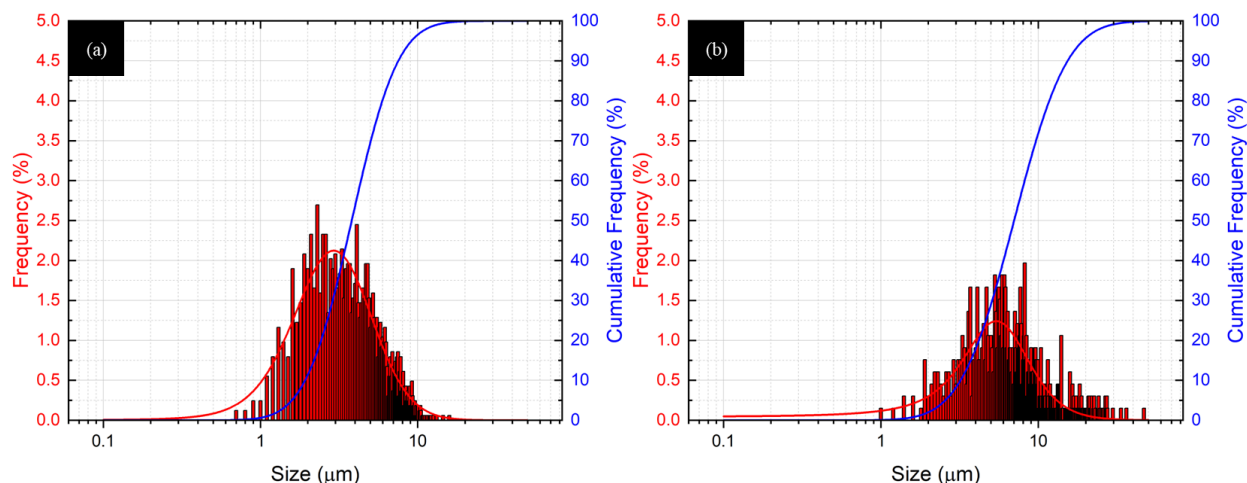


Figure 90. Particle size distribution and cumulative number frequency of (a) D05 α -1,3-glucan and (b) D15 α -1,3-glucan

The Minitab software was used to analyze the DOE. The normal probability plot of the effects was used to identify the most significant factors that influence the average particle size and the yield (Figures 91 and 93). The number average diameter was mostly affected by the slurry concentration and the rotameter height (gas flow rate), based on the normal plot shown in Figure 91. The concentration has a positive effect, indicating that the particle size would increase if the concentration increased. Conversely, the rotameter height has a negative effect, thus increasing the rotameter height would decrease the particle size. Since the goal is to minimize the average particle size, decreasing the slurry concentration and increasing the rotameter height, and therefore the gas flow rate, will produce the smallest particle size distribution.

The main effects for the average particle size are summarized in Figure 92. Though not significant, the plots show that decreasing the pump rate and the temperature will decrease the average particle size as well.

There are several literatures that report the change in the spray dried particle size based on the spray drying conditions, where lowering the feed concentration, decreasing the feed rate,

increasing the gas flow, and decreasing the inlet temperature all contributed to the reduction of particle size.^[148–152] By reducing the concentration of the feed solution, the number of particles that can be present in a droplet formed by the atomizing gas will be less, which reduces the effect of agglomeration. Elversson et al. reported that the increased atomizing gas flow increased the relative motion between the surface layer of the liquid and the air producing kinetic energy for disintegration.^[152] As a result, smaller droplets are formed at the nozzle, which increased the air-liquid surface area of the droplets. The feed rate also influences the droplet size, where an increase in the pump setting, or the feed flow rate, resulted in larger spray droplets, thus larger particles.^[149] The effect of the inlet temperature varied with literature. In most cases, the inlet temperature had no significant effect on the particle size, while some reported an increase in particle size as the temperature increased as a result of agglomeration and hardening of the droplet.^[151]

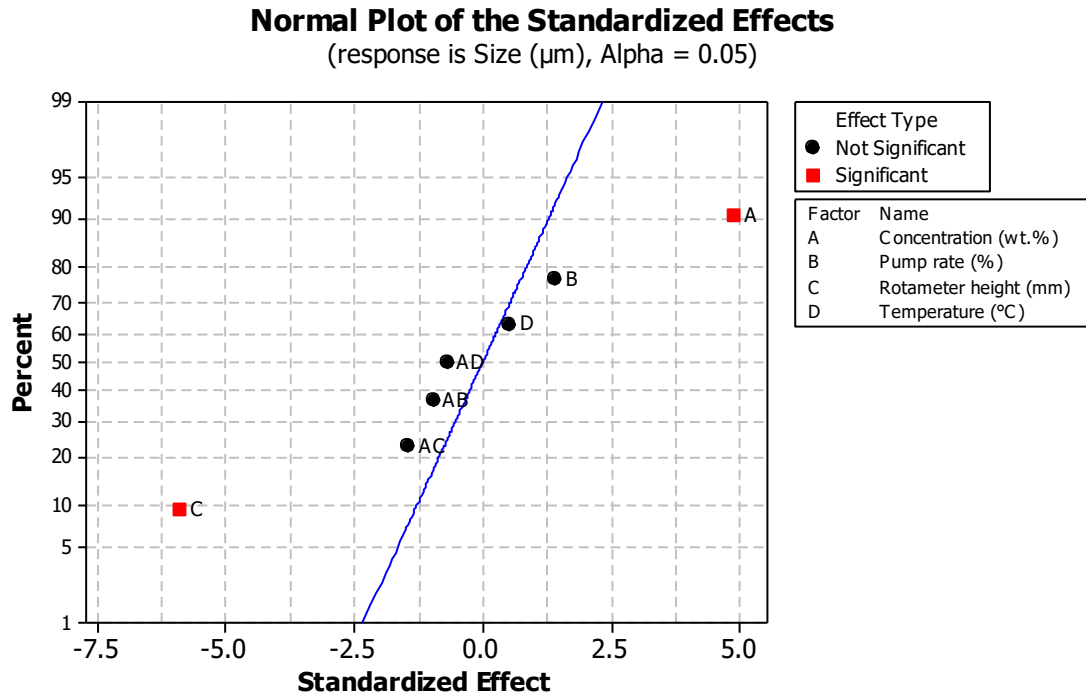


Figure 91. Normal probability plot of the DOE with number average particle size (μm) as response

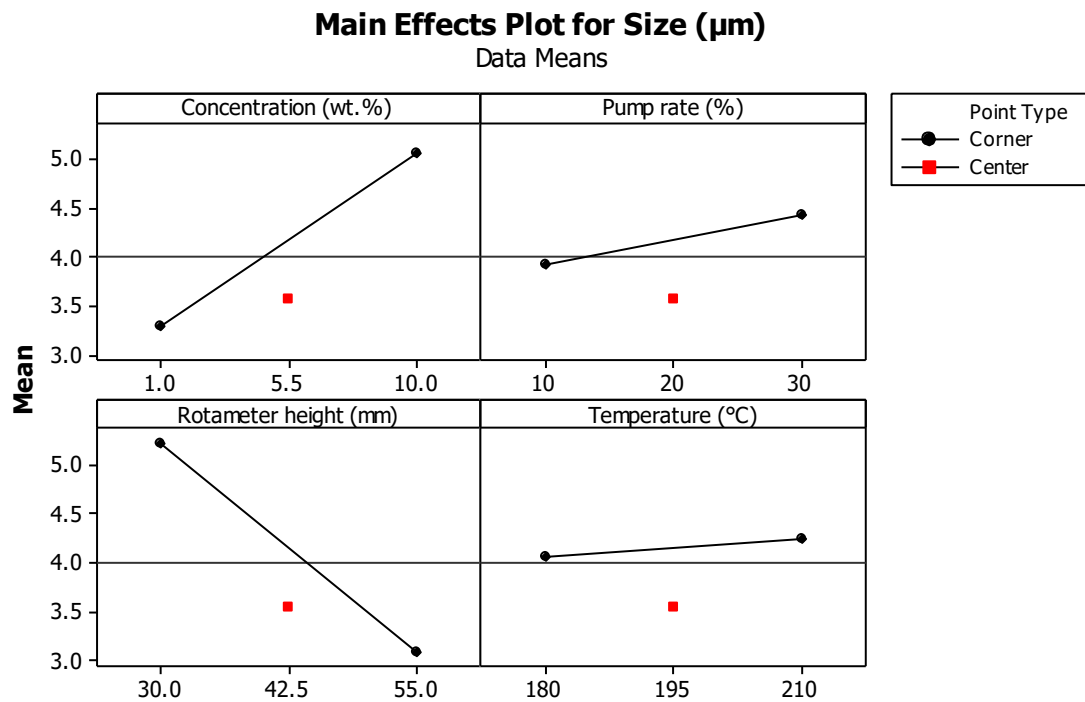


Figure 92. Main effects plot for number average particle size (μm)

The spray drying yield is another response that relates to the overall process efficiency and production rate (yield). The normal probability plot of the yield in Figure 93 shows that the slurry concentration and the pump feeding rate affected the yield significantly. Both parameters have a positive effect, thus increasing both the slurry concentration and the feeding rate will maximize the overall yield. However, based on the effect of the slurry concentration on the average particle size, increasing the concentration to increase the yield will produce larger particles, which creates room for optimization. The main effects for the yield are summarized in Figure 94. The approximate time required to obtain a total of 100 g of dried wet cake is shown in Figure 95.

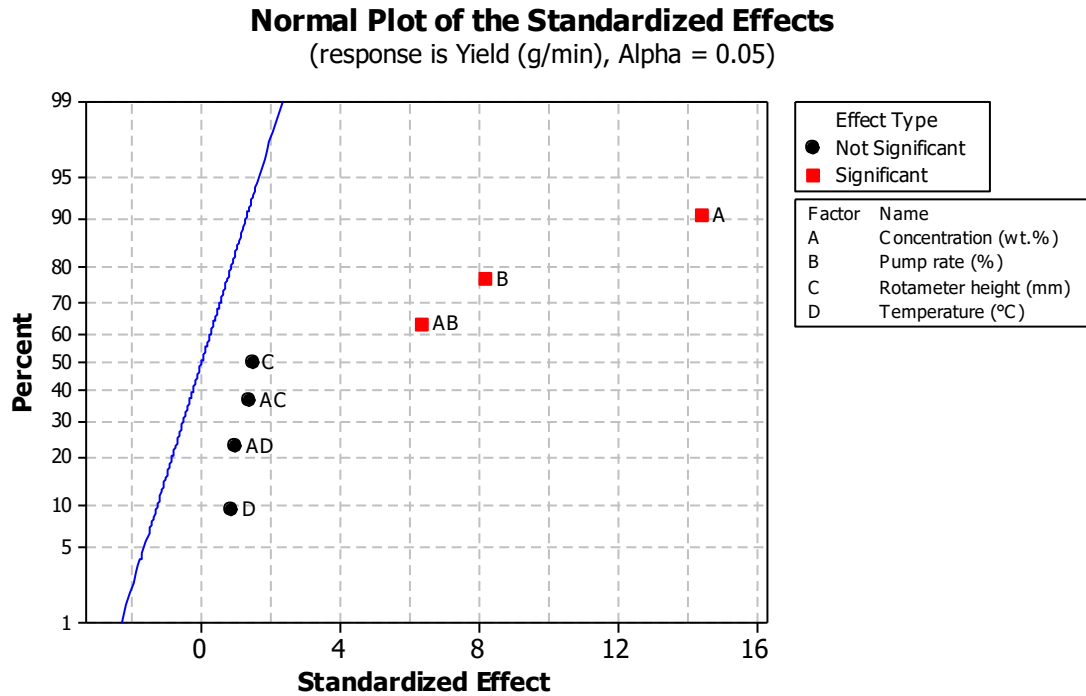


Figure 93. Normal probability plot of the DOE with yield (g/min) as response

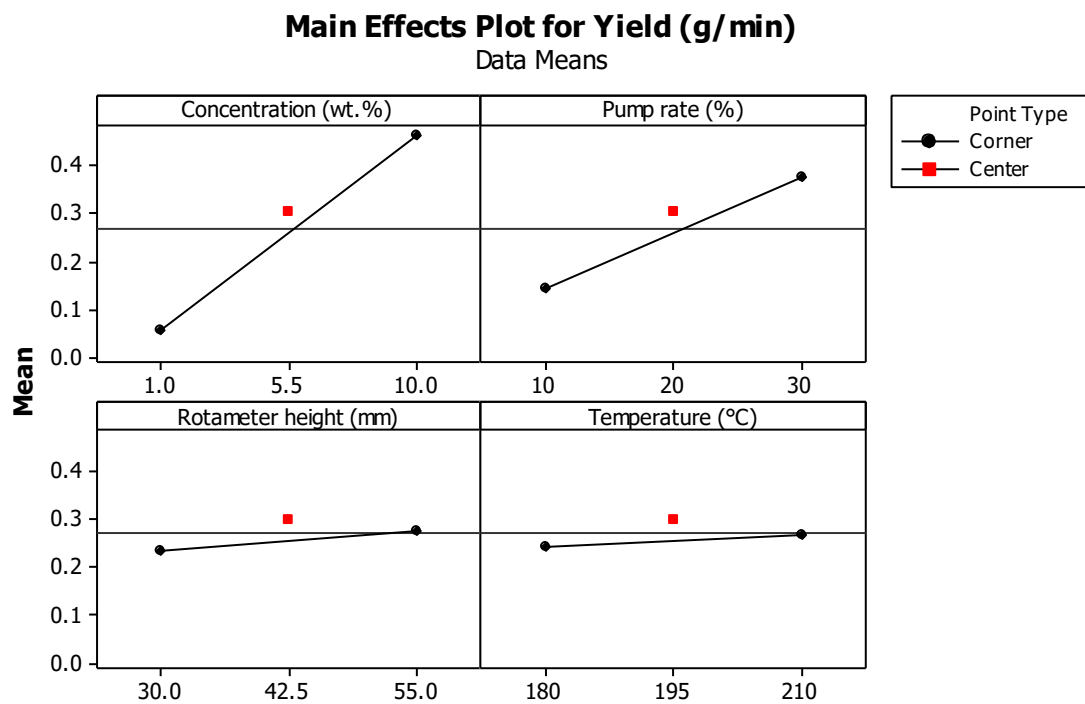


Figure 94. Main effects plot for yield (g/min)

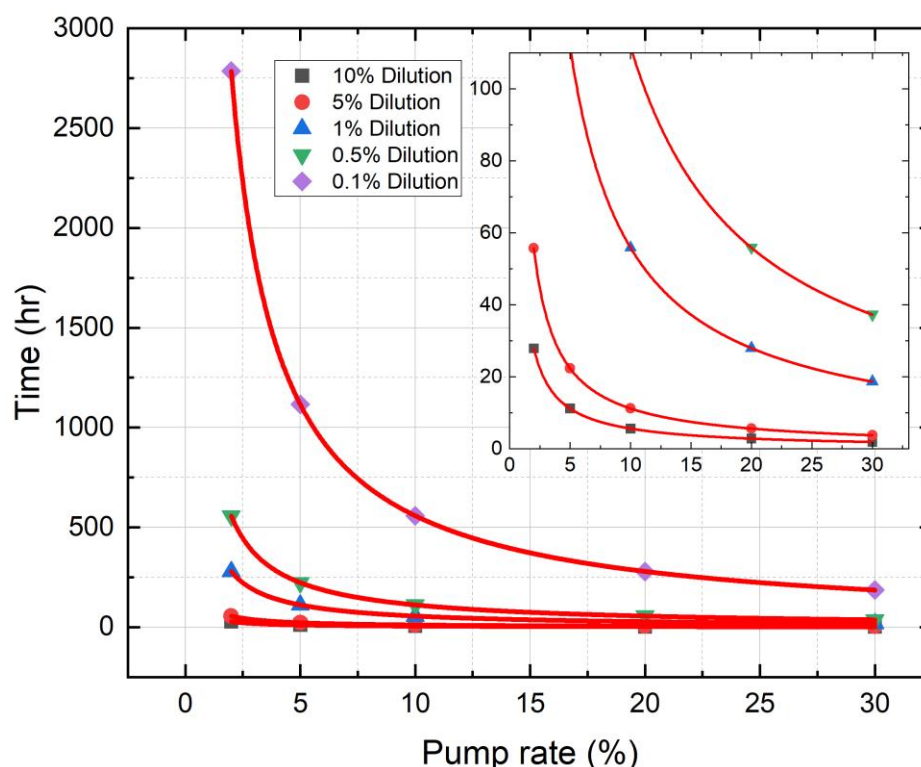


Figure 95. Spray drying time as a function of pump rate to dry 100 g of wet cake solids

Ideally, selecting the lowest slurry concentration and the pump rate will produce the smallest particles, but the time required increases exponentially when the pump rate goes below 10%. The advantage of using the spray dryer is the time that is required to process the samples, so selecting conditions that requires more than 100 hours for 100 g of sample would be counter productive. Based on the plots, increasing all four spray drying parameters will result in a higher yield. The increase in yield when the feed rate was increased was observed by several authors.^[148,149,151] Since the high feed rate results in larger volume of solution being dispersed per unit time, the overall production rate increases. Likewise, increasing the slurry concentration meant more particles were being dried per unit time, thus increased the yield.

The plot in Figure 96 provides a different perspective on the yield and the average particle size. In Figure 96, the ideal operating range would be the upper left corner, where the sample collected per minute is maximized while keeping the particle size to a minimum. However, the factorial design revealed that in order to minimize the average particle size, the slurry concentration must be lowered, but that results in low yield. Therefore, this plot establishes essentially a boundary of yield versus the average particle size that can be theoretically obtained.

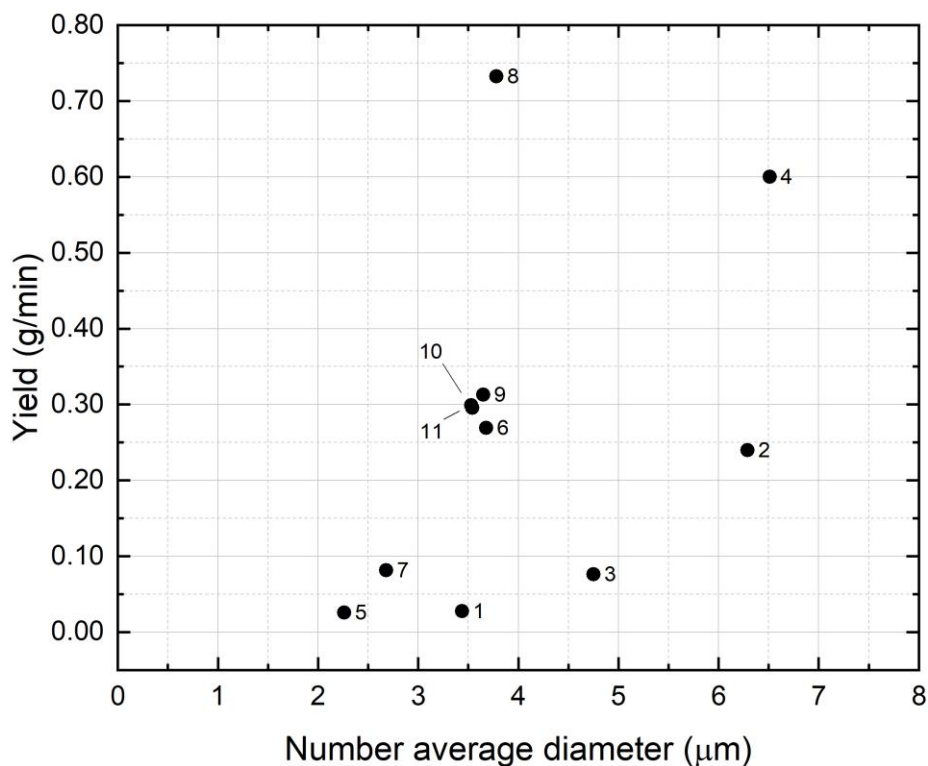


Figure 96. Spray drying yield vs. number average diameter; the numbers correspond to the standard order of the principal fraction from Table 25

8.2. Conclusions

In this chapter, the spray drying method was investigated as a method to prepare an α -1,3-glucan powder. The D05 and D15 α -1,3-glucan powders used from previous chapters for the TPU, PBAT, and PBS systems are obtained by drying the wet cake, followed by mechanical grinding and filtration to obtain a specific particle size distribution. The spray drying of the wet cake allows to by-pass the mechanical grinding step entirely, since a smaller particle size distribution can be achieved by altering the spray drying parameters. These preliminary spray drying experiments revealed that four parameters, sample concentration, feed rate, gas flow rate, and temperature play an important role in reducing the particle size. Specifically, the sample concentration and the gas flow rate had the biggest effect on the resulting particle size, with an average diameter of about 2 μ m.

CHAPTER 9:

CONCLUSIONS AND RECOMMENDATIONS

9.1. Contributions and summary

The objectives of this thesis were to evaluate the applications of the α -1,3-glucan particles as a reinforcing filler in different thermoplastic resins, specifically TPU, PBAT, and PBS. The new enzymatic polymerization technology allowed for the production of α -1,3-glucan with controlled molecular weight and no branching, making different batches to have consistent quality. Unlike starch and cellulose, the usage of α -1,3-glucan in different thermoplastics is minimal. This thesis serves as a first investigation on the preparation of TPU-, PBAT-, and PBS- α -1,3-glucan composites. A different method of producing the α -1,3-glucan powder was also investigated, with the goal of generating smaller average particle size using the spray dryer.

Chapter 2 presented relevant background information obtained from the literature. The concepts of polysaccharides, thermoplastics, and their applications were introduced.

Chapters 3 and 4 discussed the TPU and α -1,3-glucan composite materials and their performances. A highly filled TPU system was achieved with excellent modulus when α -1,3-glucan was used as a reinforcing filler. Different citrate-based plasticizers were used to improve the processability while DCP was added to improve the compatibility between the TPU and α -1,3-glucan.

Chapters 5 and 6 explored the PBAT- and PBS- α -1,3-glucan composites with varying α -1,3-glucan filler content from 0 to 70 wt.%. It was shown that α -1,3-glucan acted as a reinforcing filler as the concentration increased, while using PBAT as the base polymer offered greater flexibility and PBS offered more strength and stiffness. Different filler materials were compared with the α -1,3-glucan.

Chapters 7 and 8 investigated different drying technique to obtain the α -1,3-glucan powder using a spray dryer. Several drying conditions and parameters were methodologically adjusted to understand how they influence the particle size distribution and the yield.

9.2. Main conclusions

The α -1,3-glucan produced via enzymatic polymerization is an unbranched, free flowing polymer made from sucrose. It is a type of polysaccharide like starch and cellulose, that can be utilized as a filler material in different thermoplastics to reduce cost and improve properties. Mechanical analysis revealed that α -1,3-glucan successfully improved the stiffness and modulus of TPU, PBAT, and PBS. As well, it showed good thermal stability up to 250°C, which is beyond most thermoplastics processing conditions. Due to the hydrophilicity of the α -1,3-glucan, some incompatibility existed between the filler particles and the hydrophobic base polymer. DCP as a compatibilizer was investigated for the TPU system, and it showed some improvement in strength. The addition of α -1,3-glucan at a high concentration increased the water uptake and the water permeability of the films. Large affinity towards moisture and water may assist with natural biodegradation, but depending on the application of the composite materials, the moisture barrier property needs to be improved when large quantity of α -1,3-glucan is used. Overall, the α -1,3-glucan shows great potential as a filler material in different thermoplastics resins, as a large amount (up to 70%) can be incorporated without affecting the processing steps significantly. This is important since a high level of the α -1,3-glucan can reduce the cost of the material while improving the properties as a reinforcement.

When the thermoplastics and α -1,3-glucan were compounded together using an extruder, there were no signs of particle size reduction. Generally, the reduction of the particle size improves the mechanical properties and reactivity due to the increase in the surface area of the particles. To achieve smaller particles, different drying technique, specifically the spray drying technique, was investigated to produce smaller α -1,3-glucan particles. Upon initial assessment of the spray drying process using a half-factorial DOE approach, it was determined that a smaller particle distribution than the D05 or D15 α -1,3-glucan can be achieved by optimizing the spray drying parameters.

9.3. Recommendations

This project mainly focused on finding different applications of α -1,3-glucan, specifically as a filler material in different polymer resins. Three different systems, TPU, PBAT, and PBS have been investigated, with the goal of maximizing the α -1,3-glucan content and understanding the performance range that can be obtained. Additional studies that involve improving the

compatibility between α -1,3-glucan particles and the base polymer matrix is recommended. There are a few approaches; derivatizing or chemically modifying the α -1,3-glucan to be more hydrophobic, or adding compatibilizers during the compounding step. As well, performing rheological studies, such as parallel plate rheometer, is highly recommended.

When a specific application of the α -1,3-glucan composites is established, optimization of the composite recipes, as well as some scale-up trials may be beneficial. Since the biodegradability and sustainability are key characteristics of the α -1,3-glucan, conducting a biodegradation study will provide more insight on the sustainability of the composite material.

The spray drying of the α -1,3-glucan wet cake has room for more optimization. In this project, an image processing software was used to obtain the particle size distribution. Utilizing different analytical equipment, such as laser diffraction particle size analyzer, may expedite the process. Once the spray drying parameter has been optimized, producing some composites with TPU, PBAT, and PBS then comparing the performance may shed some light on the different between the morphology of the particles, specifically between the D05/D15 particles and the spray dried particles.

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APPENDIX A: SUPPLEMENTARY DATA

Chapter 4 supplementary data:

Table 28. α -1,3-glucan-TPU-TEC composition in wt.% and vol.%

Sample ^a	Wt. %			Vol. % ^b		
	α -1,3-glucan	TPU	TEC	α -1,3-glucan	TPU	TEC
0/0	64.9	27.8	7.2	58.0	33.2	8.8
-/-	52.2	34.8	13.0	44.8	39.9	15.2
+/-	66.7	16.7	16.7	59.7	20.0	20.3
+/+	80.0	20.0	0	75.0	25.0	0
-/+	60.0	40.0	0	52.9	47.1	0
0/0*	64.9	27.8	7.2	58.0	33.2	8.8

^a A level / B level; e.g., -/+ indicates lower bound for A and upper bound for B; 0/0* is a replicate of sample 0/0.

^b Volume calculated by using the following densities: 1.55, 1.16, and 1.14 g/cm³ for α -1,3-glucan, TPU, and TEC, respectively.

Chapter 6 supplementary data:

Table 29. PBAT- α -1,3-glucan composition in wt.% and vol.%

Wt. %		Vol. %	
α -1,3-glucan	PBAT ^a	α -1,3-glucan	PBAT ^a
0	100	0	100
10	90	8.3	91.7
20	80	16.9	83.1
30	70	25.8	74.2
40	60	35.1	64.9
50	50	44.8	55.2
60	40	54.9	45.1
70	30	65.5	34.5

^a PBAT density is 1.26 g/cm³

Table 30. PBS- α -1,3-glucan composition in wt.% and vol.%

Wt. %		Vol. %	
α -1,3-glucan	PBS ^a	α -1,3-glucan	PBS ^a
0	100	0	100
10	90	8.2	91.8
20	80	16.7	83.3
30	70	25.5	74.5
40	60	34.8	65.2
50	50	44.4	55.6
60	40	54.5	45.5
70	30	65.1	34.9

^a PBS density is 1.24 g/cm³

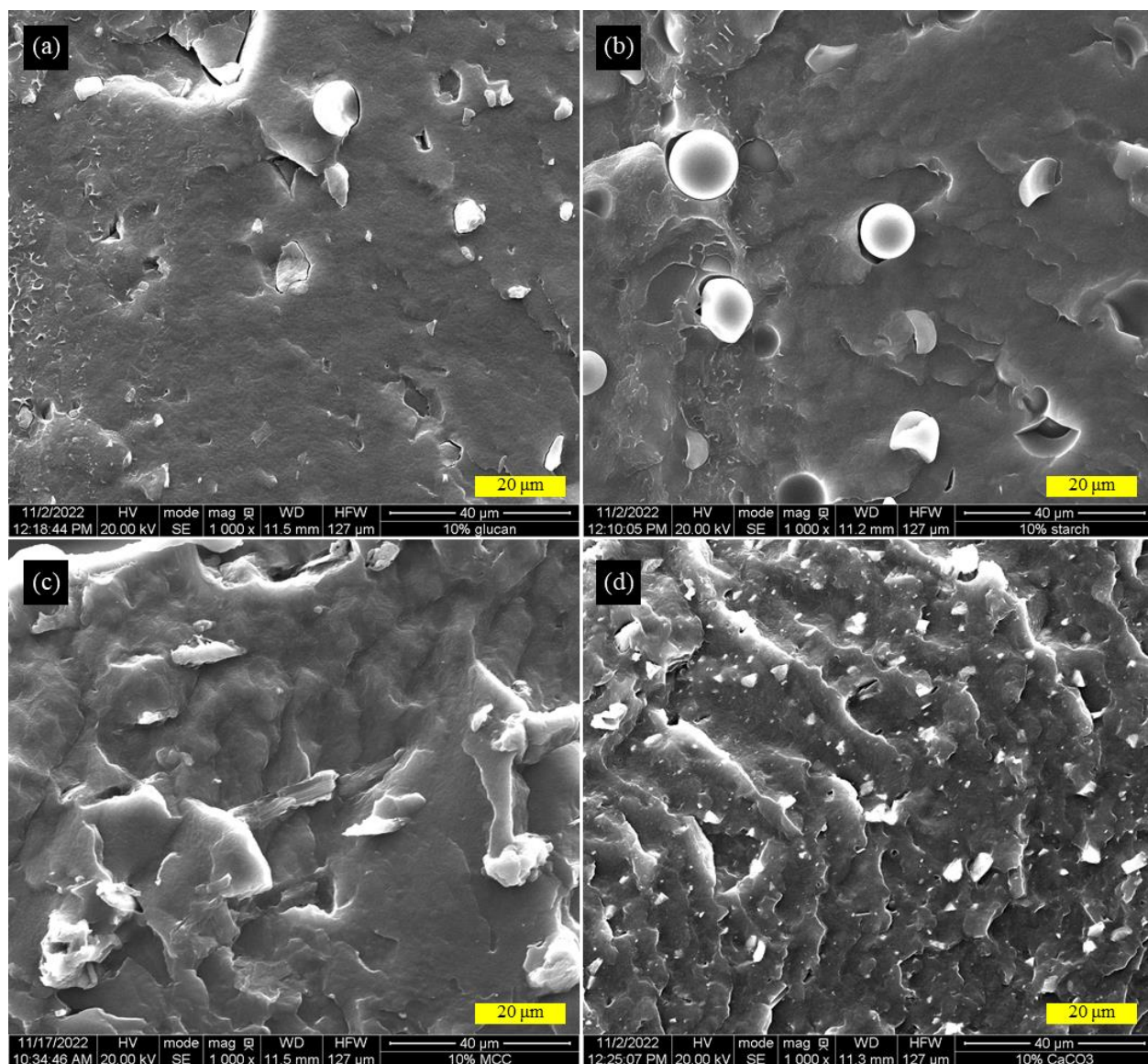


Figure 97. Film cross-section SEM of PBS composites with 10 wt.% (a) α -1,3-glucan, (b) cassava starch, (c) MCC, and (d) CaCO_3

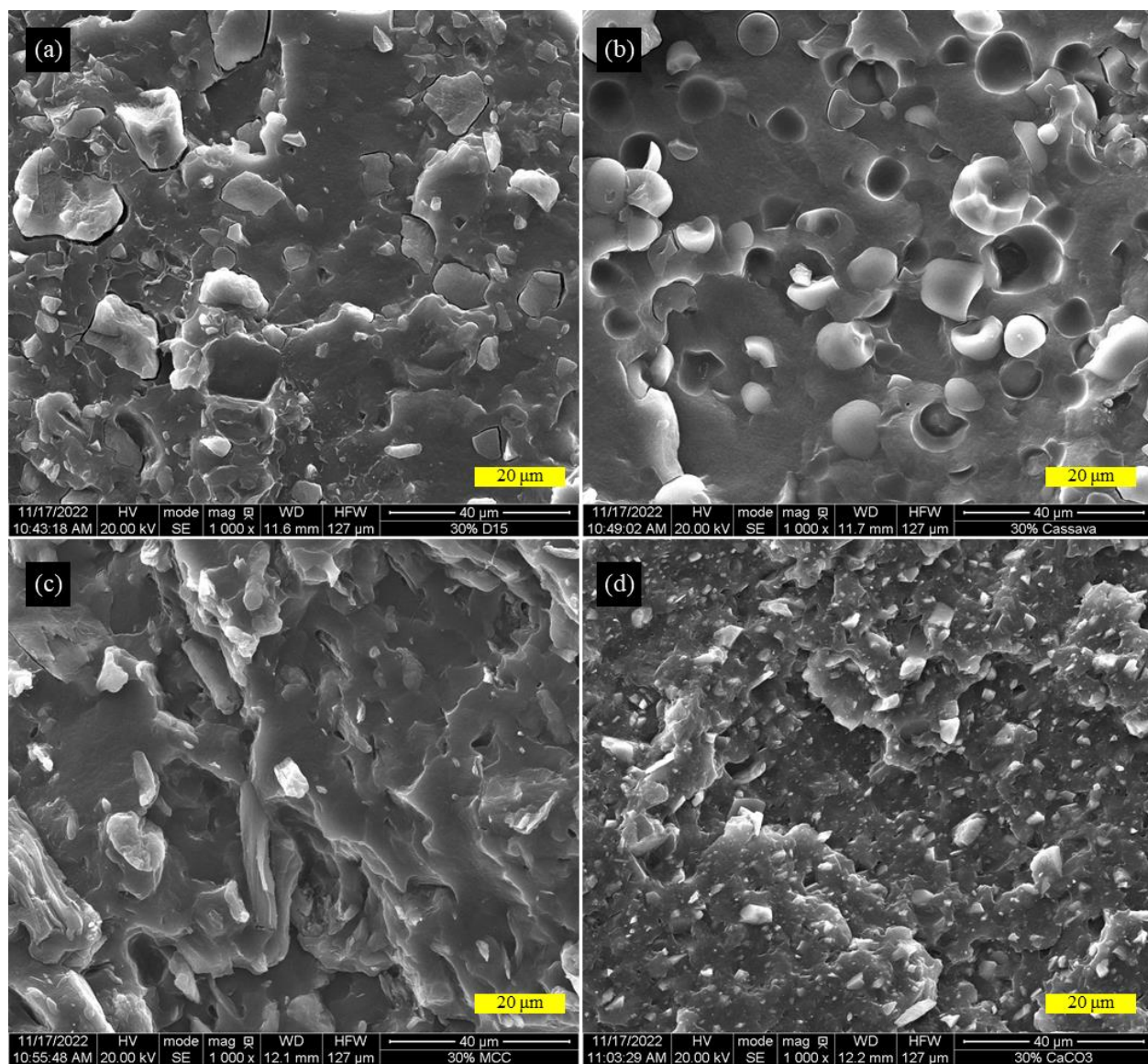


Figure 98. Film cross-section SEM of PBS composites with 30 wt.% (a) α -1,3-glucan, (b) cassava starch, (c) MCC, and (d) CaCO_3

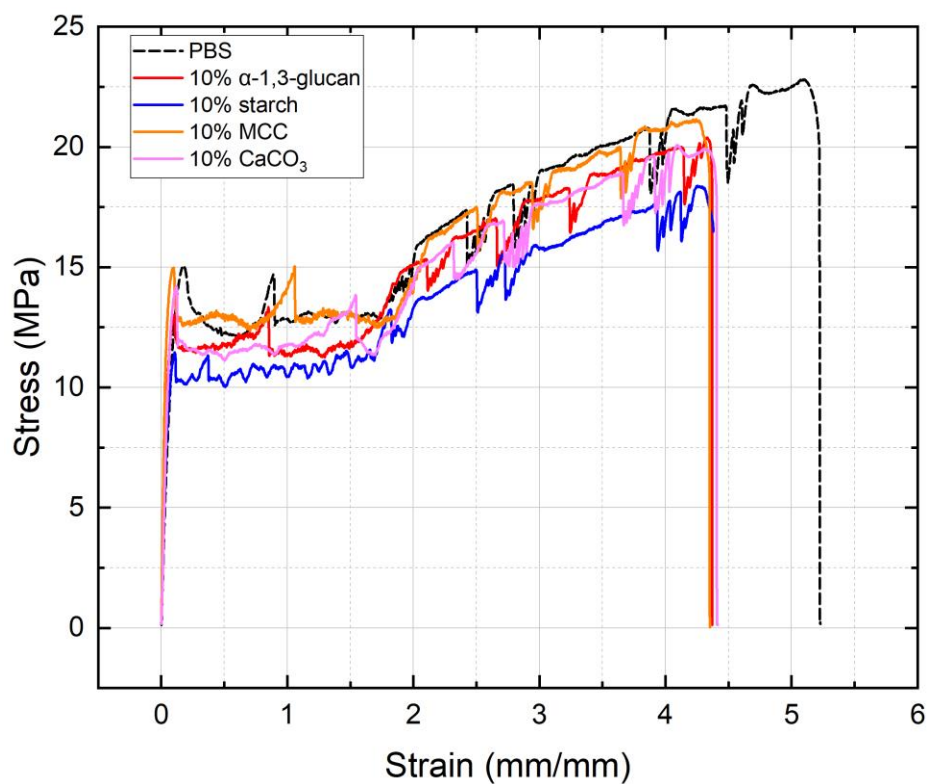


Figure 99. Stress-strain curve for PBS composites with different fillers at 10wt.% loading

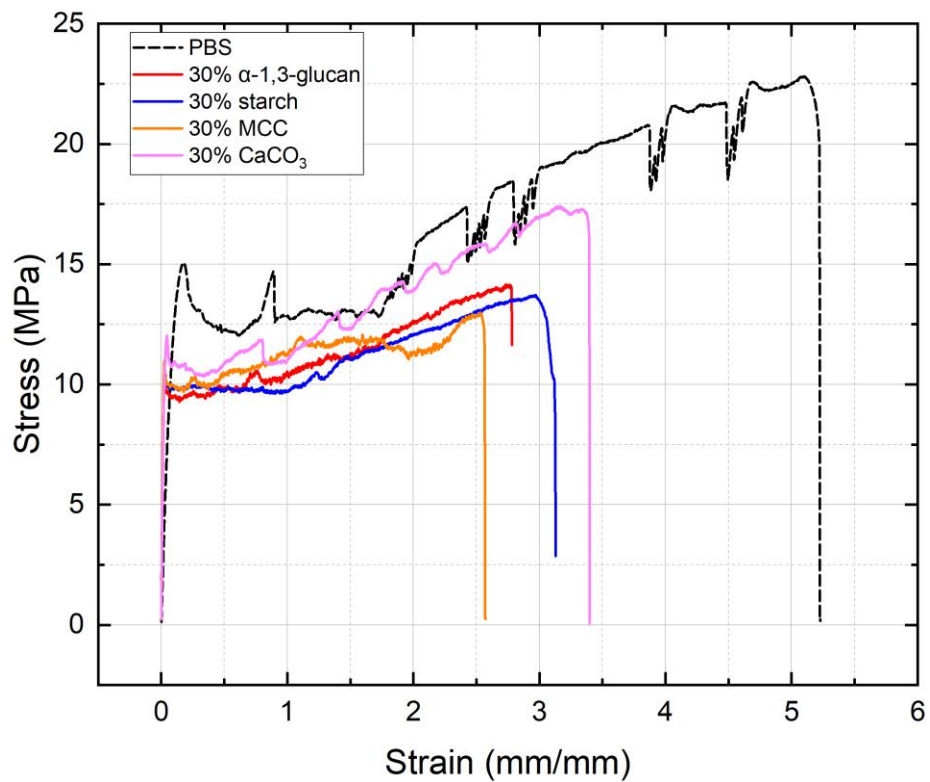


Figure 100. Stress-strain curve for PBS composites with different fillers at 30wt.% loading

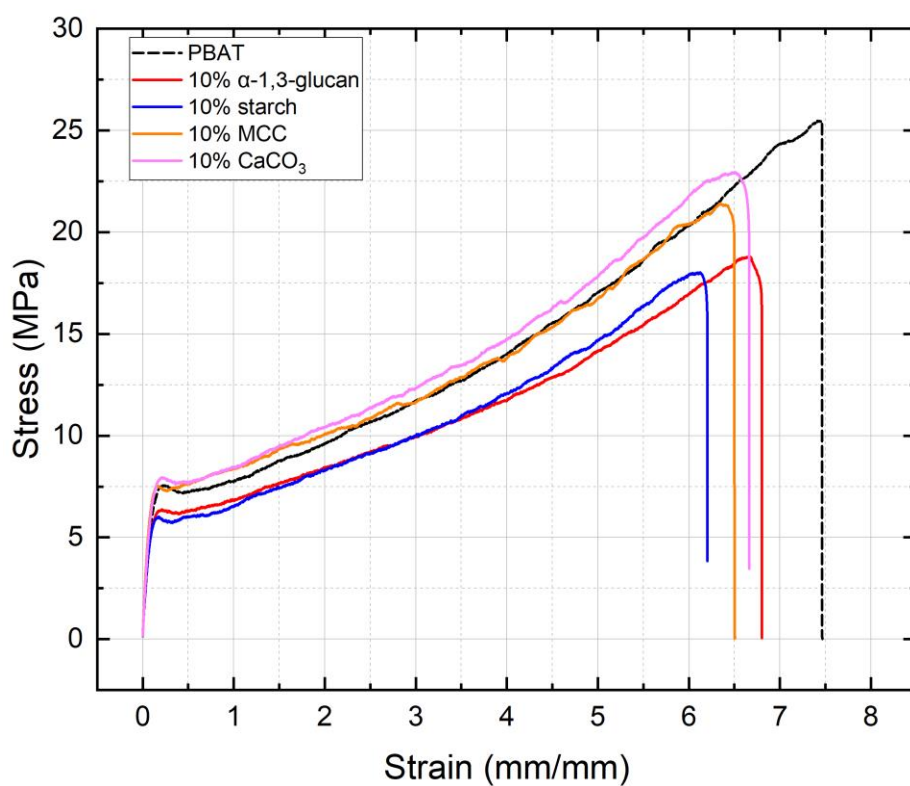


Figure 101. Stress-stain curve for PBAT composites with different fillers at 10wt.% loading

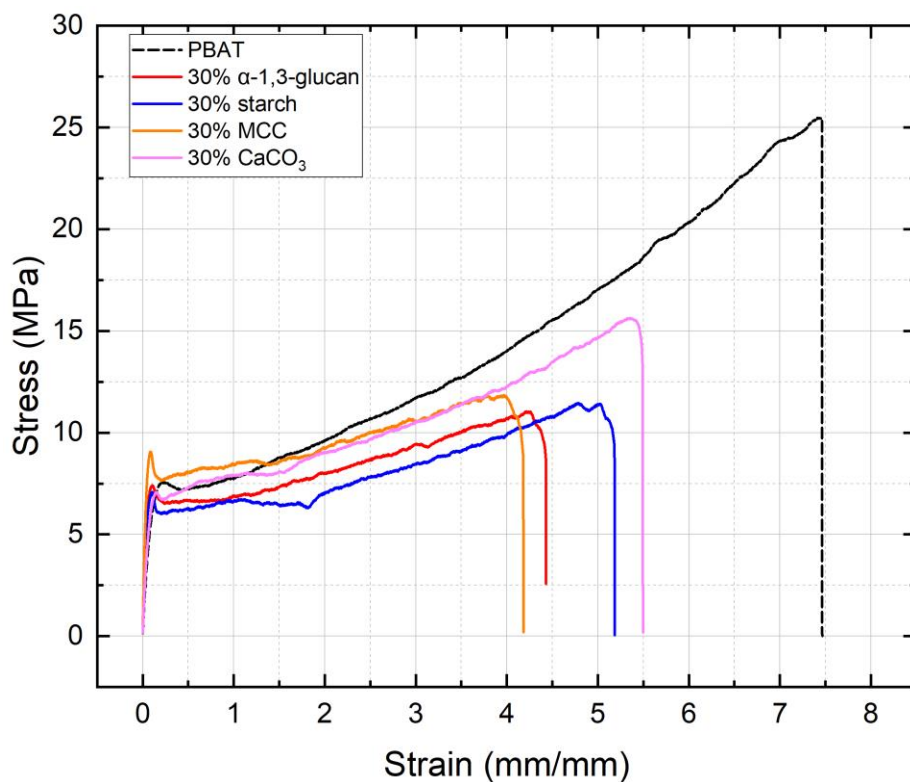


Figure 102. Stress-stain curve for PBAT composites with different fillers at 30wt.% loading

APPENDIX B: LIST OF MANUSCRIPTS

Published:

Engineered polysaccharide α -1,3-glucan in highly filled thermoplastic polyurethane systems

Description: Using α -1,3-glucan as a filler in TPU system with high filler loading (60-80%). Citrate-based plasticizers were also studied.

Work in progress:

Thermoplastic polyurethane and α -1,3-glucan composite with dicumyl peroxide as compatibilizer

Description: The role of dicumyl peroxide on the thermoplastic polyurethane and α -1,3-glucan composite to improve the compatibility.

Poly(butylene adipate-co-terephthalate) and poly(butylene succinate) composites with α -1,3-glucan

Description: Using α -1,3-glucan as a filler for polyester thermoplastics, PBAT and PBS. Different fillers will also be compared (starch, microcrystalline cellulose, calcium carbonate)

Spray drying of α -1,3-glucan

Description: Spray drying method to investigate the particle size distribution of α -1,3-glucan