The Use of Lignin in Pressure Sensitive Adhesives and Starch-Based Adhesives

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Abstract

After cellulose, lignin is the second most abundant natural polymer in the world. It has multiple functional groups, providing great potential for polymer production. In this project, we explored the use of this renewable and valuable resource in two different adhesive applications to displace petroleum-based additives, thereby providing a more sustainable and "green" product. In this regard, two types of lignin, water-soluble (Amalin LPH) and non-water-soluble lignin (Amalin HPH) provided by the British Columbia Research Institute (BCRI) were used.

In the first case, lignin was added to a pressure-sensitive adhesive (PSA) formulation via in-situ seeded semi-batch emulsion polymerization. It was seen that lignin does not readily take part in the polymerization reaction; rather, its presence results in reaction inhibition. Therefore, Amalin LPH lignin was modified via acrylation to overcome this issue. In another modification approach, maleic anhydride was used to produce maleated Amalin HPH lignin. Both the acrylated and maleated lignins were used in butyl acrylate/methyl methacrylate emulsion copolymerizations to produce PSA films. A series of controlled experiments with different lignin loadings was conducted. Adhesive properties of the PSA films were measured and compared with the corresponding acrylic base case formulation. The incorporation of lignin in the PSA formulation was a "green" solution to conventional PSA production, and led to a simultaneous increase in tack and shear strength. Further characterization of the latex films via transmission electron microscopy (TEM) showed that lignin was successfully incorporated into the polymer particles. It also showed that the use of maleated lignin at a higher concentration led to a core-shell morphology.

In the second application, unmodified Amalin LPH lignin was used to create a starch-based adhesive through the Stein-Hall process, a two-step process involving a "carrier" portion and a "slurry" portion. Several formulations with lignin loadings up to 35 wt% distributed in varying ratios in the carrier and slurry portions were prepared. It was shown that the addition of lignin to the starch-based adhesive formulation increases the water-resistance of the adhesive. Therefore, lignin addition is a solution for a common issue in starch-based adhesives, their lack

of water-resistance due to the high affinity of starch toward water. Lignin incorporation solely in the slurry portion significantly increased the strength of the glued joints in a paper board adhesive test.

The use of lignin as a renewable replacement of petroleum-based components in two different adhesive formulations was demonstrated successfully. This research strongly suggests that lignin can be used as a high value-added property modifier in adhesive applications.

Résumé

Après la cellulose, la lignine est le deuxième polymère naturel le plus abondant au monde. Il possède plusieurs groupes fonctionnels, offrant un grand potentiel pour la production de polymères. Dans ce projet, nous avons exploré l'utilisation de cette ressource renouvelable et précieuse dans deux applications d'adhésif pour remplacer les additifs à base de pétrole, fournissant ainsi un produit plus durable et «vert». À cet égard, deux types de lignine, la lignine hydrosoluble (Amalin LPH) et la lignine non-hydrosoluble (Amalin HPH) fournie par le British Columbia Research Institute (BCRI) ont été utilisés.

Dans le premier cas, la lignine a été ajoutée à une formulation d'adhésif sensible à la pression (PSA) via une polymérisation en émulsion semi-discontinue ensemencée in situ. On a constaté que la lignine ne participe pas facilement à la réaction de polymérisation; au contraire, sa présence entraîne une inhibition de la réaction. Par conséquent, la lignine d'Amalin LPH a été modifiée par acrylation pour résoudre ce problème. Dans une autre approche de modification, l'anhydride maléique a été utilisé pour produire de la lignine malée d'Amalin HPH. Les lignines acrylées et malées ont été utilisées dans des copolymérisations en émulsion d'acrylate de butyle / méthacrylate de méthyle pour produire des films de PSA. Une série d'expériences contrôlées avec différentes charges de lignine a été réalisée. Les propriétés adhésives des films de PSA ont été mesurées et comparées à la formulation de base acrylique correspondante. L'incorporation de la lignine dans la formulation de PSA était une solution «verte» au problème de production de PSA conventionnel et conduisait à une augmentation simultanée de l'adhérence et de la résistance au cisaillement. Une caractérisation plus poussée des films de latex par microscopie électronique à transmission (MET) a montré que la lignine avait été incorporée avec succès dans les particules de polymère. Il a également montré que l'utilisation de lignine malée à une concentration plus élevée conduisait à une morphologie noyau-coquille.

Dans la deuxième application, la lignine Amalin LPH non modifiée a été utilisée pour créer un adhésif à base d'amidon selon le processus de Stein-Hall, un processus en deux étapes impliquant une partie «support» et une partie «suspension». Plusieurs formulations avec des charges de lignine allant jusqu'à 35% en poids réparties dans des rapports variables dans les portions support et suspension ont été préparées. Dans ce travail, il a été démontré que l'addition de lignine à la formulation d'adhésif à base d'amidon augmente la résistance à l'eau de l'adhésif. Par conséquent, l'ajout de lignine est une solution au problème commun des adhésifs à base d'amidon, à savoir leur manque de résistance à l'eau en raison de la forte affinité de l'amidon pour l'eau. L'incorporation de lignine uniquement dans la partie en suspension a considérablement augmenté la résistance des joints collés lors d'un test d'adhésif sur carton.

L'utilisation de la lignine en tant que remplacement renouvelable des composants d'additifs à base de pétrole dans deux formulations d'adhésifs différentes a été démontrée avec succès.

Cette recherche suggère fortement que la lignine peut être utilisée comme modificateur de propriétés à haute valeur ajoutée dans les applications d'adhésif.

Statement of Contributions

I hereby declare that I am the sole author of this thesis. I performed the lignin modification (acrylation and maleation), polymerization experiments, viscosity, particle size, glass transition temperature, gel content measurements and adhesive testing. Lignin acetylation and its associated runs were done by Mr. Andrés Gardner Flores. TEM imaging was done with the help of Ms. Yun Liu.

The scientific guidance throughout the project and editorial comments of the written work were provided by my thesis supervisor Prof. Marc A. Dubé of the Department of Chemical and Biological Engineering at the University of Ottawa.

Anahita Nasiri Date: 11/9/2019

Acknowledgement

I would like to express my deep gratitude to my supervisor Prof. Marc A. Dubé, for his guidance, support and positive encouragement throughout this project. I wish to thank Andrés for his help in conducting a part of the experiments. I would also like to thank all members of our research group: Yujie, Nayara, Vida and Amir. You have all been there to help me with any expected or unexpected issues during my project. I would also like to thank my husband, Sepehr. You have always been there for me and helped me (especially in cleaning the reactor after coagulations!). Lastly, I would like to thank my family, that despite being hundreds of miles away from me, they have always listened to me and supported me.

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This thesis is dedicated to the memory of my dad, who taught me to be always keen on learning and be courageous in the face of new challenges while following my dreams.

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Abbreviations

BA	Butyl acrylate
DSC	Differential Scanning Calorimetry
DDI	Distilled, deionized water
DMF	N, N-dimethylformamide
Et_3N	Triethylamine
FTIR	Fourier transform infrared spectroscopy
HEMA	2-Hydroxy ethyl methacrylate
KPS	Potassium persulfate
MAnh	Maleic anhydride
MMA	Methyl methacrylate
MMA	Methyl methacrylate
NDM	Normal dodecyl mercaptan
PSAs	Pressure-sensitive adhesives
SDS	Sodium dodecyl sulfate
TEM	Transmission electron microscopy
T_g	Glass transition temperature
THF	Tetrahydrofuran

Chapter 1 : Introduction

Polymeric adhesives play an essential role in our lives due to their diverse applications. Adhesives come in many different forms, e.g., epoxy resins, polyurethanes and pressure sensitive adhesives (PSAs). Most adhesives are produced from fossil-based starting materials. The depletion of petroleum-based resources and their environmental and health costs has brought attention to the use of biodegradable and renewable resources. In this regard, sustainable polymer reaction engineering has been developed as a field that seeks approaches such as solvent-free production of polymers and the production of polymers and polymer composites from renewable materials.

In this project, we explored the use of lignin as a renewable source in developing more sustainable adhesive products. We employed lignin in the development of starch-based adhesives via the Stein-Hall process and in PSAs using emulsion polymerization, a water-based "greener" pathway in polymer production.

Lignin is the most abundant biopolymer in the world after cellulose. It is also the primary renewable source for aromatic structures.[1] Lignin is mainly produced from the pulp and paper industry (mainly via the Kraft process), but unfortunately, it is usually burned for its caloric value to produce part of the energy required for the pulp mill. Because of this, lignin has a relatively low cost. Recently, there has been considerable effort to transform this green material to a more value-added product rather than simply burning it. Lignin, due to the abundant presence of functional groups in its structure, shows good potential in the production of aromatic chemicals, building blocks and monomers such as vanillin and producing polymers.[2] However, its latter application was faced with some challenges because its molecular structure varies with its production process and its botanic source.

In this thesis, lignin was incorporated into an emulsion-based PSA formulation to improve the adhesive properties of PSA films. PSAs are self-adhesives that stick to almost any surface upon the application of slight pressure. PSAs are often produced from a mixture of monomers that provides a degree of control over the final properties. Usually, a monomer producing a homopolymer with a low glass transition temperature (T_g) such as butyl acrylate (BA) is

copolymerized with a monomer producing a homopolymer with a higher T_g such as methyl methacrylate (MMA). The lower T_g component provides the desired tackiness for the adhesive while the higher T_g component provides strength. Other materials such as cross-linkers, tackifiers and chain transfer agents (CTA) often are added to the formulation to modify the adhesive properties further. Typically, these additives are all petroleum-based, hazardous and toxic. Therefore, it is desirable to replace them with non-toxic and renewable materials.[3] Thus, in this case, lignin is expected to play the role of a property modifier.

The incorporation of lignin into a polymerization does present some challenges. Pure lignin causes inhibition and retardation during polymerization.[4] This is a result of lignin scavenging the free radicals during polymerization. To overcome this problem, lignin was modified, thereby introducing a more reactive functional group to its structure and changing its miscibility with the organic monomers. Modifications included acetylation (using acetyl bromide and acetic acid), acrylation (using methacryloyl chloride) and maleation (using maleic anhydride). After modification, lignin was introduced to the formulation and used in the production of PSAs.

In an entirely different approach, lignin was used in the production of a starch-based adhesive. Starch-based adhesives are mainly used in the production of paper board and corrugated boxboard.[5] Because of the hydrophilic nature of starch, the application of these adhesives in humid environments becomes limited. In this thesis, we sought to substitute part of the starch with lignin to improve the water-resistance of the adhesive as well as to modify the strength of the adhesive.

Starch-based adhesives are mainly produced via the Stein-Hall process. This process consists of the preparation of two portions: a carrier portion and a slurry portion. To start, the carrier portion is prepared with the full gelation (15-20 wt%) of the dry starch followed by the addition of Borax (aka sodium tetraborate). Borax is added to impart tackiness to the adhesive. The slurry portion is prepared by simply mixing the remaining dry starch (85-80 wt%) with water. The two portions are eventually mixed. The prepared adhesive is applied to the flutes of the corrugated board and ultimately cured by heating and compressing. Upon heating, the ungelatinized slurry portion

becomes gelatinized, and instant tack is formed. In this thesis, lignin was incorporated in both the slurry and carrier portions.

Hypothesis and thesis objectives

We hypothesize that the addition of lignin to an emulsion-based PSA formulation will improve adhesive properties. We further hypothesize that the incorporation of lignin into a starch-based adhesive will lead to improved water-resistance of the starch-based adhesive.

Thesis outline

This thesis contains five chapters. Chapter 2 presents background information on emulsion polymerization, PSA production and testing methods, adhesive properties, lignin, starch-based adhesives and their production and testing methods. Chapter 3 reports on the incorporation of lignin in PSAs and its effect on adhesive properties. In Chapter 4, using an entirely different approach, we report on the incorporation of lignin in starch-based adhesives and its impact on water-resistance and adhesive strength. In Chapter 5, we offer conclusions and some prospects for future work.

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Chapter 2 : Background

Lignin

Lignin is the most abundant biopolymer in the world after cellulose, and it is a primary renewable source for aromatic structures.[1] Lignin plays a vital role in woody plants by adding strength and structure to them. It also protects the plants from biochemical attack by inhibition of enzymatic degradation of other components.[2] Recently, the enormous potential of lignin in the production of aromatic chemicals, building blocks and monomers such as vanillin and producing polymers has emerged. However, its use as a value-added material is challenged because its molecular structure varies depending on its isolation process and its botanic source.[3]

The biopolymer, lignin, is produced via radical polymerization in the plant from monomers known as monolignols. Monolignols are phenylpropane units which originate from three primary aromatic alcohols: p-coumaryl, coniferyl and sinapyl alcohols.[4] Monolignols vary from each other mainly because of the degree of substitution of methoxyl groups attached to the aromatic ring. Figure 2-1 presents the main structure of monolignols.

There are different inter-unit linkages between monolignols which are formed by radical coupling. The main one, which accounts for 50% of linkages in lignin, includes the β carbon of one unit and the phenolic hydroxyl of the other and is called a β-O-4 linkage (Figure 2-2).[3]

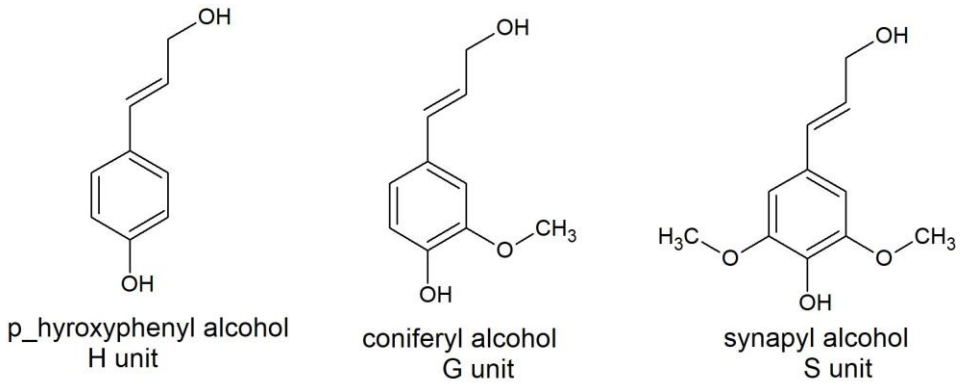

Figure 2-1: Monolignols' structure

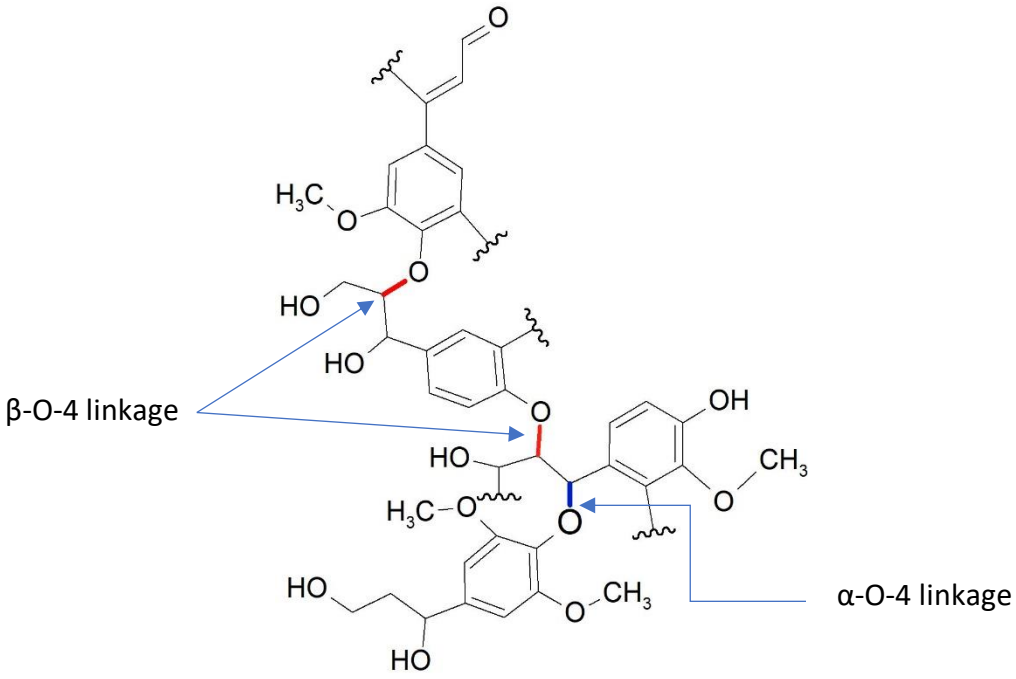

Figure 2-2: Main linkages between monolignols

Lignin Production

Lignin is extracted mainly from the pulp and paper industry.[5] In this process, the highly branched structure of lignin is degraded chemically or physically to make it soluble in the reaction medium and separate it from cellulose. Degrading lignin through extraction makes its structure different from its original botanical source.[6] There are four main commercial extraction processes described below:

Soda process

The soda process was the first chemical process in the pulp and paper industry, and was patented in 1854.[6] This process is usually used for plants with a low amount of lignin (e.g., bagasse). In the soda process, wood chips are treated in an alkaline aqueous solution. This leads to cleavage of the most common bonds like α-O-4 ether and β-O-4 ether.[6] Cleavage happens by deprotonating the phenolic hydroxyl group by sodium hydroxide. Soda lignin usually has high nitrogen and silicate content. The number average molar mass (M_n) of soda lignin is often 800-3000 g mol^{-1}.[2]

Kraft Process

The Kraft process was developed as an improvement to the soda process, and nowadays it is the most common pulping process.[3] In this process, sodium sulphide (Na_2S) is added along with sodium hydroxide to accelerate the degradation of lignin bonds. The resulting solution is called black liquor. The soluble part of the black liquor is called Kraft lignin, and it has a high content of phenolic hydroxyl groups.[3] Lignin is precipitated by adjusting the pH and applying an acidic condition to the black liquor. Residual sulphur in this process is often in trace amounts (≤1-2 wt%). The M_n of produced lignin from this process is low (1800-2200 g mol^{-1}).[2,7] Unfortunately, most of Kraft lignin is burned to provide the energy required for the mill. In this thesis, Kraft lignin was used in all of the experiments.

Organosolv Process

Organosolv lignin is the lignin that is produced at the laboratory scale, and it is considered as the purest lignin.[3] Organosolv lignin is hydrophobic. It has high solubility in polar solvents, and it is partially soluble in water and dilute alkaline solutions. Therefore, in this process, lignin is extracted by using a polar solvent such as methanol, ethanol, acetic acid or formic acid. Organosolv lignin has a higher content of phenolic hydroxyl groups compared to the lignin produced from other methods. Therefore, it retains a structure similar to that of lignin in its botanical source.[3] The M_n of Organosolv lignin is 500-5000 g mol^{-1}, and it has a low polydispersity.[2]

Sulfite process

Lignosulfonate is water-soluble lignin and is the primary source of commercial lignin.[4] Lignosulfonate has different industrial applications such as binders and dispersing agents. In this

process, three different solvents; sulphite, bisulfite and sulfur dioxide are used at different concentrations depending on which degradation mechanism is desired. The acidic condition is the most common one used in the industry. At these conditions, the main cleavage that happens is degradation of α-O-4 by sulfonation of α-carbon in lignin, and only a small part of β-O-4 ether bonds are cleaved. As a result, lignosulfonate has the highest M_n (≈ 15000-50000).[2,6]

Lignin Applications

The presence of various functional groups, its cost-effectiveness and the fact that lignin is a "green" and biodegradable material, makes it a good candidate in several applications. Recently, lignin has been used widely as a reinforcement agent for polymer matrices, whether as an additive or by copolymerization.[6,8–10] For instance, Xia et al. used modified lignin to improve the mechanical properties of styrene-butadiene rubber.[10] They showed that by increasing the concentration of modified lignin in the formulation, elongation at break and tensile strength was improved and showed better stress transfer at the interface.[10] Another example is the incorporation of lignin in a well-known biopolymer, polylactide acid (PLA). Typically, PLA suffers from some mechanical properties like a small break at elongation and low impact strength.[11] However, the copolymerization of PLA with lignin showed improvement in mechanical properties.[11] A further example is composites from olefins, which have some structural limitations leading to reduced mechanical properties.[12,13] From these types of olefins, we can name polyethylene (PE), polypropylene (PP) and polymethyl pentene (PMP), which despite their light weight, their stiffness and structural strength are limited. Lignin has shown suitability for the production of composites, and because of its high M_n, it has been suitable as a dispersed component in polyolefin composites. In this regard, their incorporation showed improvements in mechanical properties.[12,14]

In the development of adhesives, lignin has shown the greatest impact in phenol-formaldehyde (PF) resin production.[15] Here, the abundance of phenolic groups in the lignin made it a logical choice as a source of phenol in PF resins. PF is a highly reactive material, and it causes respiratory difficulties and eye irritation. The price of PF often fluctuates as a result of changes in the price of phenol. Therefore, the development of lignin-based PF had both health and economic

benefits.[12] Lignin has been used in epoxy resins by blending lignin or modified (i.e., epoxidized) lignin and using it directly in bio-based epoxy resin production.[16–18] Yin et al. produced a cross-linked bio-based epoxy resin by blending lignin with epoxy resin using a hot press moulding process. They incorporated up to 60 wt% lignin in their formulation. The resulting lignin-epoxy resin had good interfacial properties and improved thermal stability and strength.[17]

In another approach, a petroleum-based polyol was replaced with up to 70 mol% lignin in the production of polyurethane (PU). PU offers the production of a wide range of products such as low-temperature elastomers and high tensile adhesives.[19] Lignin, because of its structure, could be considered as an aromatic macro-polyol and by chemical modification, can also be considered as a polyol precursor in polyurethane production. The addition of lignin instead of polyol showed that lignin was cross-linked and successfully participated in the polymerization.[2,19]

There have been some developments on the use of lignin in emulsion and suspension polymerizations.[20–22] Pokoscielna et al. used suspension polymerization to copolymerize lignin with styrene-divinylbenzene (St-DVB), a popular polymeric sorbent, because of its hydrophobic properties. They modified the lignin with acrylic acid prior to polymerization, to facilitate lignin incorporation. The copolymerization of lignin with St-DVB sorbent brought better sorption properties toward polar moieties such as chlorinated phenolic compounds.[20]

Lignin was used in emulsion and mini-emulsion polymerization with styrene and butyl acrylate to produce a polymer hybrid latex.[21] In this study, 6.8 wt% (relative to the mass of monomer) of unmodified Kraft lignin was used in a formulation instead of styrene. Because they used an unmodified Kraft lignin, inhibition in polymerization was observed. The produced latexes were not homogeneous due to the presence of coagulum even at low concentrations of lignin. The amount of coagulum was increased by increasing lignin concentration. In the end, the authors suggested to use another method of polymerization or to use a modified lignin.[21]

Recently, Wang et al. developed a pressure sensitive adhesive (PSA) from depolymerized lignosulfonate.[22] The catalyzed depolymerization of lignin was effected at high pressure (40 bar) and relatively high temperature (250 °C) over 15 h to obtain aromatic monomers. The resulting monomers were functionalized using acryloyl chloride. Further, the functionalized lignin

monomers were copolymerized with BA in a N,N-dimethylformamide solution polymerization. The synthesized PSA films showed almost the same adhesion in comparison to a commercial product.[22]

There has been a sustained effort to convert lignin to a value-added product and take advantage of this abundant and cost-effective material. As described above, the addition of lignin to a polymer matrix usually improves the mechanical and adhesion properties of polymer composites and adhesives. However, it is important to use "greener" methods to develop lignin-based products and avoid using toxic and hazardous materials. In this regard, we explored the incorporation of lignin in PSAs, which is one of the more widely used types of adhesives.

Pressure Sensitive Adhesives (PSAs)

There has been considerable growth in the PSA market in recent years. PSAs have been produced at a rate of roughly 200 tonnes per year in Europe, and they have been used in 25000 different industrial products such as labels, post-it notes and adhesive tapes.[23] PSAs or self-adhesives are adhesives that stick to almost any surface upon applying slight pressure at room temperature without undergoing a physical transformation or chemical reaction during the bonding process.[24]

PSAs are derived mainly from fossil-based resources. Acrylic monomers, styrene block polymers and natural rubber, are three main sources for PSA production.[24] There has been a significant effort regarding the development of PSAs from renewable materials to move toward a more sustainable process.[23,25] Generally, PSAs are elastomers with viscoelastic properties because of their low glass transition temperature (T_g).[26]

PSAs are often produced from mixtures of monomers to tailor final properties according to the desired application.[26] The choice of the main monomer determines the final T_g and the characteristics of the adhesive. Usually, a combination of monomers, one with a low T_g homopolymer along with another having a high T_g homopolymer is used. The lower T_g monomer provides the desired tackiness of the adhesive, and it is considered as the "soft" polymer at room temperature. The high T_g monomer is considered as the "hard" polymer and provides strength to the copolymer.[26,27]

PSAs should have a balance of cohesive (or internal) strength and viscoelastic properties. They should have a certain degree of flowability or mobility to easily stick to the substrate and be removed without leaving any residue.[28] Various additives such as cross-linker, chain transfer agent (CTA) and tackifier often are added to PSA formulations to modify their mechanical properties. However, these additives are typically petroleum-based, hazardous and toxic. Therefore, it is highly desired to replace those with non-toxic and renewable materials.[29]

Acrylic monomers have been used in PSA formulations from 1928.[26] One of the advantages of acrylic monomers is the possession of pressure-sensitive properties without any addition of a tackifier. They are tacky by themselves because of their high entanglement molecular weight (M_e). They are sensitive toward oxidation, and their tackiness and cohesive strength do not change after an ageing period at high temperature. Acrylics are polar molecules, and they often show good adhesion toward polar substrates. They have a lack of sensitivity toward UV light, and their performance does not change easily during ageing.[26]

In this thesis, two acrylic monomers butyl acrylate (BA) and methyl methacrylate (MMA) were used (Figure 2-3).

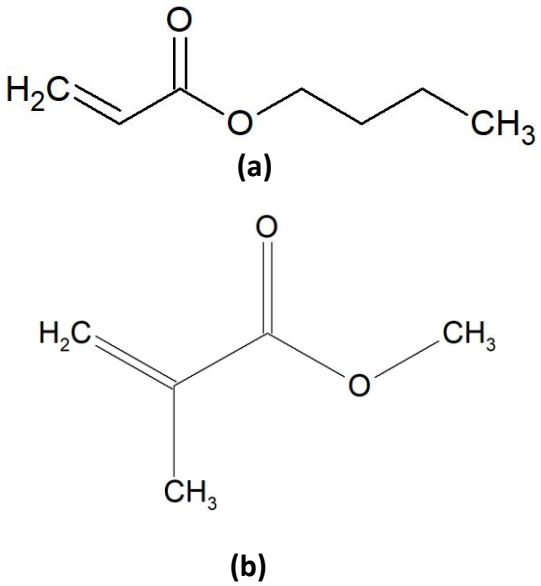

Figure 2-3: (a) butyl acrylate (BA) and (b) methyl methacrylate (MMA) structure

BA plays the role of the soft polymer as its homopolymer has a T_g of -54 ^oC. MMA is the glassy polymer and is not tacky by itself due to its high T_g (105 ^oC). However, it imparts the desired strength to the polymer matrix. Monomers should be selected in a manner that the final T_g of the copolymer suits the final application. The final T_g should be 25 to 45 °C below the application temperature of the polymer to provide enough flowability during application and to not become glassy and stiff at the application temperature.[24]

Acrylic-methacrylic copolymers are used in a variety of applications such as adhesives, paints and surface coatings.[30] They have high chemical and thermal stability, optical clarity, good adhesion and improved mechanical properties. It has been shown that alkyl acrylates have a high affinity to be copolymerized with alkyl methacrylates. Therefore, polymers with a wide range of properties from glassy to elastomeric ones can be obtained.[30] In this regard, there have been several studies on the copolymerization of BA with MMA, styrene, butyl methacrylate and 2-ethylhexyl acrylate, to name but a few. [31–36]

PSA production methods

There are three main methods for PSA production: Solution polymerization, hot melt and emulsion polymerization.[26]

In solution polymerization, all the components (i.e., monomers, initiator and all necessary additives) and the produced polymers are dissolved in a solvent. The amount of solvent is critical in the formulation. As the polymerization proceeds, the mixture's viscosity increases, therefore enough solvent should be present in the formulation. The solvent is usually evaporated at either the application stage or during the film formation process. Although controlling reaction temperature is simplified by virtue of the low viscosity in solution polymerization, there remain several drawbacks. Most importantly, the solvents used (e.g., benzene, toluene, acetone and ethyl acetate) are usually toxic and fire hazardous materials.[26,37] Therefore, there is a significant interest in moving away from solution polymerization.

Hot-melt adhesives are entirely in the solid-state and do not require any solvents.[26] These adhesives are produced through extrusion. They are solid at room temperature, and upon

heating, they melt and become more flexible, thereby enabling their application to a substrate. Upon cooling, the adhesive transforms to the solid-state, and the cohesive bond is formed. The avoidance of solvents in this process makes these types of adhesives an attractive option. However, there are still limits to their use: poor oxidation stability and marginal performance, especially at higher temperatures, are disadvantages.[26]

Another method to produce PSAs is through emulsion polymerization. In this method, water is used as a reaction medium instead of a solvent. This reduces the environmental and hazard issues compared to solvent-based adhesives. Also, water is an excellent heat sink that makes temperature control of the process manageable and reduces the risk of runaway reactions. PSAs produced from this method do not need further processing before application. However, the adhesives need to be cured, and the evaporation of water is required.[23,38–40] In this thesis, all polymerizations were performed as emulsion polymerizations.

Emulsion polymerization

Emulsion polymerization is a heterogeneous chain growth free radical polymerization technique. Monomers are polymerized in an aqueous medium. A water-soluble initiator is usually used as a source of free radicals, and polymer particles are stabilized in the water using an emulsifier. [41]

Emulsifiers are either anionic or non-ionic. Anionic emulsifiers are salts of fatty acid chains.[42] They are long-chain molecules that have one hydrophobic end (hydrocarbon chain) and one hydrophilic end, which implies electrostatic stabilization. Non-ionic emulsifiers imply steric stabilization.[42] When emulsifiers are dissolved in water above a critical micelle concentration (CMC), they form aggregates called micelles.[43] In the micelle formation process, hydrophilic chains of surfactant point toward each other while they are in contact with water but their hydrophobic ends point towards the micellar core.[44] The diameter of micelles is about 50-100 Å. In this work, an anionic surfactant, sodium dodecyl sulphate (SDS) was used (Figure 2-4). Its CMC is 9.2 mM at 60 °C (the temperature at which all our reactions were performed).[43,44]

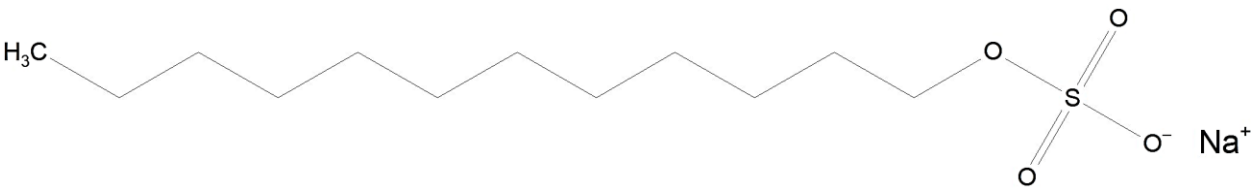

Figure 2-4: Sodium dodecyl sulfate (SDS)

When a monomer is added to the reaction formulation, it will partition into three phases. A limited amount of the monomer will be dissolved in the water phase (most monomers are typically hydrophobic), a significant amount will swell the micelles (5-7 nm in diameter), and another significant amount will form much larger emulsifier-stabilized monomer droplets (> 1μm in diameter). To start the polymerization, an initiator is added as a source of free radicals. Conventionally, a water-soluble initiator such as potassium persulfate (KPS) is used (Figure 2-5). Upon heating, the initiator molecules will cleave, and each molecule will form two radicals. The activation energy for the decomposition of the initiator is about 12-15 kcal.mol^{-1}.

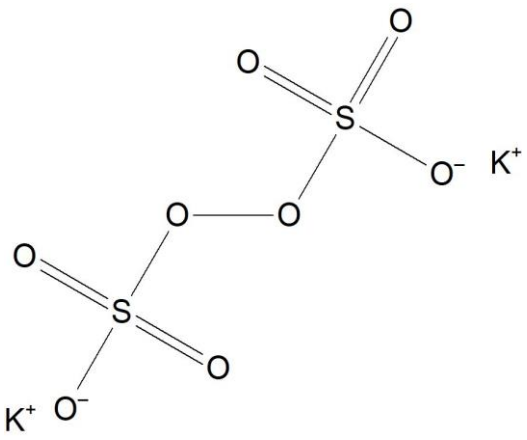

Figure 2-5: Potassium persulfate (KPS)

The free radical initiator reacts with the monomer (typically, a vinyl monomer is reacted at the carbon-carbon double bond) dissolved in the water phase. As a result, oligomeric radical chains (say 10-15 monomer units) are formed thus rendering the oligomers increasingly hydrophobic. At a critical oligomeric radical chain length, the oligomers become hydrophobic enough to enter

the monomer-swollen micelles. At this point, the micelle becomes a polymer particle (referred to as particle nucleation). It is noted that the significantly larger number of micelles compared to the number and size of the monomer droplets results in a preference of capture of the oligomeric radicals by the micelles on the basis of their significantly larger surface area. Particle nucleation continues for a short time (typically 10-20 min) until all the micelles have been nucleated. Oligomeric radicals then enter the monomer-swollen polymer particles to either react with the monomer to continue polymerization or to terminate an existing radical within the particle. Typically, only one radical exists within a growing polymer particle at a given time. Thus, polymer particles are understood to possess either one or zero radicals (known as zero-one polymerization kinetics). During the ongoing polymerization, monomer from the monomer droplets diffuses to the growing particles to maintain a thermodynamic equilibrium. Eventually, the monomer within the droplets is completely consumed and a brief period of time is needed to react any remaining monomer in the polymer particles and perhaps dissolved in the aqueous phase.[44]

Often, several materials are added to the formulation to tune polymer properties (e.g., molecular weight).[26] One of these components is a chain transfer agent (CTA), which is added to reduce polymer molecular weight. In these reactions, the free radical is transferred to another molecule, and the newly initiated molecule will continue to propagate. Thus, the growth of the polymer chain is prematurely stopped, and a new polymer chain is initiated. The most common chain transfer agents are aliphatic mercaptans. In this thesis, normal dodecyl mercaptan (NDM) was used as CTA (Figure 2-6).

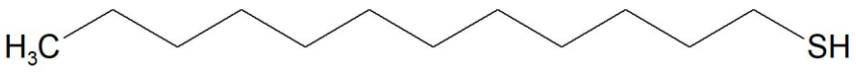

Figure 2-6: N-Dodecyl mercaptan (NDM)

Adhesive properties

PSAs require a balance between cohesive strength and viscoelastic properties, which enables them to spread quickly on the substrate and adhere upon the application of slight pressure. Three properties are used to measure adhesion: tack, peel strength and shear strength.

Tack is the ability to wet the surface instantly, or in other words, it is a property that measures the ability of an adhesive to form a bond with the surface of a substrate under light or no pressure.[28] Tack is the most critical adhesive property and the hardest one to measure. Tack not only depends on bulk properties, interfacial properties and the substrate but also it depends on the method of measurement. Therefore, measured tack with different methods should not be compared with each other.[40] In this thesis, the PSTC-16 standard was used to measure tack.[45] T_g of the polymer has a significant impact on the tack. Softer polymers with lower T_g have more flowability. Therefore, the adhesive has a better ability to form a quick bond with the substrate.[40,46] On the other hand, using harder monomers reduces tack as their incorporation in the polymer matrix will make it glassier and less flowable. Cross-linking of the polymer matrix also decreases tack.[40] The formation of a network due to cross-linking reduces the flowability of the polymer chains, leading to lower tack.[46] The addition of polar monomers also reduces tack. Intermolecular forces increase due to the presence of polar monomers, thereby restricting chain flexibility and flowability.[40]

Peel strength reflects the ability of the adhesive to remain permanently attached to the substrate in the absence of excess forces. In other words, the peel strength is measured as a force required to remove a standard strip of adhesive from a standard surface at a constant and pre-defined peel rate and angle.[24] In the peel test, not only is the peel strength important, but the mode of failure is of high interest to adhesive manufacturers. It is desired to have “adhesive failure”, which means the adhesive is removed from the substrate during the test without leaving any residue.[40] However, “cohesive failure” (i.e., adhesive remaining on the substrate during testing) and adhesive transfer (i.e., transfer of adhesive completely from its support to the substrate) are undesired. [40] In this work, the PSTC-101 standard method was used to measure peel strength.[47] Peel strength is improved by the addition of hard monomer. Therefore, an increase in T_g of the polymer will increase peel strength up to the point that the polymer becomes glassy. At this

point, the polymer will be too stiff, and it wouldn't be able to wet the surface and show adhesive properties. [40]

Shear strength is the ability of the adhesive to resist flow under an applied force. In other words, shear strength is a measurement of the shear deformation of adhesive under constant shear stress. Shear strength is related to the internal and cohesive bonds (i.e., cohesive strength) of the adhesive.[24] Like peel strength and tack, there are several standards for measurement of shear strength, but in all standard methods, the time that it takes to pull the specific area of adhesive from the substrate by applying a particular load to an adhesive strip is measured. In this thesis, the measurement of shear strength was performed according to the PSTC-107A standard.[48]

Increasing gel content and cross-linking of polymer matrix will increase shear strength. Shear strength also increases with polymer molecular weight. In this case, long linear polymer chains become more entangled, leading to a more cohesive polymer matrix.[49] Usually, shear strength changes in opposition to tack and peel strength. Therefore, a balance between these adhesive properties is required. In previous work in our laboratory, a number of different strategies were developed to enable tack, peel strength and shear strength to be simultaneously increased (or decreased). In recent work, cellulose nanocrystals were used in seeded semi-batch emulsion polymerizations of acrylic monomers to achieve this.[50]

Starch and Starch-based adhesives

There has been enormous effort to make polymer production more sustainable.[23,25,51] One of the leading examples is the production of adhesives from starch.[52] Starch-based adhesives have low cost, they are environment-friendly, biodegradable, and are available at a consistent quality. As a result of this, there has been a high demand for this adhesive in different applications such as pharmaceutical, personal care products, paper bags, laminating paperboards and textile sizing. One of the most significant applications of these adhesives is in paper board and corrugated boxboard production.[53]

Starch is one of the most abundant biopolymers and is made up of amylose and amylopectin (Figure 2-7). The ratio of these two materials differs depending on the plant source. Amylopectin has a highly branched structure and is water-soluble. In contrast, amylose has a crystal structure

and only dissolves in water by cooking under high pressure and temperature (150-160°C) or at highly alkaline conditions. Starch by itself does not show any adhesive properties unless its granules are broken down.[54] This process is usually done by gelatinizing starch.[55] When starch is heated in the presence of water, its granules will absorb water, and they swell. The swelling process will continue to the point that all the starch granules come apart. At this point, the starch is "fully gelatinized".

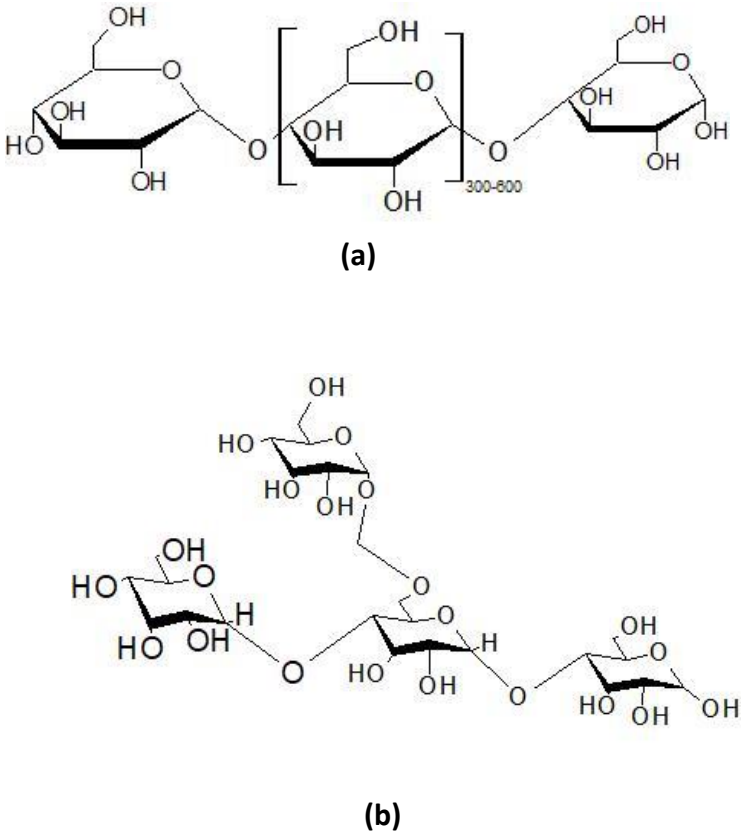

Figure 2-7: The structure of starch; a: amylose b: amylopectin

Gelation is an irreversible and endothermic process. Starches usually gelatinize at a temperature around 60-80 °C but not all the starch granules will gelatinize at the same temperature. Therefore, gelatinization occurs over a range of 8-15 °C units rather than at an exact

temperature.[56] Corn starch was used in this thesis. The percentage of amylose in this starch is 20-28 wt%, and it gelatinizes at a temperature range of 62-72°C.[56]

The production of starch-based adhesives in the industry is not a result of simple gelatinization. The starch adhesive needs to be modified to impart enough tack, water-resistance and durability according to its final application. The main methods to produce starch adhesive are the Stein-Hall process and the no-carrier process, which are described in detail below.

Stein-Hall Process

The Stein-Hall process was introduced in the 1930s.[57] This process includes the preparation of two portions, a "carrier" and a "slurry" portion. In the carrier portion preparation, about 15-20 wt% of total dry starch is fully gelatinized by the heating of an aqueous starch solution.[58] Starch granules swell upon heating in the presence of water. Upon heating, the hydrogen bonds between the starch molecules inside the granules are broken and new hydrogen bonds between water and the starch molecules are formed. When a shear force is applied to the solution, the starch granules rupture, and their content is released into the solution. At this point the starch is fully gelatinized. To reduce the gelation temperature, the process of heating is done under alkaline conditions (pH ≈ 12) by using sodium hydroxide (NaOH) solution to adjust the pH. The presence of NaOH helps to break the hydrogen bonds within the starch granules and accelerate the gelation process. Upon gelation, the viscosity of the starch solution increases, and it turns to a thick paste. In the end, usually between 0.4 -1.3 wt% (on a dry basis) of Borax (sodium tetraborate) is added to the mixture to increase the tackiness of starch adhesive.[59] Borax cross-links starch molecules through the formation of hydrogen bonds and increases the carrier portion's viscosity. Also, Borax is responsible for the formation of the "green bond", which is the hydrogen bond formed between the cellulose molecules of the paperboard and that of the adhesive (composed of starch and Borax) upon applying the adhesive to the corrugated board. The green bond holds the corrugated boards together before curing the adhesive. [60,61]

The slurry portion is prepared by simply mixing the remaining starch (80-85 wt%) with water. The slurry portion is added to the carrier portion. The viscosity of the carrier portion prevents the ungelatinized starches of the slurry portion to settle and provides the adhesive with sufficient

viscosity for its ultimate application. In the end, the total solids content of the starch adhesive is between 20-30 wt%. The adhesive is applied to the tips of flutes in the corrugated cardboard. Then, they are cured under pressure and temperature. Upon applying temperature (60-70^{o}C), the ungelatinized portion of the starch becomes gelatinized and forms instant tack.

Single container or no-carrier process

The strength of the adhesive bond in the corrugated board industry is dependent on the gelation of the ungelatinized portion (slurry portion).[62] Therefore, the ideal starch adhesive would only contain ungelatinized starch. In this regard, another process named the "no-carrier process" has been developed. In this process, a solution of sodium hydroxide is added to a starch slurry. Therefore, all the starch granules are uniformly gelatinized. The mixture is heated and, upon reaching the desired viscosity, an acid, ice or alum is added to stop gelatinization. In the end, Borax is added to increase tackiness. [62,63]

In this process, it is essential to control temperature, starch and caustic solution concentrations carefully, to be able to stop the swelling process at the right moment.[64] Although controlling the reaction conditions is difficult in this process, there are some benefits compared with the Stein-Hall process. In particular, less heat is required in the "no-carrier" process to form bonds because all the starch granules are already partially swollen and less free water is available in the mixture, leading to shorter drying times.[64] Because of difficulties in controlling the viscosity and stopping the swelling procedure at the right moment, all adhesives in this project were prepared by using the Stein-Hall process.

Starch adhesive modification

Due to the presence of hydroxyl groups, starch shows a high affinity towards water. Therefore, starch-based adhesives tend to have low water-resistance; this restricts the application of starch-based adhesives. As a result, there have been many efforts to modify the formulation of starch-based adhesives by adding different components.[65–68] Urea and melamine formaldehyde are the most common additives used, along with an acidic catalyst, to cross-link starch molecules, thereby increasing water-resistance of the starch adhesive.[65] Diacetone acrylamide-formaldehyde, acetoacetamide formaldehyde and acetone-formaldehyde condensates have also

been used.[65] The presence of free formaldehyde in the formulation is noted for its toxicity. In addition, the use of melamine and urea-formaldehyde in the presence of Borax increases adhesive viscosity severely and makes the mixing process inefficient. However, reducing the amount of Borax to control the viscosity is discouraged due to the loss of tackiness which would result.[65]

Another potential solution to the low water-resistance of starch adhesives is the use of starches with higher amylose content in the preparation of the carrier portion (> 35 wt% amylose). Amylose has a crystal structure, and it is barely water-soluble. It was believed that using starch with higher amylose content in the carrier portion would improve the rheological properties and the water-resistance of the adhesive. Although these assumptions were correct, the increase of water-resistance of adhesive was not satisfactory, and the use of other additives was still required.[65]

Recently, the addition of renewable materials such as different types of fibre and hemicellulose to overcome this issue has been explored.[68,69] It was shown that the addition of fibre, regardless of its type, in the carrier and/or slurry portion or even its addition at the end of the adhesive preparation process could improve water-resistance, tack and dry strength of the starch-based adhesive.[68] However, the impact of the fibre was mostly significant at concentrations of 25 wt% (based on total adhesive weight) and above. The cellulose fibre surrounds the starch granules and contains their moisture. In fact, the fibre acts as a moisture barrier and prevents moisture from penetrating into the fibreboard (or cardboard, in our case) from the starch granules and vice-versa. Therefore, it increases the water-resistance of the adhesive. Also, the presence of fibre in the adhesive leads to fibre-fibre entanglement between the adhesive and the fibreboard, which increases tack.[68]

The addition of hemicellulose to starch-based adhesives has also shown promise with respect to increasing water-resistance of glue.[69] Due to the presence of hydroxyl groups in starch and hemicellulose, hydrogen bonds form between them. The presence of Borax in the formulation leads to the formation of a Borax-oxygen bridge to the starch or hemicellulose hydroxyl group.

As a result, starch and hemicellulose become cross-linked, and this increases the water-resistance of the adhesive.[69]

In this thesis, we propose that lignin would be a good candidate to be used in the starch-based adhesive formulation to improve its water-resistance. Lignin has a relatively low cost, and the presence of phenol groups in its structure leads to hydrophobic properties. At the same time, the presence of hydroxyl groups in its structure suggests its compatibility with starch and gives it the potential to cross-link with starch.[70] Recent research blending lignin and starch in foam and film applications have shown that the addition of lignin decreases water uptake and increases the strength of the composite material.[70–73] This evidence supports our hypothesis that lignin could improve adhesion and water-resistance properties of starch-based adhesives.

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Chapter 3 : The Use of Lignin in Emulsion-Based Pressure-Sensitive Adhesives

Abstract

Pressure sensitive adhesive (PSA) films were produced by in situ seeded semi-batch emulsion polymerization of butyl acrylate (BA) and methyl methacrylate (MMA) in the presence of varying amounts of lignin. Two types of Kraft lignin, water-soluble and non-water soluble, were used in this study. Lignin was modified using acrylation (methacryloyl chloride), maleation (maleic anhydride) and acetylation (acetyl bromide and acetic acid) to promote its miscibility with the BA and MMA monomers and encourage its incorporation into the polymer matrix. For the case of the maleated lignin, maximum incorporation of 10 wt% was achieved whereas, for the acrylated lignin case, a maximum of 5 wt% was attained. Lignin was shown to decrease latex viscosity in all cases. At a lignin loading of 1 wt% (relative to the amount of monomer) a tack and shear strength of the PSA films increased significantly while the peel strength remained constant. Thus, maleated lignin was shown to be an effective, renewable modifier for emulsion-based PSA properties.

Introduction

Because of the depletion of fossil-based resources, high petroleum prices and, most notably, their negative impact on the environment, there has been a significant effort made towards the production of more sustainable polymeric materials.[1–4] Pressure sensitive adhesives (PSAs) are mainly produced from acrylic, and styrenic monomers, which are often hazardous and toxic materials.[5] Using non-toxic renewable materials as monomers and additives to tailor the properties of PSAs is one option towards achieving greater sustainability. However, the addition of new materials to a formulation often results in a significant change in performance properties compared to the original commercial product.[6,7] Nevertheless, one can use a number of

approaches to modify the formulation and process conditions to either maintain or improve the properties of the original product. [4,8]

Lignin is the most abundant biopolymer in the world after cellulose, and it is a primary renewable source for aromatic structures. In nature, lignin combined with cellulose provides rigidity and structure to plant cell walls; in a sense, they form one of nature's composite materials. Due to the presence of phenolic and aliphatic substrates in lignin, it provides an anti-oxidant barrier to protect the plant (Figure 3-1). In the plant, lignin is generated via radical polymerization from its building blocks, monolignols (Figure 3-2). Lignin does not have a unique chemical structure, which depends on its isolation process and its botanical source. There are different inter-unit linkages between monolignols which are formed by radical coupling (Figure 3-1). The main linkage, which accounts for 50% of lignin linkages, includes the β carbon of one monolignol and the phenolic hydroxyl group of the other and is called a β-O-4 linkage.

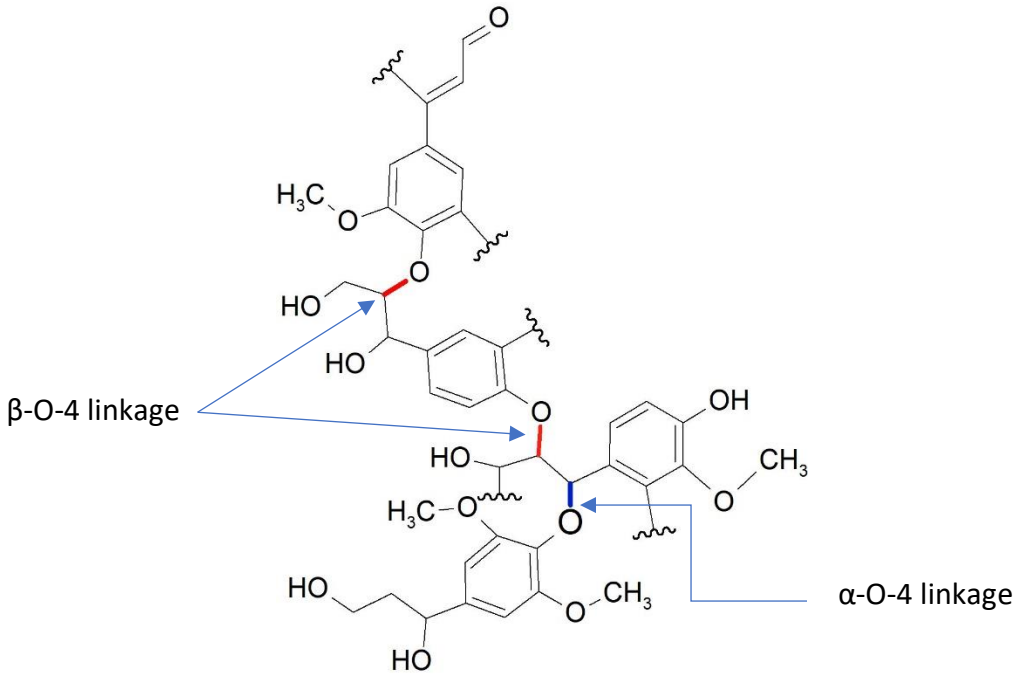

Figure 3-1: Main linkages between monolignols in a typical lignin molecule.

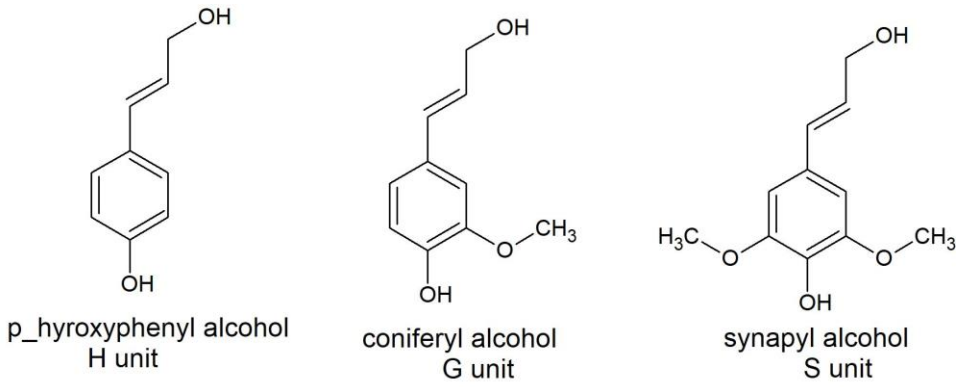

Figure 3-2: Examples of monolignols

Lignin has a relatively low cost (e.g., Kraft lignin is about 260-500 USD/MT)[9] and primarily is produced in the pulp and paper industry. The Kraft process is the most common lignin production method.[10] In the Kraft process, wood chips are treated with sodium sulfite and sodium hydroxide to separate pure cellulose from other wood parts. The soluble part of the resulting "black liquor" is referred to as Kraft lignin. The Kraft lignin is precipitated by adjusting the pH and applying acidic conditions. Typically, Kraft lignin is hydrophobic at neutral conditions, relatively high in phenolic hydroxyl groups (2-5 wt%), carboxylic acid groups (4-7 wt%) and low in residual sulfur (≤1-2 wt%).[10] The number average molar mass of Kraft lignin is relatively low (1800-2200 g mol^{-1}).[11,12]

Due to the diversity of functional groups present in lignin (e.g., phenol, hydroxyl and methoxyl groups), there is enormous potential for the use of lignin in the production of aromatic chemicals, and as monomers (e.g., vanillin) for polymer production.[13] One of the most common applications of lignin is as a precursor for the production of polyols by oxypropylation.[6,14] In this reaction, propylene oxide is grafted onto lignin through a gas-solid interaction using a high Bronsted base and applying pressure. Polyols are widely used for polyurethane foam production. The addition of lignin instead of polyol showed high incorporation of lignin in the polyurethane matrix, and the produced foam had comparable thermal conductivity and dimensional stability in comparison to those based entirely on fossil fuel resources.[6,11,15]

Another application of lignin is in phenol-formaldehyde (PF) production. The source of synthetic phenol for PF production was replaced by lignin due to the latter's abundance of phenol

functional groups. In this case, lignin is epoxidized and used in epoxy resin production. The resulting products show competitive results to PFs synthesized with synthetic phenol.[16–18]

Due to its favourable mechanical properties (e.g., high Young's modulus), lignin has been investigated as a sustainable filler to reinforce elastomers.[19,20] Attempts to blend lignin with polymer often leads to phase separation and particle aggregation.[21,22] To compatibilize the lignin with the polymer matrix, either polymer particles were grafted onto lignin or lignin particles were modified by introducing reactive functional groups (mainly vinyl groups) to its structure. The resulting modified macromolecule was used in polymer blends and copolymerizations. The resulting products were used in applications such as emulsifiers, adhesives, paints and coatings.[23,24] For example, Hilburg et al. synthesized nanocomposites by solution-based (in dimethylformamide) atom transfer radical polymerization (ATRP) using poly(styrene) and poly(methyl methacrylate) (pMMA) grafted from lignin.[25] The resulting polymers showed enhanced toughness and elongation in comparison to the pure homopolymer. In another approach, lignin was used to enhance the UV absorption of polylactic acid polymers. The miscibility of the lignin with the polymer matrix was improved by grafting lignin from poly(butyl acrylate) (pBA) and pMMA by free radical solution polymerization (using dimethyl sulfoxide (DMSO) as solvent). The grafted copolymer showed excellent UV absorption, thermal resistance and hydrophobicity.[26]

The incorporation of lignin in a polymer matrix brings unique mechanical properties in comparison to other nanocomposites. However, because of the low solubility of lignin in low hazard profile solvents like methanol and acetone[27] and the high heterogeneity of lignin due to its size, cross-linking and different functional groups,[28] polymerization and grafting of lignin often is done as a solution polymerization in hazardous solvents (e.g., DMSO, dioxane and pyridine).[29] As a result, there has been a trend towards the use of a more environmentally-friendly pathway such as suspension and emulsion polymerization, where water is used as a reaction medium. Jacob et al. performed aqueous graft copolymerization of lignin and MMA, but the graft efficiency after 8 h of reaction was less than 15 wt%.[23] This low efficiency was attributed to radical scavenging by the lignin. Using the same approach, Panesar et al. grafted vinyl acetate onto lignin, and achieved graft efficiencies of 45%.[30] Typically, lignin participates in a free radical

polymerization by subtraction of hydrogen from its phenolic hydroxyl groups. The produced phenoxy radicals are much less reactive, acting as inhibitors due to their quinonoid structure,[31] thereby inhibiting further polymerization.[32] Thus, when lignin is used in free radical polymerizations, low conversions are typically observed.[33]

Messmer et al. used unmodified Kraft lignin in emulsion and mini emulsion polymerization in order to produce a polymer hybrid latex.[34] They substituted up to 6.8 wt% (relative to the mass of monomer) of styrene with lignin in a styrene/BA/MMA monomer formulation. Inhibition was observed during the polymerization, and the formation of coagulum was noted, even at low lignin concentrations. Furthermore, the lignin was not completely miscible with the reaction medium and did not disperse adequately in the emulsion.[34]

Because of the compatibility issues noted above, several lignin modifications have been studied: esterification, etherification, reaction with isocyanate, phenolation, sylilation and reduction/oxidation reactions.[11,35] In all these modifications, the phenolic hydroxyl group is the main target of modification. This functional group is the most reactive one in lignin and could affect its chemical reactivity.[11] Esterification is straightforward and often is done using acidic compounds, acidic anhydrides and chloride acids, the last two being more effective. The reaction of lignin with an acidic compound such as acetic acid (acetylation) is a routine method to enhance the solubility of lignin in different materials and usually is used for assessment of molecular weight and structural analysis of lignin.[36,37]

Using butyric and maleic anhydride-modified lignin (via esterification) with poly(styrene), poly(ethylene) and poly(propylene) led to excellent polymer-lignin compatibility.[38–43] The aliphatic and aromatic hydroxyl groups present in lignin allow for efficient esterification. Using the esterified lignin to levels of incorporation up to 10 wt% showed excellent compatibility in blends with poly(styrene), as well as in bulk and emulsion polymerization with styrene monomer. The resulting materials showed higher thermal stability and better mechanical properties in comparison to pure poly(styrene).[30,40,42]

Another esterification pathway uses chloride acids such as acryloyl and methacryloyl chloride.[44–47] In this modification, the vinyl group is introduced into the lignin, and its reactivity is enhanced.

Triethylamine (Et_3N) often is used because it can selectively modify phenolic alcohols in the presence of aliphatic alcohols.[11,48] Often, both aliphatic and phenolic hydroxyl groups take part in the reaction.[11] Wang et al. used acryloyl chloride at relatively high pressure and temperature (at 40 bar and 250 ^oC) to modify aromatic monomers of depolymerized lignin.[49] They copolymerized the modified aromatic monomers with BA in a solution polymerization for PSA production. The modified monomers were successfully incorporated into the pBA up to 22 wt%, and the PSAs gave similar adhesive properties in comparison to the commercial equivalent.

Herein, two types of Kraft lignin (HPH which is water-soluble and LPH which is has a low pH and is not water-soluble) were identified as materials with the potential to improve the adhesive properties of acrylic PSAs. The LPH Kraft lignin was esterified using either acetylation or acrylation while the HPH lignin was modified using maleic anhydride. Each of the three functionalized lignins was incorporated in BA/MMA semi-batch emulsion polymerizations to produce stable latexes for adhesive applications.

Experimental section

Materials

Two types of Kraft lignin with the trade names of "Amalin LPH" and "Amalin HPH". Amalin LPH is light brown in colour, hydrophobic with an inorganic content <1 wt %, pH ≈ 3.3 (note: LPH refers to low pH) and dry solids about 50 wt%. Amalin HPH is dark brown in colour, with a pH of 10.4 (note: HPH refers to high pH), an ash content less than 20%, and a dry solids content of ~60 wt%. Both Amalin LPH and HPH were supplied by Noram Engineering and Constructors Ltd. (Hinton, Alberta, Canada). Butyl acrylate (BA, 99%), methyl methacrylate (MMA, 99%) and 2-hydroxy methacrylate (HEMA, 97%) monomers, 1-dodecanthiol (NDM, 99%) chain transfer agent, sodium dodecyl sulfate (SDS, 99%) surfactant, potassium persulfate (KPS, 99%) initiator, triethylamine (Et_3N, 99%) as catalyst for acrylation, N, N-dimethylformamide (DMF) as solvent for acrylation, acetic acid (99%) and acetyl bromide (99%) as reactants for acetylation were all obtained from Sigma Aldrich. Maleic anhydride (MAnh, 99%) was obtained from Fluka Analytical. BA, MMA and HEMA were purified before polymerization using an inhibitor removal column. All other

chemicals were used as received. Nitrogen gas (Linde Canada) was used to purge the reactor before polymerization. Distilled deionized (DDI) water was used throughout this project.

Lignin modification

Acetylation

The acetylation procedure was adapted from Asikkala et al.[37] Acetylation of the lignin was performed in several batches to generate sufficient amounts of modified lignin. 15 mg of untreated lignin was mixed with 2.5 g of glacial acetic acid for 1 h. Then, 0.5 g of acetyl bromide was added, and the reaction was left to react overnight at room temperature, under constant stirring with a magnetic stir bar. The excess acetic acid and acetyl bromide were evaporated in a rotary evaporator for 3 h, followed by drying at 40 °C oven for 40 min. The acetylated lignin was dried in a vacuum oven at 40 °C for 24 h.

Acrylation

LPH lignin was modified using methacryloyl chloride according to a protocol adapted from Gordobil et al.[45] In this procedure, 15 g lignin was first dissolved in 300 ml of DMF. 15 g of Et_3N was then added to the mixture as a catalyst. Separately, 30 g of methacryloyl chloride was dissolved in 40 ml of DMF, and the mixture was added to the lignin mixture dropwise over 10 h. The reaction was completed at 7 °C over 24 h. After the reaction was completed, a white precipitate was separated from the mixture and discarded by decanting the liquid (the liquid portion was retained). Acrylated lignin (AC lignin) was precipitated by adding the retained solution dropwise to deionized distilled water, and it was washed several times with water before polymerization.

Maleation

HPH lignin and maleic anhydride were mixed and ground together with a mortar and pestle at a ratio of 2:1 (wt:wt). The mixture was heated in an oven to 85 °C for 3.5 h. Due to the heating, the maleic anhydride melted, and a viscous mixture resulted. The mixture was washed with acetone several times and filtered in order to remove unreacted maleic anhydride. The insoluble part in acetone was dried in an oven at 40 °C overnight. The maleated lignin is referred to as MAnh lignin in this paper.

Latex preparation

A starved, seeded, semi-batch polymerization technique was used with different lignin loadings to produce latex polymers. It should be noted that in all but two runs, lignin was added solely via the "pre-emulsion" feed as the modified lignin was more easily dispersed, and this led to reduced production of grit. The two exceptional runs were those using 5 and 10 phm maleated lignin, wherein the lignin was added solely via the seed stage. The emulsion polymerization formulation is summarized in Table 3-1.

All runs used a solids content of 46 wt% (thus, 54% water). 1-Dodecanethiol (NDM) was used as a chain transfer agent (CTA) in order to make the polymer chains shorter and increase adhesive tack. 2-Hydroxy ethyl methacrylate (HEMA) was used as a cross-linker to increase shear strength. The polymer seed was produced as a batch reaction using the initial charge formulation (Table 3-1). The seed reactants (excluding monomer and initiator solution) were charged to a 1 L Mettler-Toledo LabMax reactor, and the reactor temperature was increased to 60°C in 0.5 h at a stirring speed of 250 rpm; the mixing speed and reaction temperature were held constant for the remainder of the reaction. The monomer mixture (12 g of 95/5 wt:wt BA/MMA) was added once the reactor achieved the desired temperature and held for 5 min. Next, the KPS initiator solution (0.4 g KPS in 13 g water) was added, and the reaction continued for 30 min. At this point, the monomer pre-emulsion and initiator feeds were begun and continued for 4 and 4.5 h, respectively, via separate feed pumps. The reaction was continued for an additional 50 min after the feeds were completed. The latex was then cooled to 30°C and the reactor was discharged.

Table 3-1: Formulation of Emulsion polymerization

Ingredients	Seed stage	Feed stage	
	Initial charge (g)	Monomer pre-emulsion (g or phm*)	Initiator solution (g)
Monomer (BA/MMA, 95:5 wt:wt)	12	240 g	-
H_2O	140/13**	90 g	70
NDM (CTA)	-	0.2 phm	-
Lignin	-	0-5 phm	-
Initiator (KPS)	0.4	-	0.8
Emulsifier (SDS)	0.65	2.2 phm	-
HEMA	-	2 phm	

*phm = parts per hundred parts monomer

** Amount of water used to dissolve initiator in seed production

To compare in situ polymerization of lignin to simple blending of lignin with a pre-made latex, a "hot blend" technique was used. In this case, the base case formulation (i.e., without lignin) was prepared, and the lignin solution was added at the end of the polymerization. The mixture was heated and stirred for an additional hour while the reaction conditions were held constant.

Characterization

Fourier-transform infrared spectroscopy (FTIR) analysis of the modified lignins was conducted using a Cary 630 FTIR with an Attenuated Total Reflectance (ATR) diamond accessory (Agilent Technologies, Canada).

During the reaction, pH was monitored by measuring the pH of all samples and the final latex using a Fisher Scientific Dual channel pH meter (XL600).

A simple gravimetric method was used to measure monomer conversion and solid content of the latex. Samples were taken every 30 min after completion of the seed stage. The seeding stage

lasted 30 min. About 1.5 g of each sample was put in an aluminum pan and dried under a fume hood at room temperature. The instantaneous conversion was measured based on the amount of monomer fed at the sampling time, and total conversion was measured based on the amount of total monomer in the reaction.

Latex particle size was measured using dynamic light scattering (DLS) with a Malvern NanoS Zetasizer at an angle of 173°. One droplet of the sample was diluted with 4 ml of water in a polystyrene cuvette. Each measurement was repeated three times, and the weighted average was reported.

Particle morphology was assessed via the drop-casting method using a Tecnai G2 Spirit Twin Transmission Electron Microscope (TEM). Three droplets of each sample were diluted with 50 ml deionized distilled water. The samples were sonicated for 10 min in a water bath sonicator. Afterwards, one droplet of the diluted solution was put on a glow discharged copper grid. The samples were dried at room temperature for 3 h and then tested by TEM.

The final viscosity of all latexes was measured using a Thermo Scientific Hakke Viscotester (Model D) using a spindle spinning rate of 100 rpm.

A TA Instrument model Q100 DSC was used to measure the T_g of the polymers. Around 7 mg of each sample was placed in a standard pan with lid. All samples were heated to 120 °C and then cooled to -80 °C and re-heated to 120 °C to complete the cycle. All the heating and cooling was done at a rate of 10 °C/min in a nitrogen atmosphere.

The gel content was measured by putting ~0.2 g of a dried latex sample in a poly(propylene) backed membrane pouch with a pore size of 0.2 μm and a diameter of 47 mm. Each pouch was heat sealed. Each sample was soaked in 30 ml of THF overnight and afterwards was shaken using a mechanical shaker for 7 h. Each pouch was subsequently dried in the fume hood for 24 h. The dry material that remained inside the pouch is referred to as dry gel. The gel content was calculated using the equation below.

$$\textbf{Gel content}\ (\%) = \frac{\boldsymbol{mass\ of\ dry\ gel}}{\boldsymbol{mass\ of\ dry\ polymer}} \times \mathbf{100}$$

The adhesive properties were evaluated by measuring tack, peel strength and shear strength. A #50 Meyer rod was used to cast latex films of 12.5" × 12.5" onto Mylar sheets. The films were dried and eventually tested at 25 °C at 50% relative humidity. All films had a thickness of approximately 6 mg of adhesive/cm^2 of the Mylar sheet. Tack and 180 °C peel strength were measured using an Instron 3000 Universal Tester along with Bluehill 2 Materials Testing Software. The PSTC-16 standard was used to measure tack[50]. A 1" × 5" sample from dried films was formed into a loop, with the adhesive facing outside. The sample was secured into the grips of an Instron tester. The loop was lowered at a constant rate of 2 mm/s until a contact area of 1" × 1" was achieved on a stainless-steel test panel. The sample was removed at a speed of 5 mm/s, and the maximum force was reported as tack. This procedure was repeated 5 times for each latex film, and the average value was reported.

The PSTC-101 standard method was used to measure peel strength[51]. Samples of 1" × 12" were cut from the latex films. The adhesive film was applied to a stainless-steel panel using a 2040 ± 50 g steel roller. The roller was rolled on the samples at a constant speed of 10 mm/s twice in both directions. The sample was peeled from the stainless-steel panel at an angle of 180° for a distance of 1" at a constant speed. The procedure was repeated 5 times for each film, and the average force was reported as peel strength.

Shear strength was measured according to the PSTC-107A standard[52]. Sample strips with a contact area of 1" × 1" were cut from the latex films. These were rolled onto the stainless-steel panel in the same manner as for the peel strength test. After preparing the samples, a 0.5 kg weight was hung to the sample, and the shear strength was measured as the time taken for the sample to detach from the stainless-steel test panel. The shear tester was in-house built, and the required time for failure was measured using Labview software.

The films cast for adhesive property measurements were also used to measure the hydrophobicity of the film surfaces. Samples of 4" × 4" were cut from each film, and three to five locations were tested on each sample. A VCA optima instrument (AST products Inc.) was used to measure the water contact angle. A 2 µl water droplet was syringed onto the film, and the contact angle was recorded using the VCA OPtimaXE software within 10 s.

Results and Discussion

As noted in the introduction, the direct use of unmodified lignin, resulted in a low incorporation of lignin in the polymer matrix, latex instability, low monomer conversion and poor adhesive properties. Therefore, it was decided to modify the lignin using acetylation, acrylation and maleation prior to polymerization with BA and MMA. Lignin acetylation yielded an improved dispersion in the comonomer mixture compared to the unmodified lignin case but ultimately led to significant lignin precipitation and agglomeration to the reactor wall and impeller during the emulsion polymerization. These results suggest that the acetylated lignin was not incorporated in the polymer matrix. Acrylated and maleated lignin samples led to good latex stability and therefore, all further emulsion polymerizations were performed with one or the other. The incorporation of acrylated lignin beyond 5 phm, and of maleated lignin beyond 10 phm led to the production of grit and latex instability.

FTIR spectroscopy confirmed the successful modification of the lignin (Figure 3-3). Unmodified Kraft lignin possesses a broad and strong peak at (3400-3500 cm^{-1}) and 2919 cm^{-1} corresponding to its phenolic hydroxyl groups and C-H stretching, respectively.[45] The aromatic stretching bands are visible at 1560 and 1504 cm^{-1}.[53] The absorbance peaks of guaiacyl units of lignin are also visible at 1256 and 1027 cm^{1}. After each modification, the phenolic hydroxyl peak intensity was significantly reduced. In addition, as a result of the acetylation process, a strong absorption band related to aromatic stretching and aliphatic carbonyl (C=O) stretching appeared at 1740-1760 cm^{-1}.[54] A new peak at 1190 cm^{-1} corresponds to ester bonds, which indicate the presence of the acetate groups and therefore, successful acetylation of lignin.[53,55] The acrylated lignin yielded two new peaks at 1200 and 1737 cm^{-1}, corresponding to C=O groups in the ester and carboxylic acid groups. The increased intensity of the absorbance at 940 cm^{-1} is due to the $=CH_2$ groups in the modified lignin molecule. The small peaks at 1640-1680 cm^{-1} correspond to C=C bonds and indicate the presence of methacrylate units.[45] For the maleated lignin, a significant reduction in peak intensity at 1027 cm^{-1} (C-O stretching of primary alcohol) was observed.[56] Increased peak intensities at 1700, 1673, and 1571 cm^{-1} were attributed to the ester groups and double bonds due to successful maleation.[40] In addition, maleation resulted in a slight shift in the location of the guaiacyl units' peaks.[38]

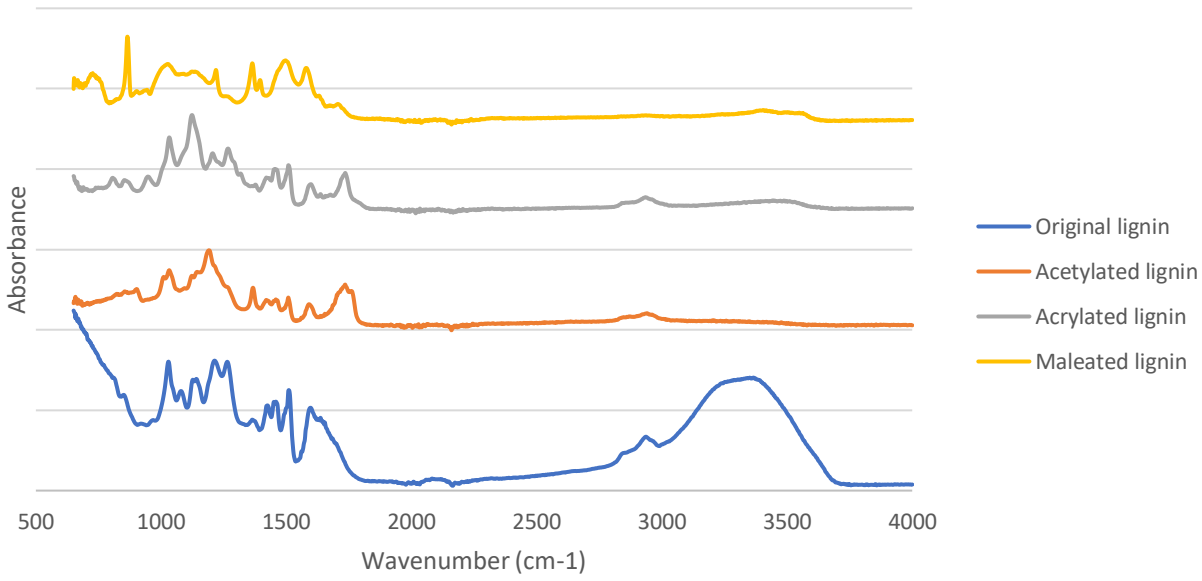

Figure 3-3: FTIR spectra of pure, acetylated, acrylated and maleated lignin

Lignin modification was confirmed further by measuring the T_g of the unmodified lignin and its esterified derivatives. HPH and LPH lignin have T_gs of 110 and 104 °C, respectively. The T_g of acrylated lignin (86 °C) and maleated lignin (89 °C) was lower than that of the unmodified ones. This suggests that the hydroxyl groups of lignin have been modified, in this case, substituted with ester groups, and the hydrogen bonds have been eliminated. Therefore, the lignin molecules have more free volume and mobility, which leads to a decrease in the T_g.[57]

Representative conversion profiles for the base case (no lignin, Figure 3-4), 5 phm acrylated lignin (Figure 3-5) and 5 phm maleated lignin (Figure 3-6) are shown below. It should be noted that the first sample was taken exactly at completion of the seeding stage. In all runs, there was no inhibition or retardation in the rate of polymerization. The base case and 5 phm acrylated lignin case show evidence of a monomer-starved condition. The 5 and 10 phm maleated lignin runs displayed a slower reaction rate (i.e., lower slope of conversion vs. time plot) due to the use of the lignin in the seed portion as opposed to the monomer pre-emulsion, which yielded a lower number of particles compared to the base case and acrylated lignin runs. All runs reached the full conversion.

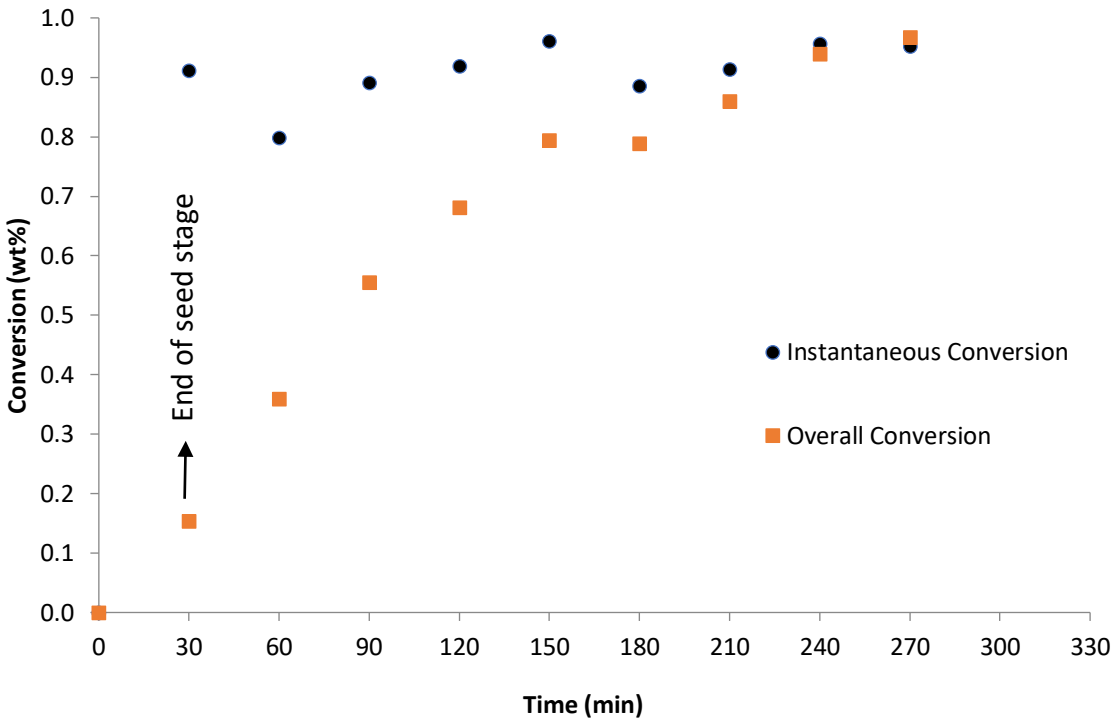

Figure 3-4: Instantaneous and overall conversion of base case run (no lignin)

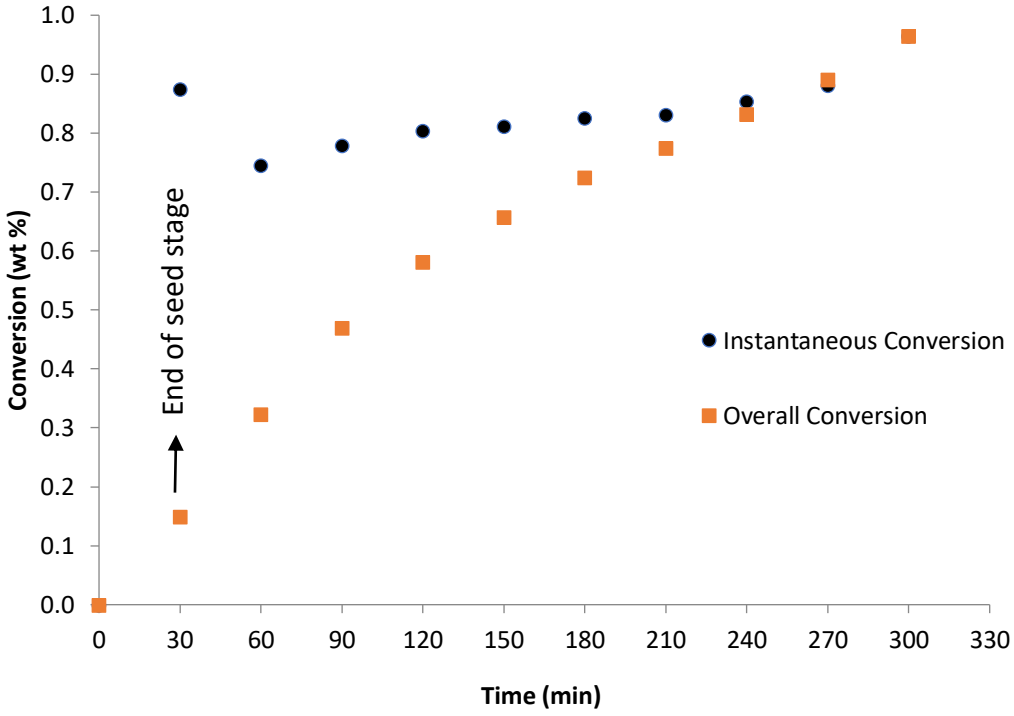

Figure 3-5: Instantaneous and overall conversion of run with 5 phm acrylated lignin

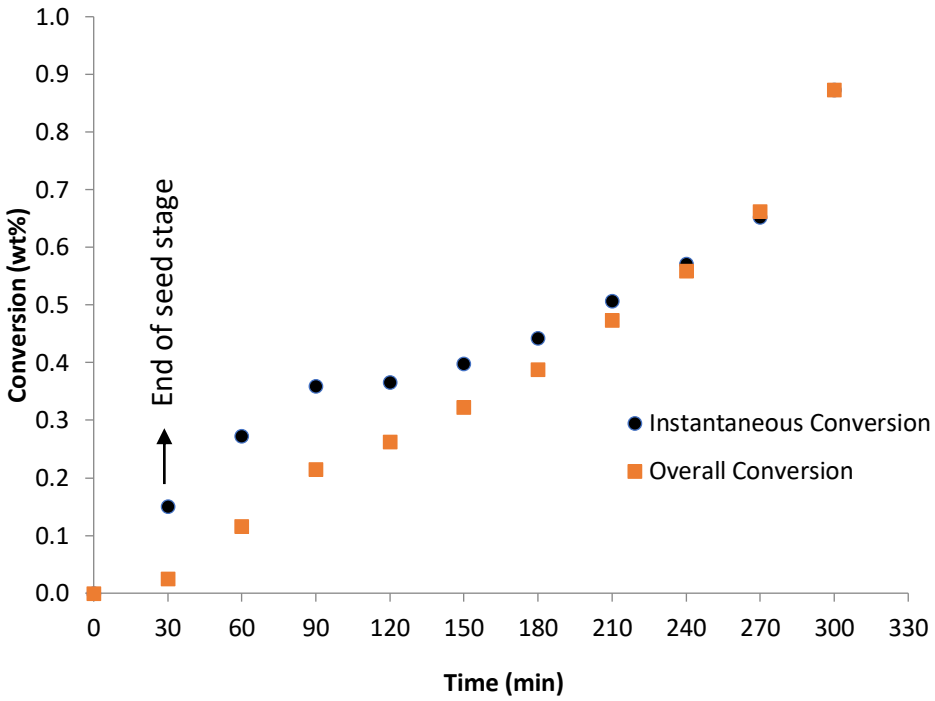

Figure 3-6: Instantaneous and overall conversion of run with 5 phm maleated lignin

The incorporation of lignin led to a slight increase in particle size when lignin was added to the pre-emulsion part of the semi-batch latex formulation (Table 3-2). Messmer et al. showed that the use of unmodified Kraft lignin led to a decrease in particle size.[34] They concluded that the lignin acted as an emulsifier and caused additional particle nucleation (beyond what was obtained in the non-lignin case), thereby resulting in more particles and lower particle size. In our case, for the addition of modified lignin to the pre-emulsion, the moderate increase in particle size is attributed to the incorporation of lignin inside of the particles. For the 5 and 10 phm maleated lignin cases, where the lignin was added at the seed stage of the polymerization, a significant increase in particle size was observed. For these two cases, some coagulum was detected at the early stages of the reaction. It is likely that "controlled coagulation" - essentially, agglomeration of lignin – led to larger seed particles and ultimately larger polymer particles at the end of the reaction. DLS measurements taken just after the seed stage showed a bimodal distribution, supporting the idea that agglomeration occurred (Figure 3-7); this was not observed for runs where lignin was added only in the pre-emulsion. As noted earlier, the larger particle sizes for these two runs corroborate the lower reaction rates (Figure 3-6). Finally, a core-shell

morphology was observed using TEM imaging, providing evidence of lignin incorporation within the polymer particles (Figure 3-8).

Table 3-2: Final particle size and latex viscosity

Lignin concentration (phm)	Modification	Final Particle size (nm)	Final latex viscosity (mPa.s)
0	Base case	123	270
0.5	Acrylation	124	233
1		130	178
2		132	187
5		136	150
1	Maleation	142	123
2		139	103
5		211*	72
10		257*	94

*Modified lignin added to the seed portion; in all other cases, modified lignin was added to the pre-emulsion.

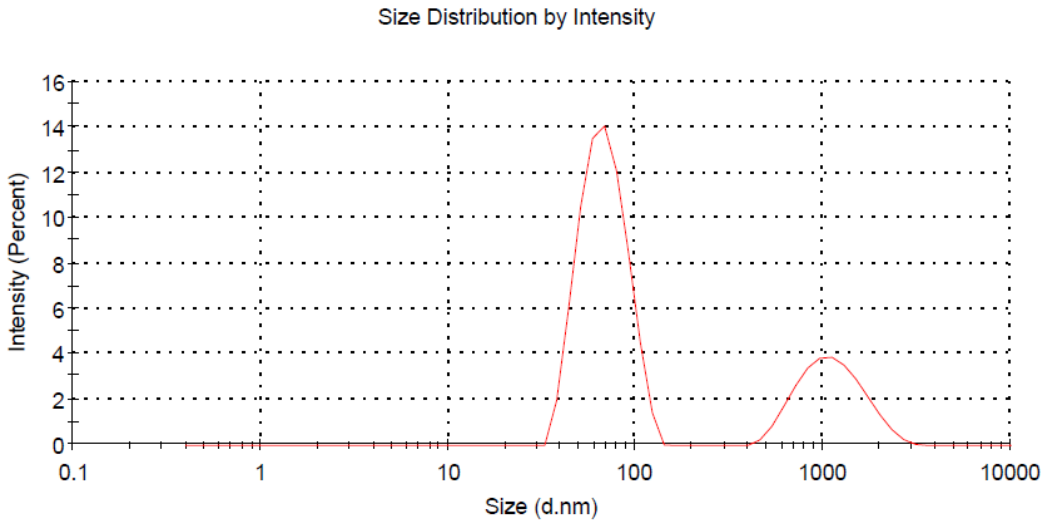

Figure 3-7: Particle size distribution for run with 5 phm maleated lignin

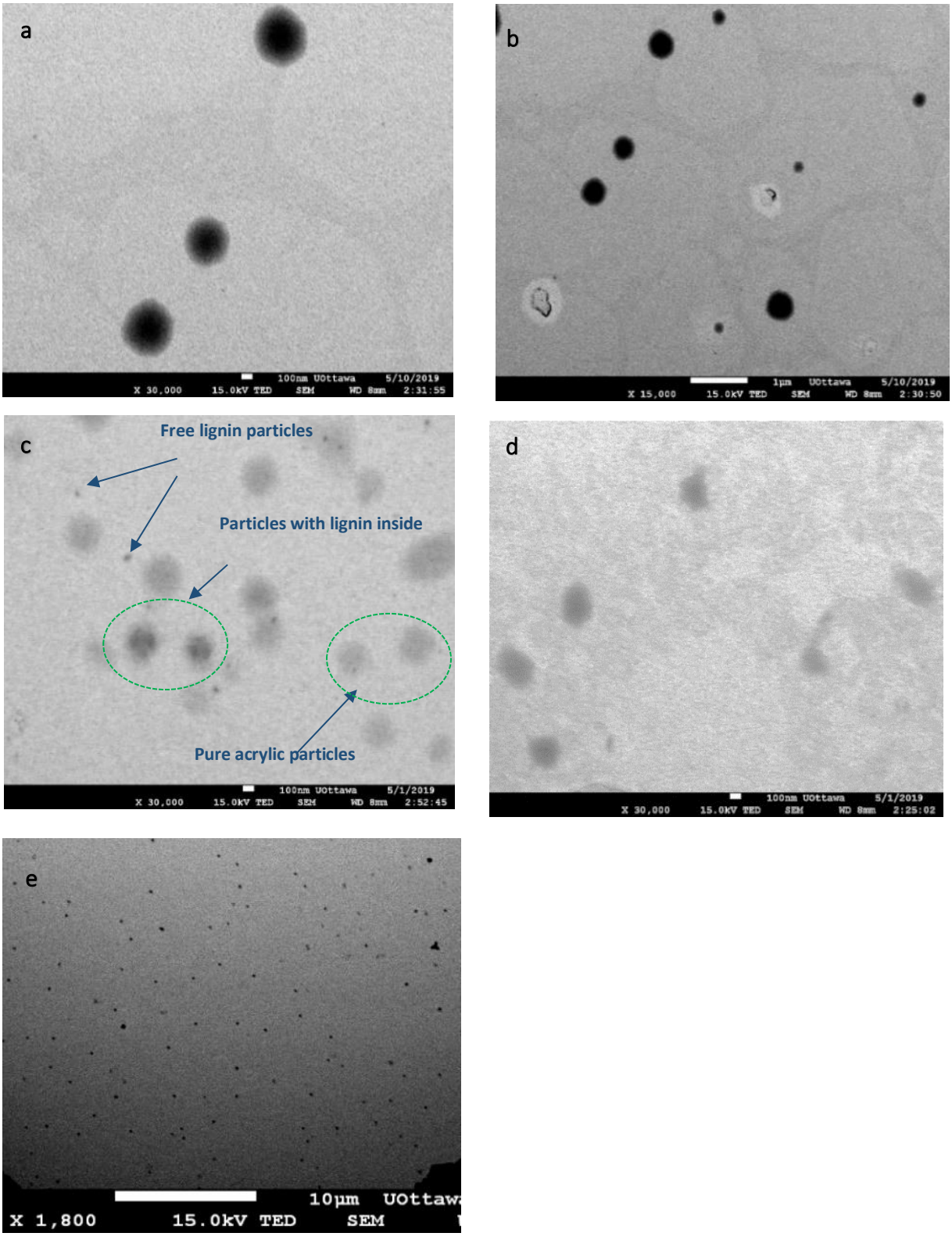

Figure 3-8: TEM images; a: run with 10 phm maleated lignin, high magnification; b: run with 10 phm maleated lignin, lower magnification; c: run with 1 phm maleated lignin; and d: run with 2 phm acrylated lignin; e: pure maleated lignin

Selected latex samples were characterized using TEM imaging (Figure 3-8). For the maleated lignin runs, incorporation of lignin into the polymer particles was evident even at low lignin concentrations and regardless of addition in the seed or pre-emulsion stage (Figure 3-8-c). As noted above, TEM images for the runs with higher maleated lignin concentrations added in the seed stage, presented a core-shell particle morphology without any evidence of free lignin in the mixture (Figure 3-8-a). In this case, at lower magnification, observing the shell layer of the particles was difficult (Figure 3-8-b) but at greater magnification, the shell became more apparent (Figure 3-8-a). This also implies that the shell layer was expanded because of the heat produced during TEM imaging. It suggests that low T_g polymer was the main component of the shell.[3] Free lignin was detected in all samples using maleated lignin added via the pre-emulsion (Figure 3-8-c, a TEM image of maleated lignin is shown in Figure 3-8-e for comparison). A core-shell morphology was not evident for any of the acrylated lignin runs (Figure 3-8-d).

The addition of lignin led to a decrease in latex viscosity (Table 3-2). As Zhang et al.[39] reported, the latex viscosity has a direct relation to the ratio of interfacial tension of two phases to the radius of the droplet (ϒ/R). As there was no significant particle size change in the runs up to 5 phm lignin, we can conclude that the addition of small amounts of lignin decreased the interfacial tension. Thus, when the concentration of lignin was low, it decreased the final latex viscosity. For the runs with 5 and 10 phm maleated lignin, a massive increase in particle size lowered the ϒ/R ratio. Thereby, resulting in a significant decrease in latex viscosity.

Multiple glass transitions were identified in the latex samples containing lignin, signalling a non-homogeneous mixture (Table 3-3). The first peak (T_{g1}) in samples using lignin, whether modified or unmodified, likely represents the T_g of the pure latex; note the similarity to the T_g for the base case. The additional peaks (T_{g2}) for the acrylated lignin cases appear to be consistent with the T_g of acrylated lignin (86 ^oC) that perhaps has been acrylated further. As the amount of lignin was increased, T_{g2} decreased. Similarly, the maleated lignin cases showed a T_{g2} aligned with the T_g of maleated lignin (89 ^oC). In three cases, at concentrations of 2, 5 and 10 phm maleated lignin, a third peak (T_{g3}) was detected. These peaks suggest the presence of a lignin-BA/MMA terpolymer; most evident when the modified lignin was added at the seed stage (i.e., using 5 and 10 phm

maleated lignin). Finally, when compared to the blended latex-lignin samples, the above results are consistent.

Table 3-3: Glass transition temperatures (T_g) of latexes

Latex type	Lignin type	Lignin concentration (phm)	T_{g1}	T_{g2}	T_{g3}
In-situ polymerization	Base case	0	-44	-	-
	Acrylated lignin	1	-44	73	-
		2	-44	65	-
		5	-44	51	-
	Maleated lignin	1	-44	75	-
		2	-45	61	-7
		5	-47	65	-9
		10	-47	63	-10
Blend	HPH lignin	5	-42	101	-
		10	-42	99	-

All formulations had a relatively low gel content (Figure 3-9). These results are not surprising given that each formulation contained NDM chain transfer agent, which decreases the gel content.[8,58] The addition of lignin in the acrylated lignin cases, resulted higher gel contents, likely due to increased cross-linking between the lignin and the polymer matrix. However, for the maleated lignin cases, the addition of lignin beyond 1 phm resulted in lower gel content. It is well known that the gel content measurement technique may be prone to high variability in the measurements; thereby, the differences herein may not be significant.

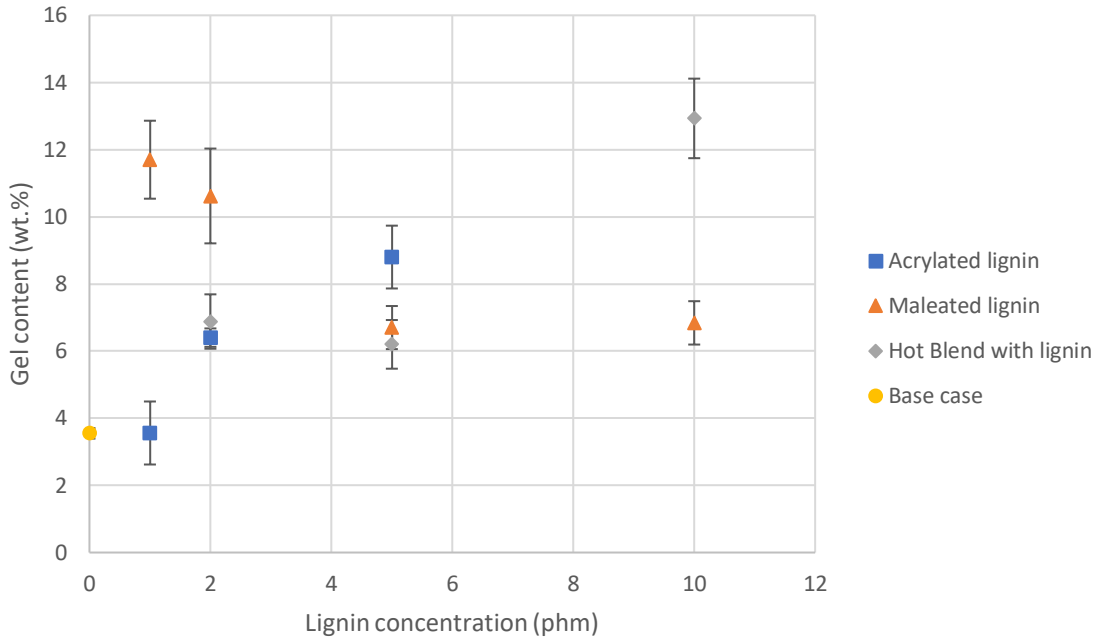

Figure 3-9: Gel content of runs

The water contact angle measurement provides useful insight into the degree of hydrophobicity and wettability of the polymer films (Figure 3-10). At low lignin loadings, regardless of treatment, the latex films became more hydrophobic. Lignin possesses both hydrophilic (hydroxyl group) and hydrophobic (aromatic rings) functional groups in its structure.[59] However, lignin esterification with acid chlorides like methacryloyl chloride and maleic anhydride will lead to increased hydrophobicity.[11,44,60–62] Thus, further increases in lignin loading tended to a recovery in hydrophilicity. This could be due to a reduction of film cohesion or increased roughness in the film surface due to the addition of lignin.[63,64] It is reported that the interaction between solid and liquid, such as affinity, adhesion, surface topography and surface charge also could have had an impact.[64,65]

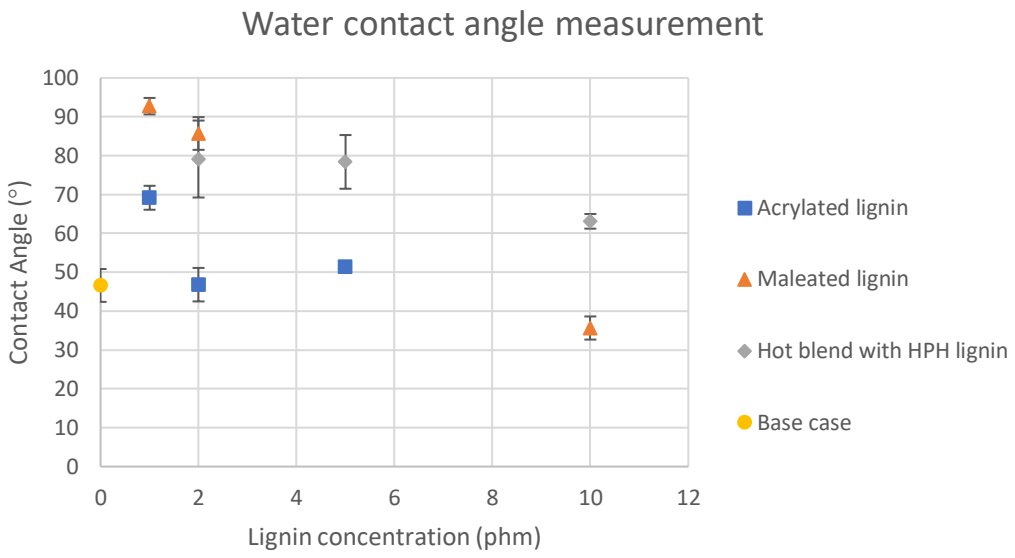

Figure 3-10: Water contact angle measurement of latex films

The adhesive properties were evaluated using tack, peel strength and shear strength measurements.[66,67] Tack provides a measure of the ability of an adhesive to form a bond with the surface of a substrate under light or no pressure. Peel strength is measured as the force that is needed to peel off a standard strip of adhesive from a standard surface at a constant and pre-defined peel rate and contact angle. Shear strength is a measure of the shear deformation of the adhesive under constant shear stress, and it is related to the internal and cohesive bonds of the adhesive.[66]

Films from the lignin-based latexes were compared to the pure acrylic latex base case, as well as the films from the HPH lignin/base case blend. In the first place, the base case formulation was chosen in a way to have balanced tack, peel strength and shear strength. These properties should be in a range that fulfils the target application, for instance, for tapes and labels, the tack should be between 60 and 160 (N/m), the peel strength between 72 and 240 (N/m), and the shear strength should range from 0.1 to 35 h.[66,68] The base case run exceeded all three of the measurement criterion, thereby presenting a fairly strong adhesive. The results are summarized in Figure 3-11 to Figure 3-13 for the acrylated lignin case, Figure 3-14 to Figure 3-16 for the maleated lignin case, and Figure 3-17 to Figure 3-19 for the hot blend with HPH lignin. It should be noted that, due to the addition of NDM in the formulation and low gel content of the

adhesives, all adhesives left trace amounts of residue on the substrate during the peel strength test, which is considered a mild cohesive failure.

In the case of using acrylated lignin, increasing lignin up to 1 phm resulted in significantly increased tack (Figure 3-11) and shear strength (Figure 3-13) compared to the acrylic base case (without lignin). However, peel strength remained mostly unchanged (Figure 3-12). Increasing lignin up to 5 phm led to subsequent decreases in tack and shear strength.

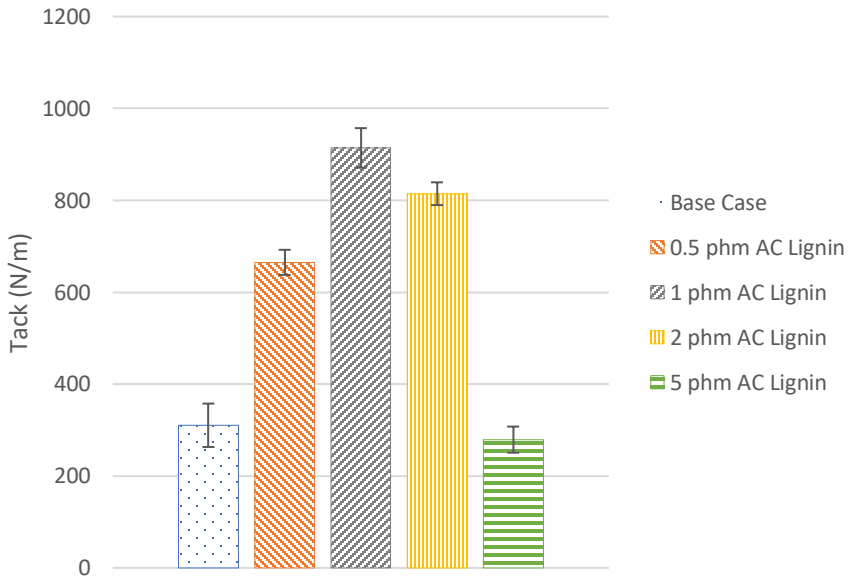

Figure 3-11: Tack for acrylated lignin runs

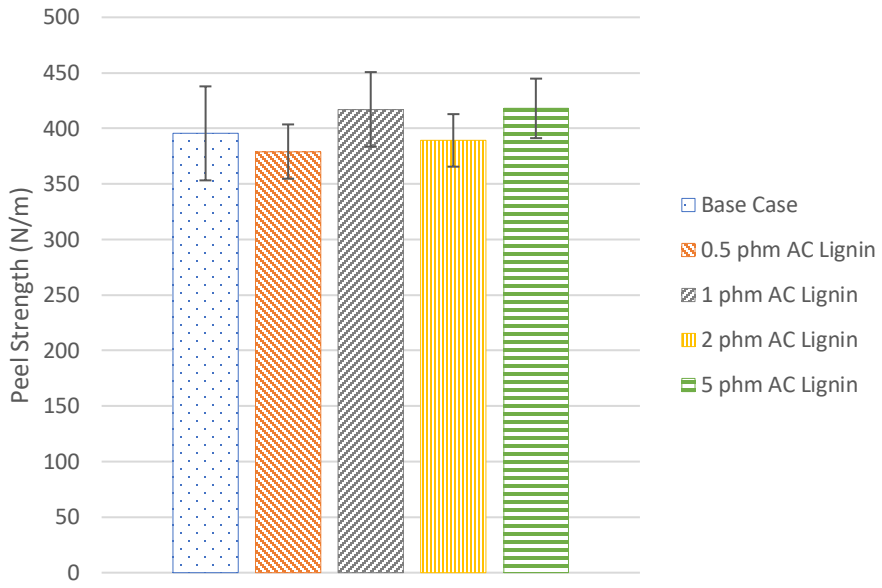

Figure 3-12: Peel strength for acrylated lignin runs

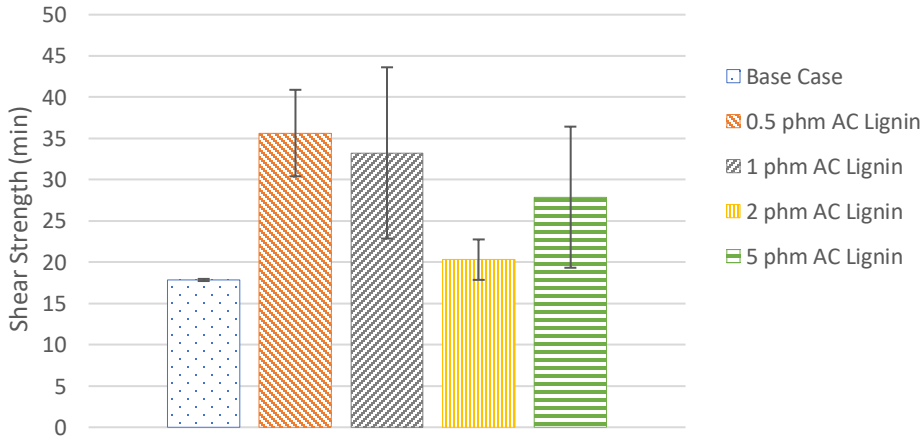

Figure 3-13: Shear strength for acrylated lignin runs

Using one phm maleated lignin increased tack (Figure 3-14), peel strength (Figure 3-15) and shear strength (Figure 3-16) simultaneously in comparison with the base case. However, further increases in lignin content reduced all three properties. These results mimic those using acrylated lignin, but the maximum performance of the maleated lignin latex films was better than that of the acrylated lignin latex films. For both the acrylated and maleated lignin cases, the decrease in

tack beyond a certain lignin content may be due to the partial incorporation of lignin into the polymer matrix with the remaining lignin acting as a glassy filler; this is consistent with the T_g values reported earlier (Table 3-3). Therefore, the increased glassy nature of the polymer leads to a decrease in tack.[69] Finally, the shear strength for both maleated and acrylated lignin correlates very well with the gel content measurements: higher gel contents led to higher cohesive strength and higher shear strength (Figure 3-9). [67]

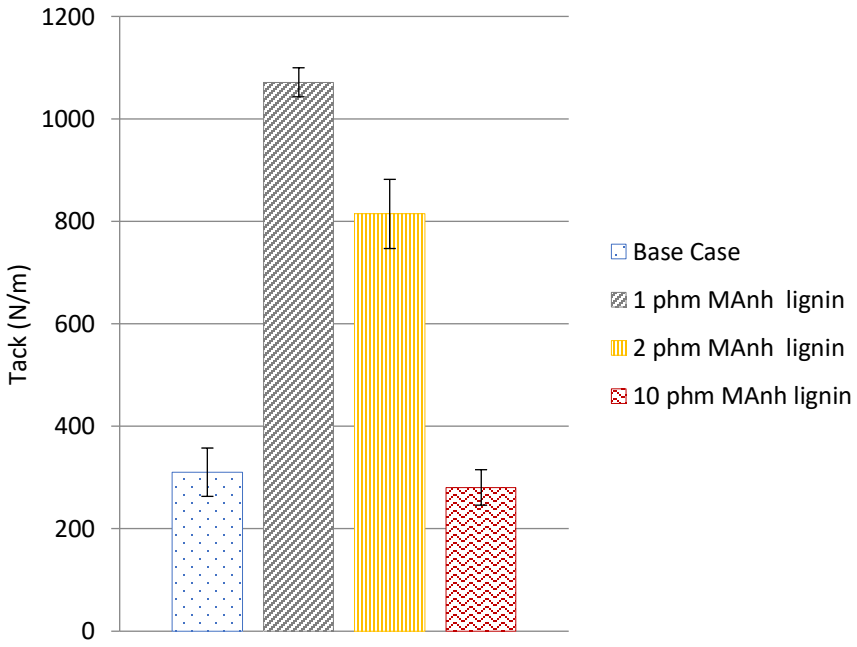

Figure 3-14: Tack for maleated lignin runs

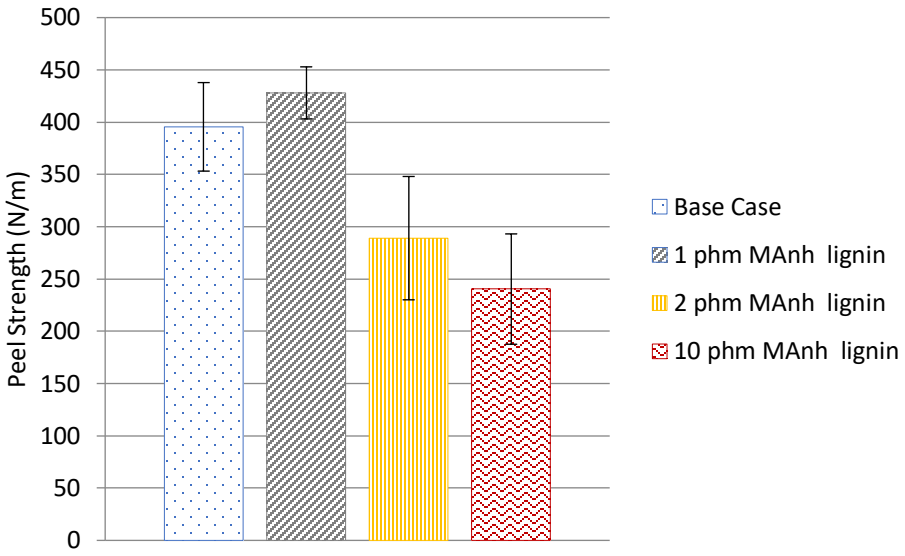

Figure 3-15: Peel strength for maleated lignin runs

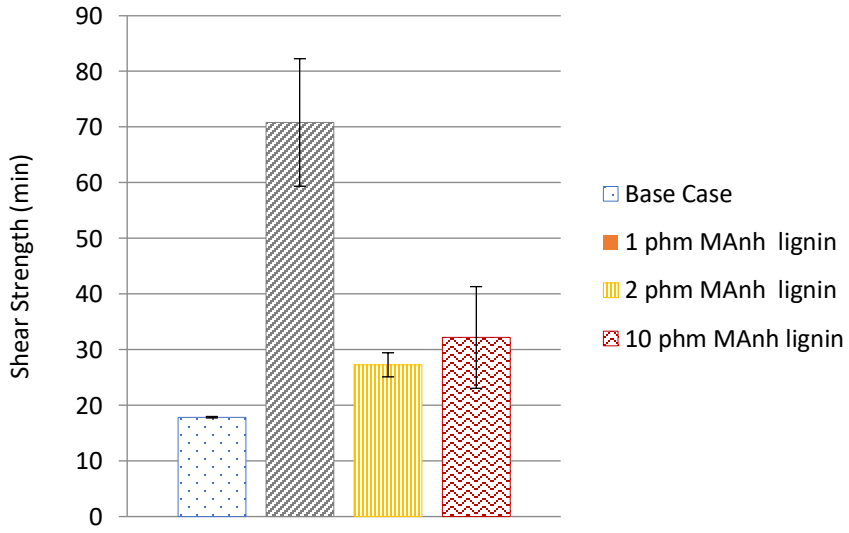

Figure 3-16: Shear strength for maleated lignin runs

While the results above clearly show the positive impact of the addition of modified lignins via in situ polymerizations, the question remains whether the same effect is present in a simple blending case. The adhesive performance of blends of unmodified HPH lignin with the base case latex was measured. Tack results displayed similar trends to the in situ cases, although the blends did not achieve the same level of performance (compare Figure 3-17). This suggests that the functionalization of lignin coupled with the in situ approach enabled a better dispersion of lignin in the latex. As in the in situ polymerization cases, the effect of lignin on peel strength for the

blended latexes was not statistically significant (Figure 3-18). Increasing the HPH lignin concentration led to higher gel contents (Figure 3-9) and as a result, higher shear strength (Figure 3-19). In this case, the blended latex films showed a better performance than their in situ counterparts.

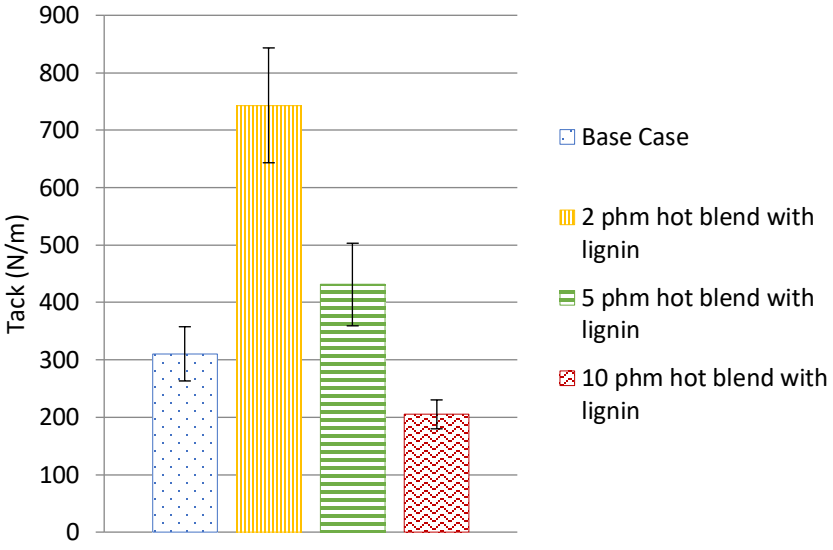

Figure 3-17: Tack for a hot blend with HPH lignin runs

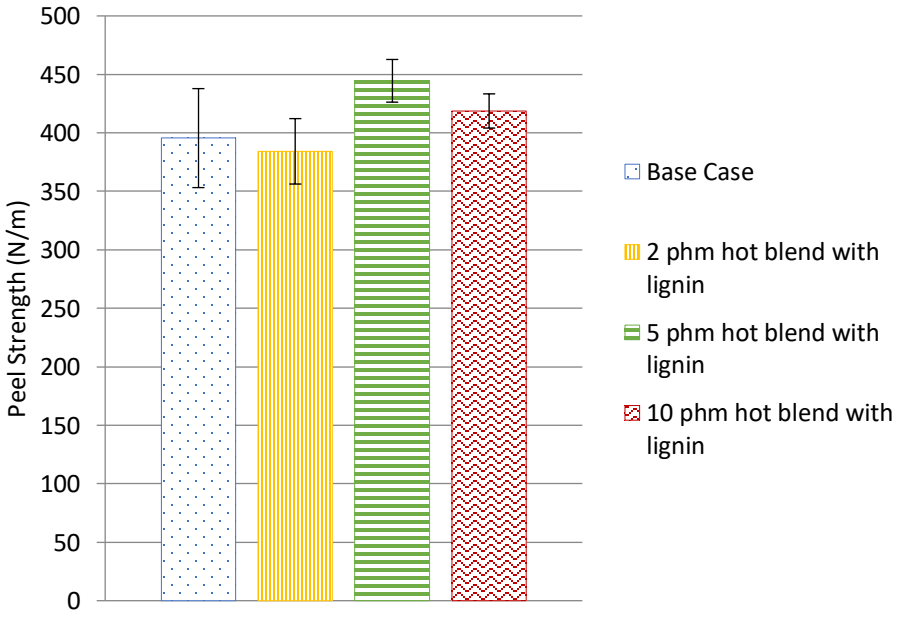

Figure 3-18: Peel strength for a hot blend with HPH lignin runs

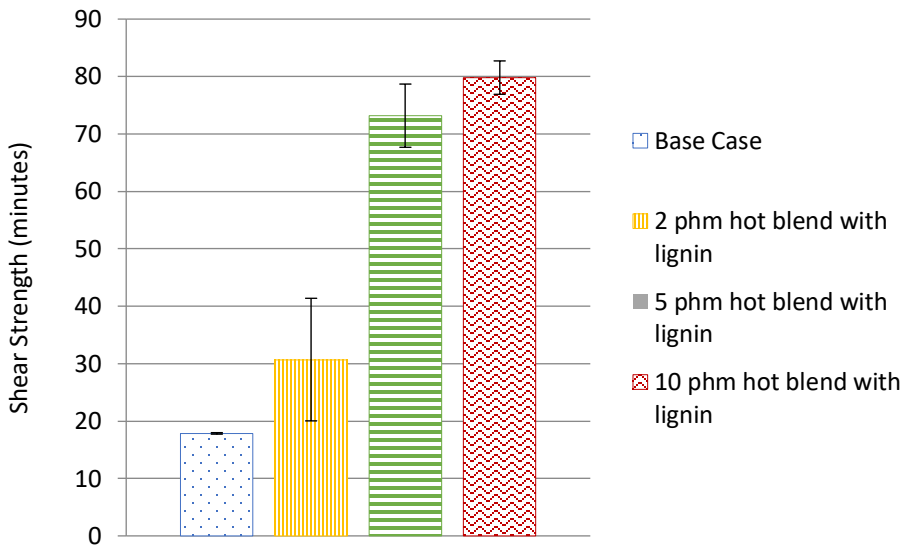

Figure 3-19: Shear for hot blend with HPH lignin runs

Conclusion

To enable the incorporation of lignin in the synthesis of latex-based adhesives, a seeded semi-batch emulsion polymerization approach along with chemical modification of lignin was proposed. The modifications led to the addition of reactive functional groups (vinyl groups) to the lignin, thereby changing its miscibility and reactivity with monomers such as BA and MMA. One approach involved the acrylation of lignin using methacryloyl chloride and another involved maleation using maleic anhydride, which is a low-hazard material. Acetylation of lignin did not lead to the production of stable latexes. The acrylated lignin and maleated lignin were successfully incorporated into latex formulations at concentrations up to 5 and 10 phm, respectively. Both the acrylated and maleated lignins were effective to simultaneously increase tack and shear strength in an acrylic adhesive formulation while maintaining a constant peel strength. The simple blending of the HPH lignin with the acrylic base case formulation led to similar results. The blend case outperformed the in situ cases for shear strength but did not achieve the same levels of tack. Thus, one may argue that lignin modification may not be necessary and that effective adhesive property modification can be achieved via blending.

However, further studies should be undertaken to fully investigate this phenomenon. In any case, a low-cost, renewable material, lignin, can be used as an adhesive property modifier.

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Chapter 4 : Using lignin to modify starch-based adhesive performance

Abstract

Unmodified Kraft lignin was used to create a starch-based adhesive via the Stein-Hall process. Lignin up to 35 wt% was used in several formulations. Lignin was incorporated in both the carrier and slurry portions of the formulations and its effect on adhesive strength, and water resistance was studied. The addition of lignin resulted in a significant increase in adhesive strength when the lignin was added solely to the slurry portion. When lignin was added solely to the carrier portion, adhesive strength decreased. Other formulations where lignin was present in both the carrier and slurry portions showed moderate increases in adhesive strength. Finally, the addition of lignin increased water-resistance of the adhesive bond in the paperboard.

Introduction

Efforts to increase the sustainability of polymer products are numerous.[1,2] One well-known example is the use of starch as an adhesive in paperboard and corrugated cardboard production. [3] These starch-based adhesives are readily available at good quality, low cost, are biodegradable, and are easy to use. They are usually available as a powder and are mixed with water prior to application. Commercially, starches that are used in adhesive production are derived from corn, wheat, potato, rice, and tapioca. [4] Starch is one of the world's most naturally abundant polymers, consisting of glucose repeat units. Starch is made up of two materials, namely amylose and amylopectin (Figure 4-1). Amylopectin is a highly branched macromolecule, while amylose has a linear structure. The ratio of these molecules differs according to the plant source, and the physical properties of the products are greatly influenced by this ratio. Moreover, the most important difference between types of starch is the molecular weight of the amylose portion and

the ratio of amylose to amylopectin. In addition, because of the presence of hydroxyl groups in its structure, starch presents a high affinity toward polar materials such as water. [5,6]

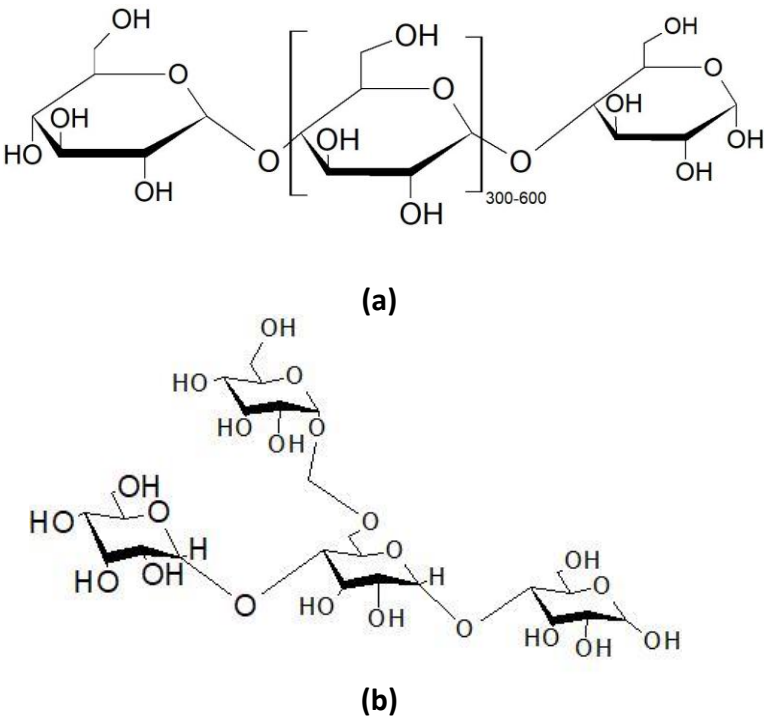

Figure 4-1: Starch structure, (a) amylose and (b) amylopectin

Because of the amylose fraction, suspended starch granules in water don't exhibit any adhesive properties due to their high crystallinity. The granules must be broken down in order to present adhesive properties.[4] Amylopectin is water-soluble, while pure amylose can be dissolved in water at high alkali conditions or by cooking at 150-160 °C under high pressure.[6] When starch is heated (say, at 60-80 °C) in the presence of water, starch granule breakdown occurs through an irreversible process called gelatinization.[7] Starch gelatinization is an endothermic process which leads to the swelling of the starch granules, loss of crystallinity and water absorption.[8] The swollen granules are rich in amylopectin because the linear amylose diffuses out of the granules during this process and forms a continuous gel phase outside of the granules. In fact, amylose plays a restraining role for the swelling of amylopectin.[9] Not all starch granules will gelatinize at

the same temperature. The percentage of amylose in different starches and their gelation temperature are summarized in Table 4-1.[10]

Table 4-1: Amylose content and gelation temperature of different starch types

Starch source	Amylose (wt%)	Gelation temperature (°C)
Corn	20-28	62-72
Wheat	17-34	58-64
Oat	18-29	56-61
Rice	17-29	68-78
Potato	25-31	59-68

The most popular process for starch adhesive production (i.e., breaking down the starch granules or gelatinization) is the Stein-Hall process, which was introduced in the 1930s by J.V Bauer.[11] In this process (Figure 4-2), there are two parts for the adhesive preparation, a "carrier" portion and a "slurry" portion. Briefly, the carrier portion consists of a gelatinized starch solution whereas the slurry portion is an ungelatinized starch solution.

In the carrier portion, part of the starch (usually about 15 -20 wt% of the total starch) is dissolved in water and heated under alkali conditions to be fully gelatinized. Heating starch in the presence of water leads the starch granules to absorb water and swell. The hydrogen bonds between amylose and amylopectin molecules inside the granules will break down and new hydrogen bonds between starch and water molecules are formed. The addition of sodium hydroxide (NaOH) accelerates this process by breaking hydrogen bonds between starch molecules inside the granules. In other words, adding an alkali solution decreases the gelation temperature of the starch. During this process, some of the linear amylose leaches out of the starch granules. Both swelling of the granules and amylose leaching thicken the paste, leading to an increase in viscosity. After a while, the viscosity reaches a plateau which indicates that starch granules are fully swollen to their maximum size. If the swelling process is not stopped at this point and shear force is applied, starch granules will burst. At this stage, it is said that the starch is fully gelatinized

and the starch solution becomes a thick paste.[12] Upon complete gelation of starch, the colour of the starch solution turns from opaque white to translucent. Sodium tetraborate decahydrate (aka Borax) is usually added in trace amounts after complete gelation of the starch, which leads to the cross-linking of hydroxyl groups between the starch molecules, thus increasing viscosity and tackiness. This thick paste is referred to as the carrier portion of the starch adhesive.[13] The carrier portion is mostly responsible for achieving the required viscosity of the adhesive and, in most processes, is made in a separate tank and is referred to as the primary mixture.[14]

The slurry portion is prepared by mixing the remaining part of the starch in the formulation (usually, about 80-85 wt% of the total starch) with water. At the end of the process, the slurry portion is added to the carrier portion. The viscous carrier portion prevents settling of the ungelatinized starch granules. It should be noted that the solid content of starch adhesives is usually between 20-30 wt%.

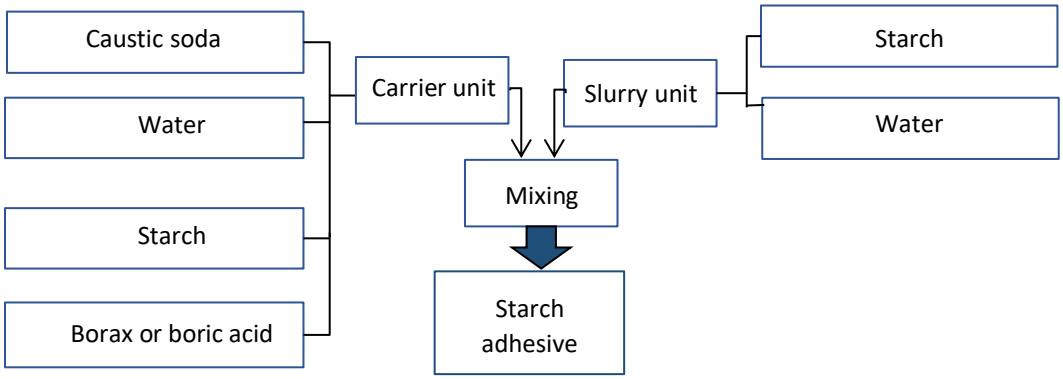

Figure 4-2: Stein-Hall process

In the corrugated cardboard production process, the starch adhesive is applied at the vertices of the fluted cardboard (Figure 4-3). Upon contact with a hot press at 60-70°C, the ungelatinized portion of the starch will quickly gelatinize and produce instant tack. The Borax added to the carrier portion is responsible for the formation of the "green bond". In this context, "green" refers to a "new" hydrogen bond formed between the cellulose molecules in the paperboard and in the adhesive (composed of starch and Borax). The green bond is responsible for holding the components of corrugated boards together prior to final heat curing.[4,15]

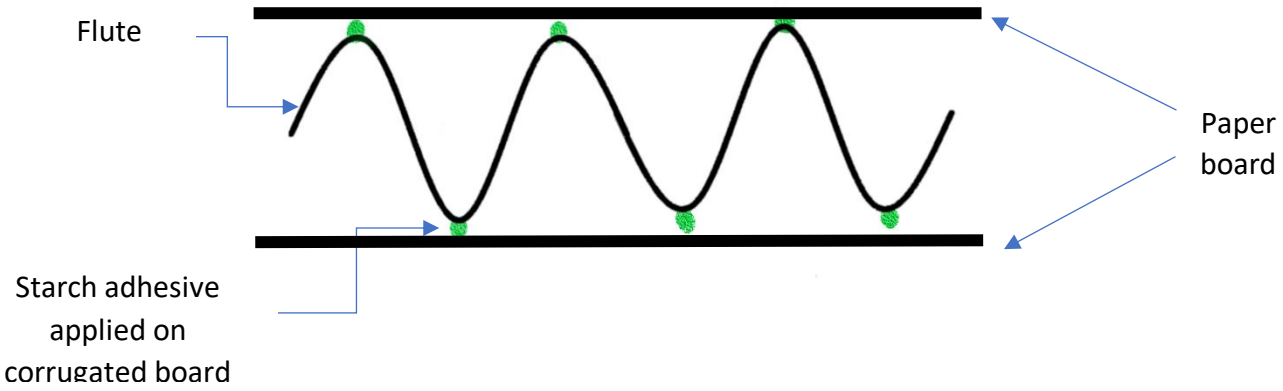

Figure 4-3: Application of starch adhesive in corrugated cardboard (cross-section view)

Selecting a proper adhesive is vital to ensure that packaging will fulfill its performance requirements. A number of different starch adhesive modifications have been proposed, which involve the addition of different compounds to the formulation, thereby leading to improved adhesive performance. For example, a variety of plasticizers (e.g., glycerol and glucose) have been used to control the brittleness of the adhesive. In addition, these plasticizers act as a hygroscopic agent, which decreases the drying rate of the film. [16] Calcium chloride, urea and sodium nitrate are commonly used to decrease the viscosity. [17] Mineral fillers such as calcium carbonate and titanium dioxide are often used to control the penetration of adhesive into porous material.[6] Formaldehyde, copper sulfate and zinc sulfate are common preservatives used in starch-based adhesives to prevent microbial activity.[6]

One important goal in the starch-based adhesive modification is to increase water-resistance of the adhesive because of starch's affinity toward water absorption. Because of the lower water solubility of amylose, one suggestion is to use starch with a higher amylose content (at least 35% amylose) in the carrier portion because it will improve rheological and film-forming properties and, to some extent, increase water-resistance of the adhesive. Nonetheless, high amylose content starch-based adhesives do not present sufficient water resistance, and thus, additives are still required. [18] Another method to increase water resistance involves the preparation of

acidic starch-based adhesives where urea formaldehyde or melamine formaldehyde, along with an acidic catalyst, are added to cross-link the starch and provide water-resistant bonds. Other cross-linking agents such as diacetone acrylamide-formaldehyde, acetoacetamide formaldehyde and acetone-formaldehyde condensates have been used. However, one should bear in mind that usage of formaldehyde is considered unsafe, and the presence of free formaldehyde in commercial products is discouraged.[19] Also, the amount of Borax in a starch formulation should be lowered when urea or melamine-formaldehyde are used because using one or both resins in the presence of Borax will increase adhesive viscosity. Such increases in viscosity are difficult to control; besides, reducing the amount of Borax leads to a decrease in the tackiness of the adhesive.[18]

In yet another method, different types of fibres were used to enhance water resistance, dry strength, viscosity and tackiness.[20] It was shown that suspending fibre in the carrier and/or slurry portion, or even addition at the end of the process was effective. The effect of the fibre was typically only significant at levels beyond 25 wt% of the total adhesive mass. The addition of fibre lowered the gel point by surrounding the starch granules, which helped maintain the moisture around the granules. This phenomenon improved adhesion and prevented moisture from being diffused into the fiberboard. The addition of fibre, along with the addition of thermosetting materials, enhanced water resistance because the moisture held by the fibres around the granules led to resin cross-linking, thereby forming a moisture barrier. The presence of fibre also improved adhesion because of fibre to fibre entanglement between the adhesive and the fiberboard. The hydrophobicity of the fibre also helped repel moisture, thereby increasing the drying rate and water resistance.[15,20]

In other achievements, hemicellulose was added to a starch adhesive formulation. [21]Hemicellulose is completely compatible with starch and could be extracted from corn fibre under alkaline conditions. Thus, in a corrugating process, there would be no need for a separate production process because, as noted earlier, the carrier portion is prepared under alkaline conditions. Despite the structural differences between hemicellulose, starch and cellulose, the hydroxyl functional groups common to all three materials allows for bond formation within the adhesive. Hemicellulose reacts positively with Borax since it forms a Borax-oxygen bridge

structure, which is common in poly-hydroxyl groups and thus enhances tackiness. As a result of cross-linking hemicellulose with starch, the availability of hydroxyl groups to form hydrogen bonds with water is reduced. Therefore, more hydrophobic and aliphatic moieties are formed.[15,21]

As mentioned, starch-based adhesives are attractive due to their relatively low cost, versatility and biodegradability, but one of their main disadvantages is that they have poor water resistance. Blending starch with more hydrophobic biopolymers possibly could improve the water-resistance of the adhesive bond. The second most abundant biopolymer after cellulose is lignin, which is an important renewable source of aromatic materials. [22] Annually, about 40-50 million metric tons of lignin are produced worldwide, largely by the pulp and paper industry. [22] However, most lignin is considered as non-commercialized waste or is burned due to its caloric value to generate part of the energy required for the pulp mills.[22] Not surprisingly, lignin is available at a relatively low price (e.g., Kraft lignin is about 260-500 USD/MT).[23] The presence of phenolic groups in lignin provide a potential for hydrophobic properties, and at the same time, the presence of hydroxyl groups in lignin suggests its compatibility with starch.[24]

Recently, the blending of lignin with other renewable materials (e.g., proteins, starch) has attracted attention because of its availability, low cost, good mechanical properties and biodegradability.[24–28] In these cases, it was shown that the addition of lignin decreased water uptake and increased the composite material strength. [24–27] In addition, lignin has exhibited antioxidant properties due to the presence of phenolic hydroxyl groups, which scavenge free radicals.[29] Research on lignin-starch blends has been focused on producing films and foams, which suggests that lignin could be used in starch-based adhesives. [24–27] In this paper, we investigate the use of lignin in starch-based adhesives. The objective was to determine the impact of lignin on adhesion and water resistance in paperboard applications.

Experimental section

Materials

Unmodified regular corn starch (27% amylose) and sodium tetraborate decahydrate (> 99%, aka Borax) were acquired from Sigma Aldrich. Distilled deionized water (DDI) was used in order to prepare both carrier and slurry portions. A 50 wt% sodium hydroxide (NaOH pellets from Fisher Scientific) solution was used to adjust the pH. Kraft lignin (light brown in colour, hydrophobic with inorganic content <1 wt %, pH ≈ 3.3 and dry solids about 50 wt%) was supplied by Noram Engineering and Constructors Ltd.(Hinton, Alberta, Canada) The lignin is also known by the trade name “Amalin LPH”.

Adhesive Preparation

The carrier portion was prepared by adding 38 g of corn starch to 260 g of DDI water at room temperature. The temperature was increased via stirring hot plate up to 40–50 °C (gelation temperature of starch in alkali). 11 g of 50 wt% aqueous sodium hydroxide solution was added to the starch solution, and the mixture underwent vigorous mixing (4000 rpm) until the starch was fully gelatinized, as observed visually when the solution became a translucent gel. Separately, 2.8 g Borax was dissolved in 80 g of water at 70 °C. The Borax solution was added to the carrier portion after complete gelatinization of the carrier portion, followed by mixing for 3 min at 5000 rpm.

Next, the slurry portion was prepared in situ, rather than as a separate solution, by adding 380 g cold water to the carrier portion. This resulted in a temperature decrease to 35-40 °C and a decrease in viscosity. The diluted solution was mixed for 1 min at 1600 rpm using a Silverson homogenizer (model L5M-A). Next, 200 g of dry starch was added in one shot to facilitate dispersion into the carrier portion. [14] The whole mixture was mixed at 10000 rpm for 30 s followed by a 1 min pause; this step was repeated for a total of 4 mixing times. The final solids content was 24 wt%.

Several batches of starch adhesive were prepared wherein up to 35 wt% of starch was substituted with lignin added either in the carrier portion or slurry portion or both (Table 4-2). Sample designations, as shown in the first column of Table 4-2, consist of a first number referring to the weight percentage of lignin used in the carrier portion based on the total starch loading in the formulation. The second number refers to the weight percentage of lignin used in the slurry portion based on the amount of starch only in the slurry portion.

Table 4-2: Batch formulations

Adhesive no.	Percentage of starch substituted with lignin (wt%)		*Adhesive no.*	Percentage of starch substituted with lignin (wt%)	
	Carrier portion	Slurry portion		Carrier portion	Slurry portion
0-0	0	0	5-20	5	20
0-10	0	10	5-30	5	30
0-20	0	20	10-0	10	0
0-30	0	30	10-10	10	10
5-0	5	0	10-20	10	20
5-10	5	10	10-30	10	30

Characterization

Viscosity: The viscosity of the starch-based adhesive was measured using a Stein-Hall viscosity cup at 30 °C immediately after adhesive preparation

Hydrophobicity: The hydrophobicity of the starch adhesive was determined via water contact angle measurements. A #20 Meyer rod was used to cast films of 12.5” × 12.5” from starch-based adhesive onto Mylar sheets. The films were dried at 25°C at 50% relative humidity for 24 h. Samples of 4” × 4” were cut, and three to five locations were tested on each sample. A VCA

optima instrument (AST products Inc.) was used to measure the water contact angle. A 2 µl water droplet was slowly dropped onto the film, and the contact angle was measured by VCA OPtimaXE software within 10 s. The average of each measurement is reported.

Glued joint strength: The strength of the glued joints was measured using an adaption of the TAPPI T-837 test.[30] The adaptation consisted of using the paper board (as opposed to corrugated board) in between two hinged plates (Figure 4-4). Paper boards were cut to 1.5" × 1.7" and attached to hinged plates with double-sided tape. The starch adhesive was applied to one surface of the paper board and sandwiched in a hot press under 500 psig of pressure at 60 °C. Each specimen was held in the hot press for 20 min to ensure that all the starch was fully gelatinized. Each specimen was stored at 25 °C and 50% relative humidity for 24 h. After drying, each hinge half was secured in Instron grips, and the force required to separate the boards was recorded using the Instron tester.

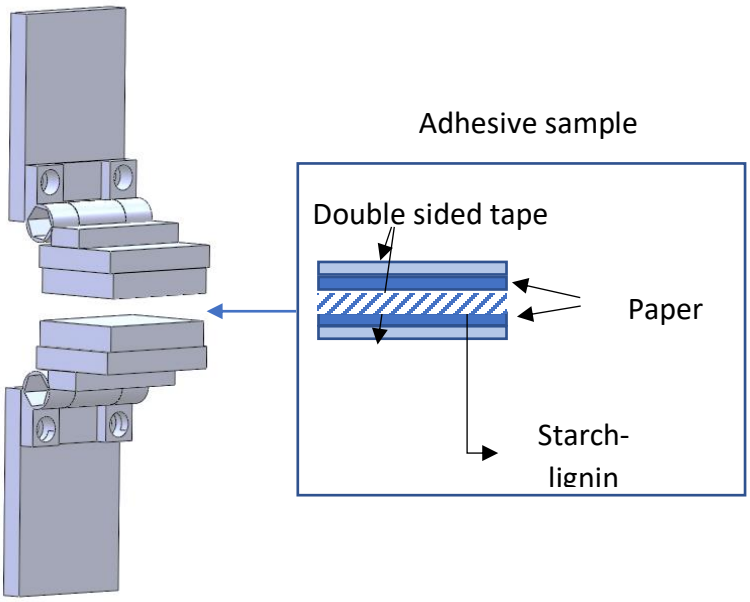

Figure 4-4: Hinges and an adhesive sample used for assessment of the glued joints with starch-based adhesive

Results and Discussion

The viscosity of all the adhesives was measured at 30 °C immediately after completing the adhesive preparation (Table 4-3). With the addition of lignin to the carrier portion, the adhesive viscosity decreased. The addition of lignin to the slurry portion had no effect on viscosity. This suggests that the incorporation of lignin in the starch matrix largely happened in the carrier portion. The low molecular weight phenolic groups and amphiphilic fatty acids in lignin may have had a plasticizing effect by interacting with the starch via hydrogen bonding. Plasticizers are known to interact with polymers by replacing interactions between polymer molecules, thereby improving polymer chain mobility and flexibility by reducing their intermolecular forces. Thus, a reduction in the Stein-Hall viscosity was observed (Table 4-3).[24,25]

Table 4-3: Starch adhesive final viscosities

Adhesive no.	Viscosity (Stein Hall seconds)	Adhesive no.	Viscosity (Stein Hall seconds)
0-0	90	5-20	20
0-10	90	5-30	20
0-20	90	10-0	15
0-30	90	10-10	15
5-0	20	10-20	15
5-10	17	10-30	15

Increasing the lignin content increased the hydrophobicity of the adhesive film according to water contact angle measurements (Table 4-4). Samples with less than 20 wt% total lignin were not measurable because the water absorbed instantly upon contact with the film surface. These results are consistent with the fact that we are using Kraft lignin, which is insoluble in water at acidic or neutral conditions because of its lack of hydrophilic chains.[3132] Contribution to film hydrophobicity is also due to lignin's hydrophobic phenolic groups.[27] The above is supported by Baumberger et al., who showed that the addition of lignin to a starch matrix via blending yielded

more hydrophobic starch films and reduced the water absorption of starch-lignin films.[33] In their case, the addition of lignin to starch increased the water contact angle from 30° to 80°. They also noted that the hydrophobicity of lignin was detectable if no plasticizer was used in the formulation. If plasticizers such as glycerol are present in the formulation, it could reduce or cancel the hydrophobicity effect of lignin. [34]

Table 4-4: Water contact angle of starch-lignin adhesive films

Adhesive no.	Water contact angle
0-20	14°
0-30	21°
5-20	22°
5-30	24°
10-20	26°
10-30	33°

Because Borax was used in the formulation, there was a strong possibility of cross-link formation between the starch and lignin via their hydroxyl groups. The formation of hydrogen bonds between both starch and lignin is highly likely due to the presence of hydroxyl groups in both materials. Figure 4-5 shows possible cross-linking and hydrogen bonding pathways between amylopectin and lignin molecules. It should be noted that the compatibility of lignin with amylopectin is higher than that with amylose.[35]

The greater hydrophobicity of the starch-lignin films, as demonstrated by the higher water contact angles, coupled with the strong likelihood of cross-link formation, implies that the addition of lignin increases the water-resistance of the films. This is supported by Baumberger et al. who showed that water solubility of a blend of starch/Kraft lignin was reduced, leading to increased starch-lignin bonds and increased adhesive film water resistance.[26]

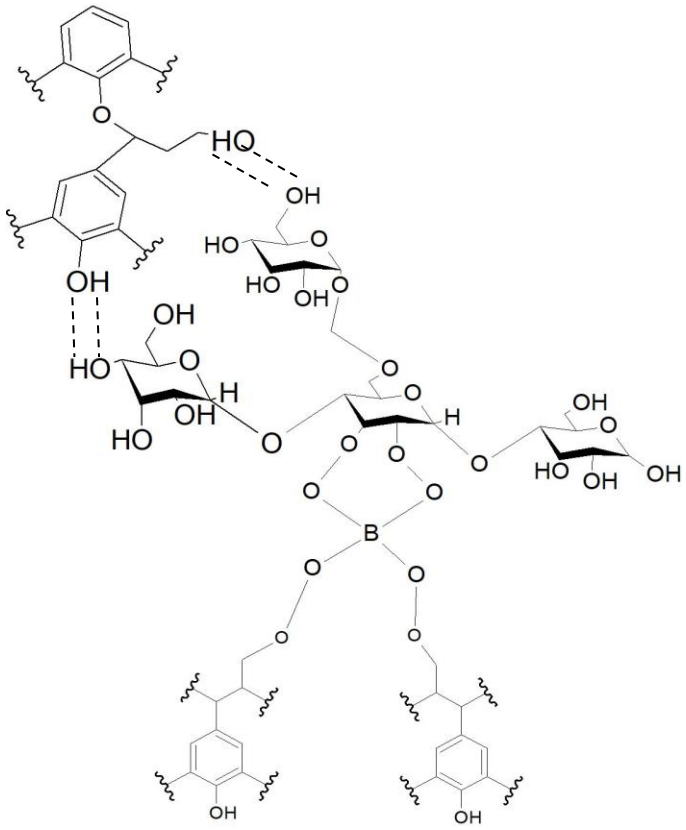

Figure 4-5: Possible cross-linking and hydrogen bonding between starch and lignin molecules

The strength of the glued joints, as measured using an Instron tester, is shown in Figure 4-6. For the cases where lignin was added solely to the slurry portion (samples 0-10, 0-20 and 0-30), the glued joint strength exceeded the adhesive performance of the double-sided tape used to attach the samples to the hinges. In comparison, the starch adhesive without lignin (sample 0-0) showed much poorer adhesive performance. On the other hand, with the exception of sample 5-30, the addition of lignin to the carrier portion resulted in a decrease in glued joint strength. It appears that the addition of lignin to the slurry portion in sample 5-30, compensated for the negative effect of having lignin in the carrier portion. For the cases where 10 wt% lignin was used in the carrier portion (sample 10-30), the lignin in the slurry portion was unable to compensate for the

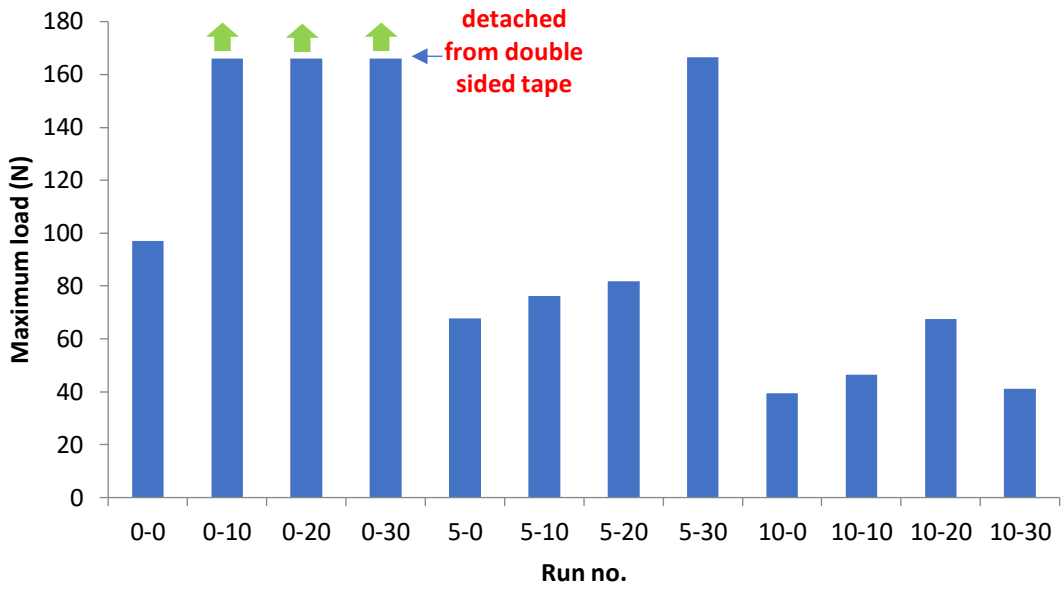

Figure 4-6: Strength of glued joints in starch-lignin adhesives

negative effect. It should be noted that the film produced from sample 10-30 was very brittle, similar to other reports.[25]

In a number of studies involving starch-lignin blends, as opposed to the use of the Stein-Hall process, some supporting conclusions are noted. With a low lignin content (say, <20 wt%), there is evidence for an increase in the tensile strength of starch-lignin blended films.[36] However, when elevated amounts of lignin were used (>20 wt%), the film structure was more compact due to high intermolecular hydrogen bonding leading to a decrease in the tensile strength of the starch-lignin films.[3637] Increases in elongation at break also were observed.[252627] The latter work suggests a plasticization effect due to the presence of lignin in the starch matrix. Spiridon et al. used SEM imaging to demonstrate that lignin particles act as a plasticizer in the starch matrix.[36] They surmised that because of their more uniform shape, the lignin particles are more likely to be covered by the softer thermoplastic material, starch.

Overall, one can therefore conclude that lignin acts as a reinforcing filler that impacts both mechanical and physical properties in starch-based adhesives but only when used in the slurry portion. This is consistent with the role of lignin as a plasticizer and cross-link participant.

Conclusion

The incorporation of an abundant natural polymer, lignin, up to 35 wt% in a starch-based adhesive has been investigated. It was shown that adding lignin improves strength and water resistance of starch-based adhesive. A common issue plaguing starch-based adhesives is their lack of water resistance due to the high affinity of starch toward the water. This means that in many cases, these adhesives are restricted to a narrower range of packaging applications. In this work, it was shown that the addition of lignin to the starch-based adhesive formulation increases the water-resistance of the adhesive.

Adding lignin to the slurry portion in the Stein-Hall process improved the mechanical properties of the glue bond. Lignin was miscible with the starch adhesive, and at low amounts (5 wt% based on the amount of starch), it exhibited a plasticization effect on the starch matrix. However, the incorporation of lignin in the carrier portion and the use of higher concentrations of lignin made the adhesive brittle and lowered its adhesive strength in a cardboard application.

This work illustrates that rather than burning lignin for its caloric value, it can be used as a high-value additive in starch-based adhesives for paperboard products. Extension to corrugated board applications is obvious.

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Chapter 5 : General discussion, conclusion and recommendations

In this project, we sought to make lignin a value-added product and find a suitable application for it, rather than burning this precious pulp and paper byproduct. We hypothesized that lignin could be added to an adhesive polymer formulation and improve adhesive performance properties. It is believed that lignin could provide a green solution to the adhesive property problem wherein tack and peel strength often act in opposition to shear strength. Further, we hypothesized that substituting the amount of starch with lignin in a starch-based adhesive, could not only lead to a better application of lignin but also it may improve the classic problem high affinity towards water and poor performance under humid conditions for starch-based adhesives.

In the first approach, lignin had to be modified in order to improve its miscibility with the reaction medium and to overcome the radical scavenging properties of lignin. In this regard, lignin was esterified via three pathways: acetylation, acrylation and maleation.

The acetylation process made lignin more miscible with the monomer mixture (BA and MMA), but it did not allow lignin to be incorporated into the polymer matrix. The acrylation process seemed promising in this regard and produced valuable results regarding the possibility of incorporation of lignin into the polymer matrix and the improvement of adhesive properties. However, in this process the involvement of solvent and methacryloyl chloride, which are toxic materials, made this process less favourable to use. On the other hand, the maleation process using maleic anhydride seems a more sustainable process. The incorporation of maleated lignin even at low concentrations was evident through TEM imaging, and it was seen that using high concentrations of maleated lignin (10 phm) led to a core-shell morphology (mainly lignin in the core and acrylic polymer in the shell) of the particles (Figure 5-1). The involvement of less hazardous materials and non-severe reaction conditions makes this process more desirable for lignin modification. Moreover, using maleated lignin gave us better results in terms of adhesive

properties. In Figure 5-2Figure 5-4 adhesive properties of latexes using 1 phm of different modified lignin and latex produced from a hot blend technique (using 2 phm lignin) are compared.

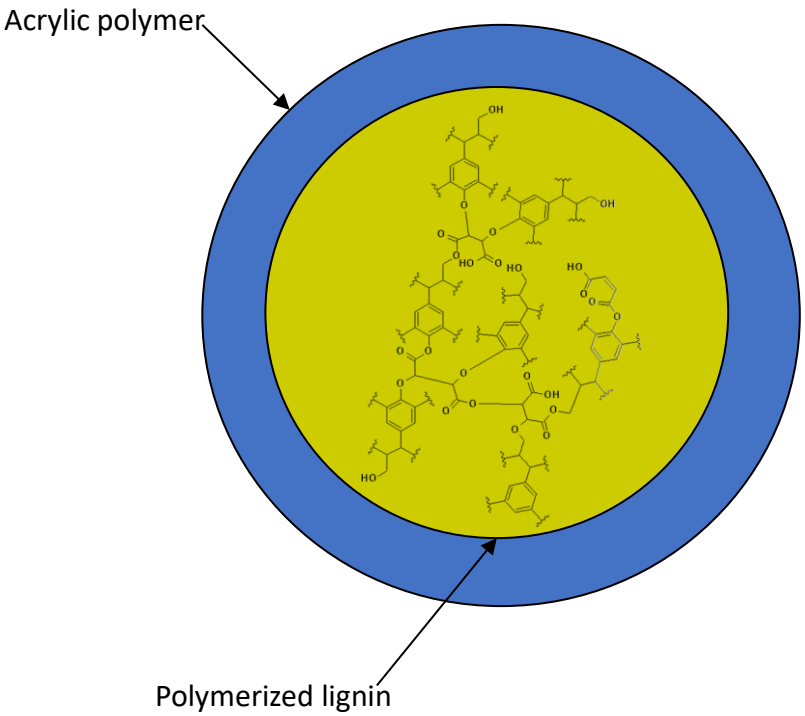

Figure 5-1: Possible core-shell structure scheme

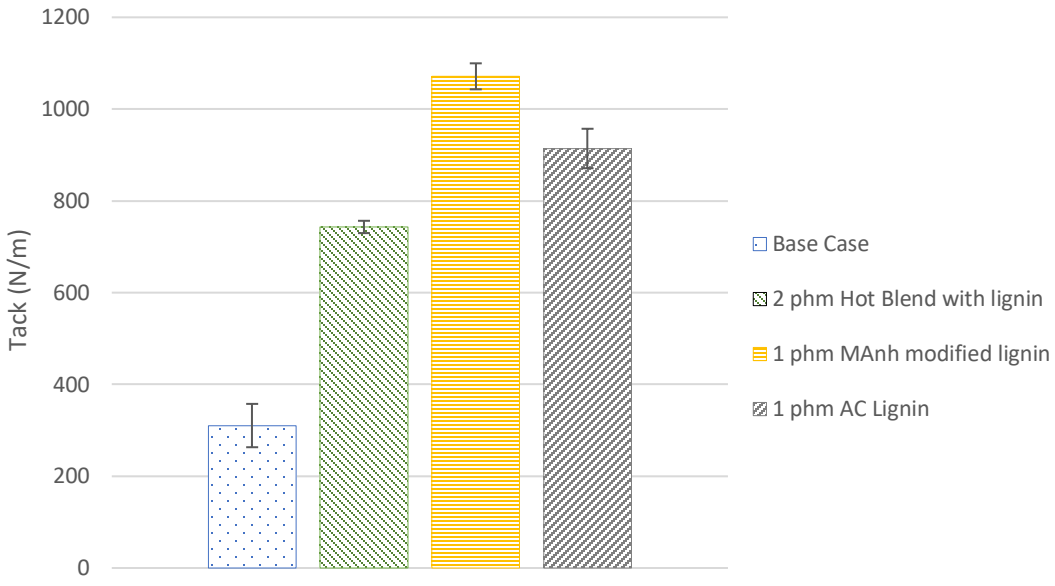

Figure 5-2: Tack for various modified lignin runs

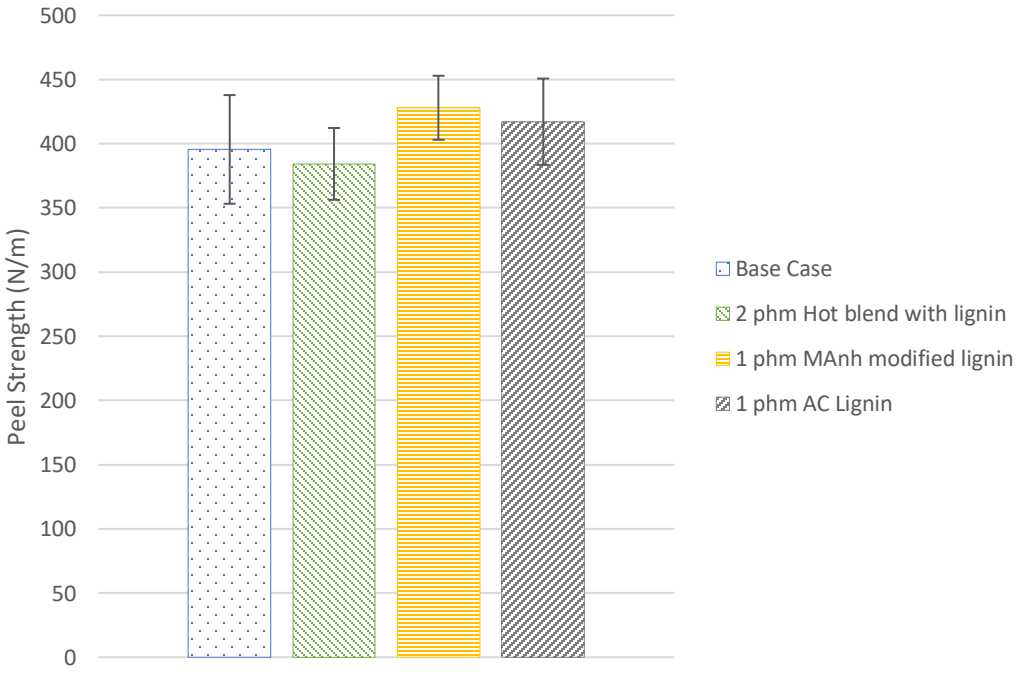

Figure 5-3: Peel strength for various modified lignin runs

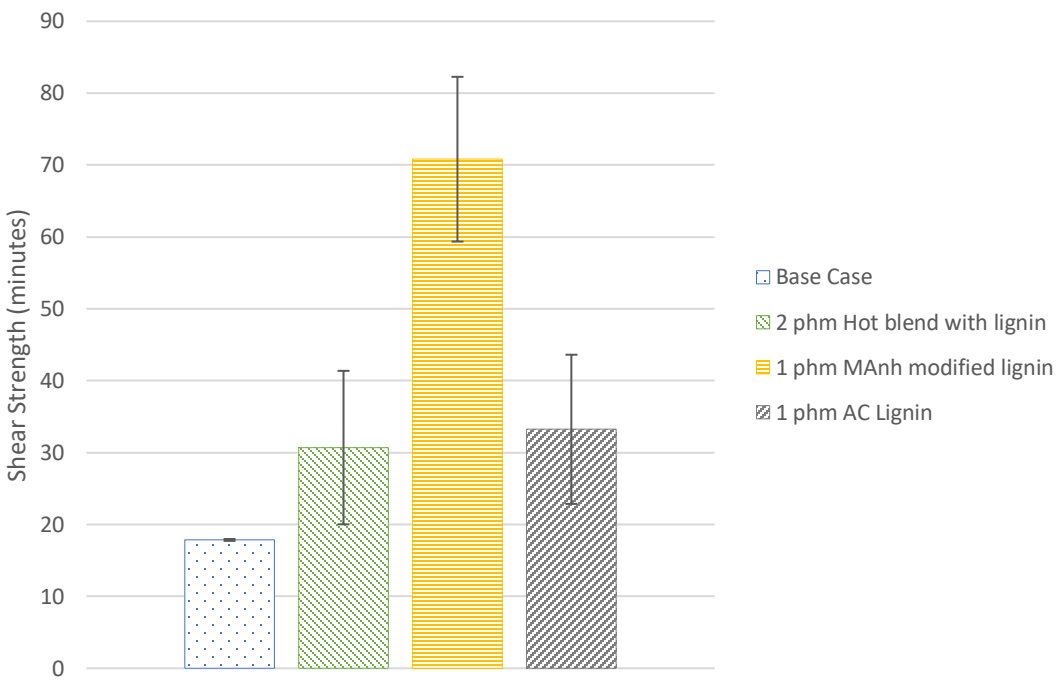

Figure 5-4: Shear strength for various modified lignin runs

Both the acrylated and maleated lignins were effective in simultaneously increasing tack and shear strength in an acrylic adhesive formulation while maintaining a constant peel strength. The simple blending of the HPH lignin with the acrylic base case formulation led to similar results. However, up to 1 phm maleated lignin, outperformed all other approaches.

Using lignin in an in-situ polymerization up to 2 phm resulted in better adhesive performance compared to the pure acrylic base case, but it is notable that using the unmodified HPH lignin as a blend also significantly improved tack and shear strength.

It can be argued that polymers themselves are not toxic, but the toxicity arises in large part due to the many additives that are used in their synthesis to tune their properties according to their final application. Lignin may act as a significant stepping stone towards more sustainable polymer production. This would include eliminating a toxic additive while providing even better performance. Therefore, it could be concluded that lignin is a “green” solution to a problem often observed in emulsion-based PSAs. However, a cost-benefit analysis of this approach should be performed to ensure that the addition of lignin is a promising replacement of petroleum-based additives.

In this thesis, the groundwork has been laid for the incorporation of lignin in PSAs as an adhesive property modifier. Our findings lead to a number of interesting possibilities for future work:

1. Lignin possesses both hydrophilic and hydrophobic functional groups in its structure. Therefore, the effect of varying monomer hydrophobicity on the miscibility of the modified lignin and incorporation of lignin in the polymer matrix should be investigated.

2. There are various types of lignin modifications. Future work could be done to improve the compatibility of lignin with the polymer matrix via etherification reactions or by oxidation and reduction reactions.

3. In this thesis, we focused on PSA applications. Of course, one should not be restricted to these low T_g applications, and the effect of lignin on other polymers with higher T_g (e.g., coatings) should also be investigated.

4. Towards the fully sustainable production of polymers, the use of lignin as a modifier with bio-based and renewable monomers could be investigated further.

5. In this project, there was a constraint in terms of concentration of lignin that could be added to the formulation due to its heterogeneous structure and its large particle size. Usually, in order to overcome this issue, lignin is depolymerized under severe conditions (high temperature and pressure). However, one could consider finding a new sustainable pathway for the depolymerization of lignin or breaking down its structure to some extent.

6. A life-cycle analysis should be performed on the entire PSA production. The question is how lignin might influence the degradability and sustainability of the adhesive.

In a second approach, starch was substituted with lignin up to 35 wt% in a starch-based adhesive. Lignin has a relatively low cost, and the presence of phenol groups in its structure leads to hydrophobic properties. At the same time, the presence of hydroxyl groups in its structure

suggests its compatibility with starch and gives it the potential to cross-link with starch. The incorporation of lignin in a starch-based adhesive regardless of its addition to the carrier or slurry phase increased the hydrophobicity of the adhesive, which indicates the improved resistance of this adhesive against humid conditions. Our investigation of the influence of lignin on the strength of starch/lignin adhesives showed that the addition of lignin to the slurry portion in the Stein-Hall process improved the mechanical properties of the glue bond. Lignin was miscible with the starch adhesive, and at low amounts (5 wt% based on the amount of starch) it exhibited a plasticization effect on the starch matrix. However, the incorporation of lignin in the carrier portion and the use of higher lignin concentrations made the adhesive brittle due to its high T_g and lowered its adhesive strength in a cardboard application.

This work illustrates that rather than burning lignin, it can be used as a high-value additive in starch-based adhesives for paperboard products. Extension to corrugated board applications is evident. The use of lignin for this purpose is evidently better than burning or disposing of it.

Our findings in these criteria lead to several interesting possibilities for future work:

1. In this thesis, due to some restrictions, a modified measurement method was used to assess the strength of the glued joints for starch-based adhesives. However, in industry, the pin method[1] is used to measure the strength of starch-based adhesives in corrugated boards. It would be useful to perform measurements according to the pin method and compare the results of the two methods.

2. Proton nuclear magnetic resonance (H-NMR) spectroscopy may help to gain a better understanding regarding lignin-starch interactions. In this project, due to the presence of Borax in the formulation, cross-linking between starch and the lignin matrix was possible, and it helped increase the water-resistance of the glue. However, by performing H-NMR spectroscopy, this issue could be further investigated, and the desired amount of cross-linking could be achieved by changing the reaction conditions.

3. The formulation that was used in this project did not contain any additives regarding the improvement of the adhesion of starch-based adhesives. The addition of lignin in the presence of different additives could be further investigated.

4. As noted earlier, the ratio of amylose and amylopectin varies with starch types. Hence, the miscibility of different lignin concentrations with the matrix could be influenced by starch source, and the adhesive properties may differ. Thus, different types of starch should be investigated.

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Appendix A : Additional figures

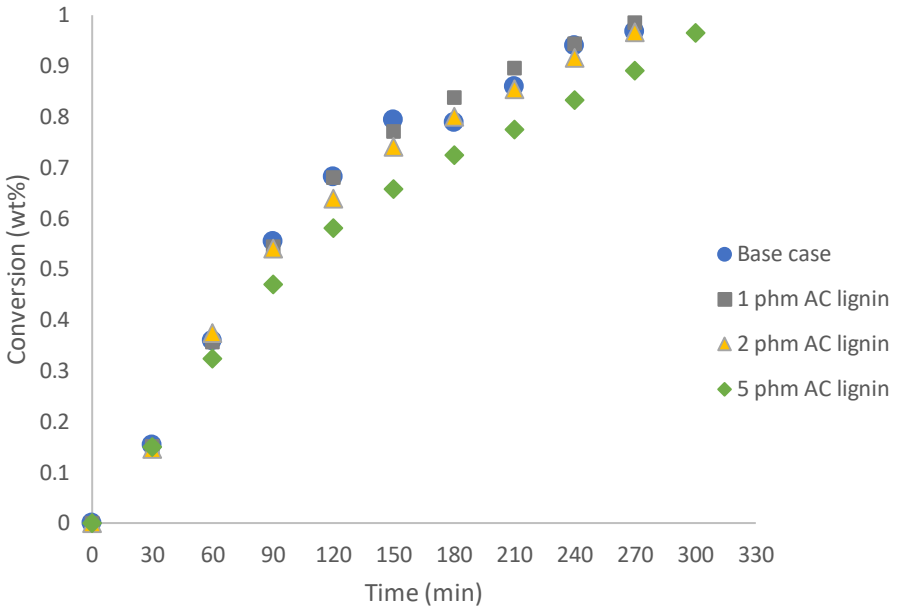

Figure A-1: Conversion vs. time for acrylated lignin runs

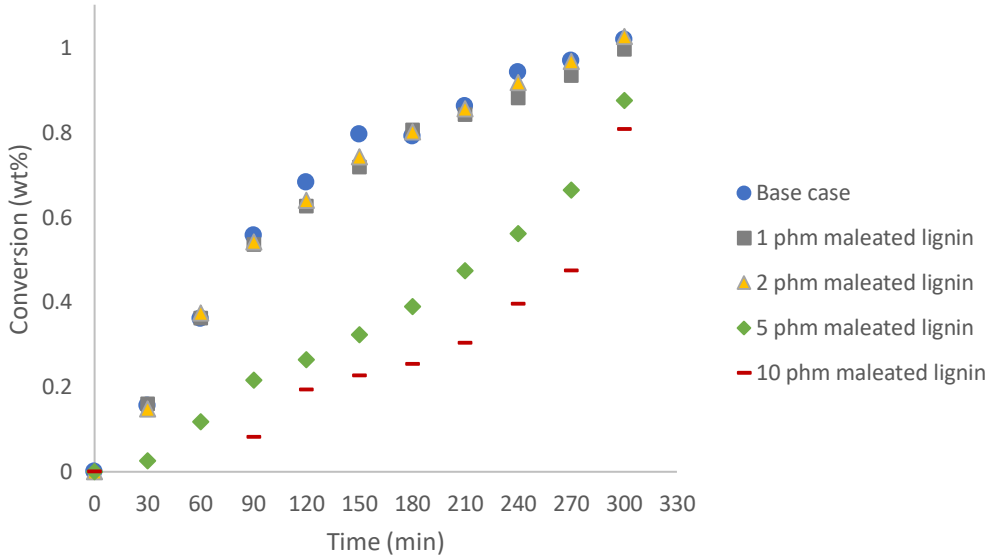

Figure A-2: Conversion vs. time for maleated lignin runs

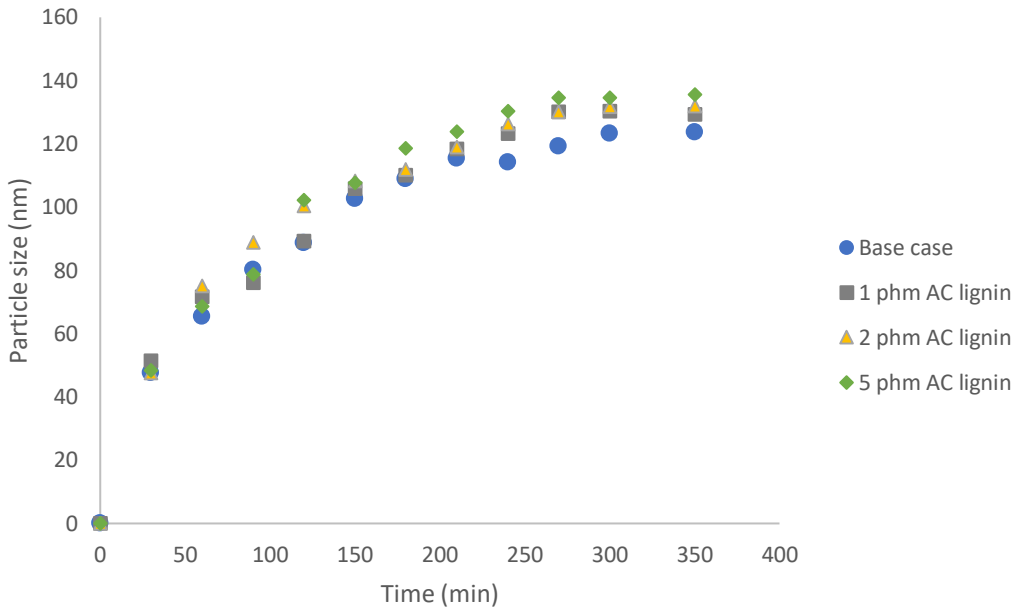

Figure A-3: Particle size growth during reaction time for runs using acrylated lignin

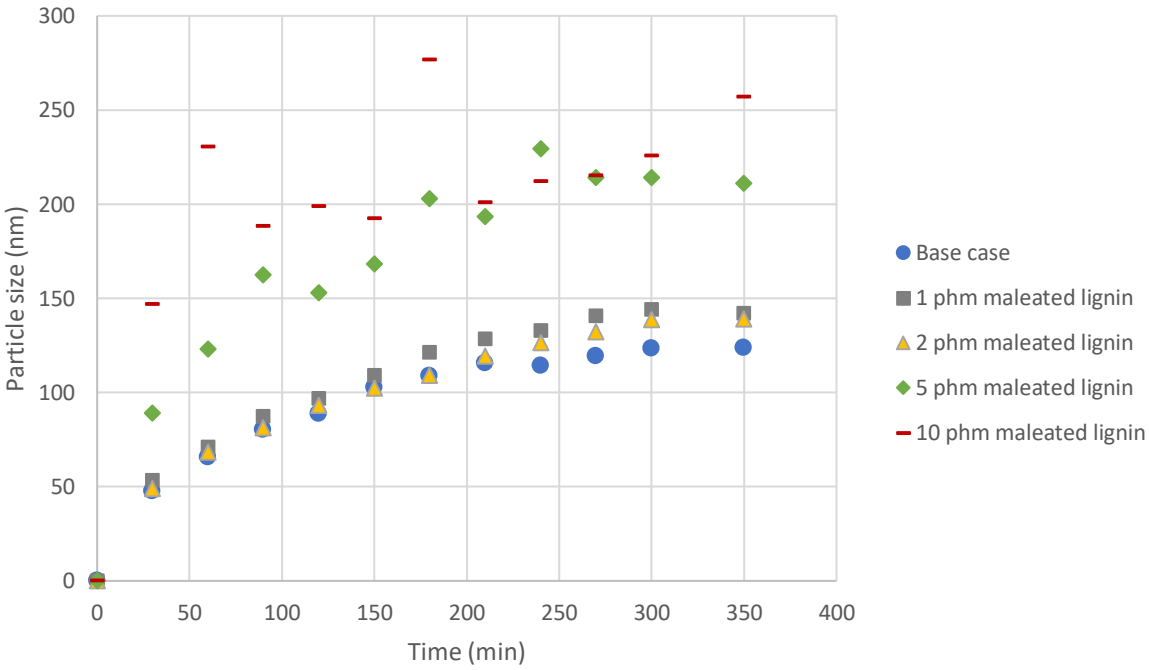

Figure A-4: Particle size growth during reaction time for runs using maleated lignin

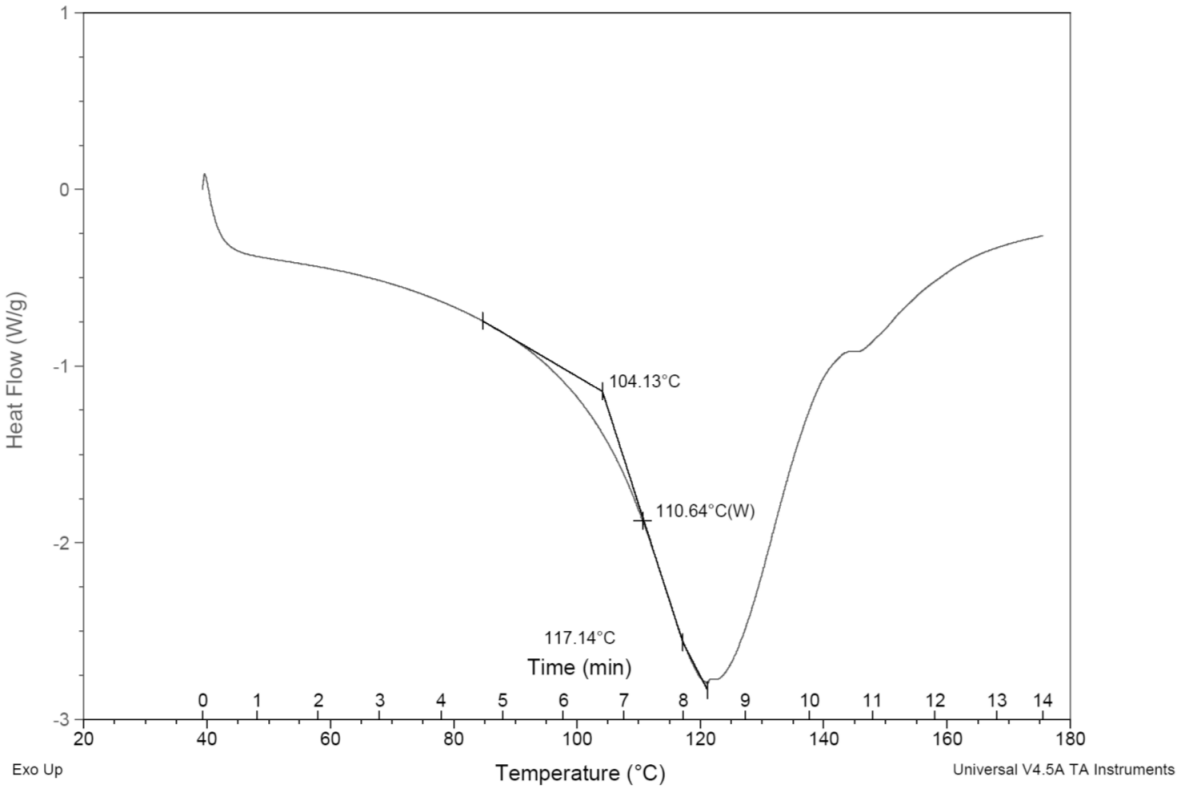

Figure A-5: Heating curve for HPH lignin

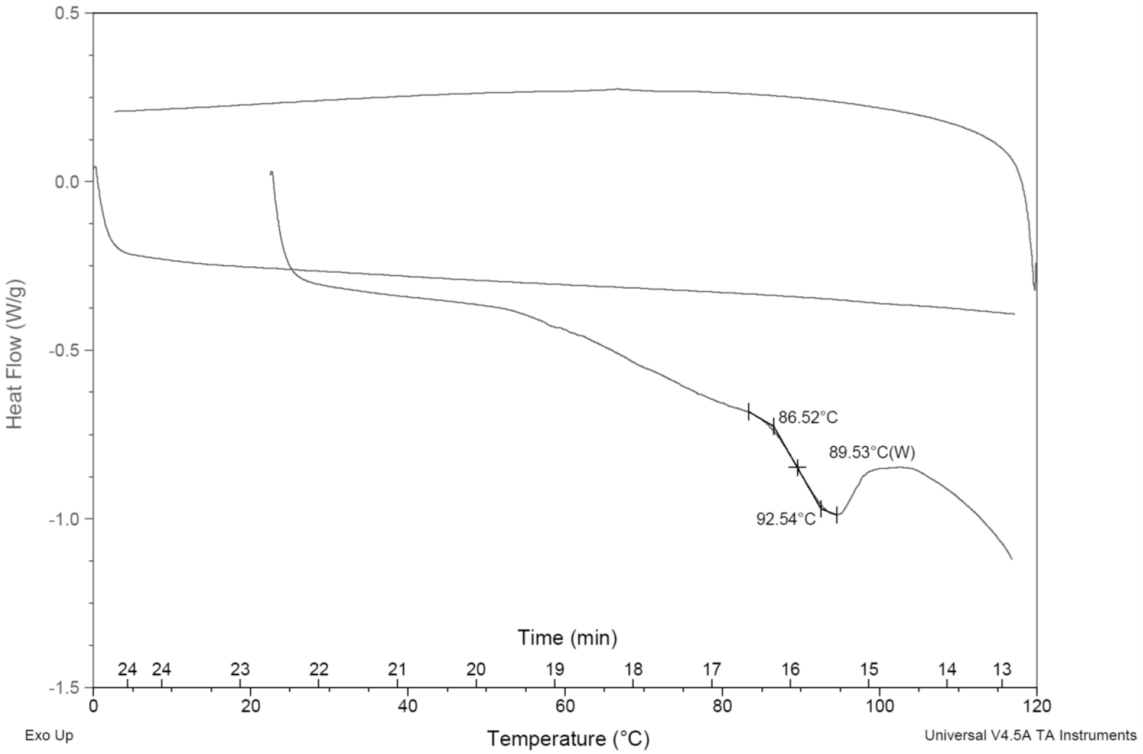

Figure A-6: Heating curve for maleated lignin

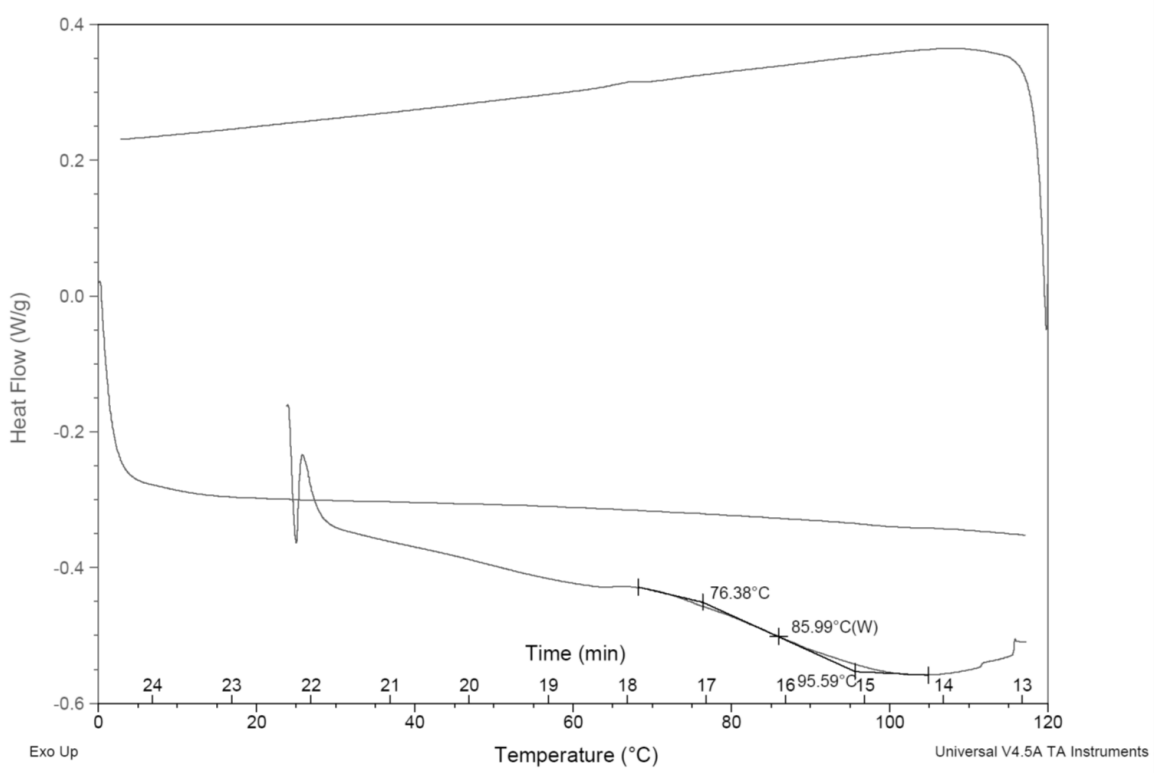

Figure A-7: Heating curve for acrylated lignin

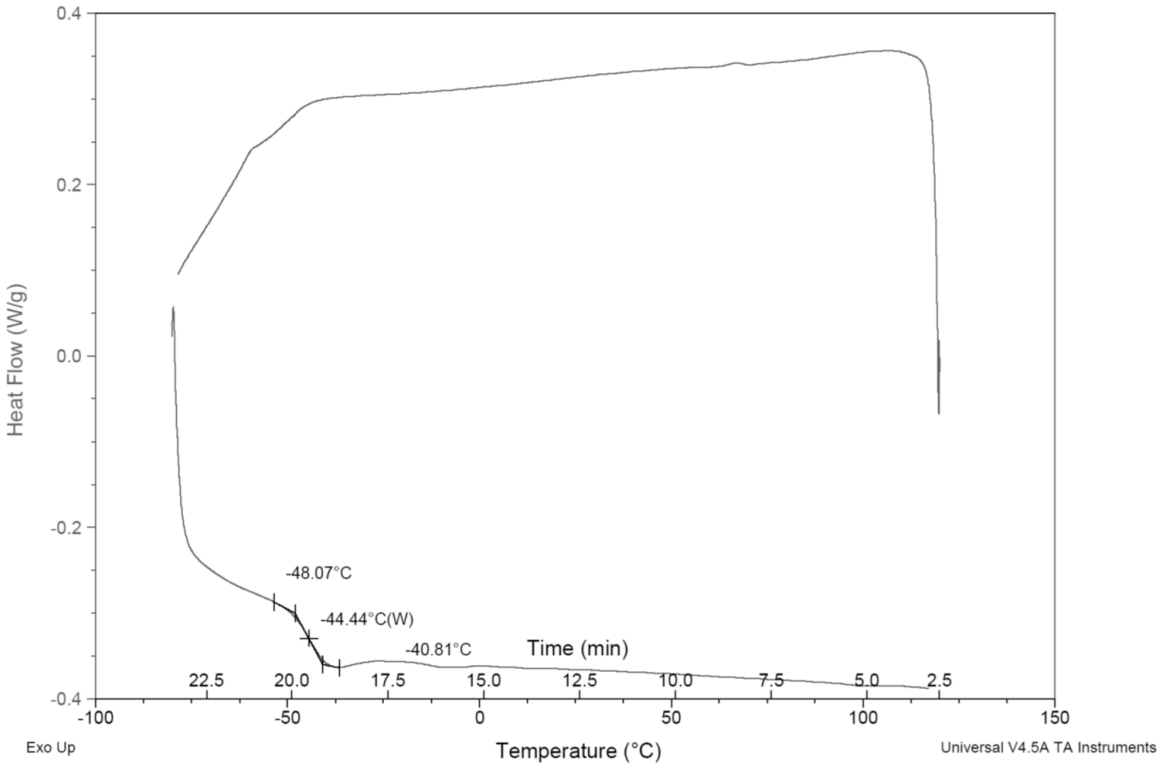

Figure A-8: Heating curve for base case run

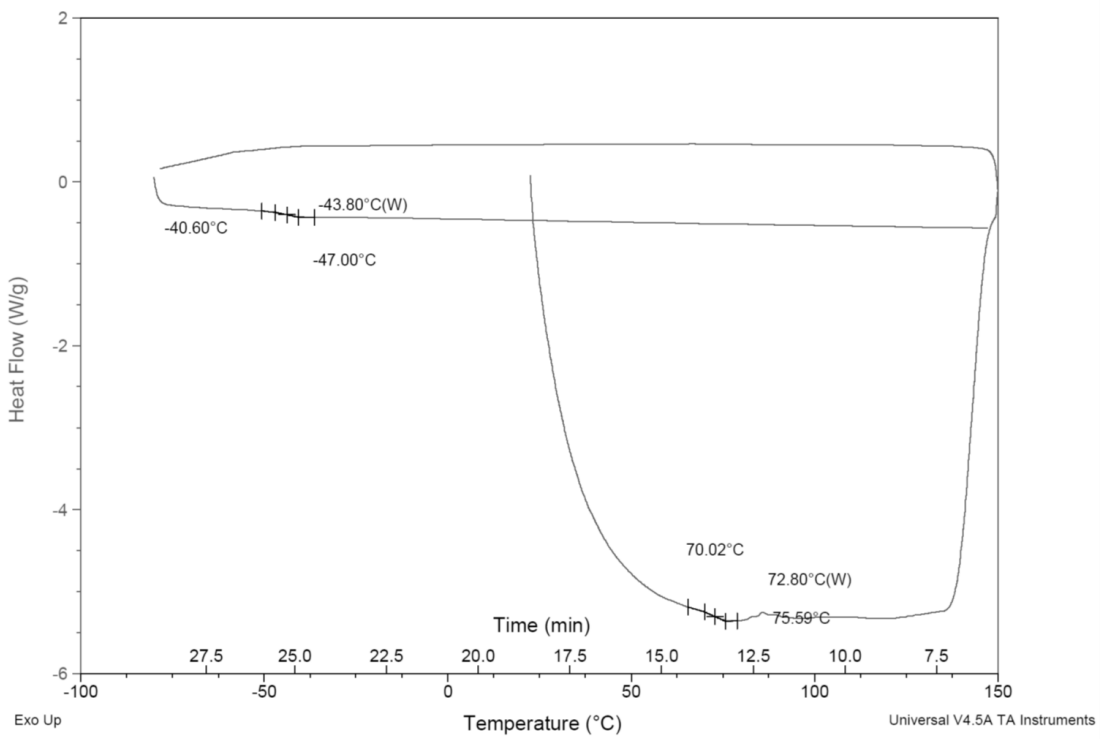

Figure A-9: Heating curve for run using 1 phm AC lignin

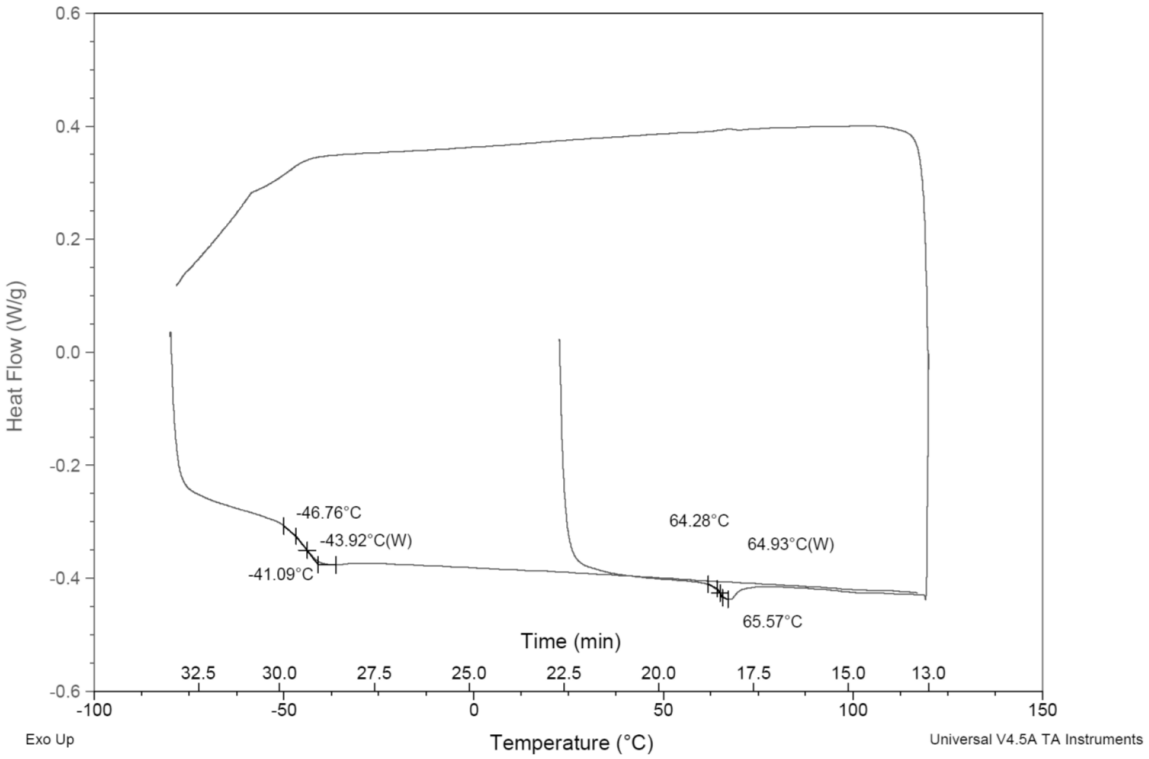

Figure A-10: Heating curve for run using 2 phm AC lignin

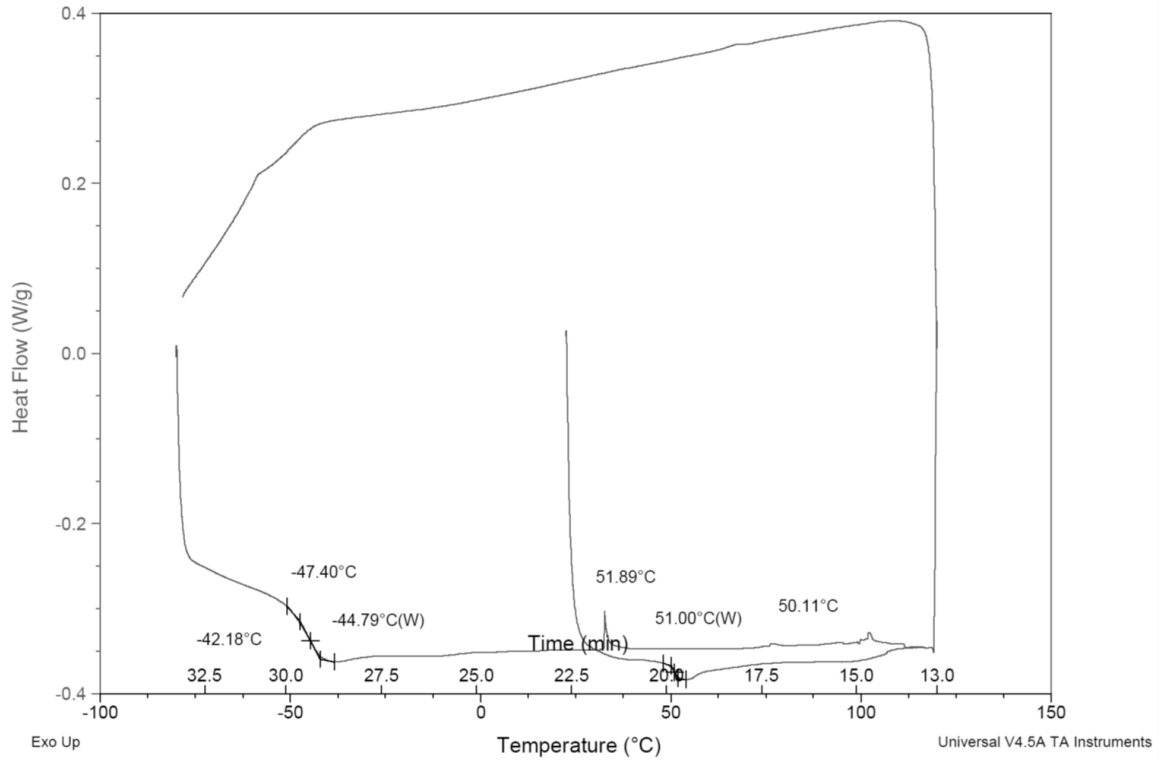

Figure A-11: Heating curve for run using 5 phm AC lignin

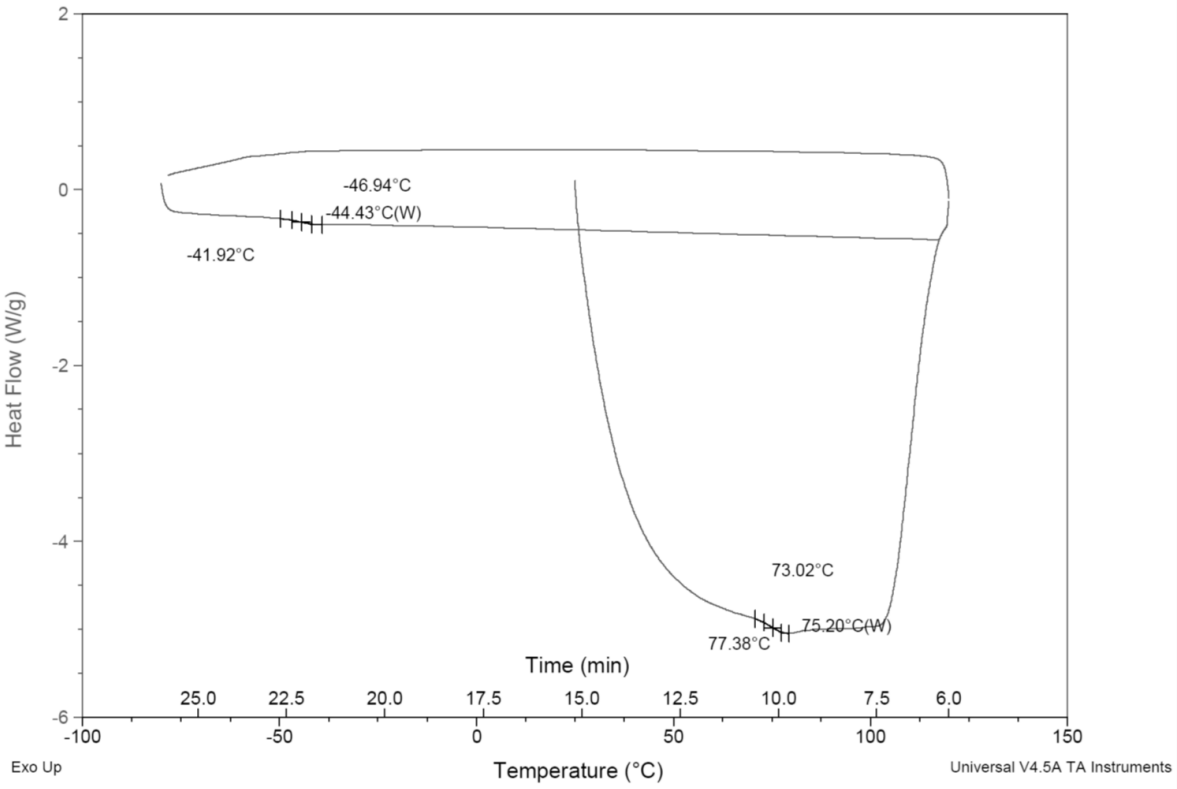

Figure A-12: Heating curve for run using 1 phm maleated lignin

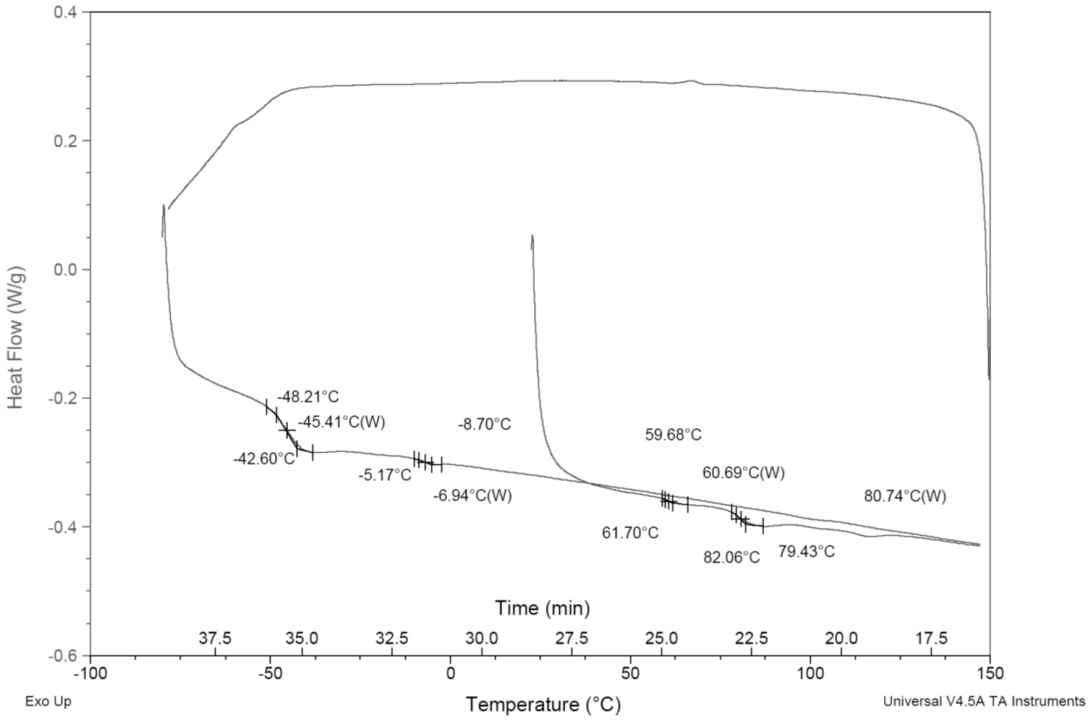

Figure A-13: Heating curve for run using 2 phm maleated lignin

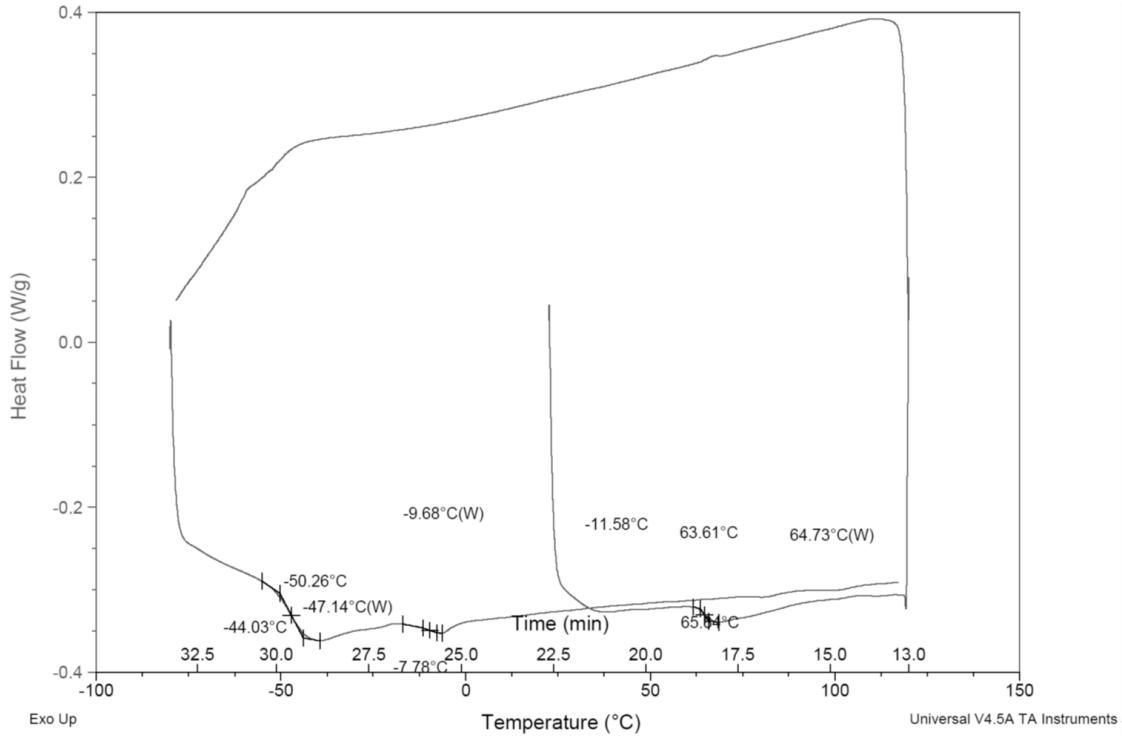

Figure A-14: Heating curve for run using 5 phm maleated lignin

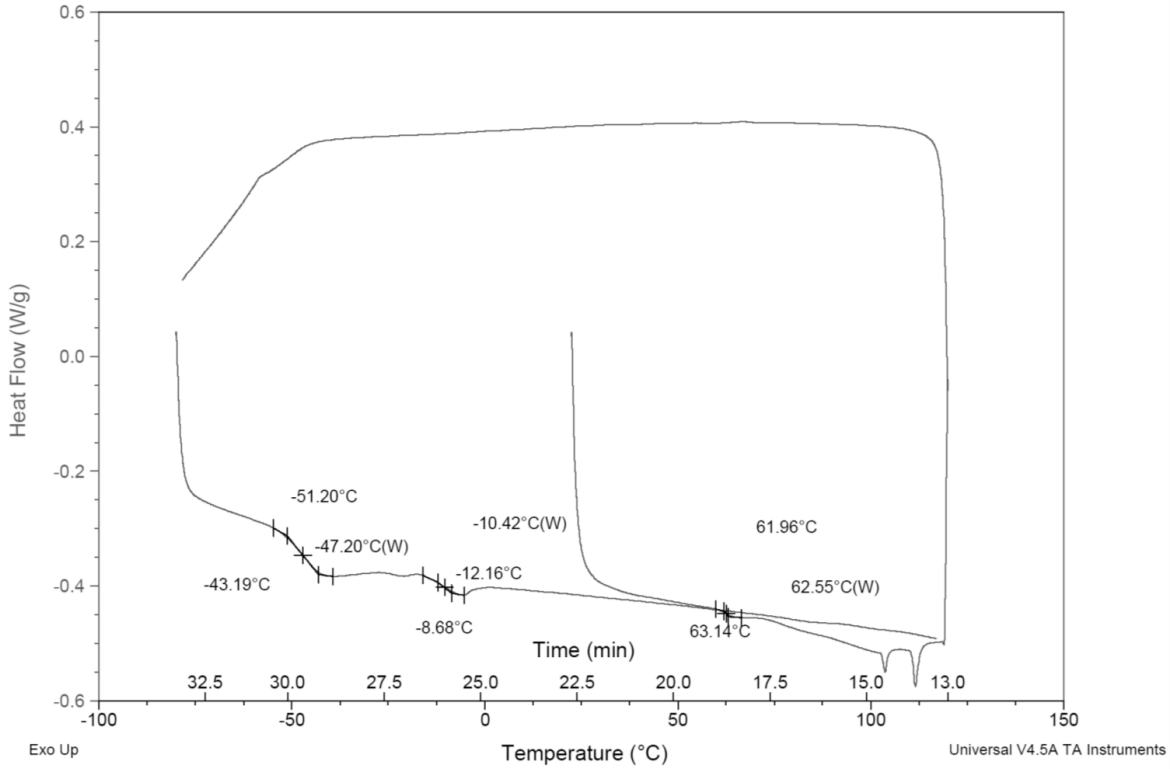

Figure A-15: Heating curve for run using 10 phm maleated lignin

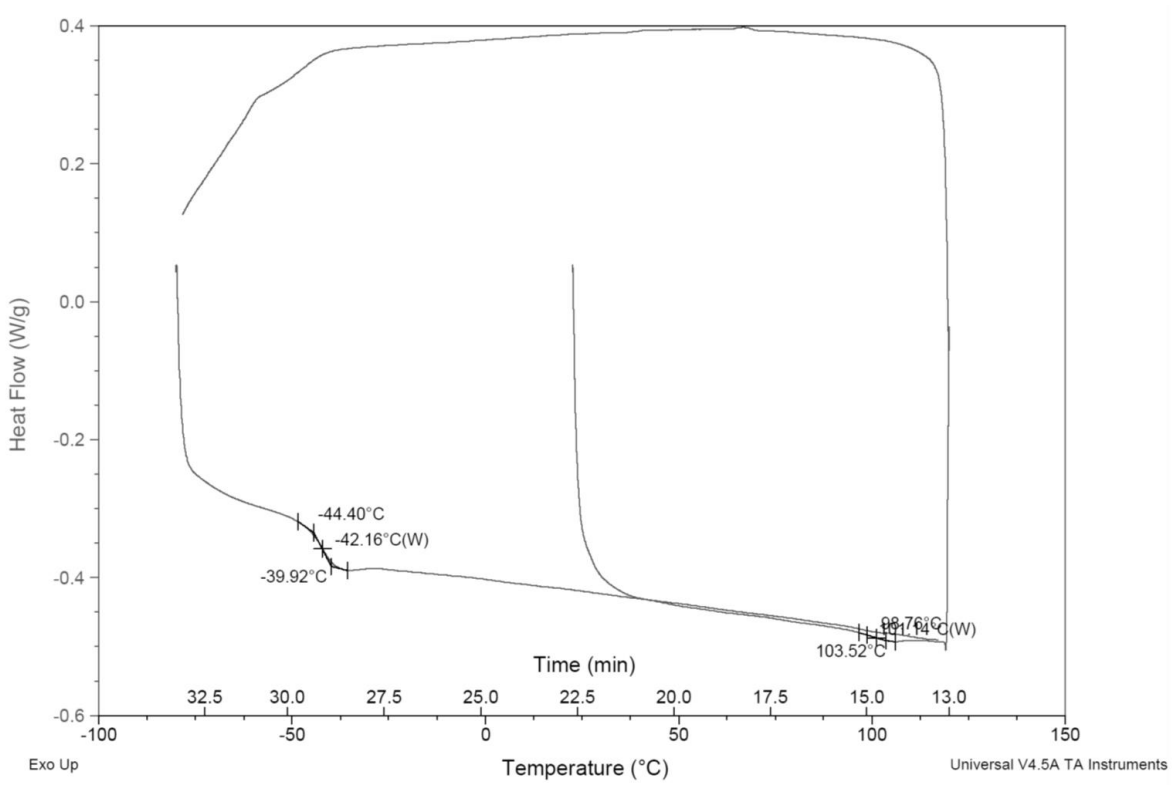

Figure A-16: Heating curve for run using 5 phm blend with lignin

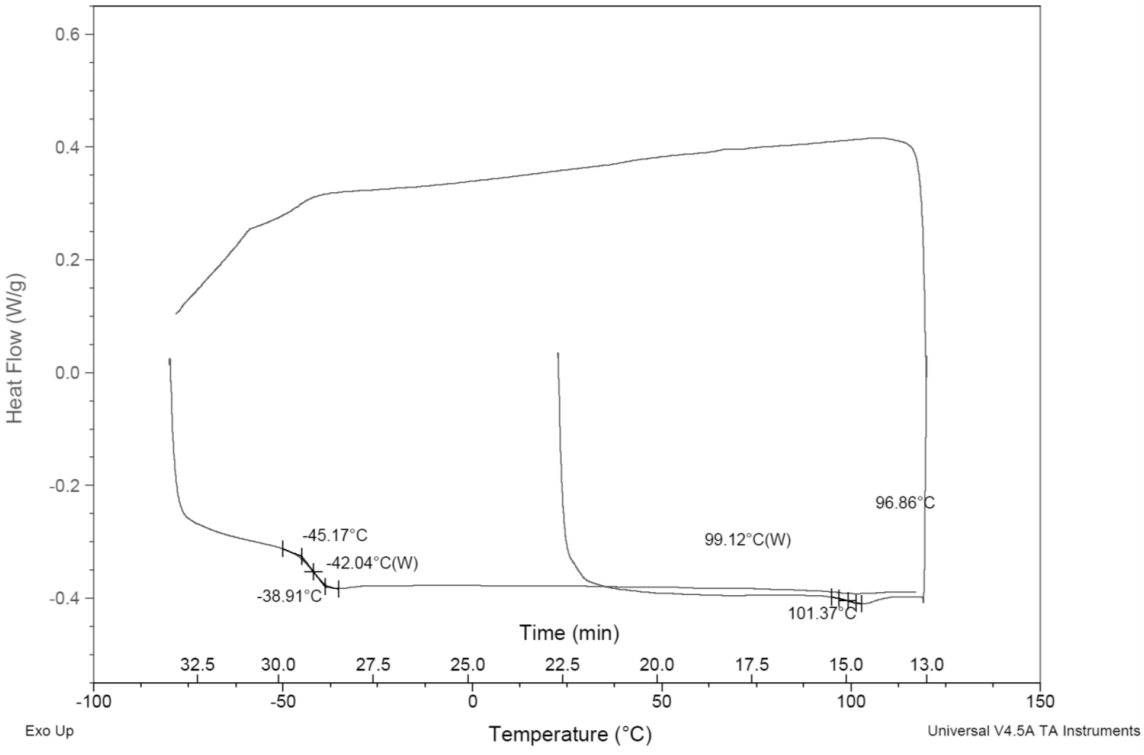

Figure A-17: Heating curve for run using 10 phm blend with lignin

Appendix B：Health and safety report

Health and Safety Assessment

Safety precautions are necessary during handling monomers, solvents, and conducting experiments. While working in the laboratory, safety glasses, nitrile gloves, lab coat and a respirator were used to protect from hazards and conduct experiments safely.

Pressure extremes

Gaseous nitrogen tank was used to perform emulsion polymerization. Proper handling and transfer of the pressurized tank was used.

Temperature extremes

In this project, the emulsion polymerization was conducted at 60 ^{o}C, and the maleation reaction was done at 85 ^{o}C. Care was taken to avoid touching any hot surfaces during polymerization, and the heat-resistant gloves were used to remove the samples from the oven during the maleation process.

Chemical hazards

In Table B-1, all chemicals used in this project, as well as the corresponding hazards, storage methods and protective measures are shown. This information was obtained from the material safety data sheets. All of the monomers were stored in a refrigerator (~5°C). Work (e.g., pipetting, stirring) related to liquid monomers was conducted in the fume hood.

Table B-1: Hazards, protective measures and storage methods of chemicals

Type	Compound	Hazard	Storage method	Protective measures
	Lignin	low toxicity, a mild irritant	Dry place	Use personal protective equipment (safety glasses, nitrile gloves, a lab coat and respirator)
	Starch	low toxicity, a mild irritant	Dry place	
Monomers	n-Butyl acrylate	Toxic; irritant (skin/eye/inhalation/ingestion)	Dry ventilated place	
	Methyl methacrylate	Toxic; irritant (skin/eye/inhalation/ingestion)	Dry ventilated place	
	Methacryloyl chloride	Extremely hazardous (skin/eye/inhalation/ingestion)	Dry ventilated place	
	2-hydroxy methacrylate	Toxic; irritant (skin/eye/inhalation/ingestion)	Dry ventilated place	
Solvents	Acetone	Toxic; irritant (skin/eye/inhalation/ingestion)	Flammables area	
	DMF	Toxic; irritant (skin/eye/inhalation/ingestion)	Flammables area	
	THF	Acute toxicity; irritant (skin/eye/inhalation/ingestion)	Flammables area	

Initiator	KPS	Extremely hazardous (skin/eye/inhalation/ingestion)	Dry area, away from the heat source	Use personal protective equipment (safety glasses, nitrile gloves, a lab coat and respirator)
Surfactant	SDS	Toxic; irritant (skin/eye/inhalation/ingestion)	Dry area	
CTA	NDM	Extremely hazardous (skin/eye/inhalation/ingestion)	Flammables area	
Starch tackifier	Borax	Mildly toxic; irritant (eye/inhalation/ingestion)	Dry area	
Starch gelation agent	NaOH	Toxic; irritant (skin/eye/inhalation/ingestion)	Dry area	