

A STUDY IN LIGNIN CAPABILITY TO IMPROVE STRENGTH AND WATER  
ABSORBENCY OF STARCH POLYMERS: A POTENTIAL HEAT-RESISTANT FLUID-  
LOSS-CONTROLLER IN WATER BASED DRILLING FLUIDS

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## **ABSTRACT**

In the oil and gas industries, drilling deep wells has rapidly become more significant to meet the global demand. The design of drilling fluids and choosing the proper additives are very important for the drilling operation's success. Rheological behaviour and filtration-loss properties are the main factors to control for effective drilling operations. So, the study of an effective fluid loss controller and a rheology modifier is necessary to designing drilling fluids formulations and determining their proper performance during operations. Starch, as a natural polymer, is broadly utilized in the drilling industry, thanks to its specific structure and solubility in water. The main duties of starch in drilling fluids formulations are reducing fluid loss and improving the viscosity of fluid during drilling operations. One of the main problems of using starch in water-based fluids (WBFs) is being inefficient in high pressure and high temperature (HPHT) condition and shear force. Numerous studies have been conducted to elevate the thermal stability of starch to strengthen it for harsh conditions. In some studies, starch was replaced by new polymers like Carboxymethyl Cellulose (CMC) and other synthetic polymers, to overcome these problems. These polymers are not effective enough and are relatively expensive, so one needs to consider using alternative materials or natural ingredients to make drilling more economical and more efficient, especially in deeper wells with higher temperatures.

The main goal of this work was to develop a novel starch-based polymer for the synthesis of a new fluid loss controller (FLC) and rheology modifier using lignin as a support to raise its mechanical and thermal stability. Starch and lignin were crosslinked in the presence of a crosslinking agent, a type of substitution reaction, leading to the formation of a new compound of starch-lignin polymers. The mechanical and thermal properties of synthesized starch-lignin crosslinked polymers were investigated to demonstrate their potential for use in drilling operations. Addressing all drawbacks of native starch, using lignin as a biopolymer with the potential of improving starch mechanically and thermally was studied in this research. It is shown that Kraft lignin can be crosslinked with starch via ether covalent bonds to successfully increase the viscoelasticity and water absorption. Rheology analysis showed that in the

temperature range of 25 to 90 °C, lignin-starch polymers are more viscoelastic and stable than unmodified starch. The results showed that the rheological behaviour of lignin-starch crosslinked polymers was different from the natural starch at the same concentration and temperature. The change in viscoelastic properties caused by crosslinking reaction and etherification significantly depended on the amount of lignin and crosslinking agent incorporated. Modified starches with higher lignin content displayed higher values of storage and loss module than those with lower lignin content. This finding was due to the fact that ether groups in modified starches were more polar than natural starch, thus forming stronger hydrogen bonds with water restricting the movement of the chain of starches and leading to an increase of the elastic modulus. In addition, the presence of lignin in starch polymers influences its thermo-reversibility characteristics significantly and increases the storage and loss modulus of starch. Moreover, water absorption of starch was found to increase when it was crosslinked to lignin via proposed reaction conditions.

Our new polymer has the advantage of being produced using a renewable source, which is biodegradable and abundantly available in nature for a very low cost. In this work, based on results from XPS and TGA, we see the impact of the new covalent ether linkages between starch and lignin(-C-O-C-) improving the thermal stability, especially at the main weight loss steps. These structural changes, as highlighted by X-ray measurements, associated with morphological ones, shown by SEM images, could affect the mechanical properties of the modified fibers, compared to unmodified ones, that we will attempt to verify by means of suitable mechanical measurements.

## **Dedication**

To my sister, Molook Rashedi who has been my support in my whole life.

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## **Abbreviation**

Crystallinity index (CrI)

Differential scanning calorimetry (DSC)

Dimethyl sulfoxide (DMSO)

Epichlorohydrine (ECH)

Fluid Loss Controller (FLC)

Fourier Transform Infrared (FTIR)

Glass transition temperature ( $T_g$ )

Ion Chromatography (IC)

Molecular weight (MW)

Polyethylene glycol diglycidyl ether (PEGDGE 400)

Scanning electron microscopy (SEM)

Thermo gravimetric analyzer (TGA)

Water-based drilling fluids (WDFs)

Water contact angle (WCA)

X-ray photoelectron spectroscopy (XPS)

## **Chapter 1: Introduction**

### **1.1 Drilling fluids**

Drilling fluids are used in oil well drilling operations in order to access the oil from the reservoir. Drilling operations is a hard and complex job involving the pumping of drilling fluids into the wellbore. During these operations, drill cuttings are transferred out of the wellbore using drilling fluids which is critical for a successful oil and gas access and production. Drilling fluids with suitable combinations of natural polymers and mineral additives provide many functions such as transferring solids and drill cuttings, lubricating metal parts, cooling the drilling bit, preventing formation damage, and stabilizing the wellbore during operations [1-3]. Different types of mineral materials, chemicals and polymers are used in drilling fluid formulation and each provides different practical fluid requirements such as pH, hardness, density, rheology, fluid loss control, etc.

#### **1.1.1 Rheological properties**

Rheology is an extremely important function of the drilling fluid to assist it to perform its needed task. This property of drilling fluids helps in well cleaning and removal of the drill cuttings, has considerable impact on carrying out of drilling cutting and influences drilling progress in many other ways, and also aid in the suspension of drilling cuttings when circulation of the fluid is placed on hold. So, it is important to monitor and continuously adjust the viscosity and other rheology properties of the drilling fluid. Unsatisfactory fluid rheology can cause serious problems such as bridging the hole, settling heavy cuttings and filling the bottom of the hole with drill cuttings, reduced penetration rate, borehole enlargement, stuck pipe, loss of proper circulation, and in some cases a blowout and stop drilling operations. Different studies have been done around the world to find the most economical and the highest performance rheology modifiers in drilling fluids. They used different combinations of natural polymers and minerals which worked better in higher temperatures [1,4,5]. Unfortunately, most of these types of additives are not resistant to harsh conditions in the bottom of the borehole with high temperature and pressure conditions.

### **1.1.2 Fluid-loss properties**

Fluid loss refers to the volume of the filtrate lost to the permeable formation matrix during the process of drilling operations. Controlling and usually lowering fluid loss is a vital function of drilling fluids and can be achieved by several means. High filtration loss of drilling fluid is a critical problem in drilling operations which can lead to several big challenges from formation damage or in some cases stop the operation.

Formation damage is a condition that can occur due to the invasion of the fluid filtrate to the formation and result in the instability of the borehole due to an irreversible change in the drilling fluid properties, for instance, density and rheology [2, 6].

Various natural polymers like starch, xanthan gum, cellulose, and guar gum have been used in drilling fluid operations to achieve desirable operational performances. These polymers have many benefits like their environmental friendliness, availability, and low cost. On the other hand, natural polymers and their modified forms are susceptible to microbial degradation and low stability at temperatures above 90 °C [7,8]. At elevated temperatures, these additives degrade, reducing the active components, and consequently, drilling fluids are likely to lose function and exhibit undesirable properties. These changes in main factors like rheological and fluid loss control properties will cause serious operational problems, such as fluid invasion, subsequently increasing drilling costs significantly.

Fluid loss controllers are the key components of drilling fluids, which especially are used at high pressure and temperature, as an essential and important task. In general, water-based fluid loss controllers, show a complex rheological behaviour at higher pressures and temperatures which must be discovered and discussed [9-11].

Drilling fluids are normally designed to continuously circulate and perform as shear-resistant fluids. In addition, these systems have a high viscosity at low shear rates in order to suspend and carry drill cuttings from the wellbores. Moreover, carrying capacity is also considered as one of the most important functions and is directly related to rheological modifiers and fluid loss controllers that are not stable in thermally and mechanically harsh conditions [12-15].

Drilling fluids are suspensions of various constituents and considered as complex products. These products show non-Newtonian behaviour, such as shear-thinning and, significant thermal and pressure sensitivity. This unstable behaviour of the drilling fluids under high pressure and high temperature is extremely important for drilling deep wells where these conditions get too high and harsh [13,16].

## **1.2 Starch**

Starch is a natural, abundant polysaccharide and mainly serves as energy storage. Starch granules are often extracted from various sources like potato, corn, wheat, or rice, each containing different ratios of amylose and amylopectin. Starch has many advantages such as easy availability, high biocompatibility, and renewable source and inexpensive which is a major advantage to any industry from the commercial point of view [17].

Starch is a biodegradable and abundantly renewable polysaccharide that is produced in all parts of the world in large quantities. Due to its unique characteristics as a natural polymer, starch has been used in different industries and it is a base for the production of a wide range of products. Chemically modified starch is produced by large companies. All of these big companies have produced a wide range of starch-based materials [17-21]. One of the main applications of their chemically modified starch production is in the drilling industry.

Generally, starch-based products are commonly used as better substitutes for native starch due to their better thermal and mechanical properties and, consequently, improved performances. Chemical modification is often used to enhance the physicochemical properties of starch-based products and to some extent their applications.

Different applications of starch have been used in different industries like in the field of pharmaceuticals, textiles, biodegradable packaging materials, hydrogels, thin films and thermoplastic materials with improved thermal and mechanical properties [22,23].

For many reasons such as hydrolyzing, low resistance to moisture, poor processability, or poor mechanical properties challenge this promising candidate to be applied directly and without



any modifications in every possible application. Several strategies have been suggested by researchers to overcome these problems [23].

### **1.2.1 Structure of starch**

Starch polymers are one of the main additives in drilling fluids and mostly are used for fluid loss control and as fluid loss controllers and viscosifiers. Generally, starch polymers are made of about 27% amylose and 73% amylopectin. As it is shown in Figure 1.1, amylose has a linear structure and amylopectin is a branched polymer. Starches are carbohydrates of a general and repetitive formula of  $(C_6H_{10}O_5)_n$  and are derived from different sources like corn, wheat, oats, rice, potatoes and similar plants and vegetables [24-29]. Starch contains an abundance of hydroxyl groups. The presence of these hydroxyl groups develops a hydrophilic nature in starch. Starch granules differ in sizes and shapes based on the organization of amylose and amylopectin, and the degree of crystallinity and branching of amylopectin [30, 31].

The main flaw of native starch is that in higher temperatures, the bonds between monomers of Amylose and Amylopectin break and convert to Glucopyranose ( $C_6H_{10}O_5$ ) monomers, and the starch loses its function.

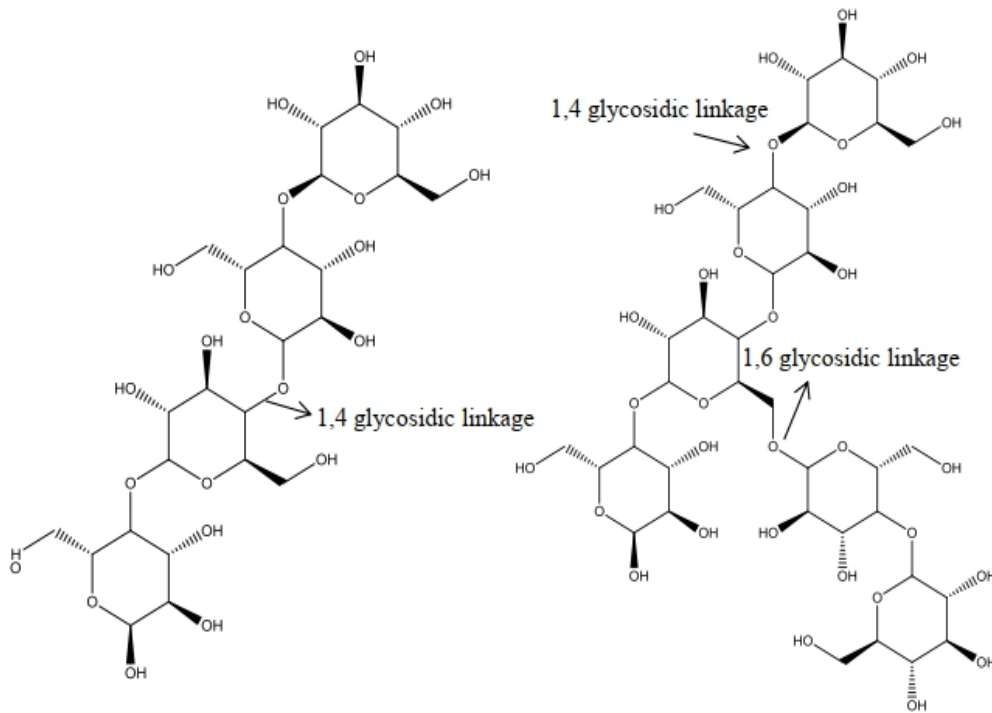


Figure 1-1: The molecular structure of amylose and amylopectin.

### 1.2.2 Using starch in drilling fluids formulations

Rheological properties and filtration loss play key roles in the proper performance of a drilling fluid. Therefore, studying the rheological behaviour of the water-based drilling fluid and using suitable polymers is essential for a safe and high-performance drilling operation. Starch is one of the main additives in the drilling fluids with specific characteristics that have made it an inseparable component of these fluids [32]. When starch dissolves in water, it starts absorbing a large amount of water and swell to many times its original size and spreads and opens its structure in the whole water system. By doing so, starch provides the viscosity of the whole water-based system to increase during mixing and circulating and acts like a sponge holding water in its molecular structure. Despite their wide usage and benefits, native starches have many disadvantages for industrial applications such as insolubility in cold water, loss of viscosity, and shear thinning after the temperature is raised [33].

### **1.2.3 Modification of starch**

Starch, the major form of carbohydrate storage in green plants, is an important natural, renewable, and biodegradable material [34-37]. However, the products provided from native starch have low stability when they are used under different environmental conditions due to their high water sensitivity and poor water resistance [38-41]. In addition, starch-based products exhibit poor thermal and mechanical performance at harsher conditions and their industrial applications have been limited [42-45].

All these properties can be modified through physical, chemical, and biotechnological means. The modifications alter the properties of starch, by creating new functional groups and raising the molecular weight, changing the whole chemical structure of the final products. The functionality and performance of starch can be modified in many ways. The most common chemical modifications for natural starch are esterification, acid treatment, crosslinking, oxidation, and etherification. Enhancing molecular stability against mechanical shearing, acidic, and high-temperature hydrolysis; obtaining desired viscosity; and increasing interaction with water will be the desired improvements for unmodified starch [46-49].

Over last two centuries, starch modification has been carried out by various methods. There are many applications for modified starches such as foodstuffs, cosmetics, pharmaceuticals, detergents, and drilling fluids. Physical, chemical, enzymatical methods, and dual modifications are the main strategies to overcome the limitations of using native starch.

Physical modifications of starch can be performed via mechanical mixing, microwave exposure, or radiation to produce modified starch with specific functional properties. The main advantages of this kind of modification were to enhance the capacity of the production and shorten the time of modification.

The whole concept of the modification of native starch is carried out to strengthen the positive attributes and fix or eliminate the shortcomings of the natural starches. Modification of starch has been growing substantially in four main categories (chemical, physical, enzymatic and genetic modification) with many possibilities to generate new products which include new applications, functions and value-added properties as a result of modification and as demanded

by the industry [50]. Over the last few decades, starch has been modified by various methods to achieve functionalities suitable for various industrial applications [51].

Chemical modification of starch is generally achieved through derivatization such as etherification, esterification and crosslinking, oxidation, cationization and grafting of starch. In some cases, different kinds of chemical treatments must be combined to create new kinds of modifications. Physical modifications such as microwave radiation have been combined with chemical modifications to produce modified starch with specific characteristics.

#### **1.2.4 Starch as a fluid loss controller**

Starch was the first polymer reagent used for drilling fluids. In 1939 it was added to salt fluids in the western part of Texas to regulate the filtration properties. However, because of drawbacks of native starch and with the introduction of cellulose based polymers such as carboxymethylcellulose(CMC), widespread demand of starch started to reduce and it was replaced with new synthetic polymers. The main reasons for limiting starch were the need to use bactericides and the low thermostability of starch reagents [52].

Currently, starch-based products are commonly used as better substitutes for native starch due to their better thermal and mechanical properties and, consequently, improved performances. Chemical modification is often used to enhance the physicochemical properties of starch-based products and to some extent their applications. All modified starches are synthesized for a good water solubility and high durability to thermal, pressure and bacteriological effects.

### **1.3 Lignin**

The consumption of naturally abundant, environmentally friendly, biodegradable, and available resources for various applications is a vital demand for the future of industrial sustainable development. At a rather low production cost, lignin, a naturally abundant substance, presents the greatest potential to be utilized as a renewable resource worldwide [53,54]. In nature, lignin is known to be the structural strength provider of plant cells and its available aromatic components make it attractive to industries, such as pharmaceuticals and oil [55-57].

Lignin, after cellulose is the second most biopolymeric component found in the cell walls of plants. By providing strength and rigidity to the plant stem, lignin plays an important role in cells. Lignin also provides plants with other biological functions such as adding compressive strength, protecting them from biological attack, providing mechanical support to the plant and assisting in water transport by sealing plant cell walls against water leaks [58, 59].

Lignin has the potential to be a value-added product and be used in various applications. The fact is the commercial use of lignin is very limited, as this polymer is primarily used as an energy source to produce heat. However, application of lignin has gained attention in order to produce new value-added products to use in various industries [60, 61].

### **1.3.1 Lignin structure**

Lignin is an aromatic biopolymer with an irregular three-dimensional structure in nature. It is generated in large quantities as the main by-product of the pulp and paper industries. This complex polymer is composed of three p-hydroxycinnamic alcohol units, linked together through radical coupling pathways to produce a complex three-dimensional polymer. The key function of lignin in woody biomass is providing strength, rigidity and resistance to degradation [62-66]. Different types of lignins can be extracted from different processes. For example, alkali lignin from the kraft process, hydrolytic lignin from enzymatic hydrolysis, organosolv lignin from organosolv process, and lignosulfonates obtained by the sulphite process [67-70].

The chemical structure of lignin is complex; it is a highly branched, amorphous biomacromolecule that normally presents a molecular weight of 1000-20,000 g/mol. To date, there has not been any specific structure to define lignin's chemical structure.

The determination of the lignin structure depends on different factors the species, location, growth duration of the plant, and the extraction process used to separate it from cellulose and hemicellulose and is extremely complex [71,72].

The structure of lignin is constituted by different structures and repeated units, p-coumaryl alcohol, coiferyl alcohol, and sinapyl alcohol. The polymerization of these three primary

monomers results in the formation of structural units in lignin: p-hydroxyphenyl (H), guaiacyl (G), and syringyl, respectively. Approximately, 90% of softwood units are G units. Figure 1.2 shows the three monolignols p-coumaryl, coniferyl, and sinapyl alcohols, that are considered the building blocks of lignin [73-76].

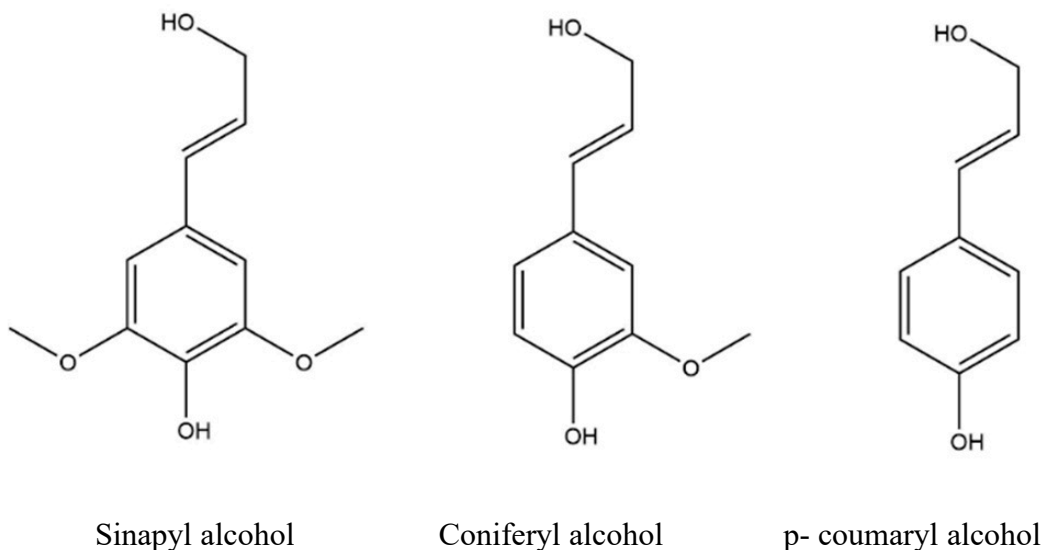


Figure 1-2: The three monolignols considered as the building blocks of lignin.

In previous studies, the chemical structure of lignin has been determined thoroughly using different chemical and spectroscopic methods. A general structure of softwood lignin is presented in Figure 1.2; among all the functional groups, the hydroxide group situated at para position on all three of the different subunits (p-coumaryl, coniferyl and sinapyl) is of great interest for lignin modification, which provides many changes in the chemical and physical properties of lignin [76-78]. The main functional groups in lignin structures are aliphatic -OH, phenolic -OH, -OCH<sub>3</sub>, -C=O, and some terminal aldehyde groups. These functional groups provide different chemical reactivities to gain specific modifications. The number and ratios of these functional groups of lignin are illustrated in Table 1.1.

Table 1-1: Functional groups in lignin (per 100 C6-C3 units)

Functional group	Softwood lignin	Hardwood lignin
Methoxyl	92-97	139-158
Phenolic hydroxyl	15-30	10-15
Benzyl alcohol	30-40	40-50
Carboxyl	10-15	40-50

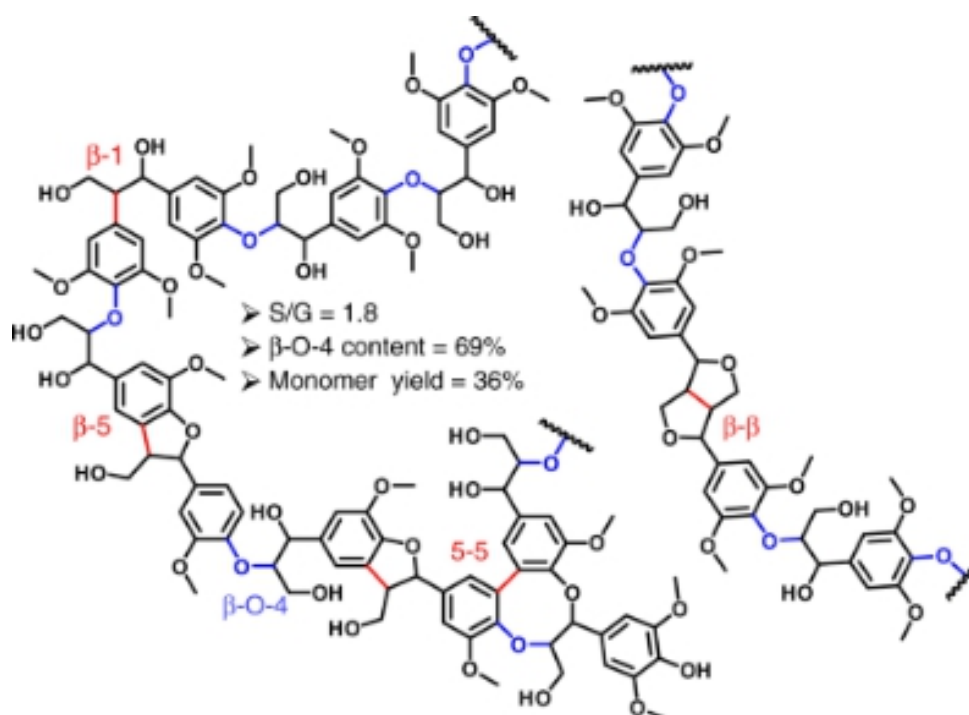


Figure 1-3: Molecular structure of lignin.

These monolignols are linked by a multitude of covalent linkages that include several types of ether and carbon-carbon linkages named  $\beta$ -O-4, 5-5,  $\beta$ -5. The structure of lignin polymers is complex and heterogeneous. The dissimilarity in the structures of these polymers depends on variations in their composition, origin plants, size, crosslinking and functional groups. This

heterogeneity depends on many factors such as the original plant from which lignin is obtained, and the processes used to separate it from cellulose [79,80].

In Figure 1-3 and Figure 1-4, different parts of lignin are illustrated and different linkages of lignin are presented. In the whole structure of lignin, the most predominant linkage is  $\beta$ -O-4, which is around 50% of all linkages in the structure.

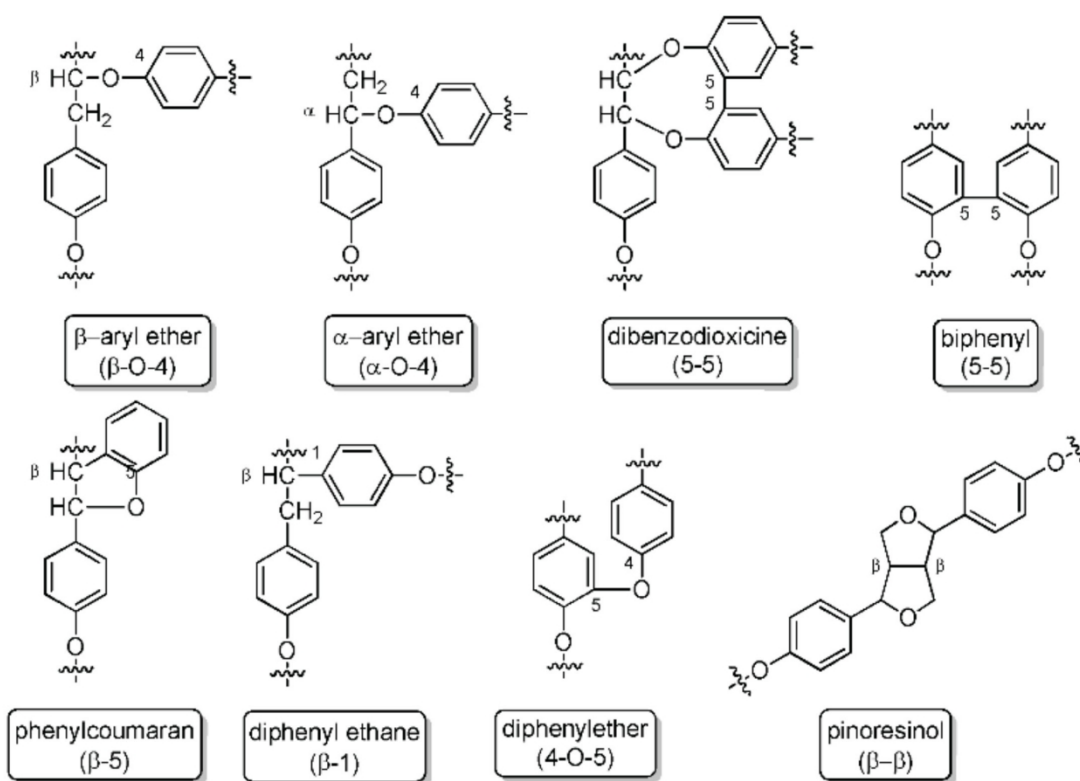


Figure 1-4: Lignin linkages: Ether bonds, carbon-carbon bonds, and more complex linkages [81]

### 1.3.2 Polymerization of lignin

For many reasons such as the low cost, availability, and versatile properties of lignin, this macromolecule has attracted great attention; it has been considered a potential candidate for the replacement of fossil-based products in many industries [82].



Annually, 120 Mt of kraft pulp is produced around the world, and this leads to the production of 70 Mt of kraft lignin. Recently, the development of both second-generation biofuel techniques and new biorefineries for various biomass types has further boosted lignin production capacity. Intensive efforts have been taken to develop value-added materials like flocculant, adhesives, emulsifiers, sorbents, carbon fibre, resin, biologically active agent carrier and animal feed additives [83,84]. Currently, the majority of lignin from the pulp and paper industry is considered as waste and will be used with low-value utilization, namely, burning for energy, and only 2% is used commercially. Different characteristics of lignin such as the polymeric nature, functionality, thermal stability, hydrophobicity, antioxidant and antimicrobial properties, have helped to incorporate lignin into different functional valuable composites, such as in films with hydroxypropyl cellulose, cellulose, polypropylene, starch and polyolefins [85-98].

In addition, numerous modification techniques such as chemo-enzymes, irradiations, UV radiation, and mechanical activation, have been carried out to make new lignin-based products for useful purposes via polymerization [89-91]. Many sites on the lignin structure offer opportunities for different reactions [92]. In order to take advantage of this characteristic, choosing the chemical reactions that would tailor lignin properties for a certain application is crucial. Different types of modification have been proposed to increase lignin's chemical reactivity, reduce the brittleness of lignin-derived polymers, increase its solubility in an aqueous solution, and improve the ease of processing lignin [93]. The phenolic OH groups of these phenyl propene subunits of kraft lignin present the most reactive sites. However, the  $\beta$ -O-4 aryl ether linkages and others interconnecting bonds create significant steric hindrances or occupy these reactive sites, which leads to limited reactivity of kraft lignin for possible chemical reactions. Therefore, depending on the application, a lignin molecule can take part in chemical reactions via copolymerization to make it more reactive [94,95].

The abundance of carbonyl and carboxylic groups and phenolic and aliphatic hydroxyl groups provides lignin the ability to establish a strong interfacial interactions with other polymers, making this natural biopolymer a suitable candidate for creating new polymers. Many

researchers put forward the use of lignin to blend with various synthetic polymers, either in their native state or after compatibilization, such as poly(vinyl alcohol), poly(ethylene oxide), and poly (lactic acid) [96-97].

The presence of polar and aromatic groups in lignin structure, which render lignin thermally and mechanically unique and stable was the inspiration point of this study to modify starch by lignin to be utilized as a rheology modifier for fluid loss controllers in harsh conditions.

### **1.3.3 Using lignin in drilling fluids**

Lignin has been used in drilling fluids formulations as thinners and clay deflocculants in many forms like lignosulfonates and lignin graft polymers.

Lignin has been incorporated into many biopolymers, such as starch, protein, cellulose, PLA and PHB, to form different composites for various applications. Many investigations have been done to improve mechanical properties of starch with lignin. In these studies, lignin was introduced to starch for different applications like plasticization, hydrogels, and packaging [98-102]. Many references show that lignin and starch are compatible biopolymers that can overcome many of the drawbacks of each. Introducing lignin to starch as a filler in starch films and bio-plastics is currently under investigation, with several goals: the utilization of industrial lignins produced by the pulp and paper industry, the improvement of the starch matrix hydrophobicity, and the knowledge of starch-lignin interactions [103-107].

Apart from new linkages between lignin and starch via crosslinking agents, some researchers [1-2], believe that due to the presence of hydroxyl groups in both materials, there is a high possibility of hydrogen bonding between the starch and lignin via their hydroxyl groups. The formation of these intramolecular interactions between both starch and lignin is highly likely (Figure 1-5) with hydrogen bonding pathways between amylopectin and lignin molecules possible. It should be noted that the compatibility between the molecular structures of lignin and starch should help to provide a stronger polymer in terms of mechanically and thermally [3, 108-112].

In addition, since the application of these new polymers are in water-based systems and they need to be dissolved in water, these hydrogen bonds will help to prevent the degradation and hydrolysis of modified starch polymers in high temperatures. This hypothesis is limited to low-temperature conditions and can not be taken into account at higher temperatures. However, these hydrogen bonds will help starch-lignin polymers stronger at lower temperatures than native starch.

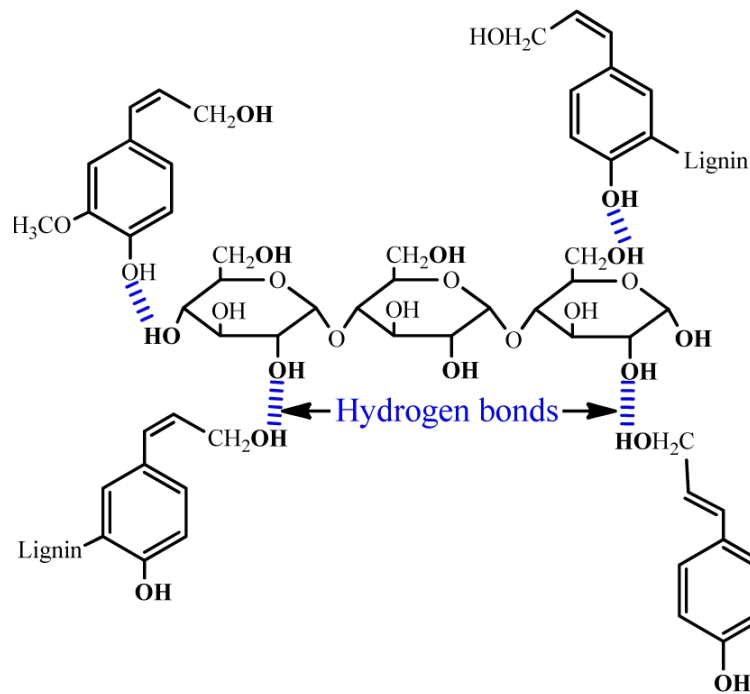


Figure 1-5: Shows the hydrogen bonding between starch and lignin polymers.

#### 1.4 Motivations & objectives

It is well-known that the addition of lignin within the starch matrix significantly improves the physical and chemical properties of starch. As we mentioned during this chapter, it has been previously investigated that the incorporation of lignin into starch can reduce the water permeability and increase the thermal stability and tensile strength of the resulting starch-lignin polymers [113-116]. The main goal of this thesis was to develop a new polymer by

crosslinking starch with lignin in order to produce a low-cost, environmentally friendly fluid loss controller with enhanced thermal and mechanical properties. The rheological properties, thermal stability, and water absorption of the produced fluid loss controller were determined and compared with those of unmodified starch.

The objectives of this thesis were to:

- Determine if lignin can strengthen starch to work in high temperature and high shear rates.
- Prepare crosslinked polymers of starch and lignin, improve many native properties of starch such as the thermal stability and mechanical strength, by crosslinking to lignin by applying PEGDGE 400 as crosslinking agent in different ratios.
- Investigate the impact of lignin content and PEGDGE 400 on the surface tension, interfacial tension of polymers of glass slides coated with modified polymers and as well as wettability.
- Investigate the impact of new covalent linkages between starch and lignin if that will improve its thermal stability, especially at the main weight lost steps.

### **1.5 Novelty of this study**

The study is novel as the following aspects have not been previously studied:

- The production of a new starch based polymers via crosslinking with lignin and alkoxylation with PEGDGE 400 chains.
- The properties of these modified starches are investigated, including their performance as rheology modifier and water absorbent in water based fluids.

Chapter one, which is the current chapter, covers the overall goals of this MSc thesis work and provides a general introduction to the current research and its importance. It also includes a brief summary of other chapters. The objectives of this research study are also presented herein. Then reviews literature relevant to this work, which includes the properties, production, starch-lignin polymers, and reactions to enhance its hydrophilicity, thermal stability, and

mechanical strength. In addition, general background information on the literature related to the current studies was briefly written here. This chapter also discusses the various methods used in literature and in this study to analyze the physiochemical characterizes of lignin and starch polymers. The instruments that evaluate the rheology and water absorbency of starch-lignin polymers are also discussed.

Chapter two is the experimental section and discusses the materials and methods used in this thesis to characterize polymers before and after modifications. It focuses on the production and analysis of starch-lignin and the polymerization process. Attempts to find the optimum conditions for polymerization to produce high-performance lignin-starch polymers with the highest performance.

Chapter three presents the results and discussion of this thesis. Modified and unmodified starches were utilized in water-based formulations and they were evaluated in terms of thermally and mechanical stabilities in order to find the best product.

Chapter four states the overall conclusions and future work of this thesis.

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## **Chapter 2: Experiments and analysis**

In this chapter, the preparation and characterization of the polymers is provided. Polymer characterization and analysis of performance will be discussed, including scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), hybrid rheometer, thermogravimetric analyzer (TGA), and differential scanning calorimetry (DSC), and a rheometer, TA Instruments, Discovery HR-2, with a Peltier temperature control system was used for analyzing the viscoelastic properties of the polymers.

### **2.1 Raw materials**

Softwood kraft lignin (KL) was supplied by FPInnovations from its pilot plant facilities located in Thunder Bay, ON, Canada. ACS grade natural Starch (99.9%), Poly(ethylene glycol) diglycidyl ether (PEGDGE 400) (99%), epichlorohydrin (ECH), tetrabutylammonium bromide (TBAB), sodium hydroxide (98%), H<sub>2</sub>SO<sub>4</sub> (98%), DDW, toluene, N,N-dimethylbenzylamine (BDMA), petroleum ether, hydrochloric acid (37%), dimethyl sulfoxide (DMSO), dimethyl sulfate, pyridine, deuterated chloroform (CDCl<sub>3</sub>, 99.8%), cyclohexanol, 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane (TMDP, 95%), potassium hydroxide solution (8 M), ammonium hydroxide (NH<sub>4</sub>OH), methanol, all analytical grade, were purchased from Sigma Aldrich and used as received. A dialysis membrane with a molecular weight cut-off of 1000 g/mol was obtained from Spectrum Labs Inc., USA.

### **2.2 Preparation of starch/lignin crosslinked polymers with DMSO as solvent**

Lignin and starch were crosslinked with PEGDGE as follows. In a 250 mL round-bottom three-neck glass flask equipped with a mechanical stirrer, 2 g of lignin, 0.2 g of crosslinking agent and different amounts of starch from 0.2 g, 2.0 g and 4.0 g starch were dissolved under vigorous stirring in 80 mL DMSO. Then, BDMA (0.45 g) was added as a catalyst, followed by PEGDGE addition at different molar ratios relative to lignin's hydroxy group content. The mixture was purged with nitrogen gas to remove oxygen. The first 30 min of the reaction occurred at room temperature, then the mixture was heated to 100 °C and reacted for another 5

h. The reaction was stopped by adding 2 M HCl (5 mL), and the mixture was stirred for another 30 min at room temperature to cool down. The solvent (DMSO) was then removed from the mixture using membrane and via dialysis process for the next two days. The resulting water-insoluble product was separated via centrifugation at 1500 rpm for 5 min and oven-dried at 60 °C.

### **2.3 Preparation of silylated starch**

Silane modified starch was prepared by physical adsorption, chemical grafting and condensation reaction between hydroxyl and silanol groups. First, natural starch was pre-hydrolyzed in water/ethanol = 1/4 (volume ratio) at room temperature for 2 h while keeping the pH = 4 by acetic acid. The starch dispersed in water was transformed to ethanol dispersed by centrifugation since the excess water could result in self-condensation of the hydrolyzed hexadecyltrimethoxysilane (HDS). The ethanol dispersed starch and pre-hydrolyzed hexadecyltrimethoxysilane was mixed (starch = 0.6%, w/v; HDS = 0.05%, v/v) and stirred at pH = 4 for 2 h to make H-HDS adsorb onto starch polymers. Then, the chemically grafted starch was centrifuged at 5000 rpm for 10 min, vacuum dried at room temperature to remove the water and ethanol and heated at 120 °C under a nitrogen atmosphere for 2 h [1].

### **2.4 Preparation of lignin-starch crosslinked using Epichlorohydrin as a crosslinking agent**

The aqueous phase has been prepared by dissolving 4 g of starch and 4 g lignin in a 12 g alkaline solution till pH 11 under mechanical stirring. The aqueous phase has been mixed in 100 ml of a cyclohexane/chloroform mixture (4:1 v/v). The mixture was homogenized for 3 min either with a laboratory blade stirrer or a high-speed mechanical. Varying amounts of epichlorohydrin, expressed as molar ratios of epichlorohydrin (ECH) to starch, were added under mechanical stirring at various stirring rates. The stirring was maintained for 18 h at 40 °C. Products were then isolated by centrifugation and washed twice with cyclohexane, and extensively with deionized water. Finally, they were dried in a 60 °C oven [2-6].

## **2.5 Reaction procedure, crosslinking reaction between starch and lignin, and PEGDGE**

### **400**

Varying amounts of starch (1.0–10.0 g) and lignin (0.0–10.0 g) were dissolved in round-bottom glass flasks using deionized distilled water. The pH of each solution was then adjusted with 20% sulfuric acid and 10% sodium hydroxide to 10.0–11.0 prior to purging with nitrogen gas for 30 min. Water was added to each flask to generate a total mass of reaction (40 g). The flask was placed in a water bath and heated to the steady-state temperature (65–85 °C) and the reaction was allowed to proceed with a constant flow of nitrogen gas at 220 rpm. Then, different amounts of a crosslinking agent were added, and the reaction was run for 3h. After completion, all samples were removed from the flask and rinsed with water to remove unreacted materials. Products were then rinsed with water to prevent degradation and freeze-dried at –50 °C for over 24 h in a Labconco FreeZone 1L freeze-dryer [7,8].

## **2.6 Lignin content analysis by UV spectroscopy analysis**

For modified and unmodified starch samples analysis, dried precipitates were mixed with deionized water, NaOH and placed in a water bath at 30 °C and 50 rpm for 12 h. Lignin content of these mixtures was evaluated using a UV spectrophotometry (Genesys 10S UV–Vis, Thermo Scientific) at 205 and 282 nm (these are related to aromatic parts of lignin) in accordance with TAPPI UM 250 [9,10].

For the preparation, after being dried overnight at 80 °C, a precisely weighed amount of the FLC samples were dissolved in 5 mL of dioxane and 5 mL of 0.2 M NaOH. Some of the samples did not completely dissolve and were filtered using a membrane filter with a pore size of 0.45 µm. Out of the prepared volume of each sample, 2 mL was further diluted to 25 mL using 0.2 M NaOH solution. Different solutions of our synthesized polymers with specific concentrations were prepared. The prepared lignin samples were used as standards and the lignin content of FLC solutions was determined by detecting their absorbency at the wavelengths of 205 and 282 nm which are assigned for conjugated bonds and aromatic rings in lignin structures.

## **2.7 IC analysis**

The concentrations of polysugars and mono sugars in the hydrolysis polymers were determined using ion chromatography, Dionex, ICS 5000, Thermofisher Scientific, equipped with CarboPac™ SA10 column and an electrochemical detector (ED) (Dionex-300, Dionex Corporation, Canada). Deionized water and KOH Eluent Generator (EGC 500 KOH, ThermoScientific) were used to generate an eluent of 1.00 mM of KOH at a flow rate of 1.2 mL/min. The column temperature was set at 30°C. The monosugar concentration in the liquors was measured without pretreating the liquors but after adjusting the pH of the liquors to 7. The hydrolysis and soda liquors were acid-hydrolyzed under the conditions of 4% sulfuric acid at 121 °C for 1 h in an oil bath (Hakke S45, Instruments, Inc., Portsmouth, N.H., USA) based on the method described in the literature. This acid hydrolysis is widely used for converting oligosugars to mono sugars. Afterward, the concentration of mono sugars in the hydrolysis liquors was measured, and it reflected the concentration of total monosugars (after conversion of oligosugars to mono sugars) in the hydrolysis and soda liquors. The concentrations of polysugars were determined via subtracting total sugar concentrations from monosugar concentrations [11].

## **2.8 Elemental analysis**

The elemental analysis of starch-lignin samples was performed using an Elementar Vario EL Cube elemental analyzer by a combustion analysis method. The samples were first dried in a 105 °C oven overnight in order to remove any moisture. Approximately, 2 mg of unmodified and crosslinked samples were weighed in silver vessels and loaded in the integrated carousel of the elemental analyzer. Furthermore, the samples were automatically transferred into a combustion tube and burned at 1200 °C. Afterward, the combustion gases were reduced and analyzed for carbon, hydrogen, nitrogen, and oxygen content of the samples [12].

## **2.9 Fourier Transform Infrared (FTIR) Spectrometry**

Fourier transform infrared (FTIR) spectra of freeze-dried starch-lignin samples (5 mg) were recorded at 25 °C by a Bruker Tensor 37 FTIR spectrometer (Tensor 37, Germany) using a

universal attenuated-total-reflection (ATR) probe in the wavenumber range of 4000–600  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  [13].

### **2.10 Thermogravimetric Analysis (TGA) and DTG**

The dried powder polymer samples were placed in a desiccator overnight before undergoing thermal analysis using a thermogravimetric analyzer (TGA i-1000 series, Instrument Specialist Inc.). Approximately, 8 mg of sample was heated under a constant flow rate of nitrogen (35 mL/min) from room temperature to 700 °C at the heating rate of 10 °C/min. The freeze-dried polymers were cut and divided into samples weighing approximately 0.2 g. The dried samples (with a known weight) were immersed in 200 mL of deionized water for 24 h [14].

### **2.11 Differential Scanning Calorimetry (DSC) Analysis**

The thermal behaviour of lignin-starch derivatives was investigated with a differential scanning calorimeter (TA instrument, Q2000 DSC) using the standard cell RC mode. All samples were dried overnight at 60°C before the DSC analysis. Approximately, 10 mg of each sample was loaded into a hermetic aluminum pan and analyzed in the heat/cool/heat mode between 30 and 250 °C at a rate of 5°C/min under 50 mL/min nitrogen flow. In the second heating cycle, the glass transition and melting temperatures of the samples were determined [15].

### **2.12 X-ray Diffraction Analysis**

The XRD analysis was conducted on starch powder, lignin powder, and lignin-starch polymers. The freeze-dried samples were utilized in this analysis using an XRD (Panalytical X-pert Pro) with a high-resolution goniometer and a Pixel solid-state detector. The X-ray tube contained a copper anode and was set to 45 kV and 40 mA. The samples were set to research from 6° to 96° ( $2\theta$ ) with a step size of 0.0263° [16].

### **2.13 SEM analysis**

The surface morphology of starch-lignin derivatives with different lignin contents was analyzed using a field-emission scanning electron microscope (FE-SEM, Hitachi SU- 70,

Japan) with an accelerating voltage of 5 kV. All SEM samples were freeze-dried and sputtered with a skinny layer of gold to extend the conductivity before observation. Energy-dispersive X-ray spectra (EDX) attached to the FE-SEM unit were used for the basic analysis of LCNC samples. In the EDX analysis, the assessment was conducted at an accelerating voltage of 10 kV [17].

## 2.14 Contact angle analysis

The contact angle was determined by a combination of the intermolecular and surface forces (surface tension) and external force (gravity). The contact angle analysis is defined as the angle formed by the surface intersection of the liquid-solid interface in a specific environment. In Figure 2.1, a drop of liquid rests on a horizontal solid surface, which may result in three different scenarios; 1)  $\theta < 90^\circ$  indicates that the wetting of the solid surface is favourable and the wetting will increase overtime over a larger surface area, 2)  $\theta > 90^\circ$  implies that the wettability of the surface is unfavourable, and 3)  $\theta = 0^\circ$  indicates a flat puddle and a complete wetting.

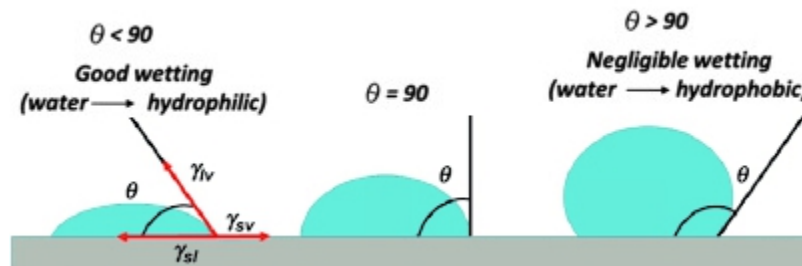


Figure 2-1: Illustration of contact angles formed by sessile liquid droplet on a smooth solid surface [ 18]

In this set of experiments, the contact angle of each lignin sample in solutions was measured using an optical tensiometer instrument, Theta lite (Biolin Scientific, Finland) equipped with a camera with sessile liquid drops on a smooth solid surface (microscopic glass slides). At first,

starch-lignin samples were prepared at various concentrations (0.2, 0.4, 0.6, 0.8 and 1 g/L) in water by stirring at 500 rpm overnight and at room temperature. It is worth mentioning that the volume of the droplet (3  $\mu$ L) and the recording time (20 seconds) were constant in all measurements. An average of three independent experiments and five droplets were considered in each experiment [19-21].

### **2.15 Contact angle of water on coated glass slides**

The contact angle of water with starch-lignin derivatives coated on microscopic slides was also measured by the sessile drop method using the optical tensiometer, Theta lite (Biolin Scientific, Finland) equipped with a camera. Approximately, 5  $\mu$ L of a water droplet was loaded on the microscopic slides coated with lignin samples and the contact angle between the water droplet and coated slides was determined via an optical tensiometer. In another set of experiments, a droplet of water (3 L) was loaded on the coated films and the contact angle was recorded at different times (5 s. and 20 s.). Five replicates were performed for each sample solution and the average values were reported [22].

### **2.16 Interfacial tension analysis**

The wettability of starch-lignin derivatives was determined via an optical tensiometer instrument, Theta lite (Biolin Scientific, Finland) equipped with a camera. The tensiometer's OneAttention software was utilized to measure the surface tension of kraft lignin via Zisman equation (1).

$$\cos \theta = 1 + b(\gamma_{SV} - \gamma_{LV}) \quad (1)$$

where  $\gamma_{SV}$  and  $\gamma_{LV}$  are surface tensions (mN/m) of solid (kraft lignin) and liquid (water), respectively.  $\theta$  is that the contact angle between the solid (kraft lignin) and liquid (water) in degrees.

The  $\cos \theta$  is plotted against  $\gamma_{LV}$  yielding a straight line with slope  $b$  and  $\gamma_{SV}$ .



The interfacial tension between solid (kraft lignin derivatives) and water droplets was measured via utilizing the Young's equation (2).

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL} \quad (2)$$

where  $\gamma_{LV}$ ,  $\gamma_{SV}$  and  $\gamma_{SL}$  are the surface tensions (mN/m) of liquid vapour, solid vapour and solid-liquid, respectively. The contact angle of water droplets on the kraft lignin derivatives coated slides [23].

### **2.17 Preparation of surfaces coated with starch-lignin samples**

To form thin uniform films of kraft lignin solutions on flat substrates, spin-coating is generally used. In this set of experiments, an excess amount of solutions containing starch-lignin derivatives were placed on microscopic glass slides. The substrate was then rotated at various rpm (100, 500 and 1000 rpm) using a spin coater, WS-650 (Laurell Technologies Corp) under vacuum with 60 Psi pressure to spread the fluid on the elapse the force. Rotation was continued for 60 seconds with the fluid being spun off the edges of the substrate until the desired film was formed.

The water contact angle (WCA) of the suspensions of prepared starch-lignin derivatives (1.5 wt%) was determined by a Theta Lite optical tensiometer (TL100, USA). For measuring WCA, the starch-lignin derivatives suspensions (1.5 wt%) were coated on clean glass slides using a spin coater (WS-400B-NPP) spin-processor (Laurell Technologies Corp) at 500 rpm for 30 s under a nitrogen environment. Then, the WCA was measured in 60 seconds [24].

### **2.18 Water absorption behaviour of unmodified and modified starches**

The test was performed with 0.5 g of a sample using a Sigma 700/ 701 optical tensiometer (Espoo, Finland) after conditioning its temperature at 20 °C. A vessel containing water (100

mL) was placed on the platform of the machine and moved until water touched the sample bed, after which capillary force caused water absorption by the sample.

The mass uptake by the polymers was subsequently recorded every 1 min for 300 seconds. The  $W_U$  of each sample at different time intervals was calculated according to eq 3.

$$W_U\% = \frac{W_D - W_W}{W_D} \times 100 \quad (3)$$

where  $W_D$  and  $W_W$  are the weight (g) of polymers before and after exposure to water at different time duration, respectively. The swelling experiment of unmodified starch and modified starch polymers was performed manually by immersing the freeze-dried samples in deionized water to swell. At different time intervals, the samples were removed and blotted by a paper towel to extract excess water from their surface. The swelling ratio of polymers ( $Q$ ) was determined following eq 4.

$$Q = \frac{W_S - W_O}{W_O} \times 100 \quad (4)$$

where  $W_S$  and  $W_O$  are the weights of swollen polymers and dried polymers, respectively. The  $W_U$  analyzed by the tensiometer measures the water penetration in only axial direction, whereas the water swelling measurement includes  $W_U$  in any direction of axial, radial, and tangential [25].

## 2.19 X-ray photoelectron spectroscopy (XPS) measurements

The analysis was performed on a Kratos Axis Supra spectrometer (UK) with a monochromatic Al  $K\alpha$  radiation (1486.7 eV) at a base pressure of about  $3 \times 10^{-10}$  mbar. The detection depth and spot diameter were 5 nm and 1 mm, respectively. High-resolution spectra were obtained using an energy analyzer operating at pass energy of 40eV. The binding energy scale was calibrated to the C1 line peak at 284.6 eV. Data analysis and peak fitting were conducted using ESCApe software [26,27].

## 2.20 Rheology Analysis

A rheometer, TA Instruments, Discovery HR-2, with a Peltier temperature control system was used for analyzing the viscoelastic properties of polymer samples. The upper geometry was a 40 mm steel parallel plate with a gap of 1 mm and a loading gap of 60 mm. The dynamic oscillatory measurements were carried out at a constant temperature of 25 °C unless stated otherwise. The Lignin-Starch polymers were prepared for the rheology test according to the method described elsewhere [28]. The polymers were saturated in deionized water before testing and were loaded onto the Peltier plate to cover the surface area of the parallel plate. Attempts have been made to ensure that the same amount of polymers with similar thickness was loaded on the Peltier plate for each test. Three tests of frequency sweep, amplitude sweep, and temperature ramp have been applied on the samples in this set of experiments. The frequency test was carried out at a shear stress of 0.2 Pa throughout the frequency range of 0.2– 20 Hz (1.267–125.7 rad/s). The amplitude sweep was obtained at a constant frequency mode of 10 rad/s over a strain rate range of 0.01–1000%. The temperature ramp was recorded at a constant strain rate of 2%, with a low frequency of 10 rad/s over a temperature range of 0–50 °C. The temperature ramp rate was 5 °C/min [29].

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## Chapter 3: Results and Discussion

### 3.1 Introduction

One of the important findings of this work was that we synthesized a new starch-lignin crosslinked polymer that can work in high-temperature water-based fluids. An improved viscosifying ability of starch-lignin crosslinked polymers was observed as the lignin percentage and crosslinking agent content increased.

#### 3.1.1 Crosslinking agent

Among all of the chemical methods to modify starch, crosslinking has been commonly used to modify native starch. There are many crosslinking agents such as sodium trimetaphosphate (STMP), PEGDGE, and phosphoryl chloride ( $\text{POCl}_3$ ), to use for crosslinking of native starches. These crosslinking agents are capable of forming either ether or ester inter-molecular linkages between hydroxyl groups on starch molecules [1].

In other cases, native starches have been crosslinked using polycarboxylic acids such as citric acid, polyphosphates such as sodium trimetaphosphate, sodium tripolyphosphate as well as epichlorohydrin (ECH), phosphorus oxychloride and 1, 2, 3, 4-diepoxybutane [2-4]. Also, carboxymethylated starch has been further crosslinked using malic, tartaric, citric, malonic, succinic, glutaric and adipic acid to synthesize crosslinked hydrogels [5, 6].

Crosslinking of starch and lignin with bi or polyfunctional reagents is a key modification technique widely utilized in industrial applications. Generally, crosslinking is a thermosetting modification that interconnects the polymer molecules by covalent bonding, thus it not only increases the molecular weight but also enhances the mechanical properties. The most common crosslinking agents for lignin are polyethylene glycol diglycidyl ether, and ECH to produce different materials like epoxy resins and lignin-based hydrogels [1, 6-9]. Based on the literature, some crosslinking agents for lignin and starch are ECH, urea crosslinked starch-lignin films [10,11]. Polyethylene glycol glycidyl ether (PEGDGE) is another common crosslinking agent for biopolymers. Figure 3.1 shows a schematic of this chemical and Figure 3.2 shows a crosslinked lignin with PEGDGE [10,11].

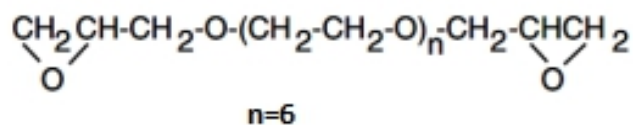


Figure 3-1: Formulation of various PEGDGE 400 with two epoxide groups to use as a crosslinking agent.

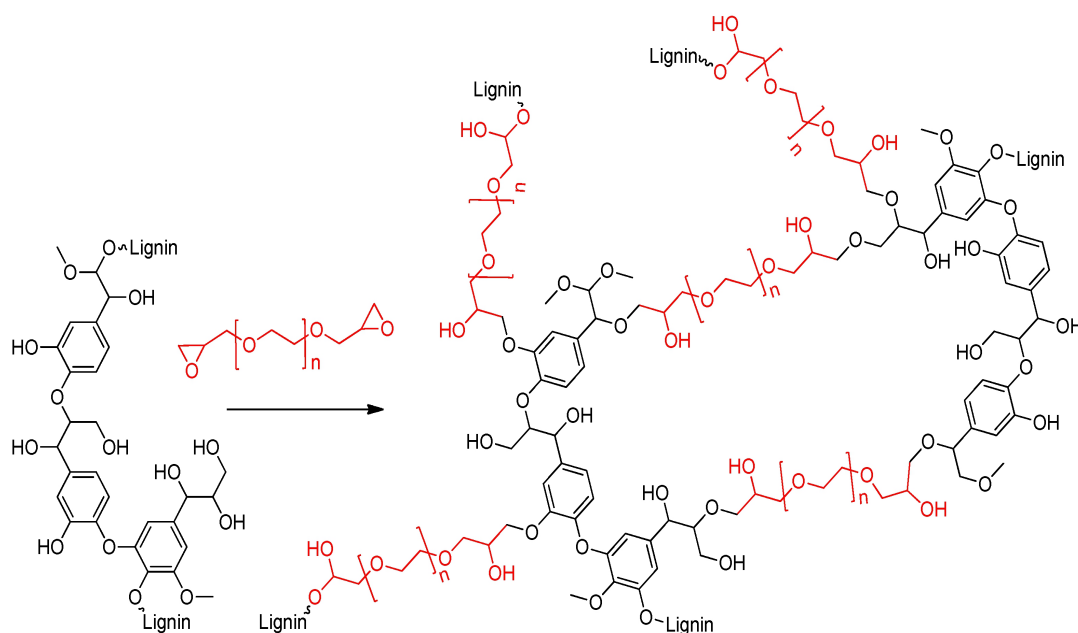


Figure 3-2: Simplified reaction scheme of crosslinking process between organosolv lignin and PEGDGE.

### 3.1.2 Applying different crosslinking agents

Epichlorohydrin is a common crosslinking agent for both lignin and starch modification, so it was investigated first as a crosslinking agent. Crosslinking starch with ECH is one of the common chemical modification techniques used in polysaccharide chemistry. The reaction of starch with epichlorohydrin leads to the formation of distarch glycerols which are highly resistant to pH changes and mechanical shear due to the formation of ether linkages with the starch hydroxyl groups [12].



Since the ECH is a small molecule compare to the groups it is crosslinking, it is not efficient enough to connect a big starch polymer to lignin or to another starch molecule. This small crosslinking agent maybe can connect some starch or lignin polymers to the same polymers and we need to have a longer crosslinking agent with higher MW. The second choice was PEGDGE 400, for many reasons including a long molecular chain, polar hydroxyl groups, and having two functional epoxy groups to connect two polymers.

### 3.1.3 Mechanism of reactions

This kind of reaction proceeds through the  $S_N2$  reaction mechanism (Figure 3.3). Epoxides are three-membered rings containing an oxygen atom. They are associated with high ring strain and this is the basis of their reactivity towards nucleophiles despite lacking a good leaving group. Either hydroxyl group may be involved in the reaction of the starch molecule with PEGDGE400 (Figure 3.4)

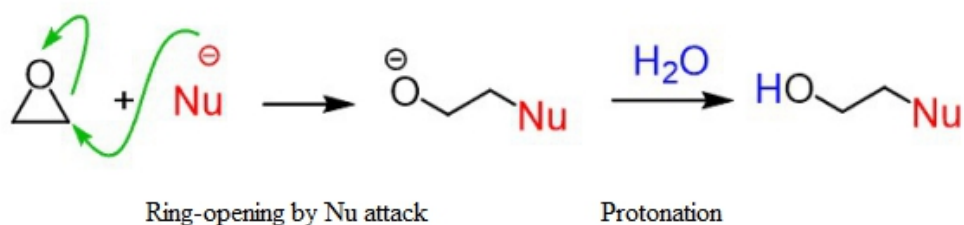


Figure 3-3: The ring-opening reactions of epoxides (PEGDGE400) occur via  $S_N2$  mechanism where the oxygen of the epoxide is the leaving group.

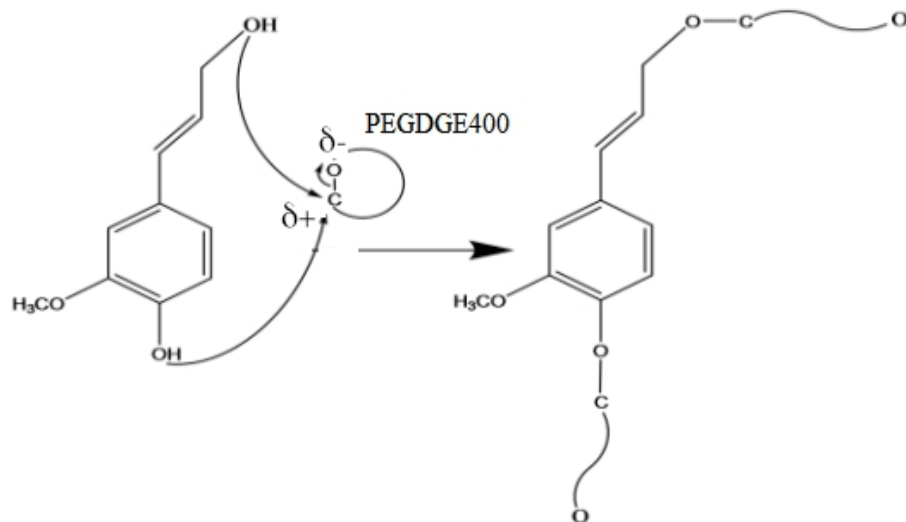


Figure 3-4: General  $S_N2$  reaction with ring-opening. Electrophilic center (carbon) is partially negatively-charged, and oxygen is partially positively-charged.

In Figure 3.5, a schematic of crosslinking reaction between two polymer and producing a complex network with different connections and ether bondings is shown.

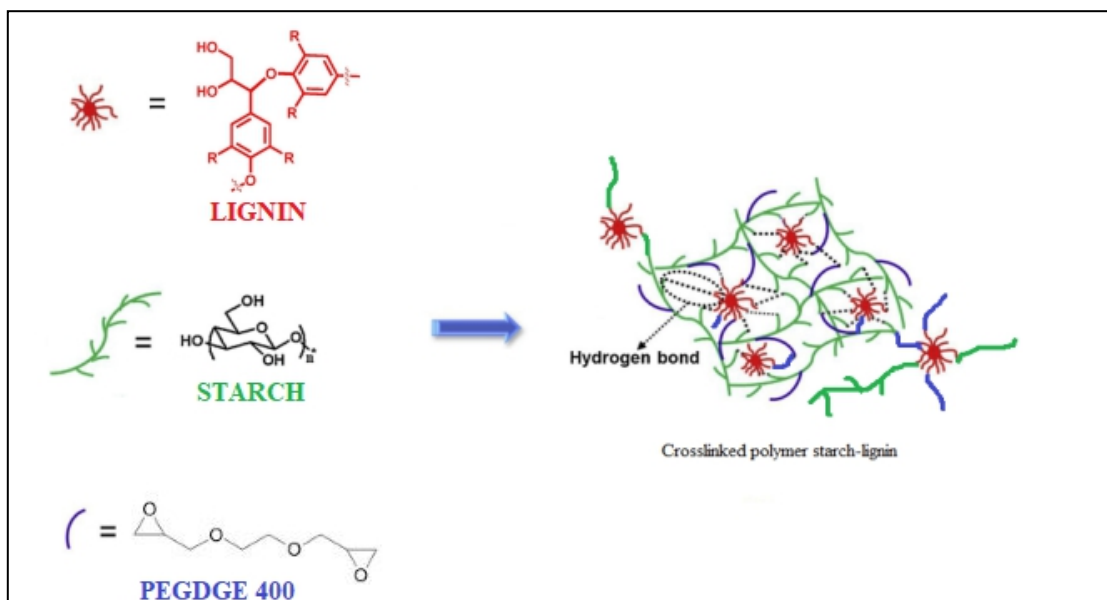


Figure 3-5: Reaction scheme of the synthesis of crosslinked starch-lignin polymers shows the reaction procedures followed to produce various modified starches.

## **3.2 Synthesis**

As it was mentioned in chapter 2, before selecting PEGDGE 400 as the crosslinking agent and water as solvent, different reaction conditions were considered: Using 1. by applying DMSO as a solvent, 2. using Epichlorohydrin as the crosslinking agent, and 3. silylation of starch. All reactions failed by dropping viscosity instantly, so we moved to the next step changing the crosslinking agent to PEGDGE400 and using water as solvent.

### **3.2.1 Reaction of starch, lignin and PEGDGE400 with water as solvent**

A series of samples were prepared with different molar ratios of PEGDGE400 to lignin and starch content in both glasses of water at different temperatures for different amounts of time, with both lignin and starch as starting materials.

## **3.3 Composition**

### **3.3.1 Sugar analysis**

The concentration of mono-sugars in the hydrolysis liquors was measured as stated in chapter 2, and it reflected the concentration of total mono-sugars (after conversion of oligosugars to mono-sugars) in the hydrolysis and soda liquors. The concentrations of polysugars were determined via subtracting total sugar concentrations from mono-sugar concentrations. The starch content (as glucose) content was measured and presented in Figure 3-6, along with the results of lignin content measurements.

### **3.3.2 UV analysis**

Based on the intrinsic structure of lignin, several absorption maxima attributed to the different functional groups of lignin are observed as shown in Table 3.1. According to Lambert-Beer's Law, UV spectroscopy can be used for the semiquantitative determination of the lignin content in synthesized polymers by using the extinction coefficient (EC). Due to the crosslinked structure of lignin with starch, there is not that much free lignin in the structure of modified starch, and it is expected that all applied lignin molecules are engaged in the crosslinked body of the synthesized polymer. This confirms that most of the lignin precipitated in the reaction was crosslinked with starch when the lignin dosage is not more than 20%.

Table 3-1: UV spectroscopic absorption of typical structures in lignin.

Absorption maxima (nm)	Electronic transition style	Chromophores and structures
205	$\pi$ - $\pi^*$	Conjugated bonds/aromatic ring
240	$n$ - $\pi^*$	Free -Phenolic OH
282	$\pi$ - $\pi^*$	Conjugated bonds/aromatic ring
320	$\pi$ - $\pi^*$	Aromatic ring conjugated bond with C = C
320	$n$ - $\pi^*$	C =O groups conjugated to aromatic ring
325	$n$ - $\pi^*$	Etherified ferulic acid

The peaks at about 280 nm are attributed to the absorbance of benzene rings in lignin, which is ascribed to the  $\pi \rightarrow \pi^*$  transition and vibrational effect of benzene rings in lignin.

Different copolymers from starch, lignin and crosslinking agent from 0 lignin to 100% lignin were prepared. To determine the actual percentage of lignin and starch in each polymer, UV and IC were measured following TAPPI and NERL methods. The results are shown in Figure 3-6.

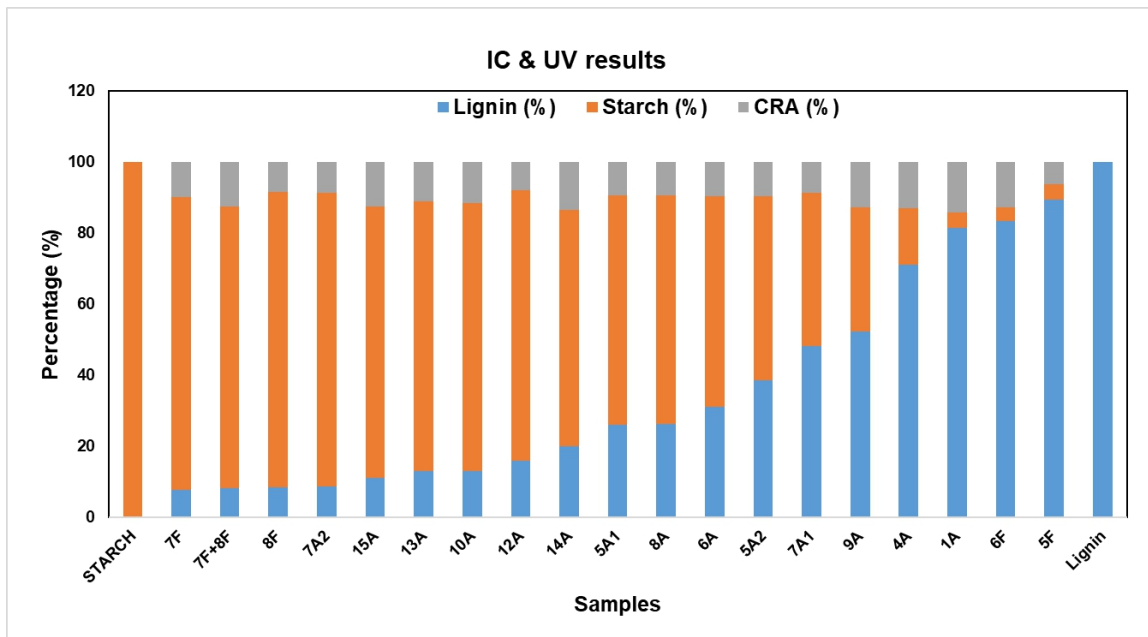


Figure 3-6: UV and IC results for modified and unmodified polymers.

### 3.3.3 XPS Analysis

To quantitatively determine the surface lignin content of starch-lignin polymers, the atomic composition of lignin-starch samples' surface was analyzed using XPS and the results are summarized in Table 3.2. Moreover, based on the proportions of O and C in the XPS data, the signals of C 1s (283.0 eV) and O 1s (529.5 eV) were observed in the XPS spectra of starch-lignin samples and displayed in Figure 3.7. Compared with unmodified starch with 36.1 wt.% of O content and 60.7 wt.% of C content, the selected modified starch (70% starch-20% lignin) showed a lower O content (30.5 wt.%) as well as a higher C content (76.8 wt.%). Correspondingly, the O/C ratio of unmodified starch decreased after modifying starch with lignin (0.60 for unmodified starch to 0.45 for 70% starch-20% lignin). The decrement of O/C ratio for modified starch might be caused by the lignin located in the structure of starch, which possesses a far lower O/C ratio (0.27) than that of unmodified starch (0.60).

Table 3-2: Atomic percentage, O/C ratios, and relative amount of C 1s peaks for modified and unmodified starches and lignin sample.

Samples	BE (eV)	Atomic conc. (%)	Error (%)	Mass conc. (%)	C/O	O/C
80% starch-10% lignin, C 1s	284.80	64.66	0.29	53.48	2.49	-
80% starch-10% lignin, O 1s	531.80	25.97	0.27	28.61	-	0.40
70% starch-20% lignin, C 1s	284.80	67.83	0.18	60.12	2.22	-
70% starch-20% lignin, O 1s	531.80	30.45	0.17	35.96	-	0.45
lignin, C 1s	284.60	78.45	0.19	72.69	3.73	-
lignin, O 1s	532.60	20.98	0.18	25.90	-	0.27
starch, C 1s	284.80	60.65	0.18	52.13	1.68	-
starch, O 1s	531.80	36.10	0.17	41.33	-	0.60

The XPS spectra of unmodified starch and produced FLCs are shown in Figure 3.7. The spectrum of each samples showed two major peaks of C 1s and O 1s as well as some minor peaks, which two of them could be assigned to S 2p and Si 2p signals. The presence of S 2p was observed in lignin and lignin containing samples (FLCs), which might be due to the preparation process of kraft pulp, as reported in the previous studies [50]. However, most probable cause for the Si 2p signal could be contamination of experimental equipment and tools. After crosslinking reaction, some new peaks were found in the spectrum of the modified starch (C 2p (192.7 eV) and O 2p (492.0 eV)), indicating that the lignin molecules were successfully introduced to the chemical structure of starch by creating new covalent ether bonds. Interestingly, these results are consistent with the results obtained from XRD and UV-Vis.

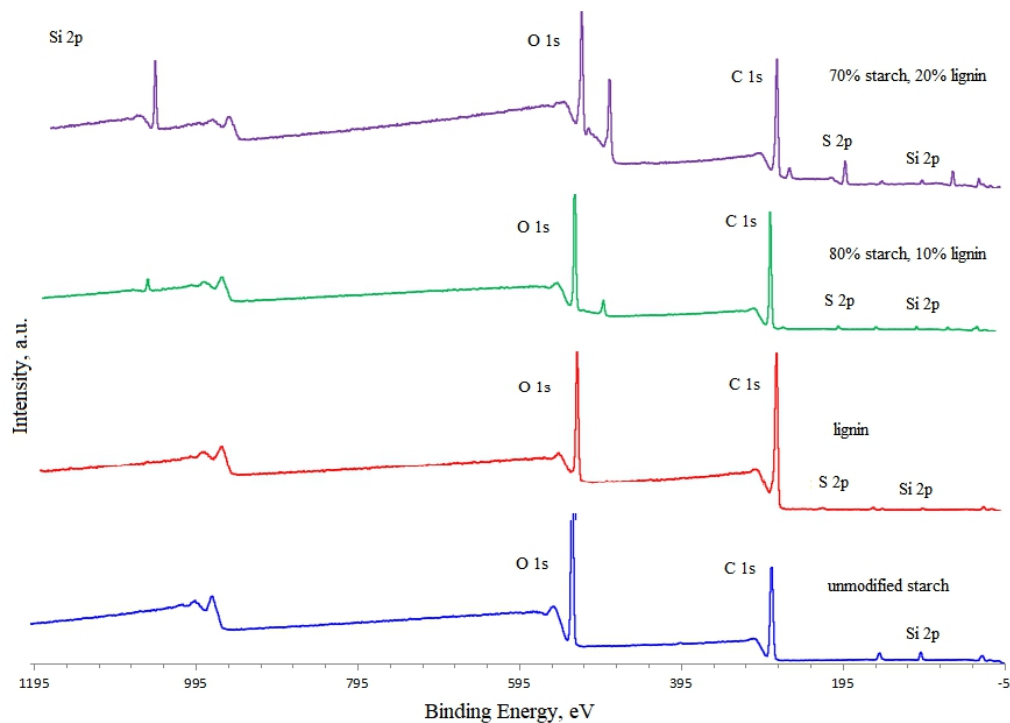


Figure 3-7: XPS high resolution C 1s spectra of lignin, unmodified starch, 70% starch-20% lignin, 80% starch-10% lignin

The high-resolution scan XPS spectrum of C 1s, O 1s, C 2p and O 2p with the fitting data for the kraft lignin, unmodified starch, 70% starch-20% lignin polymer, and 80% starch-10% lignin polymer is presented in Figure 3.8. The functional group compositions of each component in the signals of C 1s are shown in Table 3.2. The C 1s spectrum of all samples were deconvoluted into four sub-peaks shown in Figure 3.8. For lignin, the main peak located at 283.73 eV is attributed to the C-C bond. A noticeable peak can be observed in the C 1s spectrum located at 285.23 eV, which indicates the presence of C-OH bonds. The shoulder can be observed at 290.23 eV and attributes to the C=O and/or O=C-O [13-15].

For unmodified starch, the C 1s spectrum of the sample can be deconvoluted into four Gaussian peaks corresponding to four carbon-related chemical functional groups (C1: C-C at 284.15 eV; C2: C-O at 285.7 eV; C3: O-C-O at 286.8 eV; C4: C=O at 289.06 eV). In modified starch spectra, the peaks of the four carbon atoms are categorized by their bonds [16]. The

relative amount of each carbon type in the samples is determined by calculating the area of peaks and the results are also listed in Table 3.2. It can be seen that C 1s spectra of unmodified starch contained three carbon-related chemical functional groups (C-C: 31.62%; C-O: 42.17%; O-C-O: 24.05%). In addition to three chemical functional groups, the C 1s spectra of modified starch possessed C=O functional group. Also, it can be observed that the relative amount of C=O is 2.15% for unmodified starch and 4.66% for kraft lignin, and this amount for unmodified starch increased after modifying starch with lignin with a direct correlation to the lignin content of the modified starch polymers, which further supports the occurrence of a crosslinking reaction between these two polymers. In the case of modified starch, the crosslinking process created obvious changes in the structural chemical bonds displayed in the related profiles, due to the reduction of the C-OH linkages. After crosslinking reactions, the percentage of C-OH groups decreased from 30.6 % to 19.28% reflecting the decrement of C-OH linkages in the structure of produced polymer (i.e., a clear shortening in the intensity of the band at 285.72 eV, Figure 3.8). Moreover, as shown in the same figure, when the amounts of C-OH groups decreased the amounts of C-O-C groups increased, which could be attributed to the nucleophilic substitution reaction between the aliphatic and aromatic hydroxy groups and the crosslinking agent.



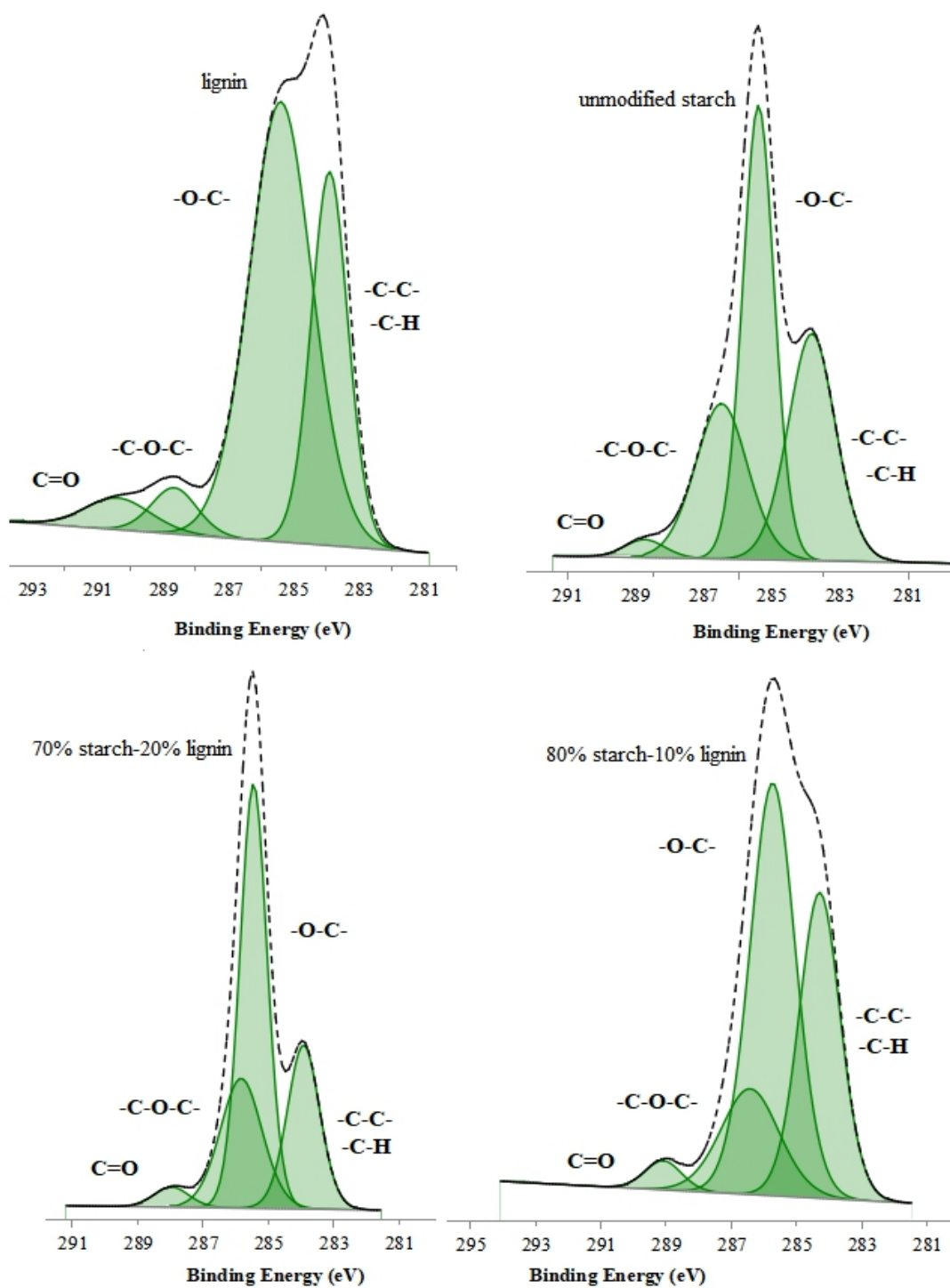


Figure 3-8: XPS high resolution C 1s spectra of lignin, unmodified starch, 70% starch-20% lignin, 80% starch-10% lignin

Basically, lignin has a higher carbon (C) content and lower content of oxygen (O) and hydrogen (H) in comparison to those of raw biomass. Table 3.3 shows the C, O, H, and N contents of all samples determined by a CHNS analyzer. As it can be seen in Table 3.3 the C/O ratio for modified starch is higher than that for starch. These results are in agreement with XPS results which will be discussed later indicated that the crosslinking reaction successfully involves lignin in the structure of starch and increases its C content as well as decreasing its O content when compared to those of unmodified starch. As the C/O ratio for lignin is higher than that for starch, this could be considered as a confirmation for the occurrence of crosslinking reaction, which creates new ether bonds during this process between hydroxyl groups of lignin and starch which increases C/O ratio of the produced polymer.

Table 3-3: Design parameters and CHNS results

Run	Lignin Content (g)	Starch Content (g)	Crosslinking agent (%)	Yield (%)	C (%)
<b>Ref-lignin</b>	100	0	NA	NA	63.08
<b>6A1</b>	90	0	10	76.07	52.27
<b>5A3</b>	80	10	10	84.4	48.37
<b>1A</b>	75	15	10	82.1	48.66
<b>8A</b>	70	20	10	93.2	45.91
<b>4A</b>	60	30	10	86.2	45.52
<b>7A1</b>	65	25	10	81.1	46.73
<b>10A</b>	55	35	10	80.2	44.44
<b>15A</b>	50	40	10	87.2	41.9
<b>5A2</b>	45	45	10	83.5	47.87
<b>8F+7F</b>	40	50	10	87.1	40.82
<b>14A</b>	35	55	10	78.3	39.78
<b>7F</b>	30	60	10	86.4	40.63
<b>8F+7F</b>	25	65	10	76.9	40.65
<b>5A1</b>	20	70	10	76.6	48.45
<b>7A2</b>	10	80	10	77.9	39.22
<b>13A</b>	5	85	10	81.2	37.66
<b>12A</b>	0	90	10	80.3	33.54
<b>Ref-starch</b>	0	100	NA	NA	37.48

\* wt. % of N was zero for all samples.

### **3.3.4 SEM analysis**

SEM analysis was carried out to highlight the structural modification as shown in Figure 3.9. Images of the resulting material show a clear morphological modification compared to those of starch, lignin and starch-lignin polymers. The crosslinked product shows integration of starch and lignin material in crosslinked polymers. To check whether the observed morphological changes result from chemical links between modified starch and lignin, morphological measurements and observations will be useful to highlight any structural variations due to chemical changes.

To explain the evolution of the mechanical and strength properties of starch, before and after crosslinking reactions, it was assumed that chemical changes are responsible for these variations affected the microstructure of polymers. Representative SEM images are shown in below figure illustrate the obvious differences, where native starch and lignin seem flattened, while crosslinked polymers present rougher surfaces.

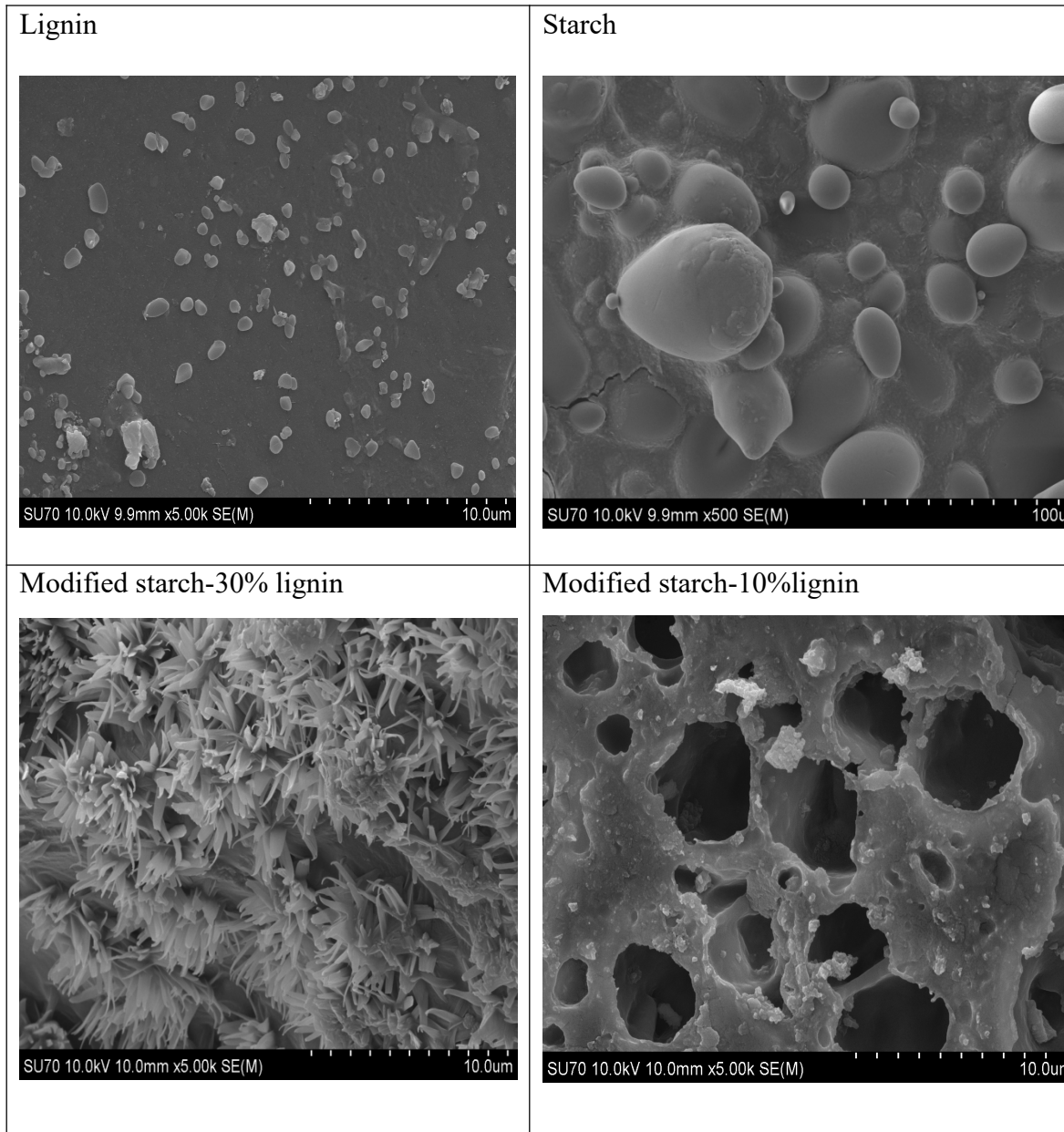


Figure 3-9: SEM micrographs of cross sections of lignin, starch, and two crosslinked polymers, that shows some details of the polymers structure.

The observed morphological characteristics of these crosslinked polymers influence their rheological behaviour and mechanical strength. For instance, the  $G'$  and  $G''$  modulus of crosslinked polymers are related to morphology and their porous structure. The surface

morphology of these 4 selected samples are shown in Figure 3.9. Based on the appearance of the polymers, the modified starches should have a higher surface area, pore volume, and pore size compared to the kraft lignin and native starch polymers. Lignin-starch crosslinked polymers are expected to become more hydrophilic than their natural forms due to the incorporation of an ether linkages between polymers.

### 3.4 Characterization

The microstructure, morphology, moisture absorbability, and thermal properties of the polymers were also evaluated. Hence, the prepared starch/lignin crosslinked polymers can be used as a biodegradable, water absorbent material in water-based fluids.

#### 3.4.1 FTIR analysis

Figure 3.10 shows the FT-IR spectrum of lignin, starch, starch/lignin crosslinked polymers. The broad peak between 3200 and 3700  $\text{cm}^{-1}$  correspond to O–H stretching of the hydroxyl groups. The C–H stretching (between 2800 and 3200  $\text{cm}^{-1}$ ) and C–O–C (at 1168  $\text{cm}^{-1}$ ) peaks should be increased after crosslinking reactions. Therefore, it was an evident that during the reaction of kraft lignin and starch with PEGDGE, its phenolic hydroxyl groups were converted to the corresponding ether linkages as the CH stretching was increased in the modified polymer (between 2800 and 3200  $\text{cm}^{-1}$ ). The FT-IR analysis also confirmed the success of the crosslinking reaction.

Peaks at 3450  $\text{cm}^{-1}$  and 2800  $\text{cm}^{-1}$  mainly account for OH stretching. Peaks for aromatic functionality in the lignin appear at 1600  $\text{cm}^{-1}$ . An aromatic skeletal vibration appears around 1500  $\text{cm}^{-1}$ . C-H deformation peaks can be observed at 1450  $\text{cm}^{-1}$  and 1420  $\text{cm}^{-1}$ . At 1320  $\text{cm}^{-1}$ , the peak mainly accounts for the C-O stretching in syringyl unit. The peaks for C-O-C soft segments appear at 1200  $\text{cm}^{-1}$ . C-H stretching of polysaccharides appears around 1100  $\text{cm}^{-1}$  and 1030  $\text{cm}^{-1}$ . There are small peaks at 830  $\text{cm}^{-1}$  and 618  $\text{cm}^{-1}$  which at for other C-H peaks [17,18].

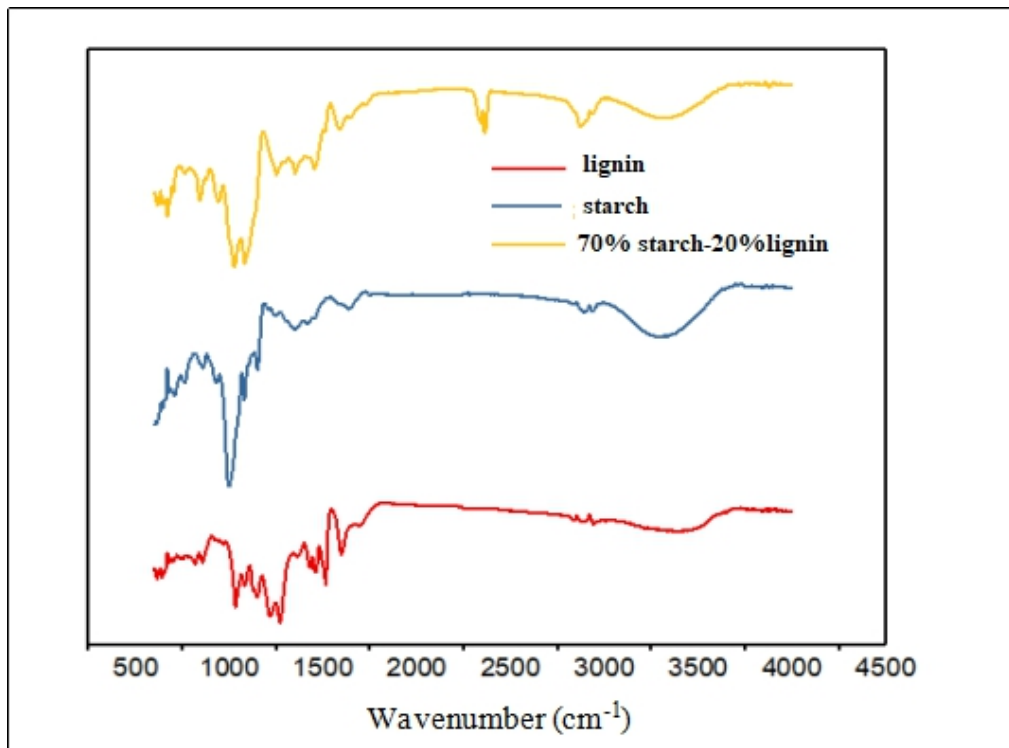


Figure 3-10: FT-IR spectrum of lignin, starch, and modified starch.

### 3.4.2 XRD analysis of unmodified starch, lignin and produced polymers

X-ray diffraction (XRD) technique has been used to investigate crystalline changes in the starch structure, after the chemical modifications. Figure 3.11 shows the diffractograms obtained for untreated starch and modified starch and lignin. The starch diffractogram reveals some characteristic peaks superimposed to a broad pattern due to the amorphous parts. The crosslinking process leads to a spectrum with more resolved peaks, probably due to the engaging hydroxyl groups of starch in new bondings. In addition, the XRD pattern of lignin is different than starch-lignin crosslinked polymer and probably this is due to the fact that the reaction has occurred, and the chemical structure changed significantly [17, 19].

The most commonly used method to determine the degree of crystallinity of unmodified starch and its derivatives is X-ray diffraction (XRD). The XRD measurements for unmodified starch, indicate the existence of two ordered and amorphous sections in its structure. The ordered

section is determined mainly by the amylose and branching points of amylopectin, while the amorphous phase is associated with the short-branched chains of amylopectin. In other words, the crystallinity of starch is due to the arranged saccharide backbone and the ordered regions formed by glucose groups on saccharide units. The crystallinity index (CrI), which defines the crystallinity degree of samples decreased significantly after introducing lignin to the structure of starch by crosslinking reaction. The CrI of unmodified starch based on the result of XRD analysis shown in Figure 3-11 was calculated to be 40.9 % which after crosslinking reaction decreased to almost zero. This is due to the significant change in hydrogen bonds between starch's granules which are cleaved and involved in ether bonds between hydroxyl groups of starch and lignin during crosslinking reaction.

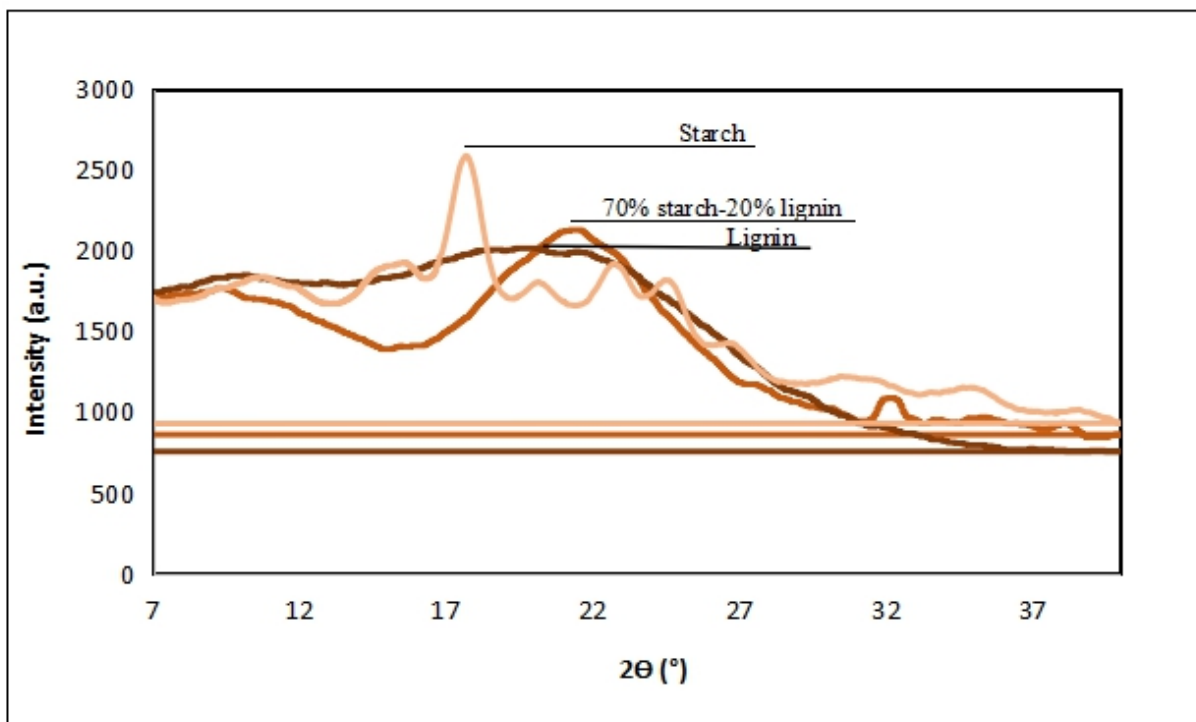


Figure 3-11: XRD patterns of 70% starch-20% lignin, pure lignin, pure starch.

Two-dimensional diffraction patterns of all samples were recorded and presented in Figure 3.11. For the unmodified starch, the crystallinity is presented by diffraction peaks well-defined at 15, 17, 19.3, and 23 degree as  $2\theta$ , which were attributed to a crystalline structure of starch.



Moreover, the XRD pattern of the modified starch was different from that of unmodified one, not showing any clear and well-defined peaks [19,20].

### 3.5 Physical properties

#### 3.5.1 Hydrophilicity

##### 3.5.1.1 Effect of crosslinking process on water absorption of starch

For the efficiency evaluation of the produced polymer in the proposed application as an FLC (fluid loss controller) in WDFs (water-based drilling fluids), swelling kinetics is one of the key points. When this product, which is a starch-lignin base, is immersed in WDFs the water diffuses into the polymer matrix and the material starts swelling. The penetration of water into dynamically formed spaces between macromolecule chains of the polymer continues until it reaches the equilibrium state where weight gain stops.

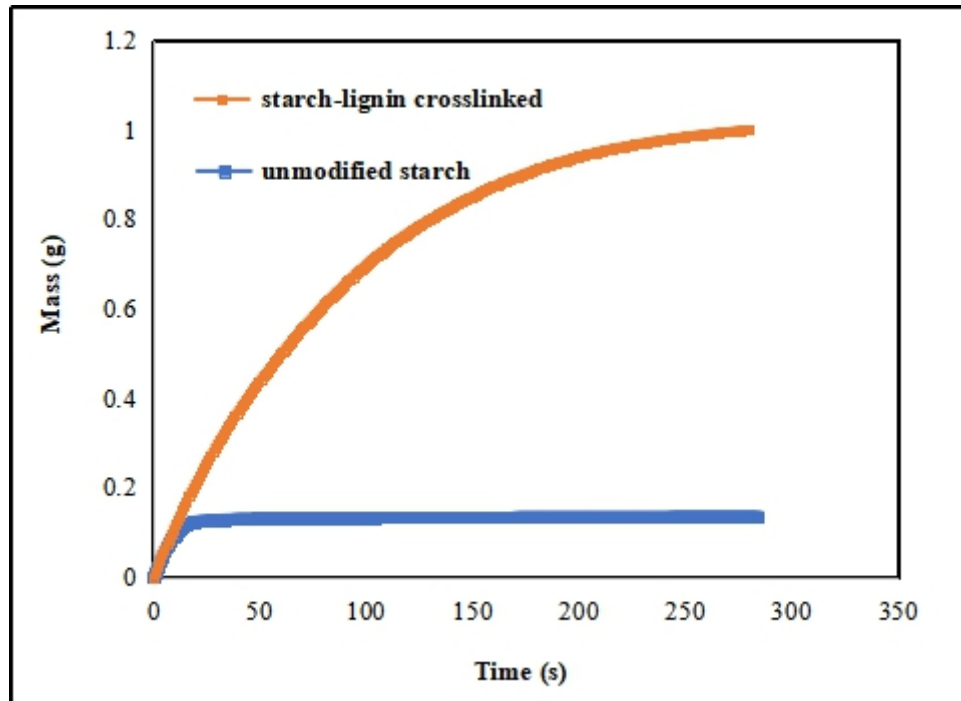


Figure 3-12: Water absorption of unmodified starch and selected modified starch.

In fact, starch molecules inflate after absorbing water through hydrogen bonding with the free hydroxyl groups in their structure without making any changes in the structural orders. With increasing the amount of starch in a structural combination of FLCs, water absorption increases forming a network that holds water, which consequently enhances the viscosity of the mixture. The water absorption capacity of these products was investigated by carrying out a water absorption test using an optical tensiometer instrument. As expected, and shown in Figure 3.12, the modification of starch by lignin resulted in higher water absorption. The mass changes of the products containing various lignin amounts versus time are shown in Figure 3.13. As it is shown in the figure water absorption rates were highest for most of the products in the first 3 min, after which the water absorption rates slowed down but kept slight increments over time [19]. In addition, the other advantage of the new polymer is when it is cold or warm, the viscosity doesn't change at all. But, for the natural starch polymer, there is a huge difference in viscosity before and after warming up the system.

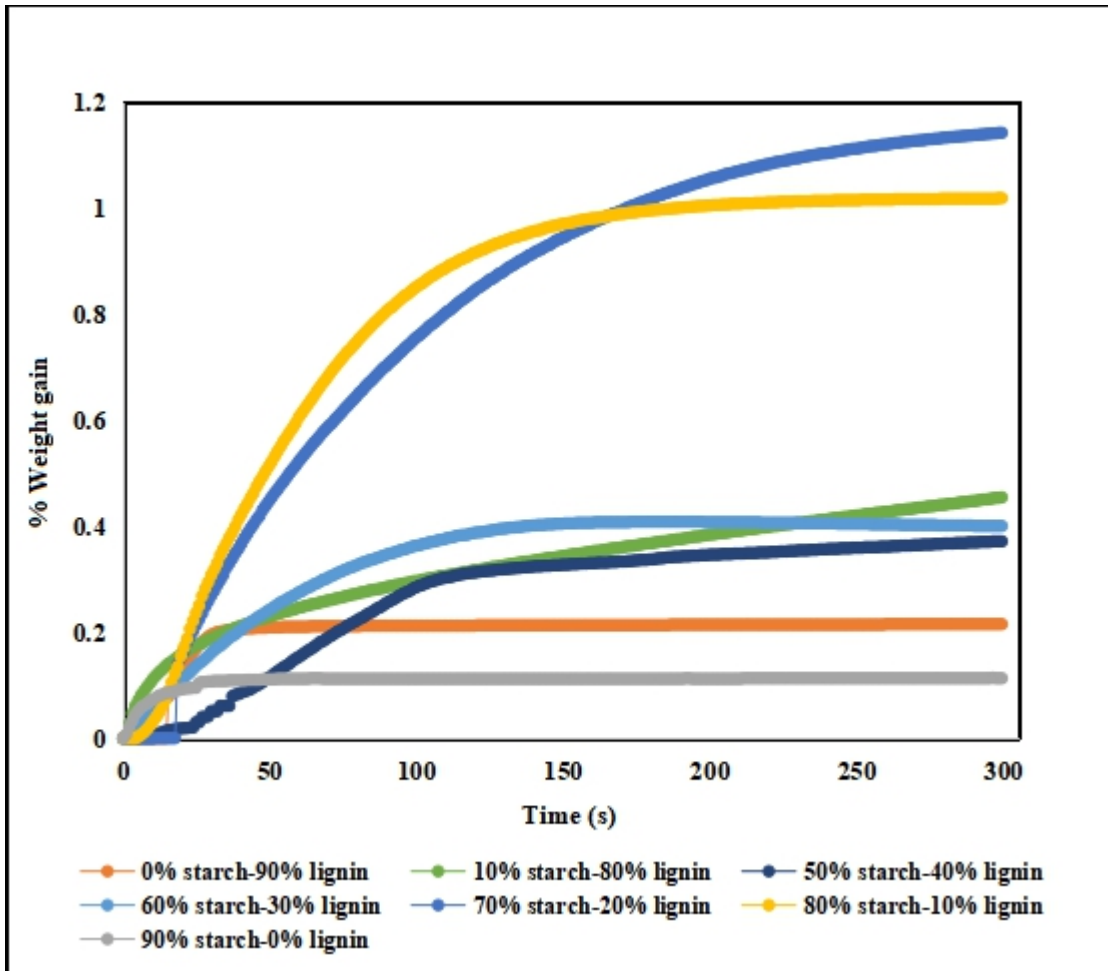


Figure 3-13: Water absorption of modified starch polymers with varied dosages of starch and lignin.

The water absorption analysis results showed in Figure 3-13 proves that the produced FLC containing 20% lignin and 10% crosslinking agent has the potential of absorbing water up to 500% of its initial mass, which ranked the highest among the all products. Furthermore, the weight gain rate at initial hydration of the polymers was fastest when it contained 10% lignin. However, the water absorption capacity of starch-lignin base FLCs decreased with increasing the amount of lignin and the product containing 90 % lignin showed the lowest water absorption capacity (100 % of initial mass). Based on the results discussed in this section, it

can be concluded that the addition of lignin to starch for producing FLCs have a positive effect on increasing their hydrophilicity and water absorption capacity to a certain point.

During the swelling of unmodified starch and modified starch-lignin base polymers, the ether groups available in the structure of polymers, which are formed between hydroxyl groups of starch and lignin, are ionized and consequently water penetrated the structural body of the polymers. This water penetration and structural swelling is facilitated via electrostatic attraction between adjacent ionized ether groups formed between starch and lignin. Therefore, it can be concluded that the number of formed ether groups between starch and lignin was highest when the amount of lignin added to starch for the crosslinking reaction was 20 %.

Therefore, the main reason for unmodified starch and produced FLCs using starch and lignin to behave differently during water absorption process is the number of ether groups found in the structure of these polymers which defines their structural polarity and hydrophilicity.

Note that water absorption capacity depends on a number of factors including not only its intrinsic hydrophilicity but the morphology, specific surface area, density, etc. Reporting absorption units per unit volume or area can shed some light about related effects. However, overall, there is clear indication of the role of the amount of lignin and crosslinking agent in starch-lignin derivatives to increase the hydrophilicity of the produced polymers.

### **3.5.1.2 Contact Angle**

Figure 3.14 displays the contact angle of water drop with the starch derivative films that were formed using different polymers. It is observed that 1) the contact angle was significantly affected by the type of polymer used, 2) by increasing the PEDDGE and lignin ratio, the hydrophilicity of the surfaces increased. The reason for more noticeable change in hydrophilicity of the surface for the samples of crosslinked polymers could be related to both the structure of the molecule and the surface texture of films.

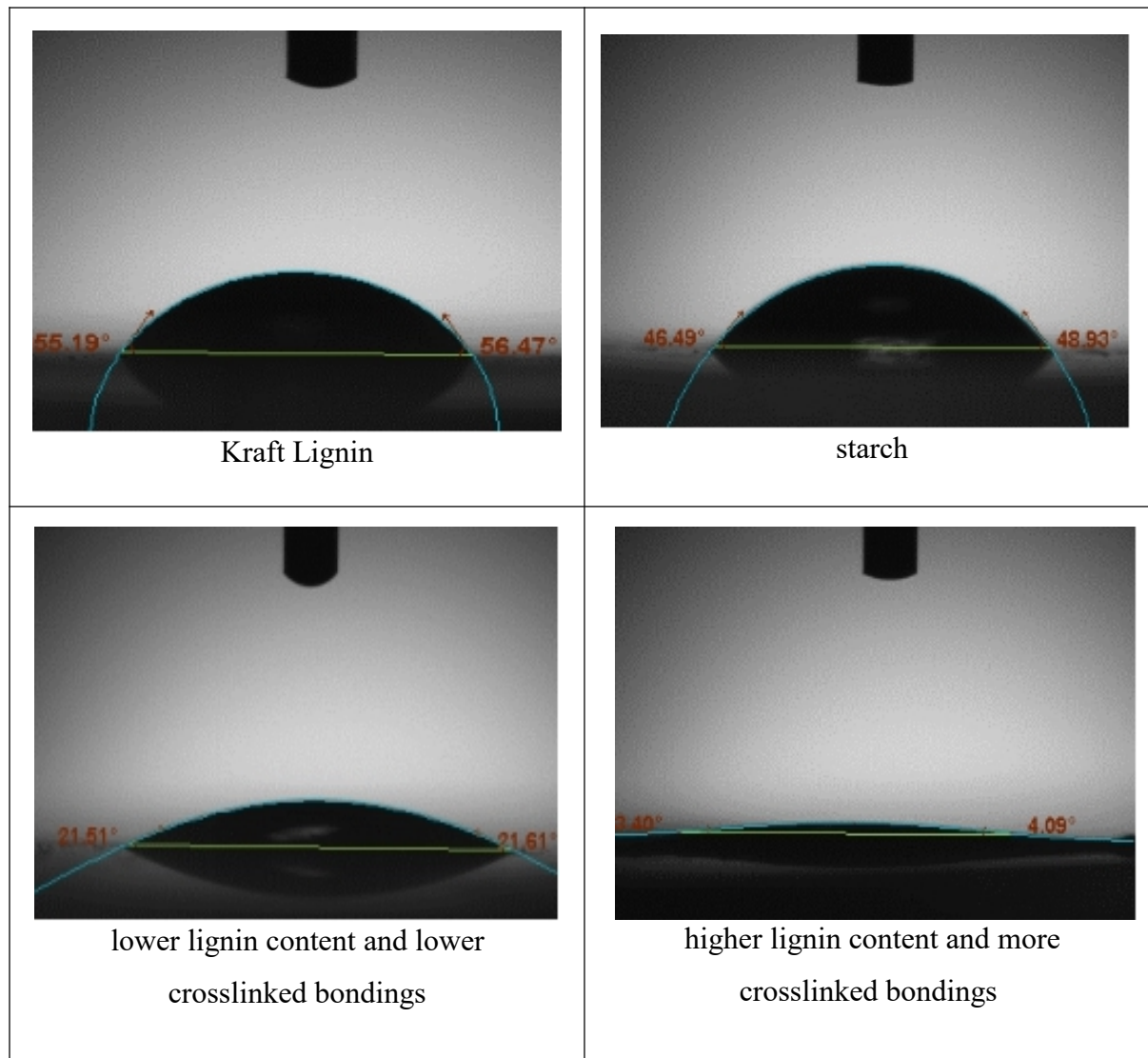


Figure 3-14: Illustration of contact angles formed by sessile liquid droplet on a smooth solid surface.

Figure 3.15 shows how ratio of bondings in natural and modified polymers were changed versus contact angle. The prediction was that when  $C2/C1$  increases, contact angle will decrease. The actual results were different. The contact angle will increase till  $C2/C1=1$ , then it starts decreasing.

In addition, Figure 3.16 shows how the percentage of lignin in modified polymers was changed versus contact angle. The prediction was that this graph will not be linear and it will

increase and then decrease. The contact angle will increase by raising the lignin content to 45% and then it will start decreasing to near zero.

The results of whole contact angle measurements indicated that increasing lignin percentage will not necessarily increase the crosslinking process and creating ether bonds. The whole crosslinking process and creating new ether bondings depend on the ratio between lignin/starch/crosslinking agent.

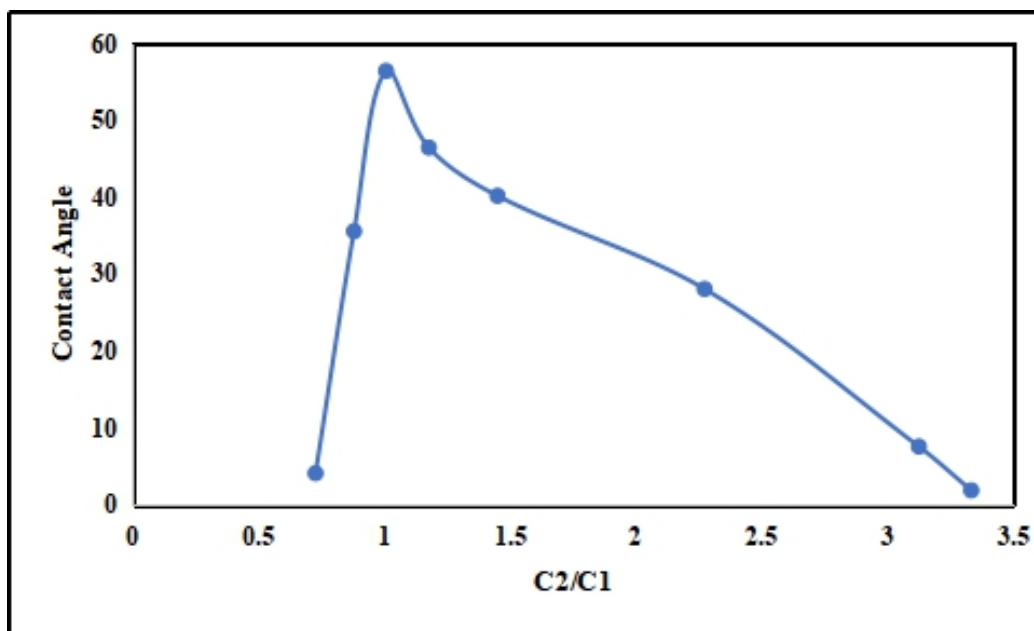


Figure 3-15: Contact angle of modified starch polymers with varied ratio of bonds in starch-lignin crosslinked polymers.

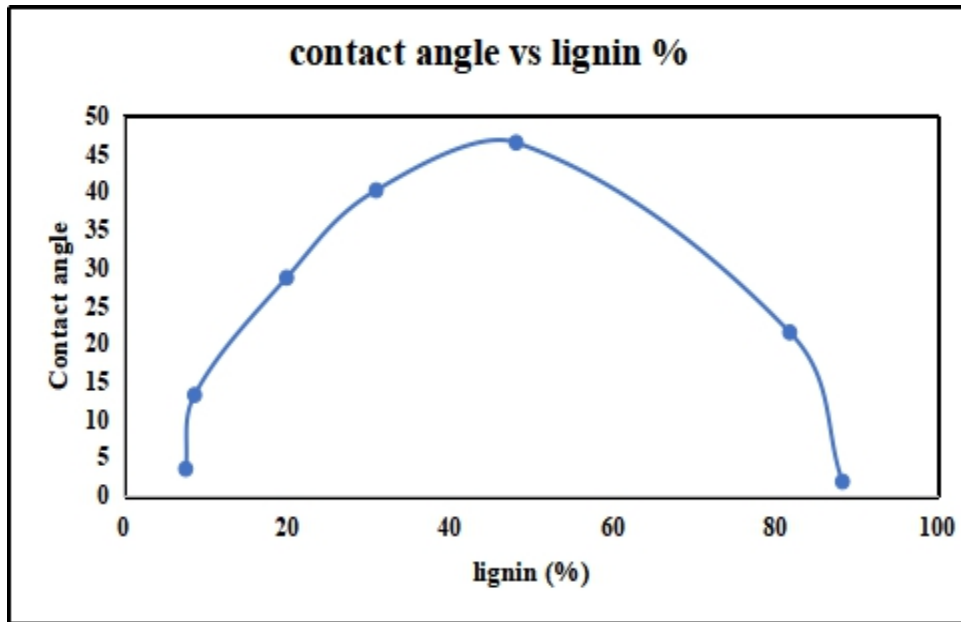


Figure 3-16: Contact angle of modified starch polymers vs the percentage of lignin in starch-lignin crosslinked polymers.

### 3.5.2 Thermal Stability

Thermostability is an important parameter to be considered during the selection of drilling fluid additives for high-temperature applications. We investigated herein the thermal stability of starch-lignin polymers using TG-DTG analyses, which have been proven to be suitable methods for investigating the thermostability and decomposition of polymeric compounds. The influence of linking chains formed between starch and kraft lignin during crosslinking reaction on the structural and thermal properties of the produced FLC was studied using thermogravimetric analysis and differential scanning calorimetry analysis.

#### 3.5.2.1 TGA and DTG (rate of weight loss) curves results

Thermogravimetric analysis (TGA) was performed to investigate the thermal response of starch, lignin, and FLCs to heat. Samples (7-8 mg) were dried in an oven at 60 °C for 24 h prior to the analysis. The analysis was performed under a nitrogen atmosphere in a thermal

analyzer (TGA i1000, Instrument Specialists Inc.), at a flow rate of 15 mL/min and heated from 25 °C to 800 °C at the rate of 5 °C/min [21-23].

For TGA investigation, we expected that crosslinking between starch and lignin will enhance thermal stability of starch.

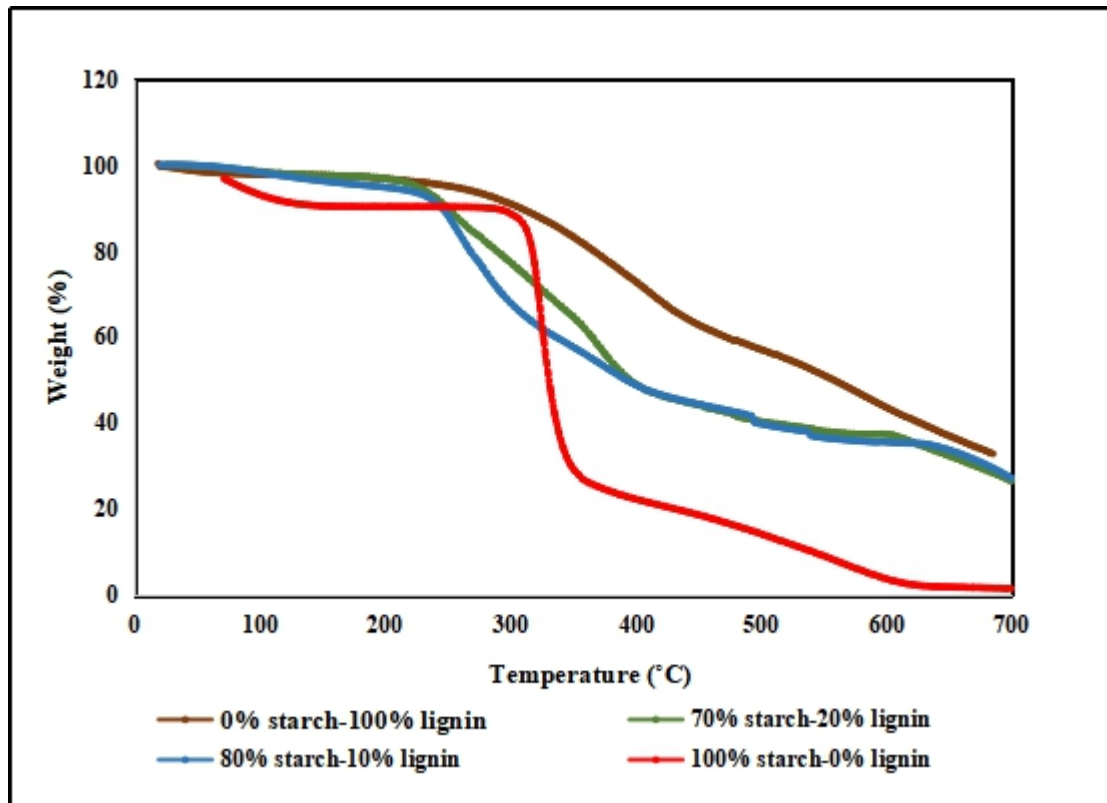


Figure 3-17: Weight loss trend of kraft lignin, unmodified starch, and modified starch polymers.

As shown in Figure 3.17, when initial decomposition temperatures of 4 polymers are compared, starch started losing weight at higher temperature (around 300 °C) than others. It might be due to strong intermolecular hydrogen bonds of starch that prevents it against structural deformation. However, these intermolecular bonds are mostly cleaved under hydrolysis reaction when starch is used in an aqueous medium with high alkalinity and temperature as a FLC. By raising the temperature further there was a point where 50 wt.% of the polymers decomposed. It is seen in the same figure that both modified starches reached



this point at a higher temperature (390 °C) than unmodified starch (330 °C). Moreover, at the final temperature (700 °C), the final mass residue of modified starch also was more than that of unmodified starch. Unmodified starch decomposed completely when the temperature reached to 600 °C. However, both modified starches (20% lignin-70% starch and 10% lignin-80% starch) could keep nearly 35% of their initial masses even when the temperature raised to 700 °C.

It is shown that the decomposition of unmodified starch occurred over a narrower range of temperatures (310 to 360°C). In comparison to the other three polymers, starch showed the fastest and highest rate of chemical decomposition. It proves that the intramolecular linkages and the intermolecular bonds of unmodified starch are less resistant against temperatures higher than 300 °C than other polymers due to its higher sugar content (70 to 80 wt. %) as the maximum decomposition temperature of sugar was reported to be as low as 290 °C [24]. Moreover, a single-step degradation process was observed for lignin and the decomposition of lignin occurred over a broad range of temperatures (175 to 500°C) which might be due to the more complex carbon-carbon bonds that exist in lignin structure when compared to that of starch and aromatic rings of lignin [25,26]. The lignin residue at 600°C is around 45% which confirms the higher thermal stability of lignin than that of unmodified starch.

Therefore, the shift of maximum decomposition temperature of modified starch-lignin polymers is most likely attributed to the unique aromatic chemical structure and its stronger intermolecular  $\beta$ -O-4 linkages. In addition, during the crosslinking process, a significant number of new covalent bonds between starch and lignin molecules are made which enhance the thermal stability of the produced polymers.

Despite relatively similar thermal behavior of modified starches (20%lignin-70%starch and 10%lignin-80%starch), the polymer with lower lignin content showed to be slightly less stable against heat in comparison to the polymer with higher lignin content. As it is shown, modified starch with 20% lignin content was found to show higher thermal stability and slower weight loss rate over the same range of temperatures (250 to 400°C).

These curves yielded different degradation steps. The initial weight loss was due to water evaporation, as well as the gaseous emissions of carbon monoxide, carbon dioxide, and other pyrolysis products. The second weight loss phase is attributed to the lignin, in the temperature interval of 200 to 450 °C. This extended range is due to the complex structure of the lignin. The thermal degradation in this region involved fragmentation of inter-unit linkages between phenolic hydroxyl, carbonyl, and benzylic hydroxyl groups, releasing monomeric phenols. At temperatures above approximately 450 °C, it was observed that the third and last stage was due to the condensation and/or decomposition reactions of the aromatic rings.

### **3.5.2.2 DTG analysis**

Thermal performance is an important parameter in industrial procedures. Materials with good thermal stability can maintain their structures and properties within a certain temperature range. Here, the thermal stability of various crosslinked polymers was evaluated by TGA.

Figure 3. 18 shows that DTG curve indicates the weight loss corresponding rate, where the peak of this curve (DTGmax) expresses the single decomposition temperature and can be used to demonstrate and compare the thermal stability characteristics of tested materials.

The DTGmax value of the lignin is thus higher than that of the modified starch which may be attributed to different C-O-C linkages content of both lignin. This could be allotted to the high degree of covalent bonds, branching and the extremely condensed aromatic structures formation in starch-lignin crosslinked polymers.

DTGmax is expressed as a single temperature value and can be used to characterize the material's thermal stability. The value of this property could be important to determine in which applications the polymer can be used, particularly if it is exposed briefly to moderately high temperatures.

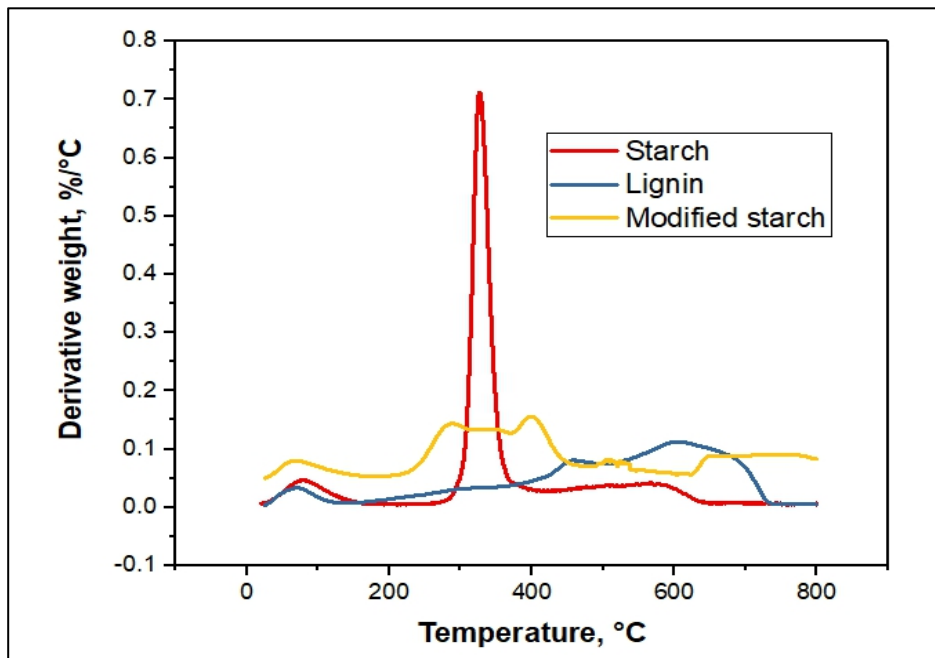


Figure 3-18: DTG curves of pure starch and pure land modified starch

### 3.5.2.3 DSC analysis

Differential scanning calorimetry (DSC) was used to determine the heat capacities ( $C_p$ ) and glass transition temperatures ( $T_g$ ) of the samples (Table 3.4). Approximately 7-10 mg of dried samples were placed in a Tzero® aluminum pan and placed into a differential scanning calorimeter (DSC Q2000, TA Instruments). Analysis was performed under  $N_2$  atmosphere with a heating rate of  $50\text{ }^\circ\text{C}/\text{min}$ . In the DSC analysis, the temperature was raised from  $20\text{ }^\circ\text{C}$  to  $150\text{ }^\circ\text{C}$  to erase thermal history, then the temperature decreased to  $20\text{ }^\circ\text{C}$  again with a cooling rate of  $5\text{ }^\circ\text{C}/\text{min}$  to cool down the sample, and finally, the second heating cycle was conducted from  $20\text{ }^\circ\text{C}$  to  $150\text{ }^\circ\text{C}$  with the rate of  $10.00\text{ }^\circ\text{C}/\text{min}$ . The maximum operating temperatures were set based on the decomposition profile of the samples obtained from TGA analysis of the samples ( $150$  to  $250\text{ }^\circ\text{C}$ ). The number of ether linkages created between hydroxyl groups of starch and lignin polymers during crosslinking reaction influences the  $C_p$  and  $T_g$  of the produced FLCs. It was expected that  $C_p$  and  $T_g$  of both lignin and unmodified starch increased through the crosslinking reaction. The DSC analysis of the samples showed

that when 20 % of lignin crosslinked with 70 % of starch, the Cp and Tg of the product significantly increased (0.3212 J/(g·°C) and 214.96 °C, respectively) in comparison to those of both lignin and unmodified starch (Table 3.4). However, when the dosage of unmodified starch increased to 80 % along with decreasing the dosage of lignin to 10%, the Cp and Tg of the product dropped to 0.2009 J/(g·°C) and 134.29 °C, respectively, which are lower than those of lignin (0.2920 J/(g·°C) and 156.00 °C, respectively). This might be due to the higher number of unreacted hydroxyl groups of starch and a smaller number of rigid aromatic units of lignin in the product structure after crosslinking reaction when the dosage of starch was as high as 80 %. It was concluded that the application of lignin as a natural biopolymer in a crosslinking reaction with starch enhanced the thermal stability and strength of the product.

Table 3-4: DSC results for unmodified and modified starches

<b>Samples</b>	<b>Tg (°C)</b>	<b>Cp (J/g °C)</b>
STARCH	123.03 °C	0.05207
7A2	152.75°C	0.5503
8F	140.23°C	0.5769
7F+8F	149.2 °C	0.9241
7F	152.22°C	1.081
7A1	159.04°C	0.8107
12A	153.07°C	0.6773
10A	158.10°C	0.664
5A	123.66°C	0.6402
6A	145.83°C	0.4966
6F	154.91°C	0.3326
1A	214.96°C	0.3212
5F	153.02°C	0.3406
LIGNIN	168.00°C	0.292

This improvement in thermal stability of starch-lignin crosslinked polymers could be assigned to the high thermal stability of the lignin molecule and the formation of a starch-lignin crosslinked network [27].

#### **3.5.2.4 The effect of lignin and crosslinking agent percentage on physicochemical characteristics of crosslinked polymers by XPS analysis**

The effect of changing bonds to create new linkages in crosslinked polymers illustrated in Figure 3.19, Figure 3.20, and Figure 3.21 show the impact of the crosslinking reaction, the percentage of lignin and the ratio between linkages in the structures on the thermal properties ( $C_p$ ) of new polymers. According to the literature data for lignin and starch polymers and from our experimental spectra, it is possible to separate the various carbons into four main classes:

C1: Carbon-Carbon or carbon-Hydrogen bonding (C-C, C-H peaks around 284.00 eV)

C2: Carbon having a simple bond with only one oxygen (C-O, peak around 286.00 eV)

C3: Carbon that bonds only one oxygen carbonyl or two oxygen atoms, (O-C-O, C=O, peak at 288.0 eV)

C4: Carbon that bonds an oxygen carboxyl group (COOH at 290.00 eV)

The prediction was that when C1/C2 increases,  $C_p$  will increase but it did not occur. That means except for increasing lignin%, we need to increase crosslinking with C2 bonding. When we have more C2 after crosslinking that means we have crosslinked more polymers and that will result in increasing  $C_p$ .

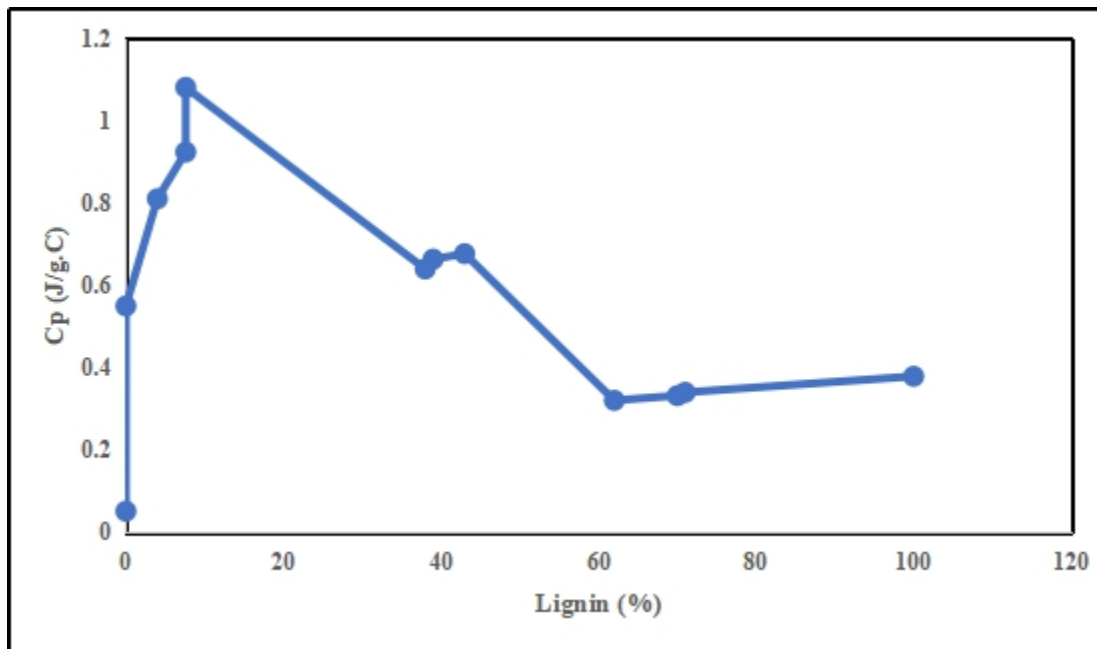


Figure 3-19: Correlation plots of Cp versus the amount of applied lignin.

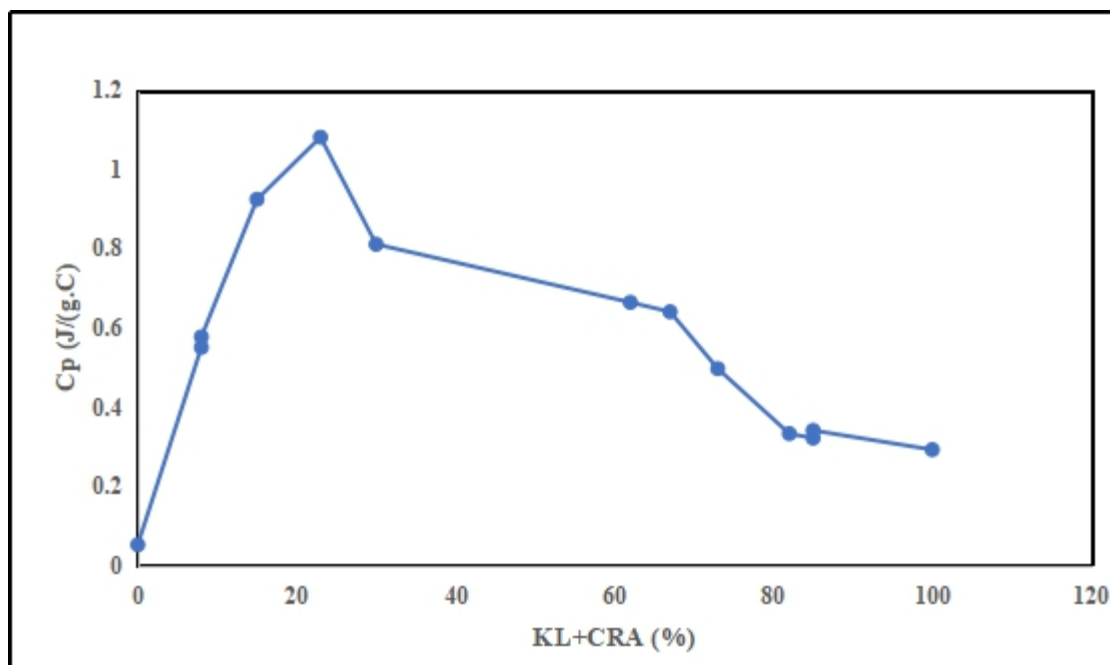


Figure 3-20: Correlation plots of Cp versus the amount of applied lignin and crosslinking agent

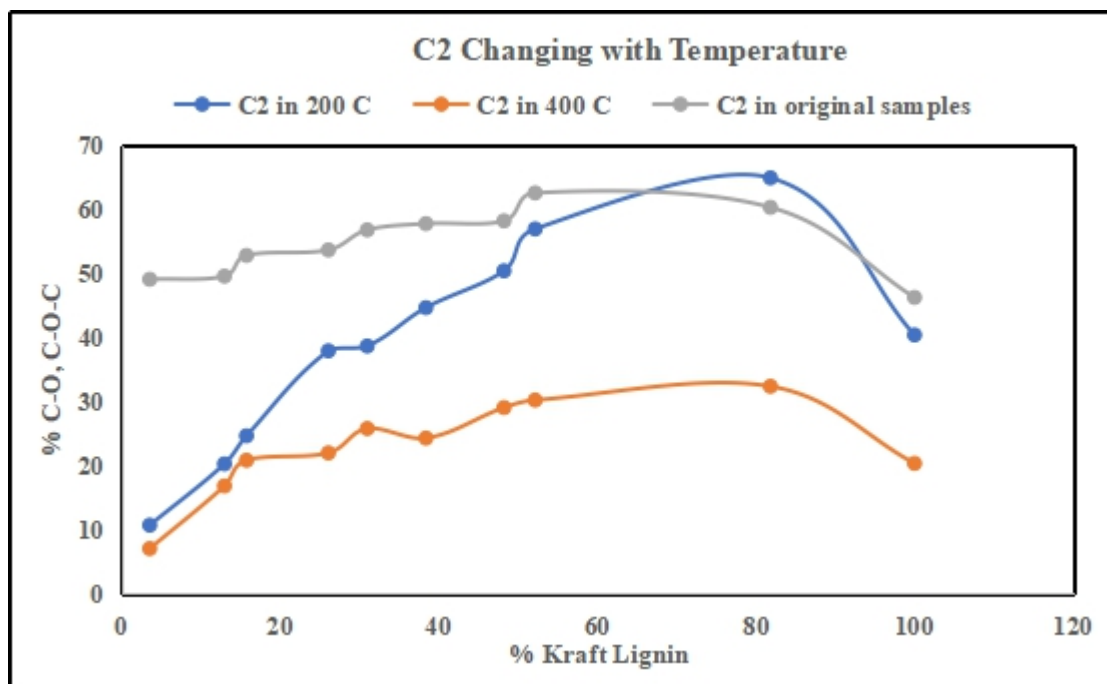


Figure 3-21: Correlation plots of the effect of changing C-C and C-O-C versus the amount of applied lignin after different temperatures.

These results in Figure 3-21 indicated that the decomposition of the substituted groups and aliphatic structures in lignin leads to CO<sub>2</sub> release from the carboxyl groups, H<sub>2</sub>O from the hydroxyl groups, CO from the weakly bound oxygen groups, such as aldehyde groups, and H<sub>2</sub> from the aliphatic and methoxy groups. In contrast, the degradation of cellulose gives carbohydrate-derived compounds that are more difficult to identify.

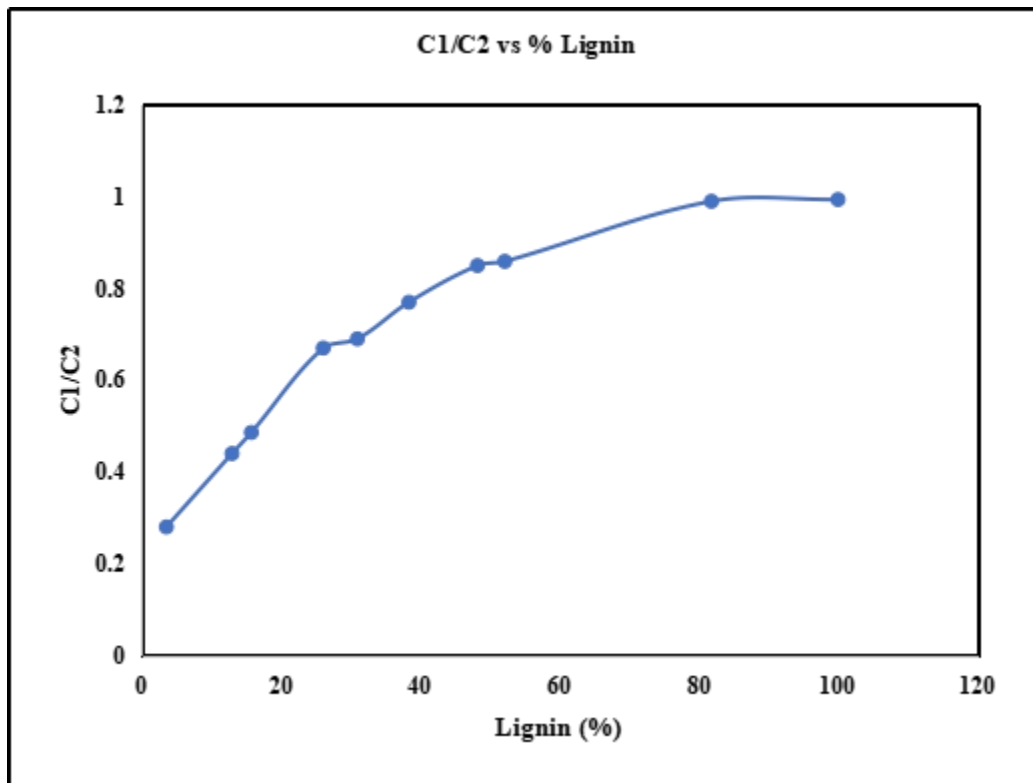


Figure 3-22: Correlation plots of the effect of ratio between C-C and C-O-C versus the amount of applied lignin

### 3.5.2.5 Changing bonds with temperature, lignin, starch, and modified starch by XPS analysis

Figure 3-23 shows that how the bonding in polymers will change by temperature, for lignin, starch, and modified starch. It will be another proof of enhanced thermal stability after modification. The results showed that C-O-C bondings will stay stable in modified starch, but in lignin and starch they will decrease significantly after 400°C. So, we can conclude that these C-O-C bondings that will remain stable even in high temperatures are from the crosslinking process and they will help starch to remain stronger at high temperatures.



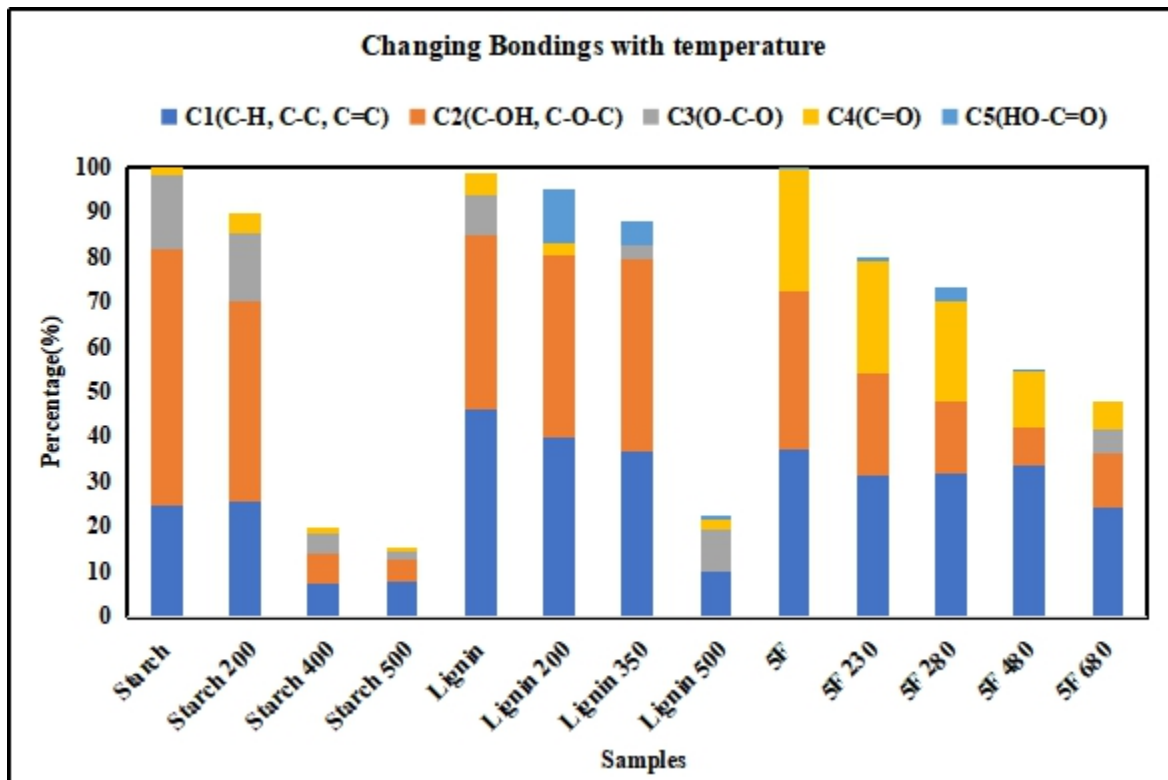


Figure 3-23: Correlation plots of the effect of changing bondings versus the amount of weight loss, by raising temperature.

### 3.5.3 Rheology

Viscoelastic properties of lignin-starch polymers were evaluated at 45 °C in a Discovery Hybrid Rheometer 3 (TA Instrument, USA) fitted with 20 mm parallel-plate geometry and a solvent trap cover. The test methods adopted in this study were oscillatory sweeps at a constant frequency of 1 Hz. The sample was placed between testing plates and the gap between the plates was set to the extent that the sample is pressed and spread out on the plates until seen from all over the edges. The excess sample then was trimmed to form an even circularly shaped sample. Three different tests of strain sweep, the storage ( $G'$ ), and the loss ( $G''$ ) moduli were carried out and recorded while the strain increased from 0.01% to 10%. The frequency sweep test was also conducted on each sample to determine their viscoelastic behaviors at a constant oscillation strain of 0.1% and over a frequency range of 0.1 to 100 Hz.

A temperature dependence test was also conducted on each sample (25 to 90 °C, 1 rad/s frequency and 0.1% oscillation strain) to evaluate the rheology behaviour of both modified and unmodified starches. Three replicates were used for each test and the average values were reported. All the storage modulus ( $G'$ ), loss modulus ( $G''$ ), complex viscosity ( $\eta^*$ ) and loss tangent ( $\tan \delta = G''/G'$ ) values were recorded and reported in this study [28].

### 3.5.3.1 Rheological properties of polymers

As mentioned previously, the main application of the produced starch-lignin polymer is to function as a FLC. Since, FLCs function practically by modifying the rheology of the WDFs in harsher conditions, evaluating the rheological properties of the product is critical to qualify the produced FLC.

Rheological properties of a substance are determined as the deformation rate and flow change during an applied mechanical stress. When characterizing starch to observe its rheological behavior, viscosity is the most important parameter since starch is often utilized as a thickener in different applications. In fact, viscosity measures the resistance of a fluid or semifluid to flow and movement when a mechanical stress is applied [29-33].

As it is shown in Figure 3.24, the unmodified starch suspension showed an average viscosity of 16.8 Pa.s at the ambient temperature. However, by raising the temperature to about 60 °C, due to the gradual cleavage of the inter molecular hydrogen bonds of starch its granules lost their crystalline structure under the hydrolysis process and consequently the viscosity of the starch decreased to about 5.4 Pa.s. Moreover, by further incremental increase of the temperature, the viscosity of the starch remained constant which confirms the total degradation of the starch at 60 °C. Interestingly, based on the results obtained from the same rheology analysis, the viscosity of the modified starch (FLC) did not show any significant decrement by raising the temperature and clearly remained stable until 90 °C. This might be a result of newly created ether bonds between starch and lignin after the crosslinking reaction, which made this product more resistant to heat. In addition, lignin is known for its complex and unique structure which brings hardness and rigidity to the FLC composed of this polymer.

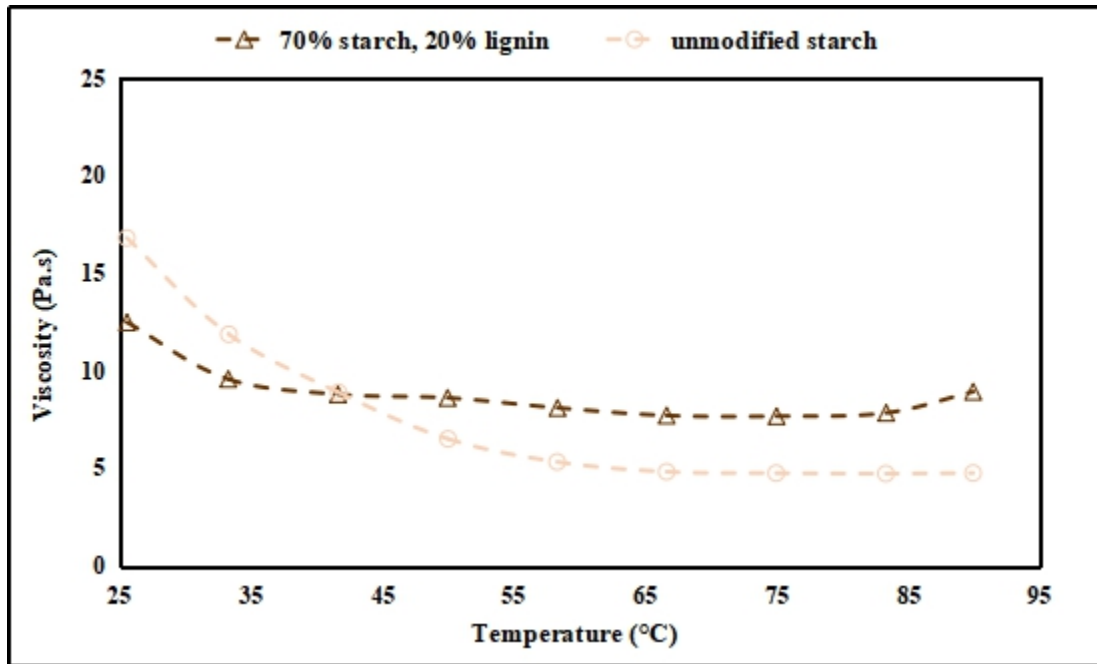


Figure 3-24: Viscosity profiles of unmodified starch and produced FLC, measured by a Discovery Viscosity Analyzer at the temperature range of 25 °C to 90 °C.

\*5 wt. % of samples mixed in distilled water.

Typically, the storage ( $G'$ ) and loss ( $G''$ ) modulus increase with frequency.  $G'$  generally represents elastic behavior of the substance while  $G''$  represents its viscous behavior. Starch basically renders elastic-like or viscous-like behaviors under different conditions during drilling operations when it is used as a FLC in WDFs. Therefore,  $G'$  and  $G''$  of both unmodified starch and prepared FLC were determined to evaluate and compare their viscoelastic behaviors [34-37]. To understand the influence of lignin crosslinked with starch on the viscoelasticity of starch, a dynamic strain sweep test was carried out in a strain range of 0.01 to 100 % under a stationary angular frequency of  $\omega=10$  rad/s at 45 °C, and the  $G'$  and  $G''$  of the tested polymers were displayed in Figures 3.25 and 3.26. The  $G'$  and  $G''$  of each sample was determined in a wide strain range of 0.01 % to 100 % first, to find out a strain (1 %) from the linear viscoelastic region (LVR) of all samples to ensure that the test was carried out in the LVR.

As shown in Figure 3.25,  $G'$  increased with increasing angular frequency due to increased inter molecular interactions between starch granules which bring them into closer contact with each other. Consequently, this makes the structure of starch firmer and more resistant against deformation. However, as seen in the same figure, the presence of lignin crosslinked to starch caused an increase of the polymer's  $G'$  and made it more stable against angular frequency. This could be explained by the formation of stronger covalent bonds between the free hydroxyl groups of starch and lignin after the crosslinking reaction as well as the unique three-dimensional structure of the lignin, which make the structure of the produced polymer more resistant against deformation and elasticity. Moreover, based on the results shown in Figure 3.26, the presence of lignin crosslinked to starch increased the  $G''$  of the polymer and made it more stable under lower angular frequencies. The increment of the  $G''$  under higher angular frequency could be due to losing the structural reordering capability of starch granules under an extra strain. It is known that when a shear force is applied to a starch suspension, starch granules need to be reordered to reduce the influence of the extra force. However, if the applied shear force is high the starch granules do not get the required time to reorder and occupy greater portion of the suspension. This leads starch granules to form a continuous network which makes starch behave in a more viscous manner [37].

It is worth mentioning the values of  $G'$  were much greater than  $G''$  at all angular frequency values showing the stronger elastic behavior of starch samples. In case of an ideal elastic behavior,  $G'$  is expected to be independent of frequency and much higher than  $G''$  ( $G' \gg G''$ ). It may be attributed to the highest swelling potential of starch and its gelatinization which results in the suspension thickening under angular frequencies.

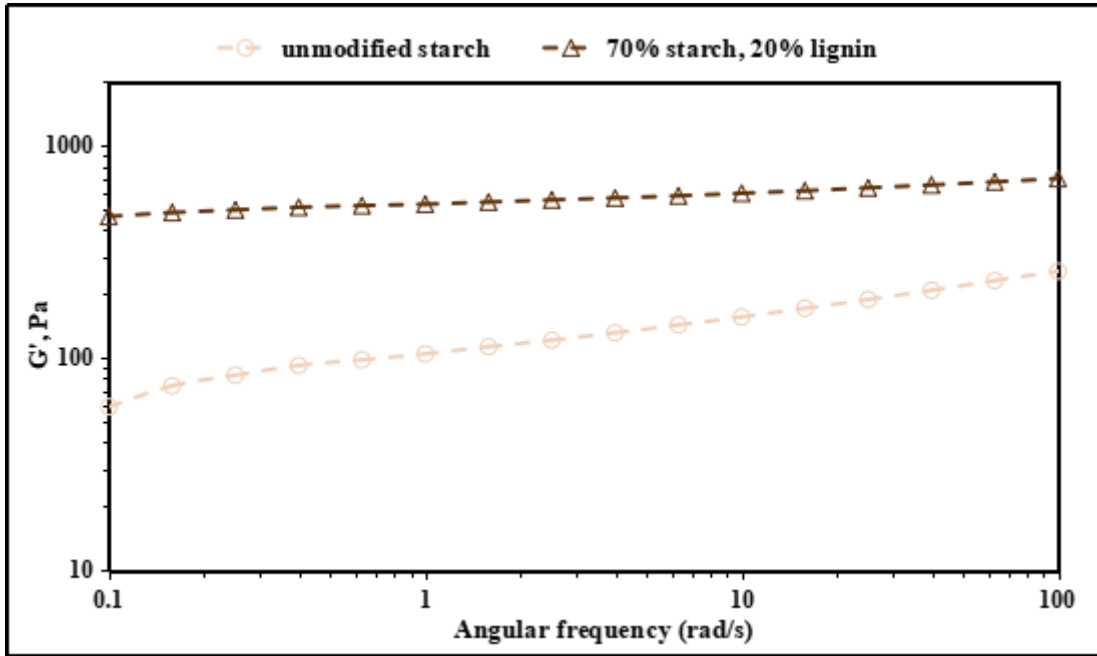


Figure 3-25: Storage modulus ( $G'$ ) trend for unmodified starch and produced FLC.

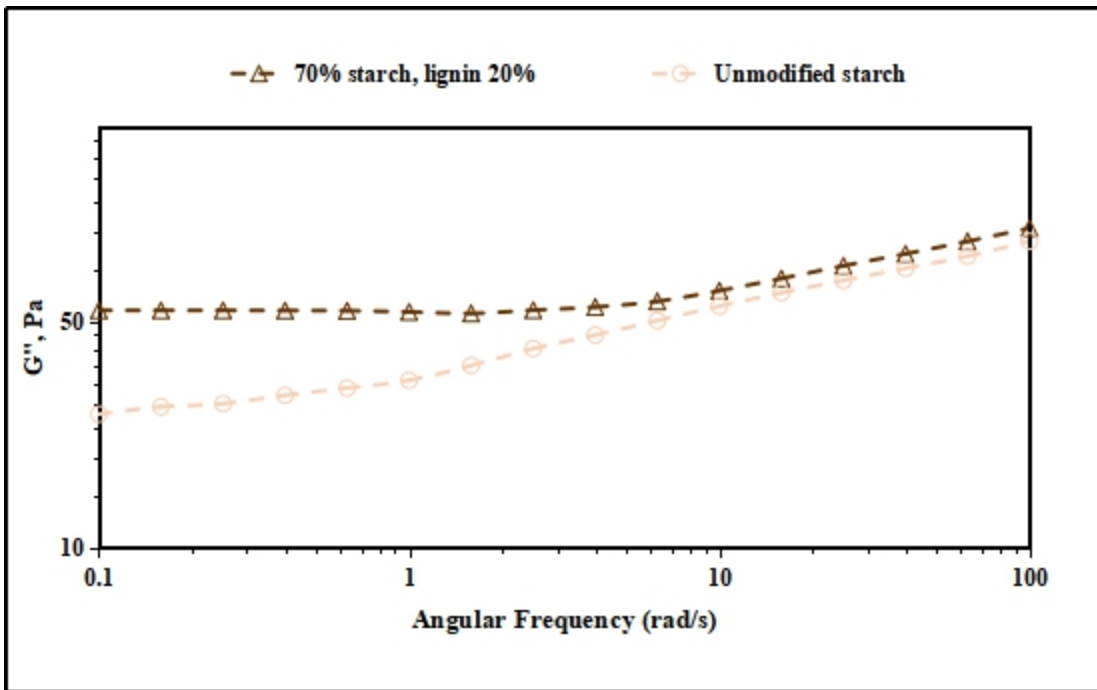


Figure 3-26: Loss modulus ( $G''$ ) trend for unmodified starch and produced FLC.

Figure 3.27 presents changes of the  $G'$  to  $G''$  ratio ( $\tan \delta$ ) versus time for the unmodified starch and the produced FLC. This ratio characterizes the viscoelastic behavior of the samples more precisely. It is known that amorphous polymers with indeterminate structures show a relatively high  $\tan \delta$  while crystalline polymers with definite structures display a relatively low  $\tan \delta$ . As shown in the mentioned figure, unmodified starch showed a larger change in the viscoelasticity ( $\tan \delta$ , 0.44 to 0.32) under the applied strain than modified starch which remained almost constant under the same conditions by time ( $\tan \delta$ , 0.12 to 0.13). However, both samples showed a different behaviour after a certain while (180 s) which implies the structural strength limitation of these polymers against external forces. Changing the  $\tan \delta$  of unmodified starch during this test proves that the structure of this polymer changes under the applied strain, which confirms the weakness of the intermolecular hydrogen bonds between starch granules and consequently the lower elasticity of this polymer. On the other hand, the constant  $\tan \delta$  of the produced FLC confirms the emphatical effect of the presence of lignin crosslinked to starch on the viscoelasticity behaviour of the produced polymer and its structural stability under the applied strain due to the created ether bonds between hydroxyl groups of starch and lignin [38-43].

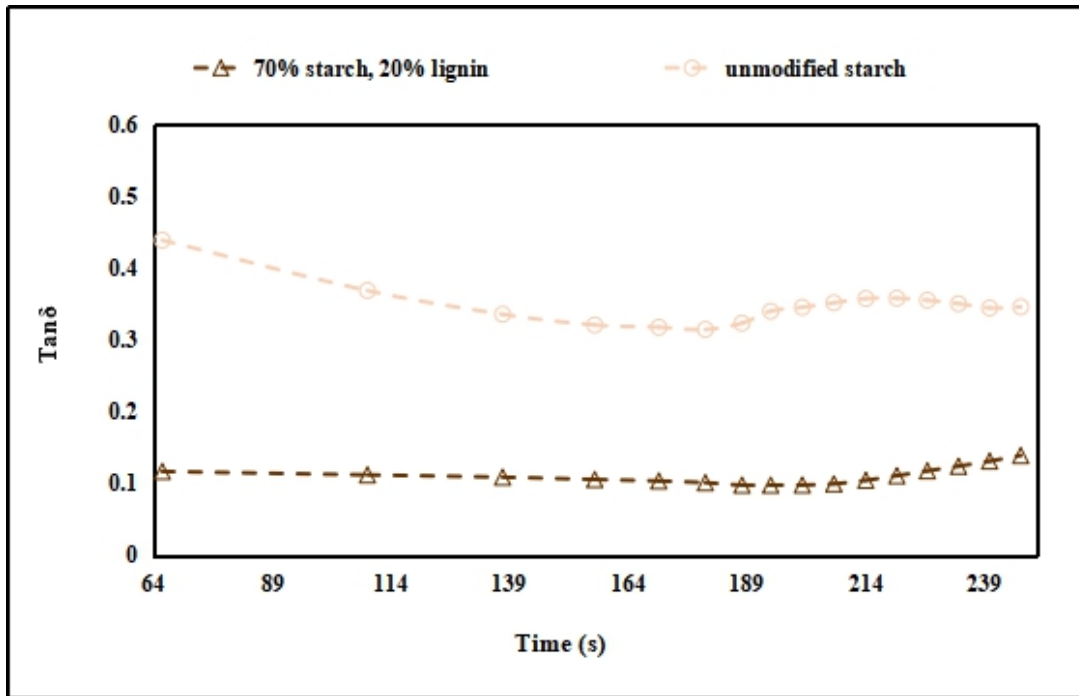


Figure 3-27: Loss tangent ( $\tan \delta = G''/G'$ ) trend as a function of time and angular frequency for the unmodified starch and produced FLC, temperature 25 °C.

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## **Chapter 4: Conclusions and recommendations for future work**

In this study, a newly developed starch-lignin polymer was synthesized, characterized, and systematically studied as a rheology enhancer and fluid-loss control agent for WBFs at elevated temperatures. The novel synthetic polymer was designed not only to boost its thermostability and viscoelasticity but also to enhance drilling fluid performance (viscosity and filtration properties) under high-temperature geothermal conditions.

### **4.1 Overall conclusions**

1. The characterization analysis of produced FLC and unmodified starch showed that both C/O ratio and C-O-C bonds quantity were much higher in the prepared FLC when compared to those of unmodified starch, which is a proof for the occurrence of crosslinking reactions between starch and lignin under the proposed conditions.
2. Water solubility of starch was improved by being crosslinked with lignin, it was shown that starch could be successfully converted to a FLC soluble in ambient temperature water.
3. Viscosity investigation showed that the viscosity of our produced fluid FLC remains stable (10 cp), when the temperature increased from room temperature to 90 °C. In comparison, native starch loses its viscosity more than 50% during this temperature increment.
4. It was shown that the starch-lignin FLC absorbs water almost six times more than unmodified starch does and consequently prevents losing water much more efficiently during the drilling operations. This will result in the usage of a lower dosage of the FLC during the operations.
5. Commonly used starch-based FLCs suffer impotent ether bonds between glucose units in their structures, which causes starch fragmentation in high pressure and high temperature conditions and consequently limited thermal and pressure resistance. In this work, we produced a starch-lignin FLC with a significantly higher thermal stability. The  $T_g$  and  $C_p$  increased from 123 °C to 214 °C and 0.05207 J/(g·°C) to 0.3212 J/(g·°C), respectively.

6. Based on rheological analysis, starch-lignin FLC showed significantly higher  $G'$  and  $G''$  in compare to those of starch-based FLC. This might be due to higher physical-chemical interactions of starch crosslinked with lignin during the process in compare to those of native starch. However, both FLCs are viscoelastic polymers with  $G' > G''$  and provide a higher storage modulus than loss modulus.

#### **4.2 Recommendations for future work**

In this study, the results suggested that starch derivatives with higher thermal stability, viscoelasticity, and hydrophilicity could be obtained. In the future, the hydrophobic modification of lignin could also be conducted with a chemical that has a higher alkyl chain. The application of the products on composites would disclose the potential use of these lignin-based products. The sulfonation of the lignin derivatives might also show potential to produce sulfonated products for different applications, and thus recommended as future work.

Free radical copolymerization is one of the simplest, economical, efficient and appropriate method for industrial purposes. One idea for future works can be focusing on free radical copolymerization of native starch and kraft lignin with a suitable cationic or nonionic monomer and offers an effective approach to produce new starch-lignin crosslinked polymers with different solubility, MW and charge density.

These starch based polymers can be used in other applications like, flocculants in water based systems.