CHEMICAL THERMOPLASTICIZATION OF LIGNOCELLULOSIC FIBERS BY REACTIVE EXTRUSION

CHEMICAL THERMOPLASTICIZATION OF LIGNOCELLULOSIC FIBERS BY REACTIVE EXTRUSION

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A thesis submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree Doctor of Philosophy

DOCTOR OF PHILOSOPHY (2020) McMaster University

(Chemical Engineering) Hamilton, Ontario

TITLE: Chemical thermoplasticization of lignocellulosic fibers by reactive extrusion

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NUMBER OF PAGES: xix, 156

Lay abstract

Wood biomass is the most abundant renewable material on the planet and comprises polymer chains like plastics. These polymer chains in wood biomass are locked by strong bonds, which limits their mobility. It is for this reason that wood biomass can not “melt” like commercial plastics such as polyethylene, and thus limits its application in the manufacture of objects with complex shapes. Using chemical modifiers to react with the wood biomass can unlock those bonds among the chains and convert it into a “meltable” thermoplastic. The current preparation of thermoplastics from wood biomass is very costly because of using expensive purified cellulose and solvents to assist the reaction.

This thesis describes the development of an economical reactive process for converting less purified wood biomass into thermoplastics. It used low-cost lignocellulose, practically forestry waste, and discovered a low-cost but effective reaction method for using less expensive reactants. Finally, a rapid mechanically assisted reaction process (called reactive extrusion) was adopted based on the new chemistry to convert the lignocellulose biomass with significantly fewer reactants than needed in a batch system.

Abstract

Cellulosic thermoplastics are anticipated as promising replacements to petroleum-based thermoplastics, but their high manufacturing costs have limited wide-spread application. The primary objectives of this thesis were to use low-cost lignocellulose, practically forestry waste, as the raw material rather than more expensive purified cellulose in the preparation of new plastics and, consequently, to develop an economical reactive process focused on diminishing the use of expensive solvents in the thermoplasticization of lignocellulose.

The thermoplasticization of lignocellulosic fibers started by developing a high solids content (60 wt%) twin-screw extrusion technique to defibrillate the raw material for the subsequent chemical modification. By this approach, the received lignocellulosic fibers showed improving handling as a feedstock for extrusion as well as chemical accessibility. To effectively wet the lignocellulosic fibers for chemical modification and avoid using expensive and largely ineffective solvents, a low-cost additive was derived by mimicking aspects of an ionic liquid using benzethonium chloride (hyamine) and sulfuric acid. The effectiveness of the hyamine/sulfuric acid wetting agent was demonstrated initially in a bench-top method where the additive also became chemically bonded to the lignocellulose and strongly contributed to its thermoplasticity. During acetylation, this new and low-cost wetting/functionalizing agent converted the lignocellulosic fibers into a compression-moldable thermoplastic. The molar ratio of benzethonium chloride to sulfuric acid was found to be the most significant variable to determine grafting behaviour as well as degradation of the polymer chains.

Subsequently, this new modification chemistry was translated over to the environment of a twin-screw extruder to devise a continuous, greener method of thermoplasticization for lignocellulose. The new reactive extrusion process had a short reaction time of 45-90 s and yet showed a good tendency for producing a flowable thermoplastic suitable for melt molding without plasticizers. A notable benefit to the method was the moldable lignocellulosic bioplastic maintained the excellent stiffness inherent to cellulose. Moreover, by the reactive extrusion method, the properties of the lignocellulosic thermoplastics were found to be tunable with the selected esterifying agents (butyric anhydride versus acetyl anhydride) and the molar ratio of benzethonium chloride to sulfuric acid. A statistical analysis based on a Design of Experiment method revealed details on desirable extrusion conditions.

The project concluded with improvements to the high solids-content process was exploring the novel concept of a recycle stream for reactive extrusion. The excessive esterifying agent content used in the initial studies was necessary to lubricate the fibrous mass inside the extruder else it would jam the process. This meant that the extrudate left the extruder with an unnecessary amount of reactant and required costly cleaning. The idea of recycling a portion of the newly made cellulosic thermoplastic was to add a natural lubricant and thereby lower the content of the esterifying agent in the extruder. Under optimal recycling conditions, a significant 50% decline in reactant was possible without decreasing the degree of modification or harming the thermoplasticity of the modified lignocellulose.

Acknowledgements

Throughout my Ph.D. studies, I have received a great deal of support, help and encouragement.

I would first like to thank my supervisor, Dr. Michael R. Thompson, for his financial support so that I can have such a fantastic opportunity to study and do research at McMaster University. I am so thankful for his excellent mentoring and guidance throughout the four years, and his expertise and critical thinking show me how to be a better engineer and researcher. I am grateful for his patience, encouragement and valuable advice when I was struggling.

I would like to thank my supervisory committee members for many useful suggestions. Dr. Guerino G. Sacripante, who has more than 30 years of industrial research experience, can always give me constructive suggestions from unique perspectives. Dr. Michael A. Brook and Dr. Charles de Lannoy, from the beginning of my studies, gave me lots of useful suggestions on how I can make more progress to my research and helped to correct my research plans.

I would also like to thank our collaborator David Lawton in Xerox Research Center, Canada, for his helpful suggestions and technical support for my work on this research project.

Thanks to my summer students Vishrut Panchal and Emma Seese, for their help and contributions to the reaction design experiments, and Thomas Baker, for his help and contribution to the extrusion experiments.

Thanks to Paul Gatt for his technical help in creating various mechanical devices for facilitating my research. Thanks to our lab manager Heera Marway who is always ready to help me.

I would like to thank all previous and current members of our CAPP-D research group for your discussion, encouragement and help. Thanks to my friends, Chinese, Canadians and International friends that I have made over the four years, I truly enjoyed the amazing four years that we had lots of fun together.

I would like to thank my parents for their love, constant encouragement and unconditional support. Finally, very special thanks to my beloved wife, Xiu Sun, for her accompany and for always giving me the most robust support in the past four years.

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ATR	Attenuated total reflectance
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAP	Cellulose acetate propionate
DMA	Dynamic mechanical analysis
DMAc	Dimethylacetamide
DMSO	Dimethylsulfoxide
DOE	Design of experiment
DS	Degree of substitution
DSC	Differential scanning calorimetry
FTIR	Fourier-transform infrared spectra
NMR	Nuclear magnetic resonance
R	Molar ratio
SEM	Scanning electron microscopy
SME	Specific mechanical energy
TBA	Tetrabutylammonium
T_g	Glass transition temperature
WRV	Water retention value

Chapter 1 Introduction and literature review

1.1 Introduction

The increasing concern about the environmental impact of fossil fuel-based plastics has led to more interest in renewable resources, considering that renewable-based materials might be biodegradable. Lignocellulosic biomass, an immiscible composite mainly containing cellulose, hemicellulose and lignin, is the most abundant renewable material on Earth with an annual production of 170-200 billion tons.[1,2] However, despite its abundance, the broad utilization of lignocellulosic fibers to produce bioplastics is negligible by its general insolubility in conventional solvents and non-thermo-processability, consequences of the intense inter- and intra-hydrogen bonding in lignocellulosic. Chemical modification of the hydroxyl groups in lignocellulosic fibers is an effective method to disrupt those hydrogen bonds and change the processability of lignocellulose. In the late 19th century and early 20th century, thermoplastics (cellulose esters) chemically derived from lignocellulosic became common and could be conveniently processed into sheet, film or other objects by thermal extrusion and injection molding methods.[3] Being a thermoplastic, such that it flows readily within a range of reasonable temperature conditions, was essential to the expansion of using this material in manufacturing. Cellulose esters once dominated the plastic market because of their relative ease in processability and satisfactory material performance. However, these properties were relatively poor compared to emerging petroleum-based alternatives such as polyethylene and polypropylene, and hence, were gradually replaced in the market. Although cellulose ester plastics continue to satisfy some specified market needs, the majority of commercial plastics in use nowadays are petroleum-based. One of the main reasons for the high cost of cellulose esters is the use of high purity cellulose as its source material, which has already been separated from lignocellulosic biomass by pulping and bleaching treatments. In contrast, petroleum-based polymers are derived from considerably inexpensive feedstocks such as ethylene and propylene. Besides using an expensive feedstock, the current processes for manufacturing cellulosic thermoplastics consume more reactants than many polymerization examples from petroleum-based monomers.

With the progressive concerns on sustainability and plastic waste management, the demand for renewable thermoplastics is ever-increasing. Among the different biomass sources available, cellulosic materials offer the best opportunity for a family of thermoplastics targeted towards structural applications while maintaining biodegradability. Much of the research with cellulosic materials have centered on their blending with other synthetic and biopolymers, limiting their beneficial contributions but also avoiding the challenges in causing them to flow.[4] To exclusively use cellulosic biomass as a continuous matrix, the costs associated with the manufacturing of a thermoplastic need to be reduced, which means looking at less expensive raw materials and reactant-saving reaction processes. From the point of cost, lignocellulose is much less expensive than cellulose, and has attracted considerable attention to developing all-lignocellulose biomaterials.[5–9] The presence of lignin in lignocellulose reduces the clarity and transmittance of the final material, which detracts from the main applications of the cellulosic thermoplastics industry (ex. supporting films for optical displays). However, with the current breadth of the plastics industry, a great many applications do not require transparency, making the inclusion of lignin realistic for commercial material. This leaves the other primary need in developing more wide-spread cellulosic thermoplastics, as a much needed reactive process that is economical (and preferentially with low environmental impact). However, there is no commercially available technology to satisfy these requirements so far, recognizing as well that lignocellulose is even more difficult than cellulose to modify due to its substantial intra- and inter-chain interaction.

In this chapter, the structure and physical properties of lignocellulosic biomass are introduced, the current research progress on thermoplasticization of lignocellulose or cellulose is reviewed, and lastly, the goal of the project is laid out.

1.2 Structure and property of lignocellulose

Lignocellulose is the main constituent (dry base) of the cell wall of plants except for a small portion of pectin and extractives (wax). As shown by Figure 1.1, it is primarily composed of lignin, hemicellulose, and cellulose, where the latter is embedded in a matrix of hemicellulose and lignin. Wood is the largest commercial source of lignocellulose, although other plants, including bast plants, bamboo, bagasse and cotton, are also important commercial sources; the composition of lignocellulose varies depending on the botanical source.[10–14] Wood lignocellulose roughly contains 43-47% cellulose, 25-35% hemicellulose, 16-24% lignin and 2-8% extractives.[12] In plants, lignocellulose exists in the form of fibrous bundles, in which cellulose, hemicellulose and lignin interact by hydrogen bonding and covalent bonds such as ether and ester bonds.[10]

Due to the presence of strong inter- and intra-hydrogen bonding, tightly packed cellulose chains form crystallites with inter-dispersed amorphous regions that arrange themselves as fibers. The semi-crystalline nature of lignocellulosic fibers brings the material necessary mechanical strength and stiffness. Depending on the botanical source, a single lignocellulosic fiber usually has a tensile strength of 300-700 MPa and a tensile modulus of 10-30 GPa.[11,14–17]

Extraction of lignocellulosic fibers from bast plants normally uses a “retting” process, which utilizes bacteria and fungi in the environment to degrade the pectic polysaccharides, thereby loosens and separates the fibril bundles from the bast plants,[11,14] but this process is slow and labour intensive. The extraction of lignocellulosic fibers from wood uses a much faster process by pulping than the “retting” process used for bast plants; thus, wood is the primary commercial source for lignocellulosic fibers. In principle, pulping of wood to liberate lignocellulosic fibers can be achieved either by mechanical or chemical pulping.[18] Mechanical pulping employs mechanical force by a grinder or refiner to release fibers from wood. Wood can be steam or chemical-steam pretreated to soften the lignin binding fibers before mechanical treatment, thus reduces the energy input required to defibrillate fibers and produces more long flexible fibers. Mechanical pulping process makes use of practically the whole material and needs less amount of chemicals, and thereby has a high yield and a relatively lower cost than chemical pulping. Chemical pulping, like the popular kraft process, break down and dissolve the lignin binder in a cooking liquid; the fibers are then easy to be defibrillated by agitation. The fibers produced are generally longer, better isolated and more flexible than by mechanical pulping, but at a higher cost as it consumes more chemicals and is more process-complex. From the perspective of cost and better utilization of whole material, mechanical pulp fibers are more desirable than chemical pulp fibers in preparing an economical lignocellulosic thermoplastic.

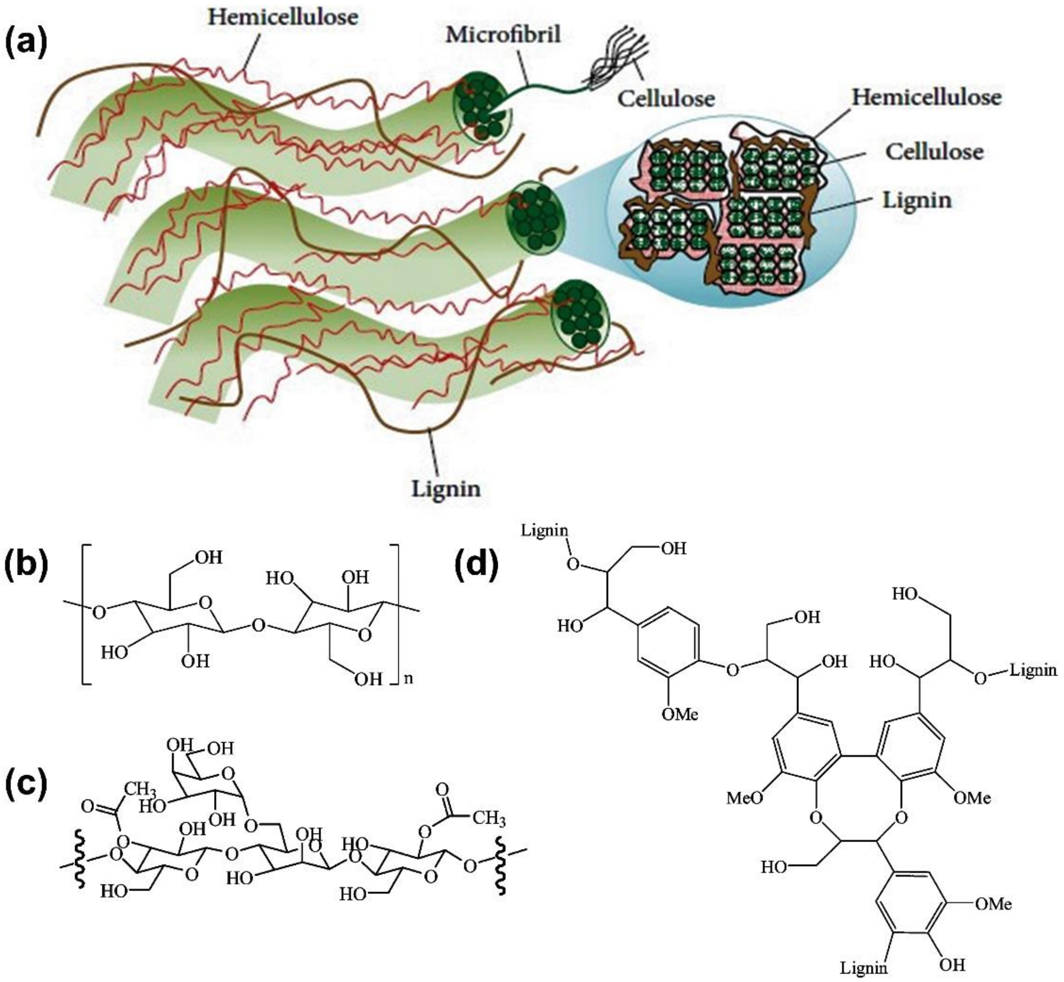

Figure 1.1. (a) Recalcitrant structure of lignocellulosic fibrils and representative molecular structures of (b) cellulose, (c) hemicellulose and (d) lignin. Picture adapted from Lee et al[19] and Sun et al[20].

The structural units of cellulose, hemicellulose and lignin in lignocellulosic fibers all have hydroxyl groups, which participate in the hydrogen bonding linkages among the three polymers. Besides hydroxyl groups, ester and ether linkages exist among cellulose, hemicellulose and lignin.[10,19] The strong interactions among cellulose, hemicellulose and lignin produce a so-called "recalcitrant" structure, which produces excellent strength in the material but also renders little mobility between the neighbouring molecules. The amorphous lignin in a lignocellulosic fibril can be softened at temperatures above 140 °C,[21] but the overall morphology of material still shows no large-scale mobility for thermoplasticity and hence maintains a solid-like nature right up to its thermal decomposition limits (220-300 °C).[22,23] Equally problematic, lignocellulose shows negligible solubility in water or most commonly used organic solvents, that might otherwise disrupt these strong interactions so that the material may flow or be dispersed/dissolved. Even for cellulose, which has a less "recalcitrant" structure than lignocellulose after removing hemicellulose and lignin, only some specific solvents such as dimethylacetamide/LiCl, N-methylmorpholine N-oxide solution, NaOH/urea solution and imidazolium-based ionic liquid are effective.[24–27] Pre-treatments like intensive mechanical pulping and hydrolysis are usually required to loosen the "recalcitrant" structure of lignocellulose so that it can dissolve in these same solvents for cellulose.[20,24,28,29]

1.3 Chemical thermoplasticization of lignocellulosic/cellulosic fibers

Understandably, to introduce a flowable nature to lignocellulose, the recalcitrant structure of this biomass must be disrupted by interfering with the hydrogen bonding. Chemical modification is an effective method for the thermoplasticization of lignocellulose. As shown by Figure 1.2, ideally, the reactions chosen for thermoplasticization should (1) primarily target hydroxyl groups so that hydrogen bonding interactions are reduced without damaging the length of chains themselves (and consequently the material's strength), and (2) introduce steric functional groups to increase segmental mobility in the otherwise rigid polysaccharide backbone (i.e. internal plasticization by grafting polymerization or substitution reactions).

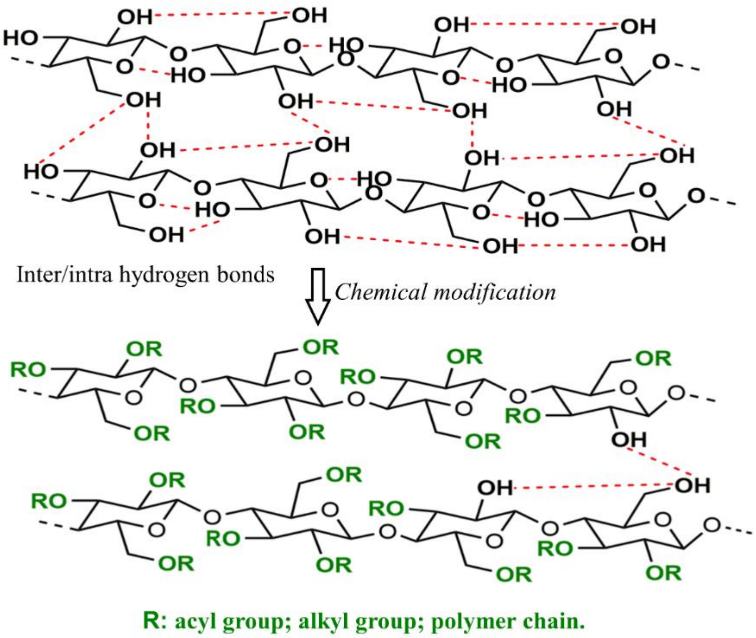

Figure 1.2. Transition in chemical state for cellulose to introduce thermoplasticization by esterification, etherification and graft polymerization.

The induced thermoplasticity by such a reaction depends on the type of substituents added and the degree of substitution (DS). Among them, esterification is the most common reaction used for preparing cellulose thermoplastics because of the ease of achieving a great extent of conversion and can give more oleophilic attributes, which in turn, minimizes moisture sensitivity and reduces swelling. Although esterification of cellulosic species appears simple, it is practical hard because of the low accessibility of these hydroxyl groups, while suitable wetting/solvating agents are absent. Below is a comparison of heterogeneous and homogenous processes for esterification, primarily for cellulose (which is far more often studied) but noting lignocellulose whenever a study was conducted.

1.3.1 Heterogeneous process

Industrial manufacturing of cellulose thermoplastics, mainly cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB), utilizes an "acetic acid" heterogeneous esterification process. In this process,[30] cellulose is first activated by glacial acetic acid to partially loosen the hydrogen bond network of the raw material. Then, acylation agent, catalyst and more acetic acid are added to start the reaction. The acylation initially takes place at the surface of fibers, and then the generated cellulose ester is dissolved/dispersed in acetic acid; thus, new hydroxyl groups on cellulose can be exposed and accessible to the acylation agent. In this process, to guarantee the homogeneity of the material in property, cellulose is first fully substituted, then back hydrolyzed to the desired degree of substitution. The acylation agent used is a carboxylic acid anhydride; for example, manufacturing cellulose acetate propionate uses a mixture of anhydrides of acetic and propionic acids. Sulfuric acid is the most often catalytic species used because of its efficiency and relatively low cost. Since the esterifying reaction is exothermic and takes hours to complete, the temperature of the reaction system is preferentially kept below 80 ℃ to minimize cellulose degradation. At the end of the reaction, acids in the reaction system are recycled preferentially or otherwise washed away. Although a series of solvents have been discovered over the past 20 years that can dissolve cellulose, this "acetic acid" heterogeneous reaction system is still the only process used industrially for the manufacturing of cellulose esters due to its relatively low cost.

Table 1.1 gives some examples of the thermoplasticity gained by the “acetic acid” process, as reflected by the glass transition temperature (T_g) of the modified cellulose manufactured. For cellulose thermoplastics prepared by the “acetic acid” process, there is a narrow temperature window between their melt flow state and thermal decomposition state. For example, the recommended flow temperature of a CAB thermoplastic (T_g = 134 ℃) for melt spinning is 240 ℃, whereas the material reportedly starts thermal degradation (1% weight loss) at 275 ℃.[31] To broaden the useable temperature window of these polymers, plasticizers are usually needed in commercial cellulose thermoplastics.

With innovations in cellulose chemistry, cellulose esters with longer side-chains have been prepared in recent times, demonstrating greater thermoplasticity (lower viscosity at the same processing temperature) with increasing side chain length (C_2-C_{20}).[32,33] However, following the “acetic acid” process makes it difficult to manufacture cellulose esters with side chains length greater than C_5,[3] because of the increased steric hindrance, lower acidity and nonpolar nature of long-chain carboxylic acid anhydrides.

Table 1.1. Examples of thermoplasticity of cellulose thermoplastics prepared by industrial "acetic acid" heterogeneous process.

No.	Type	DS_A	DS_P	DS_B	T_g* (°C)	Reference
1	CA	2.46	--	--	218	Kamide et al[34]
2	CA	2.92	--	--	180	Kamide et al[34]
3	CAP	0.25	2.45	--	153	Scandola et al[35]
4	CAP	0.04	2.67	--	140	Sand et al[36]
5	CAB	1.10	--	1.83	134	Ghosh et al[37]
6	CAB	0.49	--	2.37	103	Scandola et al[35]

*T_g are all measured by differential scanning calorimetry (DSC); DS_A: degree of acetylation; DS_P: degree of propionylation; DS_B: degree of butyrylation.

1.3.2 Homogenous process

Over the past 20 years, with new solvents identified for cellulose, novel long-side substituted cellulose esters have been achieved that was not feasible by the "acetic acid" process. The advantages of a homogenous solution method include (1) improved accessibility of hydroxyl groups to chemical modifiers and more efficient diffusion among reactants in solutions, which is beneficial for the incorporation of long and bulky side chains, (2) a single step can be achieved to control the extent of reaction, and (3) produce thermoplastics with uniform properties because of the homogenous reaction conditions. The intensive hydrogen bonding of cellulose results in a limited number of solvents that can dissolve the polymer. As shown in Figure 1.3, some of these solvents for cellulose are aqueous-based, which makes them unsuitable for being used as a reaction medium for esterification due to the interfering water species. Only the listed non-aqueous solvents in Figure 1.3 would be suitable for preparing cellulose esters.

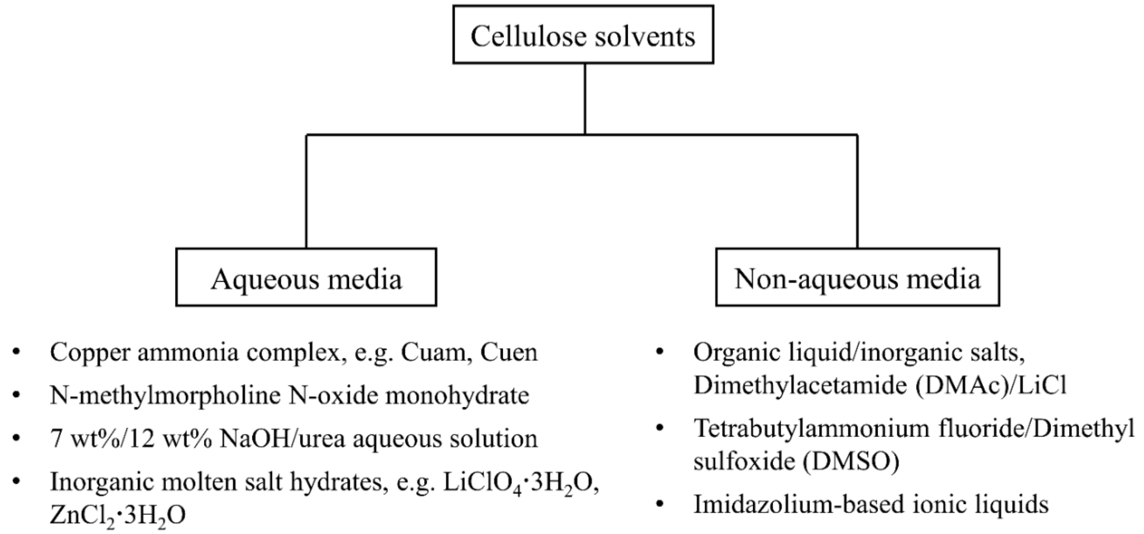

Figure 1.3. Summary of typical solvents for cellulose.

DMAc/LiCl solvent was designed for the dissolution of cellulose back in the 1980s for the preparation of cellulose esters. One advantage of the DMAc/LiCl combination is that it can dissolve cellulose of different molar masses and crystallinity.[38] By a DMAc/LiCl homogenous process, Sealey et al. reported that highly substituted (DS = 2.8-2.9) cellulose esters with long linear aliphatic acyl side chains from C_{12} to C_{20} could be prepared.[39] These cellulose esters had T_g of 94-134 ℃ and thus generated better thermoplasticity than currently available commercial cellulose ester thermoplastics. Low T_g, distinct side-chain crystallization and defined melting transitions were seen for these long-chain cellulose esters, unlike commercial cellulose mixed esters. Tanaka et al. reported that long chains containing aromatic ring could also be grafted onto cellulose backbone by the DMAc/LiCl solution system, and those modified polymers demonstrated bending and impacted mechanical properties that were tunable by changing the composition of the long-side chains.[40] A problem for the DMAc/LiCl solution method, besides its high cost, is that the high polarity of the DMAc/LiCl solvent makes the effective combination of nonpolar long-chain carboxylic acid anhydrides with the solvent difficult, and long reaction time (6-24 h) is usually required. This problem could be solved by using a polar esterifying agent carboxylic acid chloride, but an acid scavenger such as pyridine was required for the generated HCl during modification to avoid cellulose degradation,[41] and it is costly to isolate afterwards. Although the DMAc/LiCl solvent system creates new routes for preparing cellulose ester thermoplastics, it is not currently a practical route for industry because it is hard to recycle the DMAc/LiCl, and the lithium salt is expensive.

The non-aqueous solvent, tetrabutylammonium (TBA) fluoride (or acetate)/dimethylsulfoxide (DMSO) mixed solvent has also been found suitable for the homogenous esterification of cellulose.[42,43] By this reaction medium, a series of long-chain substituted cellulose esters (DS = 1.4-2.5), such as cellulose laurate, hexanoate and stearate, have been prepared.[44,45] A very bulky cellulose bis(benzyloxy) benzoate (DS = 0.7) with 15 aromatic rings in a single grafted species was prepared by this method to demonstrate further its capacity to handle bulky substituents.[46] However, no information on the thermoplasticity of these cellulose esters prepared by the TBA/DMSO method was provided in the publications. Similar to the DMAc/LiCl system, TBA/DMSO system suffers from issues with recycling the solvent at the end of the reactions.

Ionic liquids were first reported in 2002 ss a new group of solvents able to dissolve cellulose.[47] Ionic liquids typically refer to molten organic salts with melting pointing below 100 °C. The ionic liquids notedly useful for dissolving cellulose possess a cation of 1-alkyl-3-methylimidazolium, where the alkyl group of the cation and the associated anion can be varied. Ionic liquids are considered as potentially green solvents due to their practical recyclability. Like DMAc/LiCl solvent, ionic liquids can dissolve various types of cellulose with different molar masses and crystallinity.[48] Esterification studies[47,49–52] have demonstrated that using ionic liquids allow (1) milder reaction conditions and shorter reaction time, (2) a broader range of different esterifying agents, and (3) properties of the resultant cellulose esters that are easier to control and more reproducible, compared to the heterogeneous reaction system. Chen et al. conducted a detailed investigation of the synthesis of melt-flowable cellulose ester thermoplastics in ionic liquid.[53] In their research, a series of cellulose esters (13 samples) with T_g ranging from 80-248 °C were prepared by changing the nature of the esterifying agents; the sample with the best thermoplasticity (T_g = 80 °C) was flowable without shear, even at a relatively low temperature of 150 °C; bulky side groups containing aromatic rings were incorporated onto cellulose by mild reaction conditions. At the end of the modification, an excess amount of water or ethanol is usually added to the reaction system to precipitate the modified cellulose, and ionic liquids were recycled by evaporating out of these water or ethanol.

Although ionic liquids are practically recyclable, their usage in the industrial manufacturing of cellulose thermoplastics has not been realized. Ionic liquids are highly expensive now because of their complex synthesis and purification processes. Additionally, the reusability of ionic liquids is questionable because (1) thermal degradation or hydrolysis occurs during the recycling process[54–56] and there is no information on how many times these ionic liquids can be reused, and (2) the recycled ionic liquids contain unused esterifying agents, catalyst and degraded polysaccharides.

1.4 Challenges for chemically introducing thermoplasticization in lignocellulose

Studies on the chemical conversion of lignocellulosic fibers into thermoplastics basically used the same strategies as pure cellulose, focusing on esterification by either heterogeneous[57–59] or homogenous process.[60,61] For example, Abe et al. prepared wood acetylate and propionate for compression molding by a similar acid swelling process that is used for industrial manufacturing cellulose thermoplastics;[59] it is worthwhile pointing out that in their research, a much stronger trifluoracetic acid was used instead of acetic acid, which might be due to the more recalcitrant structure of lignocellulose. Similar to modifications of cellulose, imidazolium-based ionic liquids have demonstrated effectiveness as reaction media for chemical modification of lignocellulose. For example, Xie et al. prepared wood-based lignocellulosic thermoplastics (T_g = 125-132 °C) by homogenous acylation in multiple ionic liquids.[60] Chen et al. reported similar work using an ionic liquid for a homogenous reaction to chemically convert sugarcane bagasse lignocellulose into thermoplastics (T_g = 133-175 °C).[61] The dissolution of cellulose by ionic liquids is mainly driven by forming new hydrogen bonds between cellulose and the solvent to disrupt the original hydrogens bonds between cellulose chains.[38] In lignocellulose, there are not only hydrogen bonds but also covalent bonds among hemicellulose, cellulose and lignin, which means that it is much more difficult to dissolve lignocellulose than cellulose.

Depending on the source of lignocellulose and ionic liquids used, in some cases, lignocellulose is just partially dissolved in ionic liquids (or needs more solvent to dissolve), or use of pre-treatments such as mechanical grinding to assist the dissolution.[28,58,62,63] The low solubility problem of lignocellulose will undoubtedly increase the cost of making lignocellulosic thermoplastics.

1.5 Reactive extrusion of lignocellulosic/cellulosic fibers

Extrusion has advanced well beyond its original use in plastics processing, being extended into all fields of chemical modifications. Chemical reactions in extruders are practical because (1) the flexible configuration of screw elements is suitable for different reaction conditions, (2) high shear forces generated by the rotating screw(s) can intensively mix viscous reactants, and (3) highly effective heat transfer can be achieved in the shallow screw channels.[64] Further advantages of reactive extrusion include its continuous operation, ability to handle high solids content (for cellulosic modification), and short reaction time (though short residence may also be considered a significant disadvantage).

A key benefit to this method of conversion is that extrusion treatment of wet lignocellulose or cellulose can defibrillate fibers,[65–68] which improves their accessibility to reactants. This accessibility improves the potential for greater extents of reaction with lignocellulose or cellulose and reduces the demand for large amounts of solvent in the reaction. However, lignocellulosic or cellulosic has no ability to melt and remains mechanically strong, which makes the conveying of their fibers inside an extruder quite difficult. Most studies by reactive extrusion with lignocellulose or cellulose have usually involved a molten polymer matrix where the fibers are present as a filler or reinforcement agent needing in situ compatibilization.[69,70] There are, however, some reports[71–74] of the direct extrusion of cellulose fibers for their functionalization; based on the discussions so far in this chapter, it should not be surprising that such reaction extrusion processes involved a large volume of liquids to assist the conveying of fibers but also experienced a low degree of reaction due to the short residence time inside an extruder. There is no known study for using a bulk reactive extrusion process to convert lignocellulose or cellulose into thermoplastics.

1.6 Objectives

The discussion above identifies that the current industrial "acetic acid" process for manufacturing cellulose thermoplastics cannot satisfactorily justify the performance/cost requirements for the thermoplasticization of lignocellulose. Most current attempts of chemical thermoplasticization of lignocellulose have relied on using large excesses of ionic liquids to swell or dissolve the raw material for reaction, which is equally impractical for industrial due to their high costs. As a result, preparing lignocellulosic thermoplastics as potential replacements for low-cost petroleum-based polymers has seemed economically unjustifiable. Reactive extrusion has the potential to operate with reducing liquid concentrations but needs a break-through in the approach followed, so that reaction rates are high, and hence economical. The objectives of the thesis include:

1. To develop a less expensive alternative to ionic liquids to satisfy the wetting requirement of lignocellulose for chemical thermoplasticization.
2. To apply the new wetting approach in the thermoplasticization of lignocellulosic, and devise effective modification chemistry to modify lignocellulosic into thermoplastics.

The new modification method must be completed within a short residence time and not excessively damage the chain of cellulose so that the final material retains much of the strength inherent to wood products.

3. To design a reactive extrusion process to convert lignocellulose into a flowable thermoplastics appropriate for easy molding.

1.7 Thesis outline

Chapter 1 ***Introduction and literature review.*** This chapter presents the background information of the project, including a brief overview of the development of renewable-based thermoplastics based on cellulosic materials, and a review of studies related to the acylation of lignocellulosic and cellulosic fibers in preparation of thermoplastics. This chapter also provides research objectives and this outline of the thesis.

Chapter 2 ***Improved chemical reactivity of lignocellulose from high solids content micro-fibrillation by twin-screw Extrusion.*** This chapter introduces a physical pre-treatment method to compact and defibrillate lignocellulosic in a twin-screw extruder prior to the subsequent step of reactive extrusion. By this approach, the received fluffy lignocellulosic wood pulp was converted into partially micro-fibrillated fine granules, which made the wood pulp convenient for feeding in the reactive extrusion process and improved the fibers' chemical accessibility. This chapter has been published in *Journal of Polymers and the Environment*.

Chapter 3 ***Solvent-free modification of lignocellulosic wood pulp into a melt-flowable thermoplastic.*** This chapter introduces an approach mimicking aspects of ionic liquids but using less expensive species that can be equally beneficial for wetting lignocellulosic biomass for chemical modification. By this approach, lignocellulosic fibers were modified into a thermoplastic with good flowability. This chapter has been submitted to *Cellulose* for consideration of publication.

Chapter 4 ***Thermoplastic lignocellulosic polymer from wood pulp by reactive extrusion.*** Based on the new chemistry designed in chapter 3, this chapter introduces a rapid process for the chemical thermoplasticization of defibrillated lignocellulose by reactive extrusion. By this approach, a chemical modification completed within 45-90 s of lignocellulose produced a thermoplastic with excellent thermal flow properties for suitable melt molding. This chapter has been submitted to *Carbohydrate Polymers* for consideration of publication.

Chapter 5 ***Exploring the concept of a recycling stream for producing a thermoplastic lignocellulosic polymer from wood Pulp by reactive extrusion.*** This chapter introduces a newly conceived recycle stream method into the reactive extrusion process and significantly reduces the excessive amount of reactant needed to convert the defibrillated lignocellulose into a moldable thermoplastic meant for structural uses. This manuscript is under preparation for publication.

Chapter 6 ***Conclusion.*** The final chapter concludes the key findings and recommends future work.

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Chapter 2 Improved chemical reactivity of lignocellulose from high solids content micro-fibrillation by twin-screw extrusion

In this chapter, a high solid content extrusion pre-treatment was demonstrated that could micro-defibrillate lignocellulosic fibers, which was beneficial for improving the chemical accessibility of the fibers. This chapter has been published as “Li J, Thompson M, Lawton DJW (2019) Improved Chemical Reactivity of Lignocellulose from High Solids Content Micro-fibrillation by Twin-screw Extrusion. J Polym Environ 27:643–651.” Reprinted with permission from Springer Link.

Jinlei Li conducted all the experiments and wrote the draft of the manuscript. Dr. Thompson revised the draft to the final version. David Lawton provided technical guidance on the experiments.

2.1 Abstract

The low reactivity of lignocellulose limits the effective chemical conversion of lignocellulose biomass into functional bioproducts. Mechanical micro-fibrillation treatment can improve the chemical accessibility of lignocellulose but usually has limited productivity by the low processing solids content. The presented work demonstrates effective micro-fibrillation of lignocellulose at high solids content up to 60 wt% can be achieved by twin-screw extrusion. Morphological characterizations of the extruded wood pulp lignocellulose show the degree of micro-fibrillation is enhanced by operating at higher solids content. The lignocellulose treated at 60 wt% solids content presents 2.1 and 4.8 times higher water retention capacity and specific surface area, respectively than the original material. Acetylation results show the twin-screw extrusion pre-treatment can significantly accelerate the chemical modification of lignocellulose by 50%. This high productivity method for micro-fibrillating lignocellulose should be of great interest to the bioplastics industry.

2.2 Introduction

In recent decades, many stakeholders of the plastics industry have shown interest in building manufacturing capacity for bioplastics from renewable sources to reduce their reliance on petroleum and get ahead of looming regulatory restrictions. Some bioplastics, *e.g.* polylactic acid, featuring varying levels of biodegradability, have found commercial success, but have questionable futures being produced from food-based resources including corn and plant oils. As compared with food-based biomass, lignocellulose, which is the main constituent of woody plants, grasses, and crops, has more abundant availability and feasible renewability without sacrificing food security and thus is considered as a promising alternative for food-based biomass in bioplastics production.[1–3] But isolated native lignocellulose shows low chemical accessibility to its complex assembly of hemicellulose, cellulose, and lignin components on account of strong inter-and intra-molecular hydrogen bonding. Lignocellulose is insoluble in common organic solvents and incapable of flow like commodity thermoplastics, which necessitates its functional modification, whether by chemical or bio-fermentation methods, to prepare bioplastics. Both approaches require vigorous reaction conditions and long reaction time.[4–8]

It is well recognized that mechanical treatment is an effective technique that can significantly improve the chemical accessibility of lignocellulose in bioconversion processes, *e.g.* mechanical grinding of wood or wood pulps can give a 2-6 fold increase in its enzymatical digestibility.[9,10] The possible mechanism by which mechanical treatment alters the chemical accessibility of lignocellulose includes (*i*) increasing the external surface area of lignocellulose by size reduction, (*ii*) creation of more pores and voids in lignocellulose, and (*iii*) increasing the internal surface area due to fibers defibrillation.[11–13] In recent years, twin-screw extrusion has been considered as the most promising practice for continuous industrial processing of agricultural and forestry feedstocks.[14–16] As compared with other commonly used mechanical treatment methods, including ball milling, beating, and homogenization, twin-screw extrusion has the capacity to operate at higher solid loadings as well as lower energy consumption.[17–20] Several research efforts have been made on utilizing twin-screw extrusion in the pre-treatment of varied lignocellulose sources, including crops straw,[21–23] bagasse,[24,25] and hardwood pulp[26] for the purpose of maximizing yields of fermentable sugars in secondary operations. However, there have been no reports on twin-screw extrusion pre-treatment of lignocellulose for consideration of subsequent heterogeneous chemical modifications of lignocellulose, which is an important route to prepare bioplastics from biomass.

Of particular concern is whether the pre-treatment can be done without the additives used for micro-fibrillation in enzymatic hydrolysis processes. The reported additives for twin-screw extrusion of lignocellulose include glycerol,[27] ionic liquids,[24] and dilute acids or alkalines.[28–31] However, these additives in the extruded lignocellulose have to be subsequently removed so as not to inhibit the subsequent enzyme reaction, which would be similarly needed for most chemical modifications as well. The cleaning step has been reported on occasions to recover previously lost hydrogen bonding associations, *e.g.* dried powder from the dehydration of aqueous suspensions of cellulose nanofibers has shown poor re-dispersity in water.[32] In addition, these liquid additives usually cause severe degradation of the lignocellulose during micro-fibrillation, which is desired for enzyme hydrolysis but may not be accepted for chemical modifications intended to prepare a bioplastic. As compared with the enzymatical hydrolysis, chemical modifications of lignocellulose typically require higher solids loading, shorter reaction times and better heat and mass transport efficiency, which matters particularly if one eventually attempts to combine pre-treatment and modification in the same production process. Hence, it is also vital to know the relationship between the reactivity of lignocellulose in chemical modifications and its physical properties as a result of extrusion pre-treatment.

The present study examines twin-screw extrusion as a mechanical treatment for micro-fibrillation of lignocellulose, reporting on physical properties of the fibers and investigates whether the extruded product exhibits suitable reactivity for chemical modification in the absence of commonly used additives mentioned above. The goal was to demonstrate a clean approach that is effective for de-structuring lignocellulose at high solids content with minimal degradation.

2.3 Experimental

2.3.1 Materials

Aspen high yield mechanical pulp was received from Tembec (Montreal, Quebec) and used throughout this study as model lignocellulose. The initial moisture content of the pulp was 8.4 wt% determined by a moisture analyzer (HG63, Mettler Toledo, USA) at 105 ^{o}C setpoint temperature. The acid-insoluble lignin content of the pulp was 8.2 wt% determined by the TAPPI-T method 222 om-02. Congo red (analytical grade) was purchased from Sigma-Aldrich, Canada. Sodium phosphate, dibasic and sodium phosphate, monobasic both in ACS grade, were bought from Fisher Scientific, Canada.

2.3.2 Extrusion pre-treatment of the mechanical pulp

A ZSE-HP 27 mm 40 L/D co-rotating intermeshing twin-screw extruder (American Leistritz Extrusion Corp.; Somerville, NJ) was used to micro-fibrillate the mechanical pulp. As shown in Figure 2.1, a screw configuration, primarily composed of conveying screws elements and featured two kneading sections with three 90^{o} offset kneading elements, was particularly designed to generate high shear stresses for fibrillating the mechanical pulp.

Desired amounts of distilled water were pre-mixed with the pulp to prepare extrusion feedstocks with solids content at 20, 30, 40, 50, 60 and 70 wt%, respectively. The pre-wetting mechanical pulp was manually fed into the extruder at ~2.5 kg/h. The temperature inside the extruder barrel was maintained close to 10 ºC by chilled water, and the rotating speed of screws was set at 250 rpm. Each extrusion feedstock having a certain solids content was extruded for 1, 3, 5 and 7 passes. Repeated passes were used in place of modifying the screw design to determine the number of shear events appropriate to fibrillate the pulp. Samples were collected from the exit die of the extruder and referenced in the results based on a naming nomenclature of SP*x-y*, where *x*, *y* represented the solids content and number of passes through the extruder, respectively.

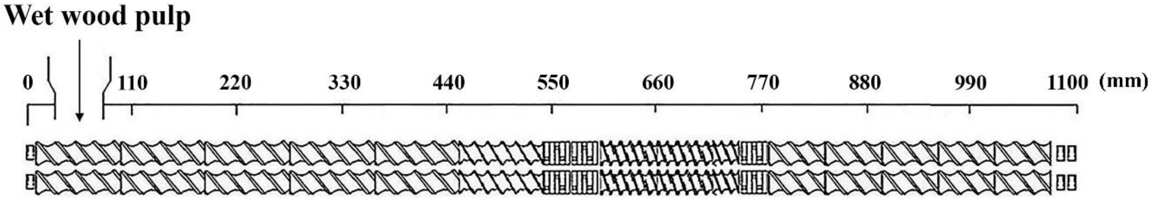

Figure 2.1. Screw configurations with conveying elements and 90º offset kneading blocks for the pre-treatment of mechanical pulp.

2.3.3 Solvent-free acetylation of the pre-treated mechanical pulp

Extruded mechanical pulp was vacuum-dried at 90 ºC for 24 hrs prior to acetylation. For solvent-free acetylation of the mechanical pulp, 2 g dried extrusion pre-treated mechanical pulp was put into a 50-mL flask containing 12 mL acetic anhydride. 0.2 g anhydrous zinc chloride acting as a catalyst for the acetylation was pre-dissolved in the acetic anhydride by magnetic stirring for 5 mins at 80 ºC. The reaction took place at 120 ºC for 30 mins, and samples were taken out at times of 2, 4, 6, 8, 12, 16, 20 and 30 mins. The reaction was stopped by adding 10-fold water into the system. Each sample was filtered and repeatedly washed with 0.5 M sodium carbonate solution until its pH value reached ~7. Finally, the wet acetylated mechanical pulp was vacuum dried at 75 ºC for 24 hrs.

2.3.4 Characterizations

Energy consumption.

The energy consumption during the extrusion treatments was estimated by specific mechanical energy (*SME*), which can be calculated by the following expression:

$$\mathrm{SME\ (Wh/kg)} = \mathrm{P_0}\frac{\tau}{\tau_0} \times \frac{\mathrm{R}}{\mathrm{R_0}} \times \frac{1}{\mathrm{Q}} \times 0.98 \qquad (1)$$

where P_0 is the drive motor power; τ and τ_0 are the operating and maximum drive torque values, respectively; R and R_0 are the operating and maximum screw rotational speeds, respectively; Q is the feed rate; and *0.98* is the motor efficiency through the gearbox according to the extruder vendor.

Solids content changes

The extruded mechanical pulp was collected and sealed in plastic bags. The final solids content of these samples was determined using a moisture analyzer (HG63, Mettler Toledo, USA) set for isothermal heating at 105 ºC.

Water retention value (WRV)

WRV of the extruded mechanical pulp was measured by a modified TAPPI method UM 256. Briefly, 1 g of the extrusion treated mechanical pulp was dispersed in 40 mL water and boiled for 30 mins. Then the suspension was centrifuged in a tube with an inserted cellulose acetate membrane filter at 9000 g for 30 mins. Obtained wet samples were weighed and dried in an oven at 105 ºC for 2 hrs. The *WRV* was then calculated by using the following equation:

$$\mathrm{WRV}\ (\%) = \frac{\mathrm{W_1 - W_2}}{\mathrm{W_2}} \qquad (2)$$

where W_1 and W_2 are the weights of wet and dried samples, respectively.

Specific surface area

Specific surface area of the extruded mechanical pulp was evaluated by Congo red dye adsorption experiments.[33,34] In brief, an extruded mechanical pulp sample with a 0.05 g dry weight was dispersed in 20 mL phosphate buffer to form the suspension with a pH of 6. The suspension was then treated with varying amounts (5-25% of the weight of the pulp) of Congo red and incubated in a shaking water bath at 60 °C for 24 hrs. The sample was finally centrifuged at 16500 g for 15 mins, and the concentration of Congo red in the supernatant was determined by UV–Vis absorption (DU 800, Beckman Coulter, USA) at 500 nm. The maximum adsorbed amount of Congo red A_{max} in mg/g by the pulp was calculated using Langmuir isotherms:

$$\frac{[\mathrm{E}]}{[\mathrm{A}]} = \frac{1}{\mathrm{K_{ad}\,A_{max}}} + \frac{[\mathrm{E}]}{\mathrm{A_{max}}} \qquad (3)$$

where *[E]* is the solution concentration of Congo red at adsorption equilibrium in mg/ml, *[A]* is the equilibrium adsorbed amount of Congo red on the mechanical pulp surface in mg/g, and K_{ad} is the Langmuir adsorption equilibrium constant. The specific surface area (*SSA*) of the extruded mechanical pulp was finally calculated by equation (4):

$$\mathrm{SSA} = \frac{\mathrm{A_{max}} \times \mathrm{N} \times \mathrm{SA}}{\mathrm{MW} \times 100} \qquad (4)$$

where N is Avogadro's constant, SA is the surface area of a single dye molecule (1.73 nm^2), and MW is the molar mass of Congo red (696 g/mol).

Light microscope

25 µL of a 0.05 wt% extruded mechanical pulp suspension was dropped on a pre-cleaned glass slide. A coverslip was put on the liquid samples immediately after dropping to minimize aggregation of the pulp fibres. The samples were air dried for 24 hrs, and then observed and imaged by an imaging microscope (Axioplan 2, Carl Zeiss, German).

Scanning electron microscopy (SEM)

Samples of the extruded mechanical pulp were diluted to approximately 0.1 wt% and vacuum filtered through a 1-µm nucleopore track-etch membrane while washing with excess water. A filtered sample was air dried and mounted on an SEM stub before being sputter coated with 6 nm Pt/Pd. Images were captured using an SU8000 FE-SEM (Hitachi, Japan) operating at 5 KV.

Sedimentation testing

Extruded mechanical pulp was dispersed into deionized water to obtain a 7 mL aqueous suspension with a solids content of 1 wt% in a glass vial. The vial was sealed and shaken while inverted for 2 hrs before being left for stabilization. Pictures were taken after 4 and 24 hrs free-standing, and the heights of the total suspension (H_0) and the sediment (H_s) were measured by ImageJ image analysis software (National Institutes of Health, USA). The sedimentation ratio is the sediment height relative to the total surface liquid height (H_s/H_0).

Degree of substitution of the acetylated mechanical pulp

Accurately weighed 0.1 g of dried acetylated mechanical pulp was put into a 25-mL glass vial. 5 mL of 0.25 M NaOH and 5 mL of anhydrous ethanol were added to the 0.1 g acetylated mechanical pulp. The mixture was left to free-standing for 24 hrs, and then 10 mL 0.25 M HCl was added to the system. After 30 mins, the mixture was titrated using 0.25 M NaOH with phenolphthalein indicator. The acetyl group grafted on the mechanical pulp was calculated by equation (5):

$$\text{Acetyl content (wt\%)} = \frac{[(V_1 + V_2)C_1 - V_3C_2] \times 43}{m} \times 100\% \qquad (5)$$

where V_1 is the volume of NaOH added to the system before the titration, V_2 is the volume of NaOH consumed in the titration, C_1 is the NaOH concentration, V_3 is the volume of HCl added to the system before the titration, C_2 is the concentration of HCl, m is the weight of the sample, and *43* is the molecular weight of an acetyl group.

2.4 Results and discussion

2.4.1 Solids content changes during twin-screw extrusion

Solids content played a significant role during the process on the morphology of the final products. It was vital to know the true solids content of the pulps during extrusion processing, especially at high numbers of extrusion passes. As shown in Table 2.1, the solids content of all pre-wetting mechanical pulps had increased very little after five passes through the extruder but after seven passes, a significant increase in solids content was reported. For the seventh pass, sample SP_{70}-$_7$ showed the highest moisture loss of ~8.25% compared to its original set point. Multiple passes in an industrial process may not be practical, but we believe a longer extruder or tandem extrusion setup would accomplish the same results as our multi-pass laboratory configuration. The loss of moisture from the pulp substrates was attributed to the heat generated from the friction between pulp fibers, which was evident by the higher extrudate temperatures relative to the barrel setpoint (10 ºC). For example, a sample of 60 wt% solids content showed a slight increase in temperature by 3 ºC for each pass, whereas temperature increased by 7 ºC in the case of pulp with a solids content of 70 wt%. Hence, a solids content ~60 wt% can be considered as the maximum solids content, which can be used for effective defibrillation of mechanical pulp lignocellulose by twin-screw extrusion.

Table 2.1. Solids content changes of wet mechanical pulps after 5 and 7 passes of twin-screw extrusion.

Sample code	Before extrusion (wt%)	Solids content at pass 5 (wt%)	Solids content at pass 7 (wt%)	Total solids content changes (wt %)
SP_{20}	20	21.47 ± 0.53	22.61 ± 0.79	2.61 ± 0.79
SP30	30	31.30 ± 0.11	33.54 ± 0.56	3.54 ± 0.56
SP40	40	42.30 ± 0.48	44.08 ± 0.92	4.08 ± 0.92
SP50	50	54.21 ± 0.014	56.62 ± 0.65	6.62 ± 0.65
SP60	60	63.59 ± 0.06	67.69 ± 2.29	7.69 ± 2.29
SP70	70	71.14 ± 1.52	78.25 ± 0.50	8.25 ± 0.50

2.4.2 Influence of twin-screw extrusion treatment on the morphological properties of the mechanical pulp

Defibrillation and size reduction

WRV quantifies the water absorption capacity of lignocellulose fibrils and has been proven to be a reliable indicator for the extent of micro- and nano-fibrillation of pulps.[35,36] As shown in Figure 2.2, the WRVs of twin-screw extruded mechanical pulps were all higher than that of the original raw material, indicating greater water absorption was achieved by the wet twin-screw extrusion. With up to three extrusion passes, WRVs of the extrusion treated pulps increased consistently with increasing solids content, suggesting beneficial fibers disintegration at higher solids content. For a greater number of extrusion passes exceeded three times, WRVs showed a drop as the solids content exceeded 50 wt% even though at lower solids values, the WRVs continued to show even greater improvement. Sample SP_{60-5} presented the maximum WRV of 215.7%, which was 2.1 times higher than that of the raw material.

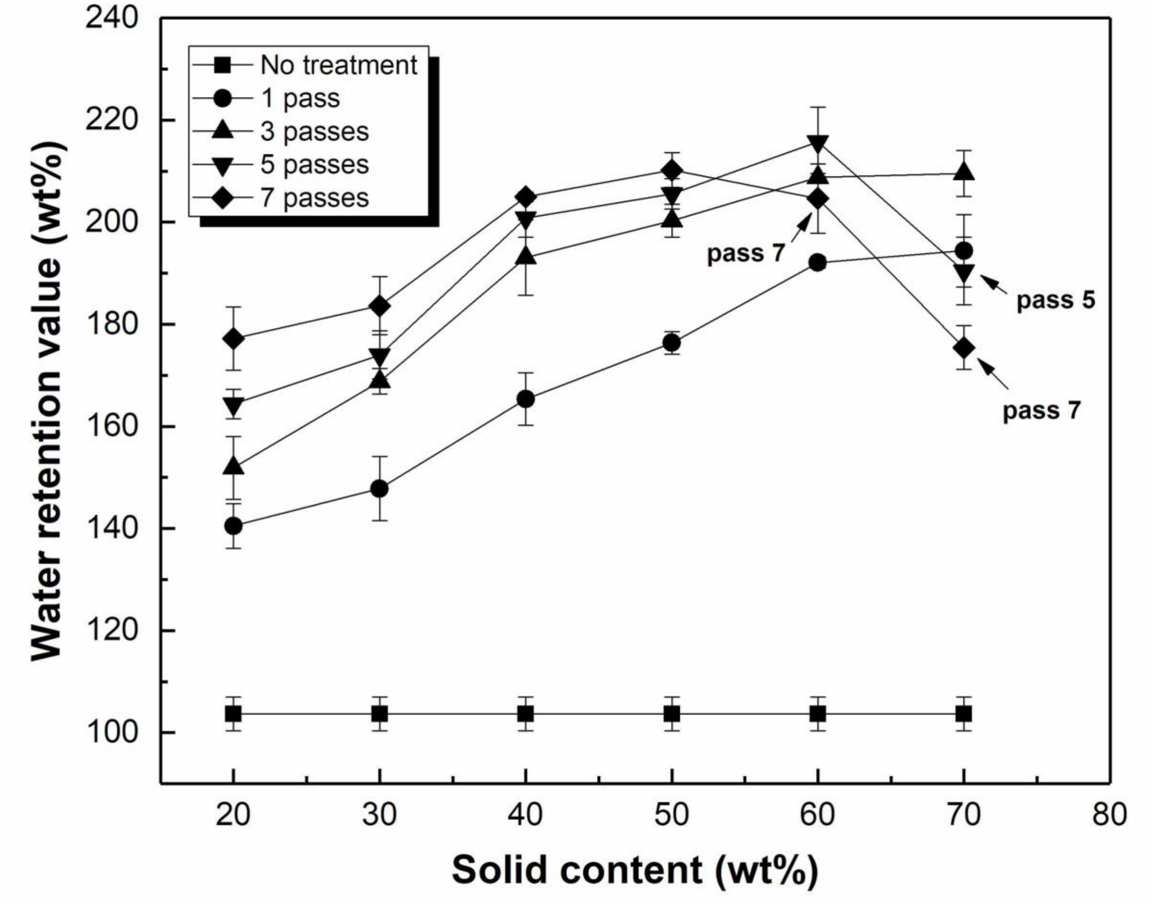

Figure 2.2. Water retention values of the mechanical pulps before and after twin-screw extrusion at different solids content.

Photographs of the collected samples reflected fiber characteristics that corresponded with the notable trend for WRVs of twin-screw extrusion treated mechanical pulps. As shown in Figure 2.3, the pulp chips of the raw material had been pulverized into smaller sized granules or fine powder after 5 passes through the twin-screw extruder depending on the water content. Sample $SP_{60\text{-}5}$ (Figure 2.3c) was processed into a fine powder, showing more apparent surface area as would be expected based on its WRV than sample $SP_{30\text{-}5}$ (Figure 2.3b) which appeared in the form of granules. But for the sample $SP_{70\text{-}5}$ (Figure 2.3d) with an initial 70 wt% solids content, hornification was observed with an obvious number of flakes appearing in the collected powder. A similar phenomenon was observed for sample $SP_{70\text{-}7}$ (not shown), which may be the reason why the WRV started to decline by the 5th pass at 70 wt% solids content. Although a slight drop in WRV was also observed for sample $SP_{60\text{-}7}$, no hornification was found in its collected powder.

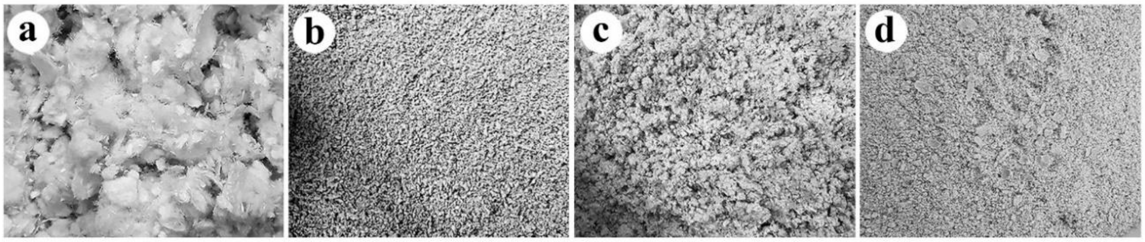

Figure 2.3. Photographs of the raw material (a) and mechanical pulps after extrusion at 30 (b), 60 (c) and 70 wt% (d) for 5 times.

Light microscopy was employed to further investigate the morphological changes of mechanical pulps after twin-screw extrusion treatments with images shown in Figure 2.4. Figure 2.4b shows that fiber length reduction was the main effect of multiple extrusion passes on the mechanical pulp at a low solids content of 30 wt%. The average fiber length observed of sample $SP_{30\text{-}5}$ was ~300 μm which was 41.7% of the length of the original pulp fibers. A small amount of microfibrils separated from the pulp substrate was also found in sample $SP_{30\text{-}5}$. Hence, the length reduction and defibrillation were both considered to be contributors to the increase in WRV at a low solids content (30 wt%). When the solids content was increased to 60 wt%, Figure 2.4c shows that not only was the length of the mechanical pulp fibers significantly reduced, but also a much greater degree of defibrillation had occurred as well compared to sample $SP_{30\text{-}5}$. Most of the original pulp fibers were processed into hair-like microfibrils for sample $SP_{60\text{-}5}$. Micro-fibrillation appears to dominate as solids content increased, reflected by the higher WRVs among the treated pulps. For more aggressive extrusion conditions, whether by an increase in the number of extrusion passes ($SP_{60\text{-}7}$) or solids content ($SP_{70\text{-}5}$ and $SP_{70\text{-}7}$), both would cause a visual aggregation of the extruded pulps to a certain extent, as displayed in Figure 2.4d-f, which seems consistent with the fact that WRVs dropped for these samples.

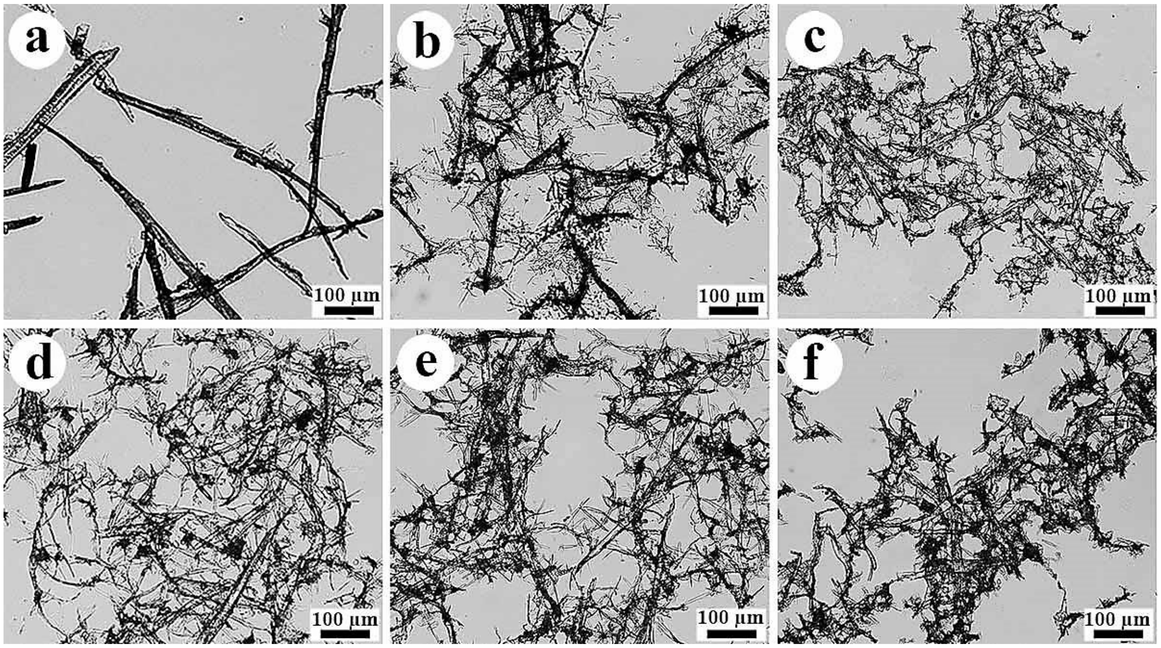

Figure 2.4. Light microscopy images of the original mechanical pulp (a), sample $SP_{30\text{-}5}$ (b), $SP_{60\text{-}5}$ (c), $SP_{60\text{-}7}$ (d), $SP_{70\text{-}5}$ (e) and $SP_{70\text{-}7}$ (f).

SEM images of the samples $SP_{60\text{-}5}$ and $SP_{70\text{-}7}$ (Figure 2.5) gave more detailed information on their difference in microstructure. For sample $SP_{60\text{-}5}$ (Figure 2.5a), it mainly consisted of individual microfibrils with the width ranging from 5-30 µm, whereas sample $SP_{70\text{-}7}$ (Figure 2.5b) mainly contained short micro-sized fragments. It was believed that highest shear damage was generated during the extrusion of $SP_{70\text{-}7}$ because it had the least amount of water working as a lubricant in the system. The calculated specific mechanical energy consumption was 249 Wh/kg per pass for trials at a solids content of 70 wt% while at 60 wt% and 50 wt%, consumption was lower at 198 Wh/kg and 150 Wh/kg, respectively. Additionally, the insufficient amount of water during extrusion of $SP_{70\text{-}7}$ limited defibrillation of the pulp fibers due to poor swelling of the raw material. Hence, the extrusion of the mechanical pulp at 70 wt% solids content was mainly in the form of cutting fibers and detaching fibrils from the surface of the pulps. A similar result was also found by[37] in the high-pressure homogenization of bleached and oxidized hardwood fibers, where hornified samples prepared by drying were cut into shorter fibers and fragments while the never-dried fibers without hornification were disintegrated directly into microfibrils.

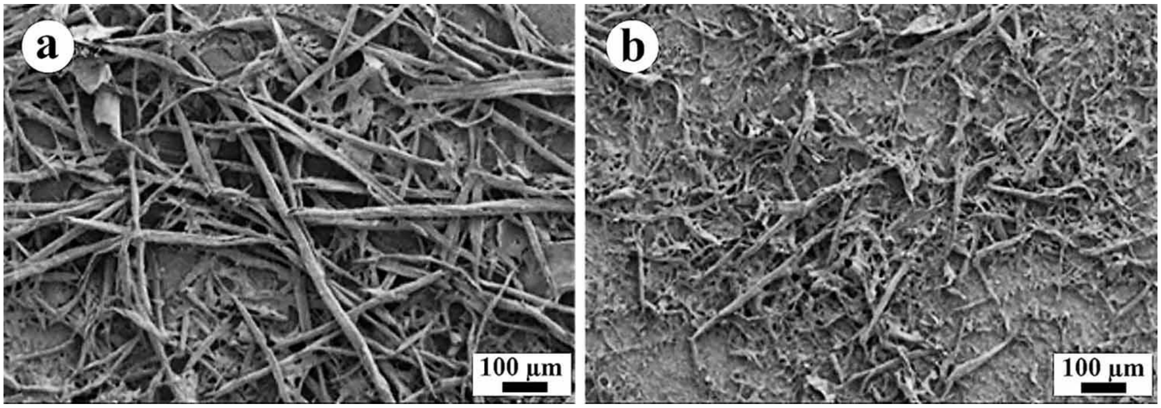

Figure 2.5. SEM images of mechanical pulps after twin-screw-extrusion at 60 wt% for 5 times, $SP_{60\text{-}5}$ (a) and 70 wt% for 7 passes, $SP_{70\text{-}7}$ (b).

Size reduction and micro-fibrillation of mechanical pulps by twin-screw extrusion were further noted by sedimentation testing of the extruded pulps. Figure 2.6 displayed the observable sedimentation behavior of all collected mechanical pulps treated at different solids content after five passes through the extruder. The nature of sedimentation after 4 hrs and 24 hrs of free-standing is seen by the images of the vials in Figure 2.6a, c, whereas the contents of the supernatant are highlighted better in Figure 2.6b, d showing the different dried liquids on glass slides. After 4 hrs of free-standing, the water-rich phase at the top of all suspensions was still turbid, indicating that a considerable amount of fine fibrils were produced by the twin-screw extrusion. After 24 hrs of free-standing, it was found that this water-rich upper region in the vial for sample $SP_{20\text{-}5}$ had become totally clear without visible pulp fibers, whereas the upper regions in the vials for samples SP_{40-5}, SP_{50-5} and SP_{60-5} were still cloudy; high solids content appeared beneficial for the generation of microfibrils from the pulp substrate.

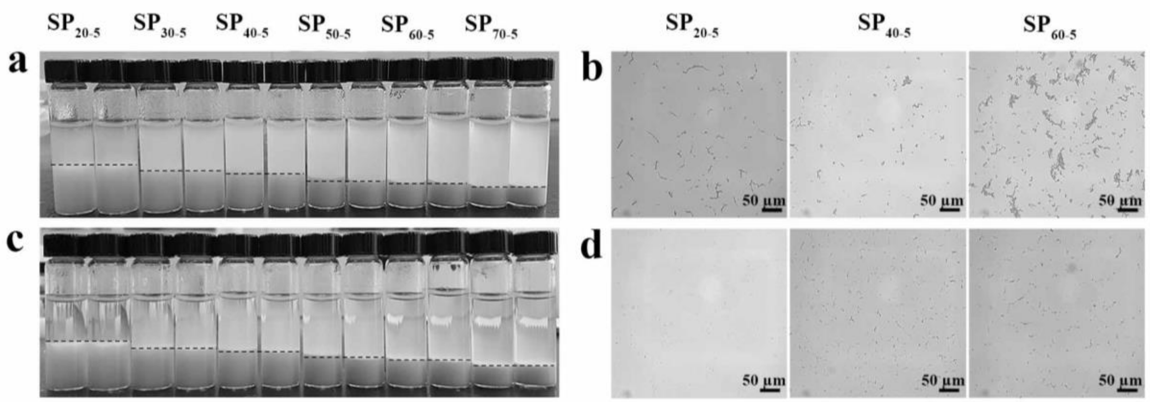

Figure 2.6. Typical sedimentation of the twin-screw extrusion treated pulp (after 5 passes) aqueous suspensions after free-standing for 4 hrs (a) and 24 hrs (c), and the light microscopy images of the fine fibrils in the supernatants after 4 hrs (b) and 24 hrs (d) free-standing.

The quantified results reflecting these observations of sedimentation are shown in Figure 2.7. Higher solids content was consistently correlated to a lower height of sediment, which can also be interpreted as higher bulk density. A major reason for this relationship was that shorter fibers were produced at higher solids content extrusion, which more easily packed together densely. On the other hand, the defibrillated fine fibrils also increased the possible contact area between mechanical pulp, that's to say, increasing the van der Waals' attractive force between pulp fibers.[38] The sedimentation ratios show deviation based on the number of extrusion runs for higher solids content than 50 wt%. The ratios show that samples, SP_{60-7} and SP_{70-7} exhibited a similar sedimentation nature as SP_{60-1} and SP_{70-1}, which was due to the decrease in fine fibrils contents of SP_{60-7} and SP_{70-7} by aggregation.

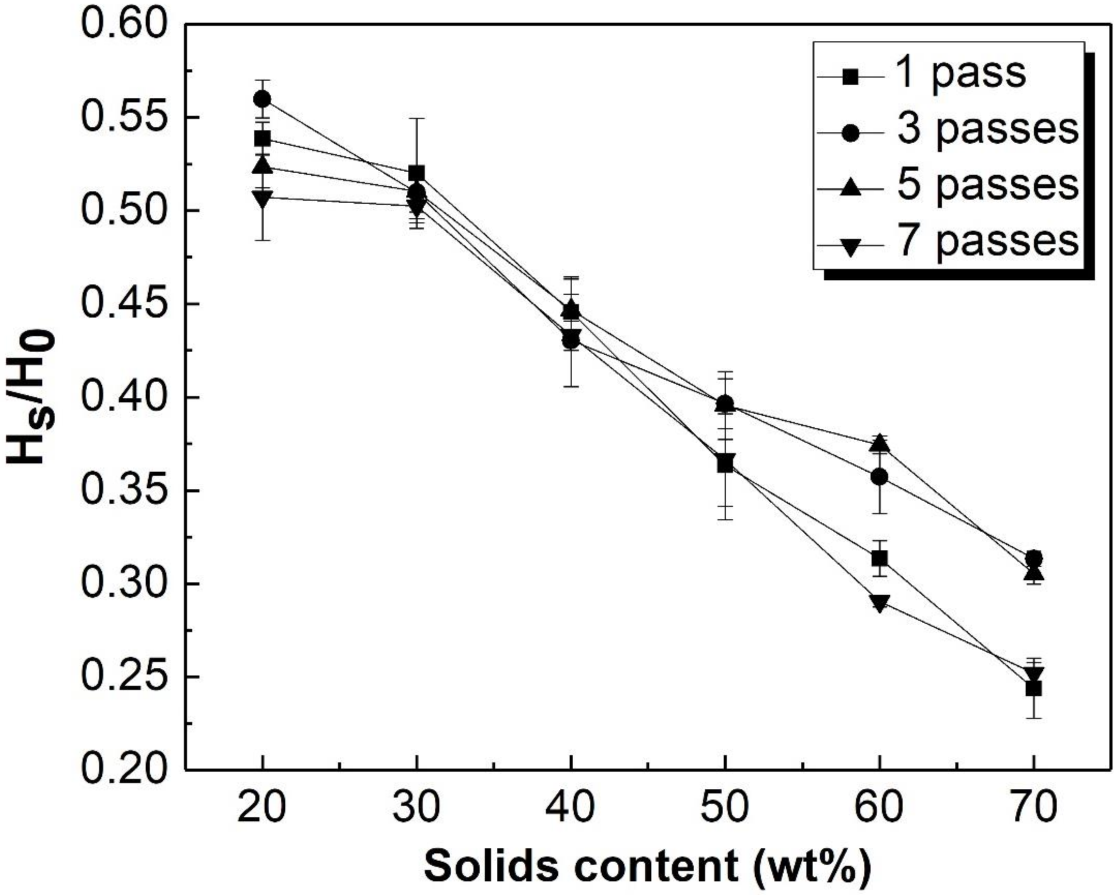

Figure 2.7. The ratios between the sediment height and total suspension height after 24 hrs free standing.

Improved specific surface area

Considering that swelling or dispersion would occur during the liquid/solid modification process of lignocellulose, the specific area was estimated by Congo red adsorption in an aqueous system rather than measured by BET with solids. As shown in Figure 2.8 of the specific surface areas of mechanical pulps, the mechanical pulps after twin-screw extrusion demonstrated higher specific surface areas than the original material. Pass 5 and 7 were compared in this analysis because notable changes in morphology of extruded pulps were observed, as shown in the above discussion. Generally, the results matched WRV with specific surface areas of the extrusion treated pulps increasing up to a solids content of 50 wt% but then decreased especially for samples SP_{60-7}, SP_{70-7} and SP_{70-5}. Slightly different from the WRVs, the specific surface areas did not significantly vary between these two passes through the extruder. The analysis indicated that mechanical pulp samples prepared in the twin-screw extruder up to 60 wt% solids content and after 5 passes can achieve the best defibrillation.

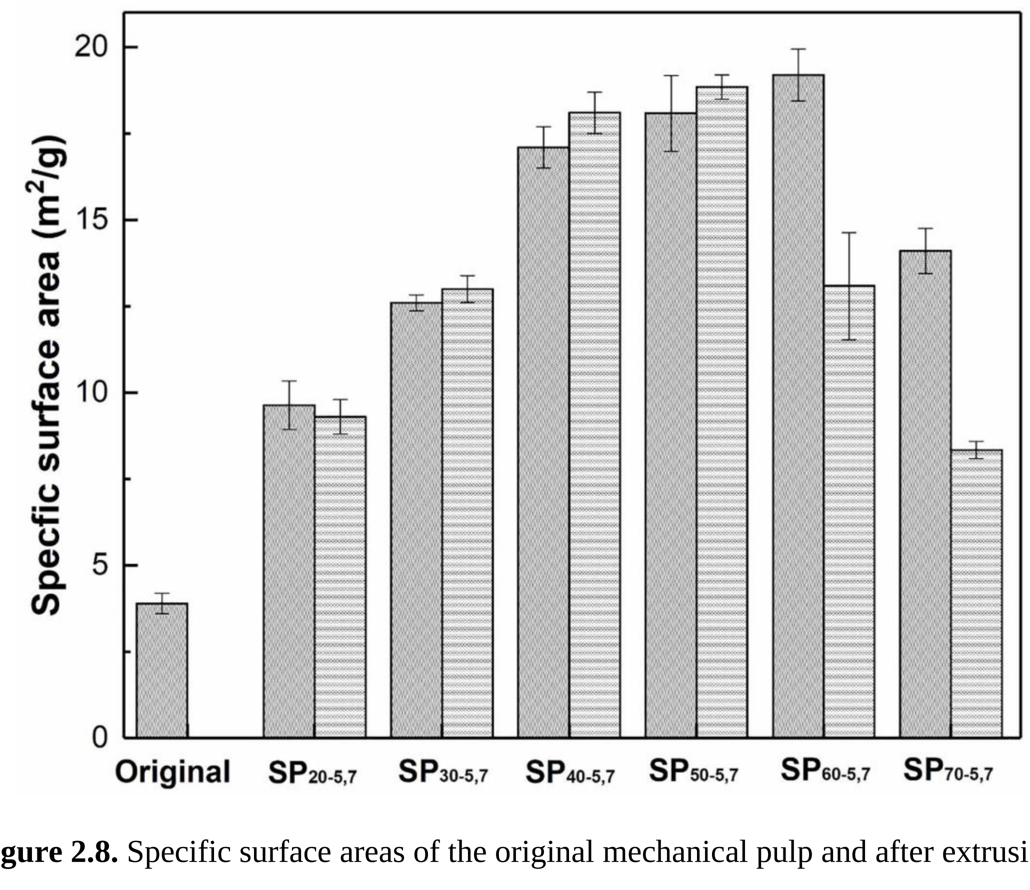

Figure 2.8. Specific surface areas of the original mechanical pulp and after extrusion at 20, 30, 40, 50, 60 and 70 wt% for 5 and 7 passes, respectively.

2.4.3 Chemical accessibility

Acetylation is an effective reaction for the chemical modification of lignocellulose, and here it was used for the evaluation of chemical accessibility of the mechanically micro-fibrillated lignocellulose. As shown in Figure 2.9 of the acetylation results of mechanical pulps, the extrusion pre-treatment not only increased the maximum content of acetyl groups that can be grafted on lignocellulose chains, but also had a noticeable effect on increasing the initial reaction rate. It was found a 96% of the maximum degree of substitution was quickly achieved for SP_{60-5} after 12 mins, whereas the original raw material needed ~24 mins. This significant increase in the initial reaction rate could reduce the feed concentration of the caustic anhydride species for the modification of lignocellulose. On the other hand, pre-treatment could allow chemical modification of lignocellulose to be carried out now in continuous reactors with short residence times, such as a twin-screw extruder, which would be beneficial for the industrialization of lignocellulose chemical conversion. SP_{30-5} showed a slower initial reaction rate than sample SP_{60-5}, which was due to the weak defibrillation of mechanical pulp at low extrusion solids content. Correspondingly, SP_{30-5} exhibited an increase in surface area by 225%, while a 360% increase for SP_{60-5} was more sufficient to make a notable impact on reactivity.

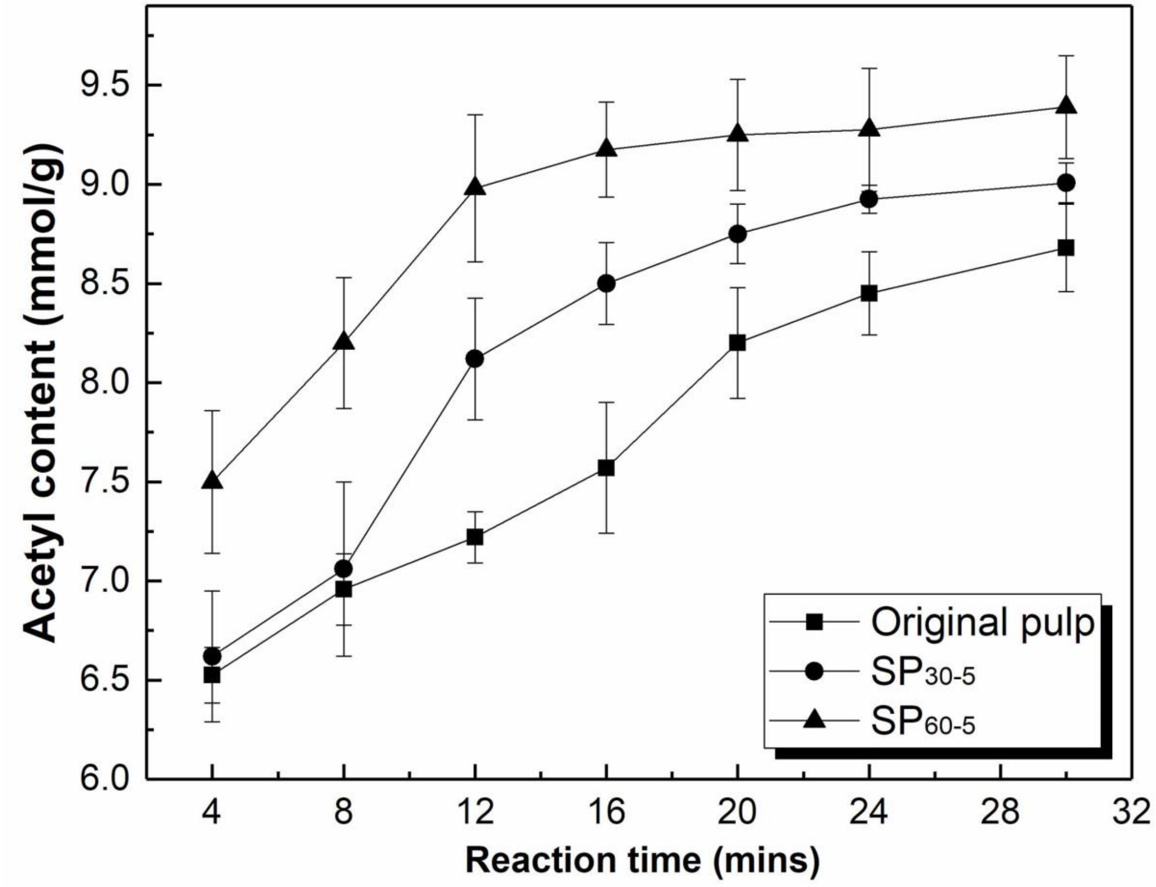

Figure 2.9. Acetylation of the mechanical pulps before and after twin-screw pre-treatment.

2.5. Conclusions

This study demonstrates high solids content twin-screw extrusion is also sufficient to micro-fibrillate lignocellulose without aggressive chemical additives, with little apparent damage to lignocellulose chains under optimal conditions. At 60 wt% solids content and after 5 passes, mechanical pulp fibers are effectively processed into 7-30 µm wide hair-like microfibrils, which demonstrated improved water retention ability (216%) and surface area (18.9 m^2/g). More interestingly, the extruded mechanical pulp still has notably improved chemical reactivity after drying. This novel high solids content twin-screw extrusion supplies an economical and clean way for the industry to pre-treat lignocellulose biomass for further processing.

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Chapter 3 Solvent-free modification of lignocellulosic wood pulp into a melt-flowable thermoplastic

This chapter introduces a new reaction method for the thermoplasticization of lignocellulose; the novelty of this method is a new wetting/functionalizing agent was designed by mimicking aspects of ionic liquids for the chemical modification of lignocellulose. The manuscript version of this chapter has been submitted to *Cellulose* for consideration of publication.

Jinlei Li conducted all the experiments and wrote the draft of the manuscript. Hongfeng Zhang conducted NMR testing and helped to analyze the results. Dr. Sacripante and David Lawton provide technical guidance on the project. Heera Marway provided technical help to mechanical testing. Dr. Thompson revised the draft to the final version.

3.1 Abstract

This paper reports on a flowable lignocellulosic thermoplastic prepared from forestry biomass by solvent-free acetylation. The non-solvent approach relies upon a functionalizing agent derived from benzethonium chloride (hyamine) and sulfuric acid that was chosen for its similar wetting attributes to an ionic liquid for the lignocellulose but was much less expensive to use. Besides acetylation, this functionalizing agent became chemically bonded to the lignocellulose by the sulfate group formed *in situ*, as demonstrated by ^{13}C NMR, infrared and elemental analysis. This attached species appeared to contribute strongly to the flowable nature of the product. The modified material showed good melt flowability by compression molding, as demonstrated in this study by the production of semi-transparent films and was characterized by differential scanning calorimetry and dynamic mechanical analysis. An experimental investigation of reaction parameters was included in the study, exploring the mechanism by which the cationic functionalizing agent modified the structure of lignocellulose.

3.2 Introduction

The decline in fossil fuel reserves will soon impact the supply chain of the polymer industry. Cellulosic thermoplastics constitute one group of many promising replacements to synthetic plastics. Cellulose is a macromolecule that is insoluble in most solvents and has no innate thermoplasticity, which is attributed to its crystallinity and strong intra- and inter hydrogen bonds. Chemical modifications can interfere with these hydrogen bonds and simultaneously introduce side groups along the cellulose backbones, which improve chain flexibility and thus afford thermoplasticity.[1–5] Often, thermoplasticization of cellulose requires substantial plasticizer content in addition to chemical modification of its chains. However, the manufacturing of current cellulose thermoplastics like cellulose acetate, cellulose acetate propionate or cellulose acetate butyrate are costly, especially as compared with competitive petroleum-based thermoplastics.[6]

The production of cellulose thermoplastics currently relies on using a large excess of acetic acid to swell and disperse the insoluble fibrillar mass for chemical modifications.[7] Using such a high amount of reactant leads to high costs in the manufacturing of cellulose thermoplastics even though this process recycles much of the residual acetic acid after the modification. Although cellulose obtains better thermoplasticity when longer side-chain substituents are incorporated,[8,9] their incorporation generally requires harsher reaction conditions, which means higher manufacturing costs. Over the past decades, some new solvents, *e.g.,* dimethylacetamide/LiCl,[10] dimethyl sulfoxide/tetrabutylammonium fluoride[11] and imidazolium-ionic liquids,[2,12,13] have been developed to dissolve cellulose for chemical modifications. Dissolving improves reactant accessibility to cellulose compared to swelling, making it easier to add long-chain substituents and giving greater access to all reaction sites along the chain backbone.[2,10,12,13] But, chemical modification with these new solvents is still questionable from an industrial standpoint because cellulose exhibits quite a low solubility (<6 wt%) in them, and these solvents are significantly more costly for industrial use than the alternative of using excess acetic acid. Some researchers have tried to improve the economics by partially derivatizing cellulose as the first step of modification to making cellulose soluble in less expensive organic solvents, then carrying out the incorporation of long-chain substituents in the second stage as solutions.[8,14,15] The reactivity of the cellulose is reportedly low in these organic solvents after the first step of derivation.

The purpose of the current study is to develop a thermoplastic cellulosic material from lignocellulose with suitable flow properties for conventional processing equipment. Working with lignocellulose rather than highly purified cellulose eliminates costly pre-processing steps and makes use of lignin, which is increasingly being considered for thermoplastics itself.[16] There are reported preparations of thermoplastics directly from lignocellulose[17–19] using similar heterogeneous or homogenous processes as used for cellulose and in those cases, lignocellulose has displayed similar or even a poorer solubility than cellulose.[20,21] The poor dispersive nature of cellulosic materials makes our investigation of an alternative wetting agent more critical, especially if solvent recovery is viewed as undesirable and we ultimately seek to develop a bulk reactive extrusion process from the studied chemistry. A novel functionalizing agent made by cationic surfactant/sulfuric acid is introduced in this work for the acetylation of lignocellulose in order to prepare a bio-thermoplastic without need of plasticizer addition. The influence of this functionalizing agent is studied in detail for its participation in the modification of lignocellulose.

3.3 Experimental

3.3.1 Materials

Lignocellulosic wood pulp containing 8.2 wt% acid-insoluble lignin (determined by TAPPI-T method 222 om-02) was received from Tembec (Montreal, Canada). The received pulp was mechanically wet pulverized in a 27 mm 40 L/D corotating twin-screw extruder

(Leistritz, USA) according to a previously published method.[22] The previous study where the method was published, showed the pre-treatment improves the degree of fibrillation of the received lignocellulose, thus improves chemical accessibility to the lignocellulose. Benzethonium chloride (hyamine, HPLC grade), dimethyl sulfoxide (DMSO) (reagent grade) and sodium bicarbonate (ACS grade) were purchased from Sigma Aldrich (Oakville, Canada), while acetic anhydride (reagent grade), sulfuric acid (trace metal grade) and anhydrous ethanol (reagent grade) were obtained from Caledon Laboratory Ltd. (Georgetown, Canada).

3.3.2 Chemical modification of lignocellulosic wood pulp

Dissolution of sulfuric acid/hyamine in acetic anhydride

Different concentrations of hyamine were dissolved in 6 mL acetic anhydride at 120 °C under constant agitation to form a solution. Similarly, different amounts of sulfuric acid were added to the acetic anhydride solution and then stirred for 10 mins. Two series of solutions were prepared to investigate the influence of the ratio between sulfuric acid and hyamine used, and the amount of sulfuric acid/hyamine added to acetic anhydride, on the modification of the lignocellulosic pulp. In the first set of trials, sulfuric acid was kept constant at 13.4% (w/w) relative to the pulp while the amounts of hyamine were varied as 0.32, 0.63, 1.25, or 2.50 g in the solution. The molar ratio of sulfuric acid/hyamine as a functionalizing agent in these trials was 1.96, 0.98, 0.49 or 0.25, respectively. The second set of trials involved a fixed sulfuric acid/hyamine ratio at 0.49 while varying the total amount of sulfuric acid (13.4, 26.8 and 40.2% (w/w) relative to the pulp) added to the solution.

To investigate the nature of the functionalizing agent formed in the acetic anhydride solution, the anticipated salt was regenerated by heating the solution (without pulp) at elevated temperature of 165 °C to evaporate the acetic anhydride. After cooling down to room temperature, the obtained salt was vacuum dried to a constant weight. The dried salt was then rinsed with water, and finally purified by recrystallization from ethanol solution.

Modification of lignocellulose in sulfuric acid/hyamine solution

In this study, the purpose of the experiments was to maximize conversion and better understand the functionalizing agent, whereas the excessive amounts of reactants will be reduced in future studies for bulk processing by reactive extrusion. A slurry was created by adding 1 g of the extrusion-fibrillated lignocellulosic pulp into the acetic anhydride solution mentioned above, and the modification was allowed to proceed at 120 °C for 30 minutes. At the end of these reactions, the modified pulp slurry or paste was precipitated in ethanol. After stirring overnight, the modified pulp was filtered, re-dispersed in deionized water, neutralized to a pH of 7 by dropwise addition of a 1 M sodium bicarbonate and then washed repeatedly by distilled water until the conductivity of the washing filtrate was close to the distilled water. Finally, the modified pulps were filtered and vacuum-oven dried at 75 °C for 24 hours before characterizations.

Modification of lignocellulose by acetic-acid process

For comparison, lignocellulose acetate was prepared by the conventional acetic acid method.[23] Briefly, 1g extrusion-fibrillated wood pulp was first activated by 1 mL of acetic anhydride at 40 °C for 30 mins, then added to a solution containing 2.8 mL of acetic anhydride, 5 mL of acetic acid and 4% (w/w) sulfuric acid catalyst relative to the weight of the pulp. The reaction temperature was gradually increased to 77 °C from 25 °C within 10 minutes, then kept at 77 °C for 20 minutes. The high reaction temperature of 120 °C used in the method with the functionalizing agent was not suitable for the acetic acid method because of the substantial degradation of the wood pulp that would result. At the end of modification, the modified lignocellulose was purified by the same procedure used for the sulfuric acid/hyamine system.

3.3.3 Compression molding of the modified pulps

Modified lignocellulose was placed between two Teflon sheets and sandwiched between two stainless plates. The sandwich was hot-pressed at 180 °C under 3 metric tons force for 2 mins in a Carver 4389 benchtop hydraulic press, then hot-pressed under 7.5 metric tons for another 10 mins to form a film.

3.3.4 Characterizations of modified lignocellulosic wood pulp

Morphology analysis

Morphology of modified lignocellulosic pulp at the end of the reaction was determined by a light microscope (Axioplan 2, Carl Zeiss, German). Modified wood pulp slurry or paste was dropped on a pre-cleaned glass slide, immediately covered with a glass clip, and then observed and imaged under the microscope.

Structural characterizations

Fourier-transform infrared spectra (FTIR) were collected on a Nicolet 6700 spectrometer with a Smart iTRT^{M} attenuated total reflectance (ATR) sampling accessory.

The data was generated from 32 scans in the range of 4000-500 cm^{-1} with a 4 cm^{-1} resolution. Solution state ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy were performed in the DMSO-d6 solvent by using a Bruker AVIII 700 MHz spectrometer at ambient temperature. Elemental nitrogen and sulfur contents were determined with a UNICUBE elemental analyzer (Elementar).

Acetyl content of the modified pulp was determined by colorimetric titration. Dried modified pulp, 0.05 g, was put into a 25-mL glass vial, to which was added 5 mL of 0.25 M NaOH and 5 mL anhydrous ethanol. The mixture was left to stand for 24 h before 10 mL 0.25 M HCl was added to the system. After 30 mins, the mixture was titrated using 0.25 M NaOH with phenolphthalein indicator. The grafted ester group content was calculated by:

$$\text{Acetyl}\left(\frac{\text{mmol}}{\text{g}}\right) = \frac{(V_1 + V_2)C_1\text{-}V_3C_2}{m} \qquad (1)$$

where V_1 (mL) is the volume of NaOH added to the system before the titration, V_2 (mL) is the volume of NaOH consumed in the titration, C_1 (M) is the NaOH concentration, V_3 (mL) is the volume of HCl added to the system before the titration, C_2 (M) is the concentration of HCl, and m is the weight of the sample.

Intrinsic viscosity was used to assess the degradation of the modified pulp samples with a Cannon Fenske viscometer (25-tube size). Dried sample was added to DMSO solvent and stirring overnight to dissolve the pulp; the insoluble part was separated by filtering and dried for determination of the concentration (*c*) of the solution. The solvent or pulp solution flowed through the viscometer held at 25 °C, and flow times through the graduated region were recorded. The intrinsic viscosity was estimated as the intercept of the plot of inherent viscosity versus concentrations. Inherent viscosity (η_{inh}) was determined from the flow times of the DMSO solvent (t_0) and pulp solution (t), according to:

$$\eta_{inh} = \text{In}\left(\frac{t}{t_0}/c\right) \qquad (2)$$

Thermal properties

Thermal transitions were analyzed using a Q200 differential scanning calorimeter (DSC; TA Instruments, USA) operating in modulated mode. Modified pulp, 9 mg, was loaded and sealed in a Tzero aluminum pan. A hole was punched on the lid to allow the release of water vapor during the test. Samples were equilibrated at -40 °C, then heated to 240 °C at a ramp rate of 5 °C /min, with an oscillation of 1.00 °C every 60 seconds.

The thermoplasticity was evaluated by a dynamic mechanical analyzer 850 (DMA; TA Instruments, USA) with tensioning cantilever geometry. DMA measurements were performed on strips with a dimension of 17 mm × 5 mm × 0.2 mm cut from the hot-pressed films at a frequency of 1 Hz and a strain of 0.01%. The temperature was ramped from 20 to 240 °C with a heating rate of 3 °C/min.

Mechanical properties

The tensile properties of compression-molded films were determined with an Instron universal mechanical testing system (Model 3366). Strips with a dimension of 40 mm × 10 mm × 0.2 mm were cut from the film. Tensile testing was performed at a crosshead speed of 0.083 mm/min, and the force was recorded with a 0.05 kN load cell. Mechanical properties were reported as the average of three repeats.

3.4 Results and discussion

3.4.1 Acetylation in the presence of the functionalizing agent

When sulfuric acid and hyamine were present with acetic anhydride, the acetylation of lignocellulose needed no solvent to improve wetting of the fibrous mass. Since sulfuric acid is a catalyst for esterification, the functionalizing agent served this purpose as well as a wetting agent. The interaction of sulfuric acid with hyamine was essential for the dispersion of lignocellulose in the non-solvent reaction system otherwise reaction conditions were notably poor with hyamine alone. Figure 3.1a shows the wood pulp displayed no dispersion in the reaction system without sulfuric acid, maintaining its granular form. With the inclusion of sulfuric acid, the molar ratio between sulfuric acid and hyamine played an important role in dispersing lignocellulose in the non-solvent reaction system. Over a sulfuric acid/hyamine ratio from 0.25-0.5, the pulp became increasingly easier to disperse in the reaction medium as the ratio increased. Figure 3.1b shows visible fibrous mass still present at the end of the reaction for a sulfuric acid/hyamine ratio of 0.25 but then, an almost homogenous system was seen (Figure 3.1c) at a ratio of 0.49. Further increasing the sulfuric acid/hyamine ratio kept the lignocellulose homogenously dispersed, but with a corresponding increase in degradation, which was denoted by the blackening of the reaction medium (referring to the inserted photo in Figure 3.1d).

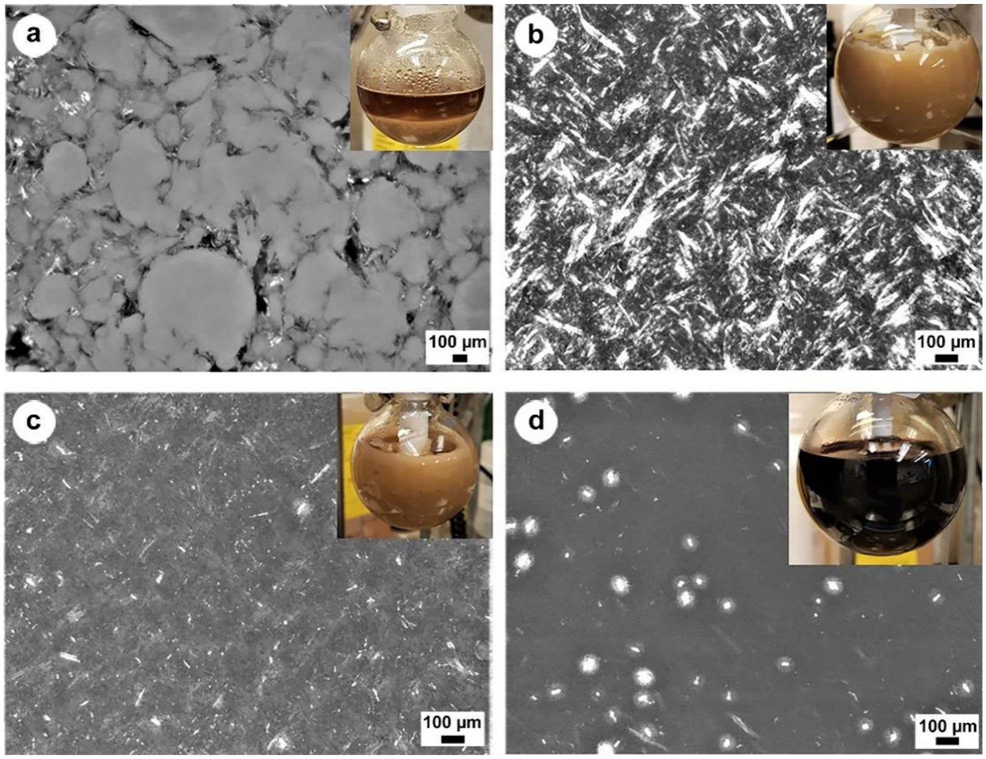

Figure 3.1. Light microscope images of the solution dried onto a glass slide at the end of the reaction with the (a) presence of hyamine or (b-d) sulfuric acid/hyamine with different ratios (0.25, 0.49 and 1.96). Inserted photo shows the state of the reaction vessel at the end of the reaction.

Degradation of pulp from the modification was quantified by measuring the inherent viscosity of the soluble part of the modified samples dissolvable in DMSO. This analysis was not possible for the sample using 13.4% (w/w) sulfuric acid at a 0.25 molar ratio of sulfuric acid/hyamine because it had negligible solubility in DMSO, similar to the original pulp. Since a baseline viscosity measurement for the original lignocellulose was not possible, this discussion is limited to commenting on trends seen in the data. As shown in Figure 3.2, lowest inherent viscosity corresponded to a 1.96 molar ratio of sulfuric acid/hyamine (sulfuric acid content fixed at 13.4% (w/w) relative to the pulp), producing the black liquid mentioned before; with lower sulfuric acid/hyamine ratios, intrinsic viscosity increased as noted by the climbing intercept values for the curves. Sulfuric acid is only considered as a solvent, with no degradative nature, towards cellulose at very low temperatures (-20 °C).[24] The presence of hyamine significantly decreased the extent of degradation by sulfuric acid, even at high reaction temperature (120 °C), but also maintained the solvation properties of the acid. The benzethonium-based salt recovered from the acetic anhydride solution displayed an additional chemical shift at 9.65 ppm within the ^{1}H NMR spectra not seen with pure hyamine (Figure 3.3). The shift corresponds to a bisulfate,[25] indicating that benzethonium bisulfate had formed in the solution. The weaker acidity of the system reduced the degradative effects on lignocellulose, but still displayed a solvation or deconstruction ability to lignocellulose. To optimally disperse lignocellulose and minimize degradation, a molar ratio of 0.49 appeared ideal.

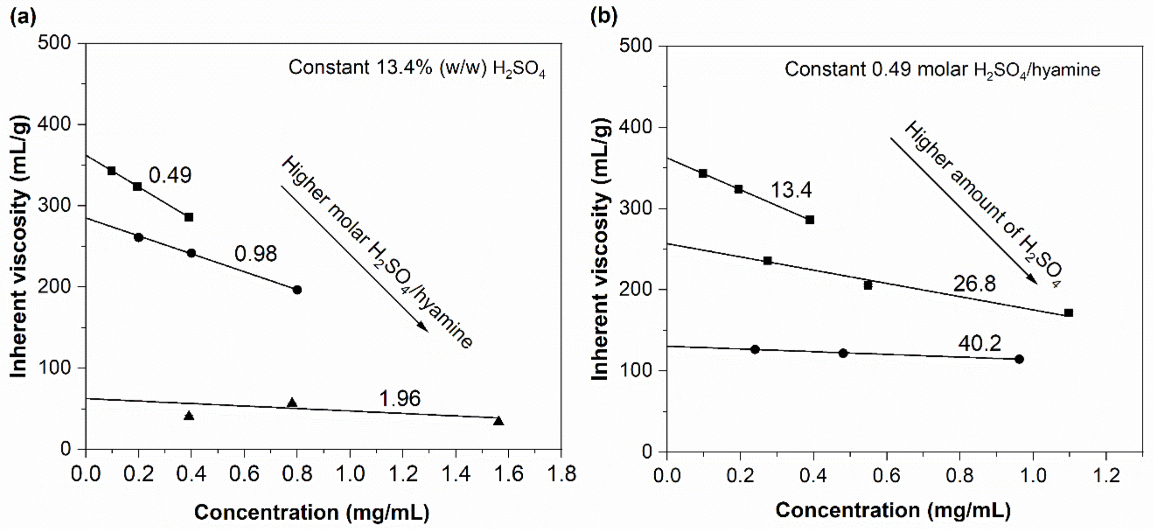

Figure 3.2. Inherent viscosities of modified pulp samples in the first (a) and the second (b) set of trials.

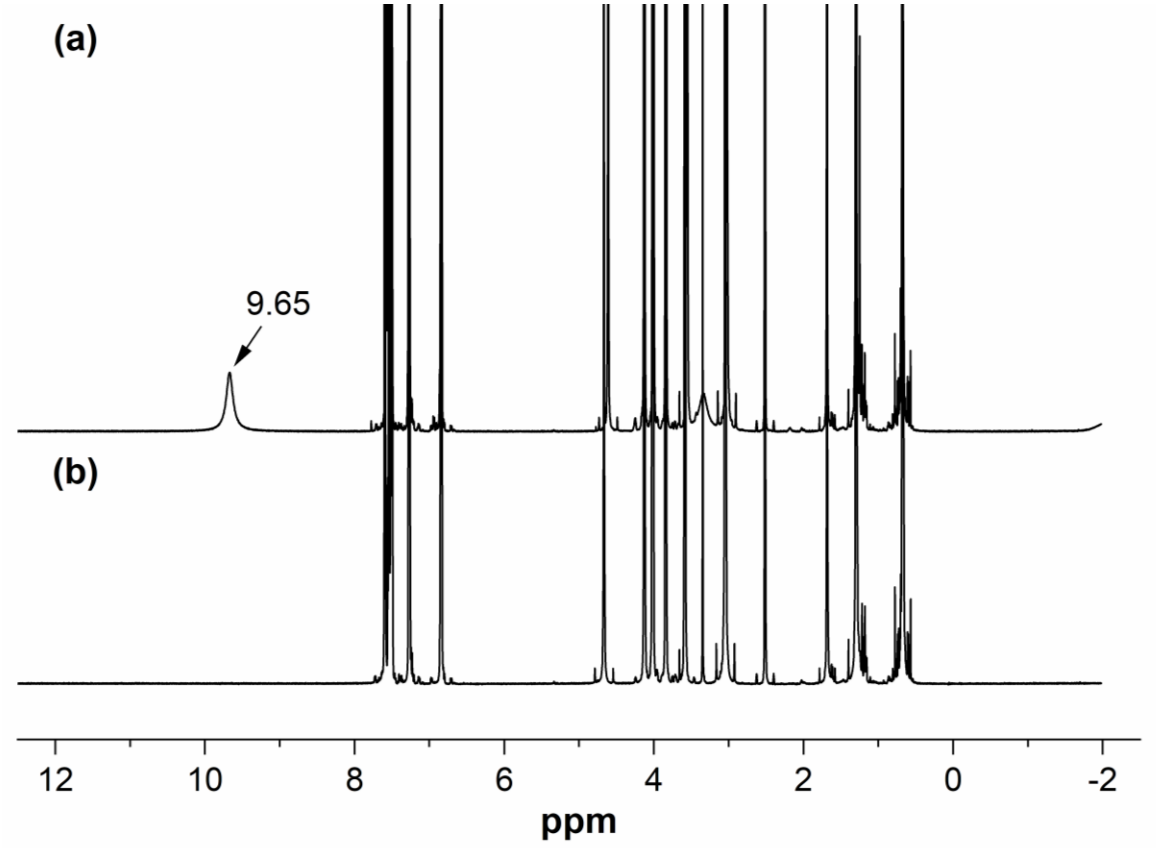

Figure 3.3. ^{1}H NMR spectra of hyamine (a) and the "hyamine" (b) regenerated from its acetic anhydride solution with the presence of sulfuric acid.

3.4.2 Chemical structures of the modified lignocellulosic wood pulp

Characteristic peaks for the acetyl groups of polysaccharide acetates are seen in the spectra at 1740 cm^{-1} (C=O ester stretching), 1365 cm^{-1} (C-H bending of acetyl groups) and 1230 cm^{-1} (-C=O- stretching of acetyl groups)[19]. Although lignocellulose naturally has trace acetyl groups, the characteristic peaks in the modified sample were much stronger than the original material (Figure 3.4), showing successful acetylation in the presence of the sulfuric acid/hyamine. Correspondingly, there was a decrease in hydroxyl functionality in the modified sample, noted by the disappearance of the strong absorbance at 3330 cm^{-1} originally seen in the lignocellulose (Figure 3.4).

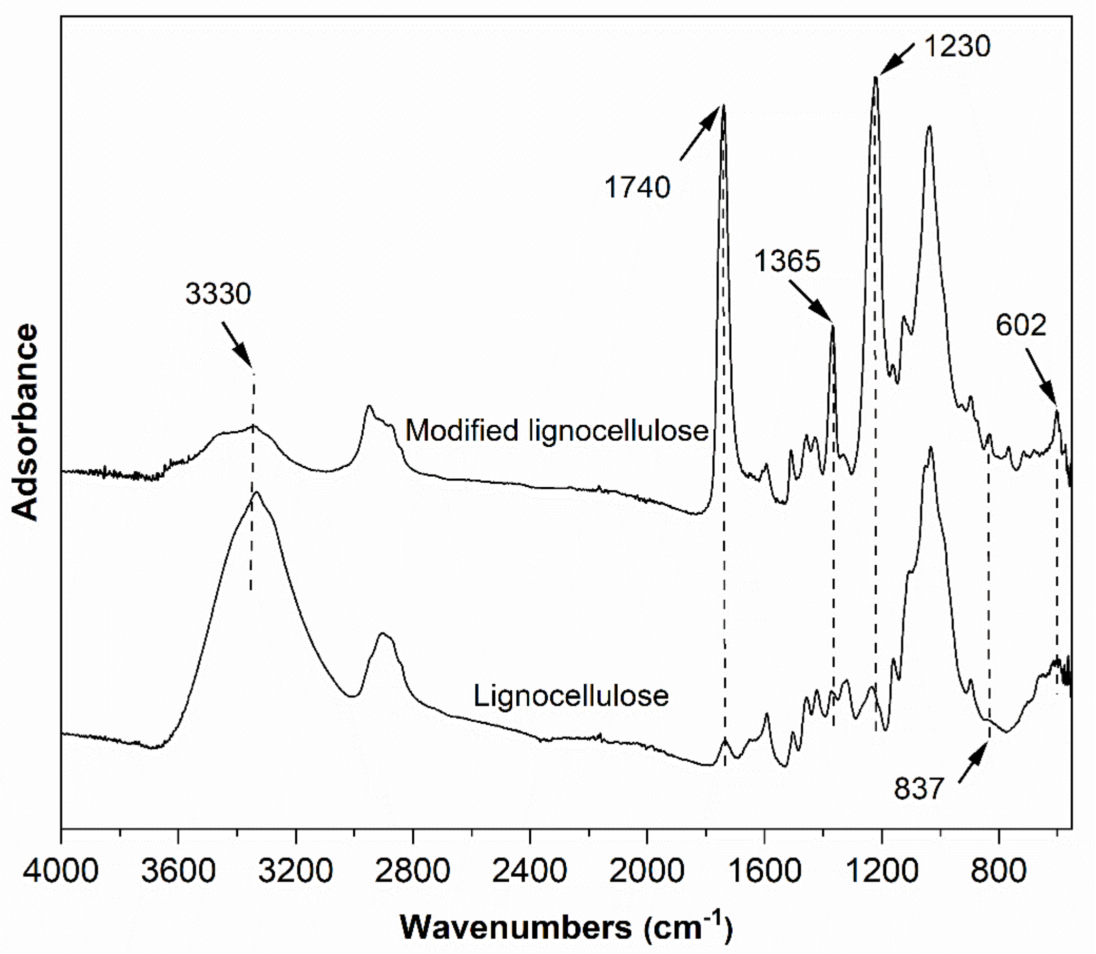

Figure 3.4. FTIR spectra of lignocellulose and modified lignocellulose using 13.4% (w/w) sulfuric acid and 0.49 molar ratio of sulfuric acid to hyamine.

The acetylation was also evident by solution-state ^{13}C NMR. Figure 3.5 shows two significant groupings of chemical shifts in the modified lignocellulose at 168.90-171 ppm and 20-20.55 ppm, corresponding to the carbonyl and methyl groups of the acetyl functionality, respectively.[26] Solution-state ^{13}C NMR also found the hyamine attachment by comparing the spectrum of the modified pulp versus hyamine. The spectrum for the modified sample includes all chemical shifts attributed to hyamine, as labelled with solid arrows (downward pointed) in the Figure 3.5. The benzethonium cation was not readily detected by FTIR, being low in concentration and typically present between 1200-1500 cm^{-1} which were indistinguishable from the broad lignocellulose peaks. It is evident by the peak intensities that few hydroxyl functionalities of the original lignocellulose became sites for the functionalizing agent compared to acetyl groups. However, a sulfate functionality was detected in the modified sample, at 837 cm^{-1} (C-O-S symmetrical vibration) and 602 cm^{-1} (bending mode of sulfate).[27,28] To investigate the nature of functionalizing agent attachment based on reaction conditions, elemental analysis was conducted.

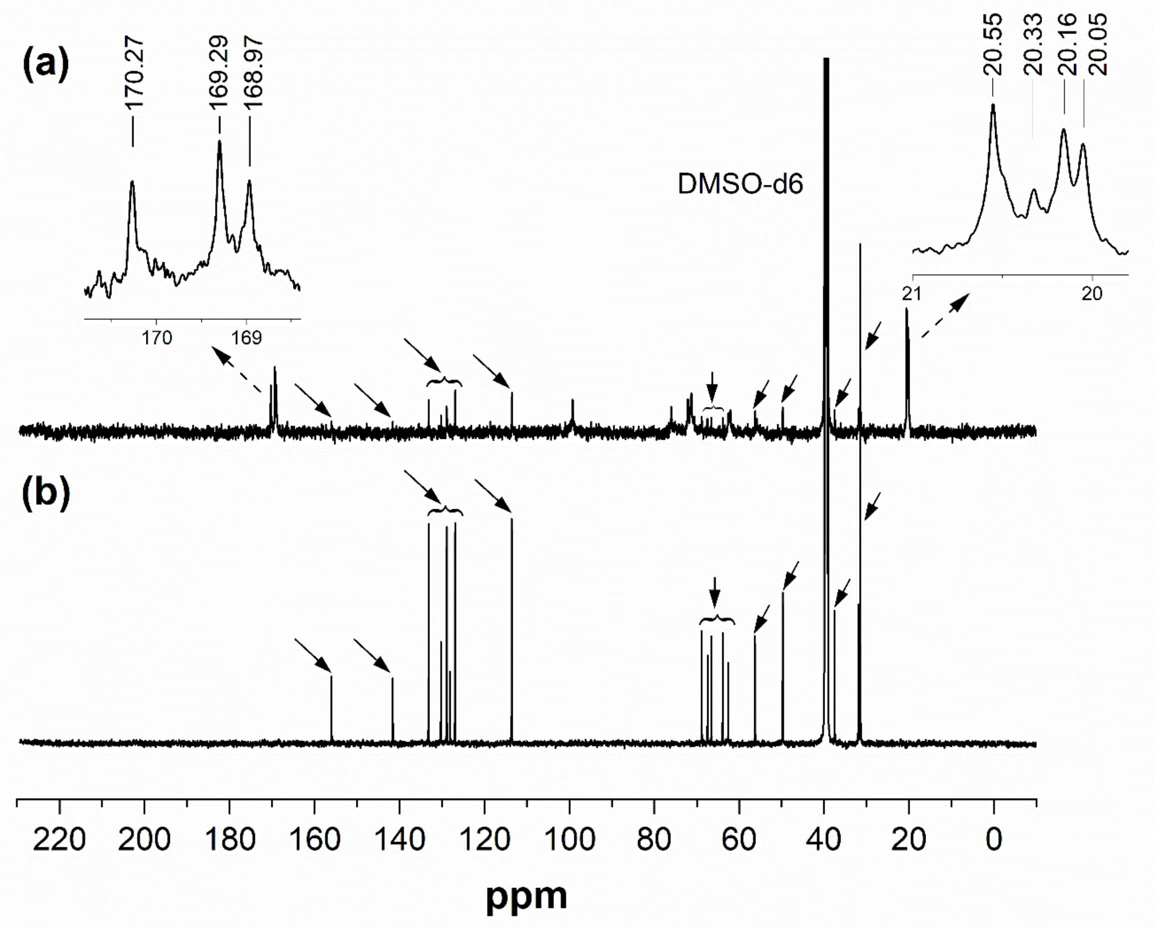

Figure 3.5. ^{13}C NMR spectra of modified lignocellulose using (a) 13.4% (w/w) sulfuric acid and 0.49 molar ratio of sulfuric acid to hyamine, and (b) pure hyamine. Downward pointed arrows highlight the chemical shifts of hyamine in the modified pulp, while upward dashed arrows are related expanded peak regions to the original spectrum.

Results of the elemental analysis are presented in Figure 3.6. In its received form, the lignocellulosic had a small but detectable elemental nitrogen (N) and sulfur (S) content; the elements showed up in repeated testing and thus were concluded as trace contaminants in the supplied wood pulp. Modified samples showed a substantial increase in N and S content when acetylated in the presence of the functionalizing agent (sulfuric acid/hyamine), reaffirming the findings by infrared and ^{13}C NMR analysis that hyamine and sulfate species had chemically bonded to the pulp acetates during the reaction. In the presence of only hyamine but no sulfuric acid (highlighted by a rectangle symbol in Figure 3.6a), the modified sample showed no increase in S relative to the supplied pulp, and only a slight increase in N; since lignocellulose itself can be negatively charged as a result of pulping,[29] the small increase in N without sulfate groups present is plausible. The need for sulfuric acid in grafting hyamine to the lignocellulose species suggested that it was primarily attached as a benzethonium sulfate. Sulfate groups readily form in lignocellulose within the presence of bisulfates or sulfuric acid,[27,30] making this mode most likely. The grafted benzethonium sulfate formed either directly by reaction of benzethonium bisulfate (which has been notably detected in the acetic anhydride solution) or by a two-step reaction via sulfation by sulfuric acid first, and then interaction with the benzethonium cation of hyamine.[31,32] The molar ratio (R) of N to S elements in the modified samples provided greater details on the modes of attachment:

$$R = \frac{(\text{N-N}_\text{i})/14}{(\text{S-S}_\text{i})/32} \qquad (3)$$

where N and S corresponded to a modified pulp while N_i, and S_i corresponded to the sample modified with the presence of only hyamine. The R values for the two experimental series were included in Figure 3.6 as dashed curves. For most sulfuric acid/hyamine conditions, R was around 1.2, which was slightly above molar equivalence. Excessive benzethonium surrounding the bound sulfate was thought to be adsorbed via hydrophobic interactions with bound hyamine.[33] The only case where R dropped below unity was at a sulfuric acid/hyamine ratio of 1.96 where N and S values closely resembled the case where only hyamine was used (i.e. sulfuric acid/hyamine ratio of zero in Figure 3.6a). Functional agent attachment was not significantly evident at both low and excess concentrations of sulfuric acid in these tests.

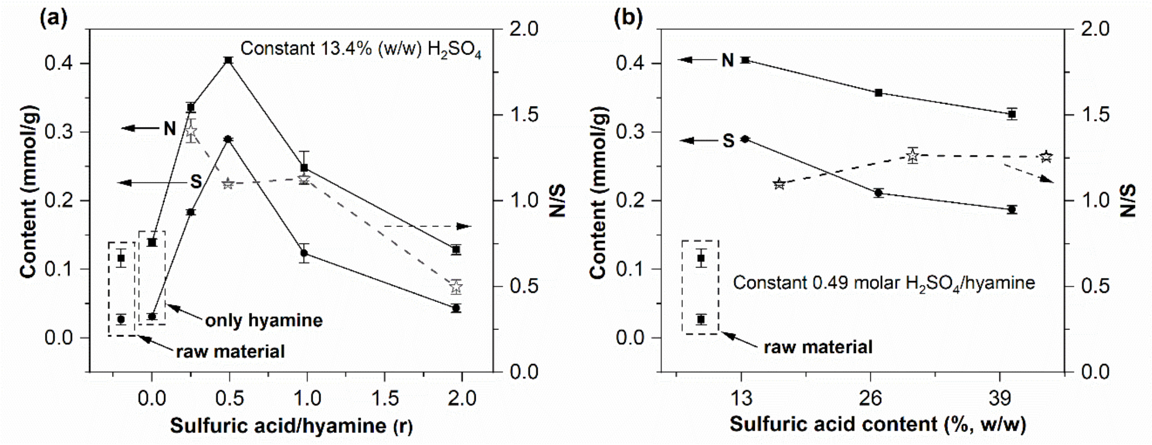

Figure 3.6. Nitrogen (N) and sulfur (S) elemental content and N/S ratio detected in the original lignocellulose and modified lignocellulose samples from the (a) first set and (b) second set of trials.

Based on the above spectral and elemental analysis, as shown in Figure 3.7, in the course of acetylating lignocellulose in the presence of hyamine/sulfuric acid functionalizing agent, hydroxyl groups were substituted with acetyl, benzethonium sulfate and possibly sulfate species; hyamine could be chemically bound to the lignocellulose pulp via sulfate anion (moiety 1) or associated with already bound benzethonium via hydrophobic end group attraction (moiety 2).

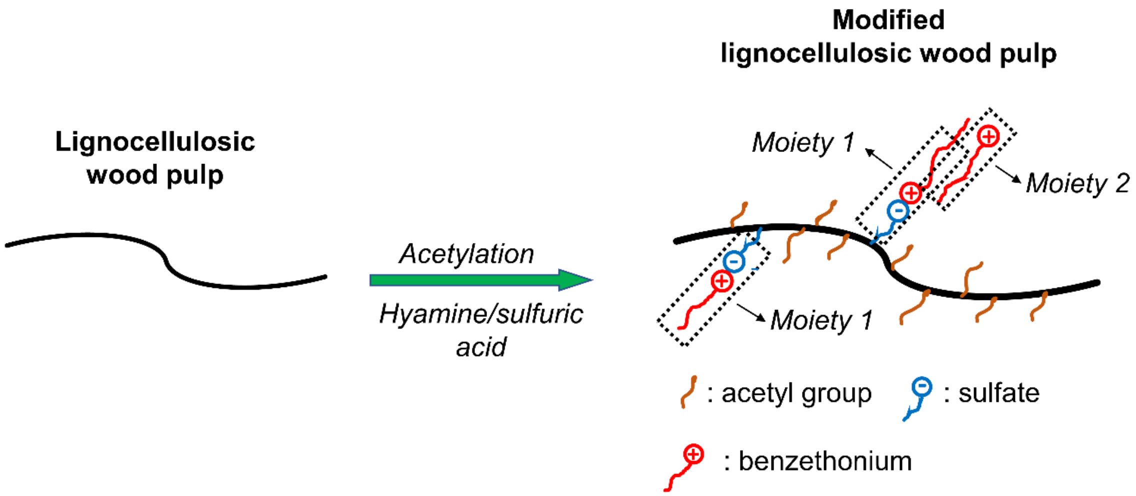

Figure 3.7. Proposed reaction scheme of modifying lignocellulosic wood pulp by acetic anhydride and hyamine/sulfuric acid functionalizing agent.

3.4.3 Influence of reaction conditions

For the purpose of estimating the extent of conversion, we assume the amount (mmol/g) of moiety 1 was molar equivalent to the sulfur content of the modified sample after subtraction of S content of the original pulp. The amount of moiety 2 was the molar difference between N and S content of the modified sample after subtraction of S and N content of the sample modified in the presence of hyamine, as indicated by Equation (4):

$$\text{Moiety 2 (mmol/g)} = (\text{N-N}_{\text{i}})\text{-}(\text{S-S}_{\text{i}}) \qquad (4)$$

where N, S and $\text{N}_{\text{i}}, \text{S}_{\text{i}}$ were nitrogen, sulfur contents (mmol/g) of the modified wood pulps with the presence of sulfuric acid/hyamine and only hyamine, respectively. In the cases of both moieties, sulfate attachment without hyamine was ignored in the calculations though at the highest sulfuric acid/hyamine ratio, such attachments may have existed. Acetyl content was estimated by NaOH hydrolysis and titration. A summary of acetyl content as well as estimated moiety 1 and moiety 2 attachments are given in Figure 3.8. Although

NaOH can also hydrolyze sulfate group, hydrolysis of sulfate species at low NaOH concentration (0.5 wt%) will be limited,[34] especially for sulfates with a large counterion (benzethonium), which normally improves stability.[35,36] The error associated with the titration should be considered small since the amount of sulfate esters (0.01-0.26 mmol, based on elemental analysis), was minor as compared to the acetyl content value determined by titration (2.4-8.9 mmol).

In the first experimental series (Figure 3.8a), the acetylation content increased with the increasing sulfuric acid/hyamine ratio, though the rate of modification relative to the ratio was highest up to 0.49. However, it was only above a ratio of 1.0 that the rate of modification significantly declined. The sample acetylated without sulfuric acid showed the lowest acetyl content of 2.5 mmol/g. All prepared samples had a lower acetyl content compared to the sample prepared by the acetic acid solvent method (10.2 mmol/g). Comparatively, functionalizing agent attachment increase with the sulfuric acid/hyamine ratio up to 0.49 (both moiety forms) and then declined at higher ratios. When sulfuric acid/hyamine ratio was lower than 0.49, excessive hyamine tended to convert sulfuric acid into bisulfate that had a low reactivity towards lignocellulose and catalyzing ability for the acetylation [30]. When the sulfuric acid/hyamine ratio was higher than 0.49, the declining presence of hyamine in the reaction system (fixed sulfuric acid content) increased the system acidity that was beneficial to the acetylation of lignocellulose,[37] but improved acetylation subsequently decreased the hydroxyl functionality sites for the functionalization agent attachment since the competition between the two reactions. The declining presence of hyamine was not beneficial to the formation of benzethonium sulfate.

Others have reported that sulfate groups (-SO_3H) will be partially replaced by acetyl group,[38,39] when sulfation and acetylation occur simultaneously in the reaction, but sulfate with large counterion (benzethonium) was more structural stable [35,36]. Additionally, high acidity causing degradation would reduce the sulfur content, thus decreased the functionalizing agent attachment in the final product.[40] The degradation of wood pulp did not have any observed negative effect on the acetylation, which was because of the degree of acetylation was much higher than that of the functionalization by sulfuric acid/hyamine.

In the second set of experiments, influence of the amount of functionalizing agent on the reaction was examined (Figure 3.8b). The sulfuric acid/hyamine ratio was constant (at 0.49, seemingly optimal in the first experiments) in this series while the sulfuric acid content was increased. The acetyl content showed little change as the sulfuric acid content increased, indicating the higher amount of functionalizing agent present did not improve the rate of reaction. In general, increasing the sulfuric acid content (and functionalizing agent content) in the reaction system resulted in small decreases in both acetyl content and moiety 1 content whereas moiety 2 showed a slight increase. However, significant hydrolysis occurred in the presence of the higher sulfuric acid was noted by intrinsic viscosity measurements earlier, indicating that system acidity was increasing. The rising acidity may explain the decrease in moiety 1. Conversely, the large amounts of hyamine in the reaction system, while beneficial to coordinating with those moiety 1 groups attached, resulting in a higher moiety 2 content, may have also reduced accessibility of the hydroxyl groups of the lignocellulose to acetic anhydride[11].

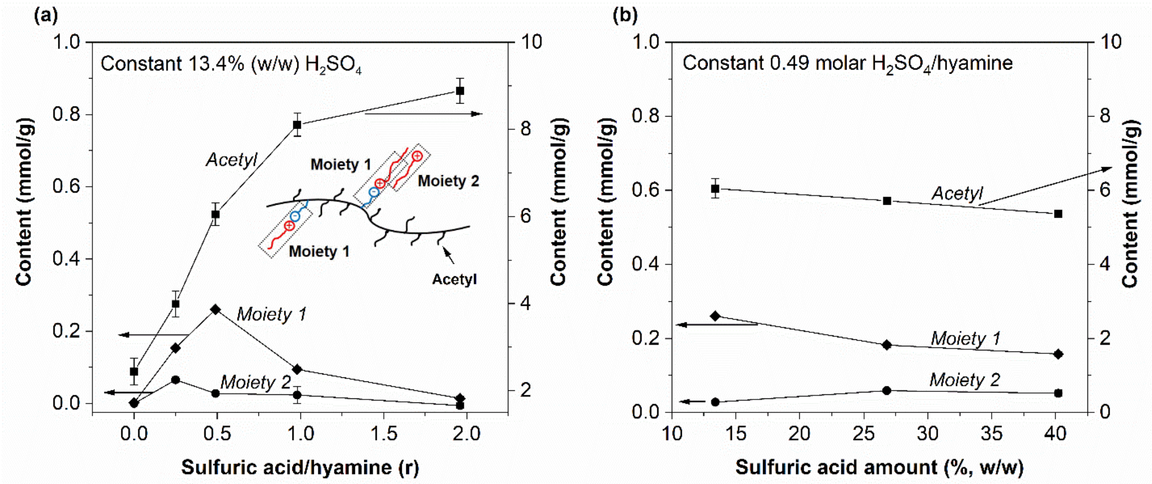

Figure 3.8. Extent of acetylation and functionalization by the functionalizing agent in the modified lignocellulose, based on the (a) first series and (b) second series of experimental trails.

3.4.4 Thermoplasticity

Figure 3.9 presents the DSC thermogram of the original pulp and sample acetylated in the presence of only hyamine showed an endothermic transition at 133 °C but no glass transition. The extractives in the wood pulp, including fats, phenolics, resin acids and waxes, contributed to this seemingly endothermic peak. This peak was not found in samples with sufficient acetylation to disrupt the hydrogen bonding of the pulp, confirming the poor extent of reaction for the sample prepared in the presence of only hyamine. The highly acetylated lignocellulose prepared by the acetic acid solvent method displayed an apparent glass transition temperature (T_g) at 164 °C, which is lower than the 180-200 °C reported for pure cellulose acetate due to the inclusion of acetylated lignin.[9] The modified pulp with functionalizing agent showed a glass transition at around 161 °C (T_{g1}), close to the acetic acid solvent modified sample, and another at 123 °C (T_{g2}). The bulky size and sparse attachment of the benzethonium group afforded greater chain mobility as a distinct phase in the modified pulp. The improved thermoplasticity seen in subsequent tests for the modified pulp by the sulfuric acid/hyamine approach compared to conventional acetylation can be directly attributed to this newly emerging phase.

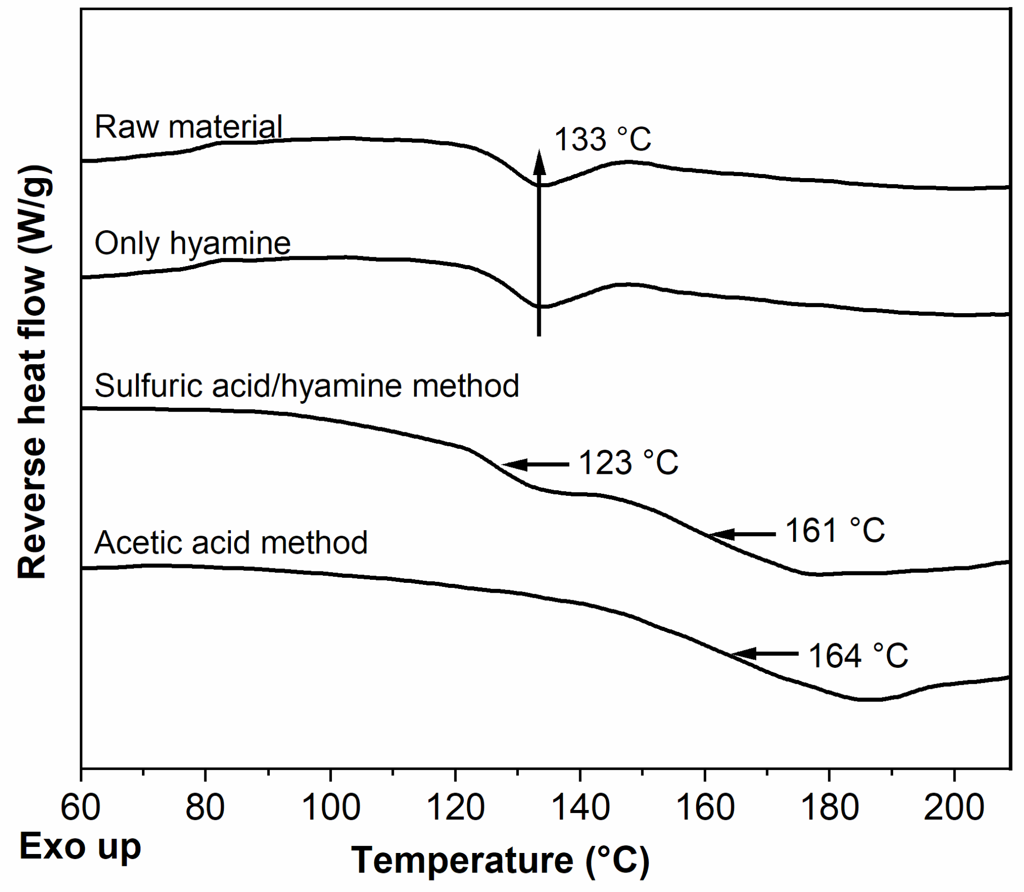

Figure 3.9. Modulated DSC results of the raw material and modified pulps by three different processes. The lignocellulose acetate had an acetyl content of 10.2 mmol/g prepared by the acetic acid method compared to 2.5 mmol/g for the case prepared with hyamine only. The modified lignocellulose prepared by sulfuric acid/hyamine method had an acetyl content of 6.0 mmol/g and 0.3 mmol/g functionalizing agent (moiety 1).

Thermoplasticity of the modified pulp was qualitatively determined by the moldability of samples from compression molding. Inserted images in Figure 3.10 show a semi-transparent yellow film was produced with the modified pulp using the functionalizing agent whereas the highly acetylated pulp sample by the acetic acid method mostly charred without evidence of flow. The modified pulp by the sulfuric acid/hyamine method appeared to be showing flow attributes comparable to synthetic plastics while the purely acetylated pulp retained its fibrous structure and solid-like nature in the mold. Quantitively, thermoplasticity of the modified pulp was evaluated rheologically by DMA, though results were limited to those samples suitably ductile for testing which did not include the sample prepared by the acetic acid method or the highly degraded sample from the first experimental series with a sulfuric acid/hyamine ratio of 1.96. Figure 3.10 shows the loss factor measured for the molded films of the modified lignocellulose; the measure is often a better indicator of processability whereas DSC results are more insightful into the composition. A single peak is seen for each modified sample tested by DMA whereas the DSC results had found two glass transitions for the modified samples, reflecting the dominant nature of the acetylated domain despite the benefits of the benzethonium-based domain on overall moldability.

Figure 3.10a shows results for the first series of experiments where the thermoplasticity of the modified wood pulp appeared to be mainly determined by the degree of benzethonium sulfate modification. At a sulfuric acid/hyamine ratio of 0.25, the loss factor had no definitive peak in the tested temperature range which indicated that there was no significant transition from the solid-like deformational nature of this lignocellulose at its low degree of acetylation and benzethonium sulfate attachment. A well-defined peak was found centered at 169 °C at a ratio of 0.49, increasing to 176 °C for a ratio of 0.96; the higher temperature required to transition from a solid-like to more liquid-like deformational response at the higher ratio negated considerations that the measure was influenced by molecular weight since the extent of degradation was greater according to intrinsic viscosity measurements. The greater tendency to flow at lower temperatures, which is a reasonable definition of thermoplasticity for this study, is noted at the optimal condition for benzethonium sulfate attachment. Figure 3.10b shows results for samples from the second set of experiments. As sulfuric acid content increased from 13.4% to 26.8% (w/w), the peak remained at 169 °C though it narrowed to reflect a sharper transition in flowability. Since the acetyl content and benzethonium sulfate attachment was not significantly different between the two conditions, the narrowing may be attributed to degradation which was significant with 26.8% sulfuric acid addition. The peak shifted to 159 °C at the highest sulfuric acid content of 40%. This improved thermoplasticity might be influenced by the ever-increasing degradation to the pulp from such high usage of sulfuric acid in the reaction; however, considering its small influence on the other results and greater sensitivity to the benzethonium group, it seems more reasonable to attribute to the increase in moiety 2. In general, the analysis shows the importance of the benzethonium sulfate attachment rather than acetyl content or extent of degradation on the thermoplasticity of the modified lignocellulose.

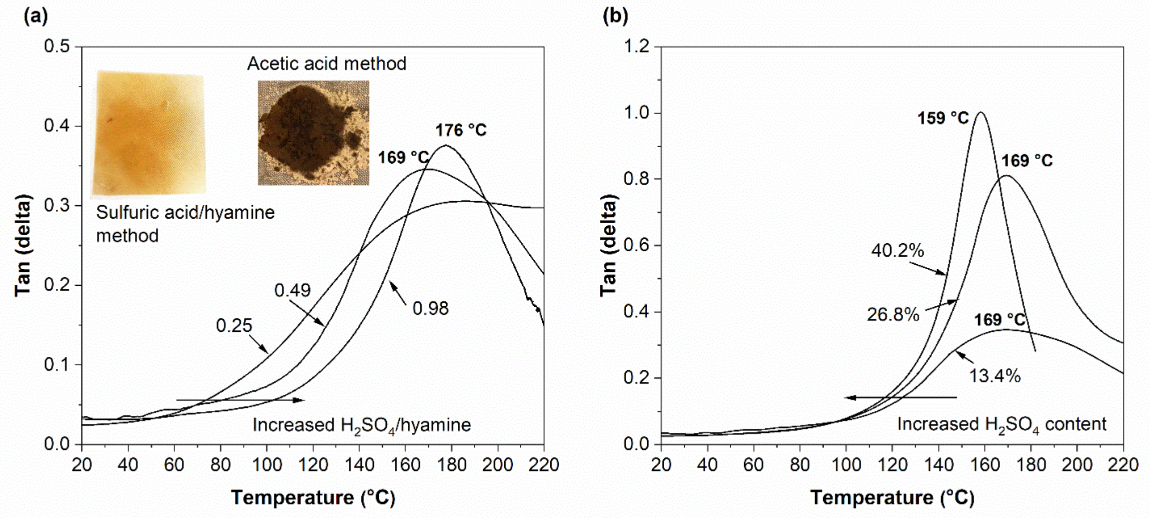

Figure 3.10. Loss factor (tan(d)) determined by DMA testing of the modified pulp-thermoplastics of (a) the first set, sample modified with a 1.96 molar ratio of sulfuric acid/hyamine was brittle for the testing and (b) the second set of trials. Inserted images are hot-pressed samples of modified pulps by two different methods.

3.4.5 Mechanical properties

Figure 3.11 shows the tensile properties of the modified pulp which has been established above as a thermoplastic. The molded films exhibited high stiffness at room temperature with Young's moduli in the range of 0.9-1.6 GPa and a low tensile strain of less than 1% (elongation at break). For the first set of experiments, Figure 3.11a shows that the modified wood pulp prepared at the ideal sulfuric acid/hyamine ratio of 0.49 had the highest modulus and strength. Though degradation should have been lowest at the ratio of 0.25, the modified sample exhibited a lower stiffness due to its relatively poor thermoplasticity. Its lower acetyl and functionalizing agent content meant it exhibited a more discrete fibrous behavior, yielding poor stress transmission through the film.

Comparably, at a ratio of 0.96, the brittle film was more prone to crumble under deformation, making the result questionable. At least the sample at the ratio of 0.49 showed thermoplastic properties and produced a reliable test specimen, which meant the analysis of samples of the second set of experiments was likely the most informative on the material properties affecting its mechanical nature.

Figure 3.11b shows a significant drop in both modulus and strength as the sulfuric acid content was increased for a fixed ratio of 0.49; the decline in tensile properties matched the loss in molecular weight detected by intrinsic viscosity. Considering the small changes in acetyl content and benzethonium sulfate attachment among these samples, the tensile properties were related to the extent of degradation. Such high levels of sulfuric acid in the reaction, as used in the second set of experiments, would seem undesirable if the goal of the synthesis is to retain the excellent mechanical properties inherent to cellulose pulp. Fortunately, the modulus and strength of the optimal modified pulp in these tests seems to be a reasonable substitute for many synthetic polymers (though more ductility would be beneficial).

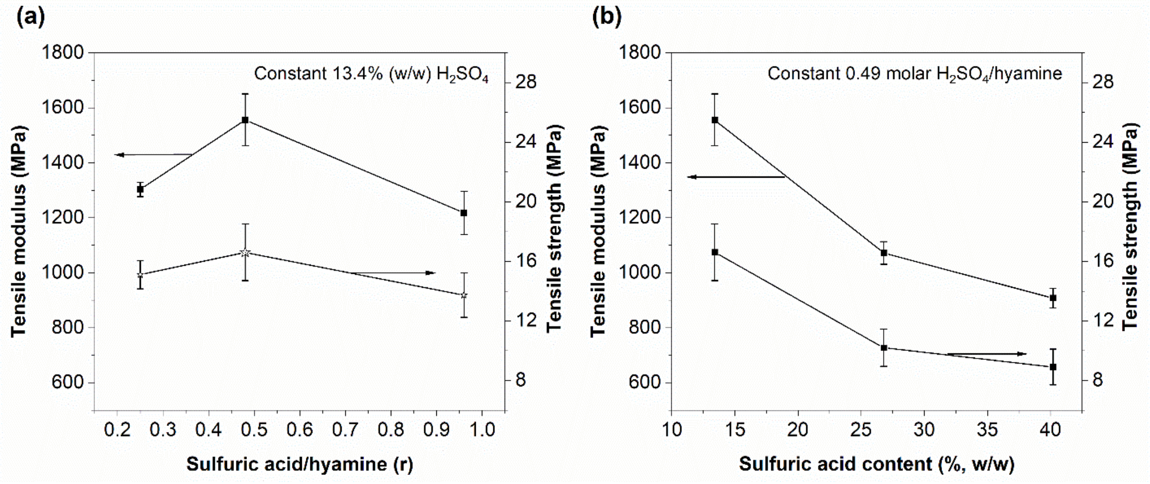

Figure 3.11. Tensile modulus and strength of modified wood pulp-thermoplastics of (a) the first set, sample modified with a 1.96 molar ratio of sulfuric acid/hyamine was brittle for the testing and (b) the second set of trial.

3.5 Conclusions

The functionalizing agent based on hyamine and sulfuric acid was seen to effectively wet the lignocellulose fibrous mass for the acetylation of lignocellulose. The presence of hyamine was essential for homogenously dispersing lignocellulose and minimizing degradation. More significantly with regards to the goal of producing a thermoplastic from the wood biomass was the spectral and elemental results demonstrating that the benzethonium species had become chemically bonded during the reaction. The grafted benzethonium sulfate rather than acetyl species appeared to strongly influence the thermoplasticity of the modified lignocellulose, which resulted in flow attributes comparable to synthetic plastics. The resulting bio-thermoplastics exhibited high stiffness at room temperature with Young's moduli in the range of 0.9-1.6 GPa and a low tensile strain of less than 1%.

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Chapter 4 Thermoplastic lignocellulosic polymer from wood pulp by reactive extrusion

Based on the new reaction method described in chapter 3, this chapter introduces a rapid reaction extrusion process for chemical modification of lignocellulose into thermoplastics for melt molding without plasticizers. The manuscript version of this chapter has been submitted to *Carbohydrate Polymers* for consideration of publication.

Jinlei Li conducted all the experiments with the help of Thomas Baker and wrote the draft of the manuscript. Dr. Sacripante and David Lawton provided technical guidance on the experimental design and results analysis. Heera Marway helped with the extrusion experiment. Hongfeng Zhang helped with NMR testing and analysis. Dr. Thompson revised the draft to the final version.

4.1 Abstract

A rapid chemical modification method has been devised for preparing flowable thermoplastic lignocellulose without the need for solvents. By reactive extrusion, forestry biomass can be converted into a high-value bioplastic. The method is demonstrated with two acid anhydrides (acetic anhydride and butyric anhydride) in the presence of another functionalizing agent (sulfuric acid/benzethonium chloride). The lignocellulosic wood pulp was modified with an ester and benzethonium sulfate group, as demonstrated by ^{13}C-NMR, infrared and elemental analysis. Twin-screw extrusion allowed for a short reaction time between 45-90 s but sufficient enough to afford excellent thermoplasticity to the lignocellulose for melt molding without plasticizers. By a Design of Experiment (DOE) analysis, the influence of extrusion conditions was studied on the thermoplasticity of the modified wood pulps. The modified wood pulp maintained much of the excellent stiffness of cellulose, demonstrating a maximum flexural modulus of 5.4 GPa and tensile modulus of 1.8 GPa.

4.2 Introduction

Lignocellulosic biomass is a structurally strong, renewable and abundant resource, considered as a highly significant alternative to declining fossil fuel reserves for the plastic industry. Lignocellulose is mainly composed of natural polymers (cellulose, hemicellulose and lignin). However, lignocellulose is not without major processing challenges due to its solid-like response to deformational strain, often right up to its decomposition temperature. This nature impedes its broader use as a polymer because it lacks the flowability comparable to synthetic polymers. Its solid-like non-thermoplasticity is attributed to the substantial intra- and inter hydrogen bonds present in the biomass as it is collected by the forestry industry. Chemical modifications [1–5] of the hydroxyl groups present among the components can interfere with these otherwise strong hydrogen bonds and beneficially introduce side groups that improve chain mobility as a result of their attachment. The challenge for modifying lignocellulose is the lack of adequate available solvents to wet and penetrate its fibrils, both quickly and extensively, such that enough hydroxyl functional groups are made chemically available for the reaction to overcome the natural non-thermoplasticity of the biomass. Innovative modification methods in the literature have turned to DMAc and ionic liquids as media to swell and disperse the fibrillar biomass in order to improve chemical site accessibility for reactions.[3–5] Despite their effectiveness, an excess amount of these liquids is needed, and due to the high expense of these chemicals, there must be costly recovery techniques deployed after a modification.

It is well recognized that mechanical techniques like milling or grinding can defibrillate wet-status lignocellulose.[6–9] Defibrillation of lignocellulose is beneficial for improving its chemical accessibility,[10–12] thereby reducing the amount of liquids required for heterogeneous chemical modifications.[13–15] Mechanically-assisted chemical modifications of lignocellulose, *e.g.*, using a ball milling, usually need long treatment times, especially when high reaction conversions are sought, which means high energy consumption is associated with generating these products. However, twin-screw extrusion has been demonstrated to be more effective in defibrillating lignocellulose or cellulose due to its capacity to handle higher solid loadings and requiring less energy in the processing.[9,16–19] The high shear forces and elevated temperatures produced in twin-screw extruders are well suited to the bulk and rapid reactions of natural polymers.[20,21] Due to this suitability for processing, reactive extrusion has naturally been explored for the functionalization of lignocellulose or cellulose.[22–24] However, this approach has its challenges as well which include the short residence time of the machine and limited mixing capacity of non-viscous materials.

A previous paper by the same authors has introduced an approach mimicking aspects of the ionic liquid but using less expensive species (benzethonium chloride and sulfuric acid) that may be equally beneficial for wetting and as a result, improve a chemical modification of lignocellulose. The approach has been demonstrated in a bench-top batch method that can modify lignocellulosic wood pulp into a thermoplastic with good flowability but in that case, lengthy reaction times were used to understand the chemistry. The current work intends to show the suitability of this chemistry for reactive extrusion. This study will examine the reactive extrusion process with a novel functionalizing agent of sulfuric acid and benzethonium chloride (hyamine), demonstrated with a common esterification method using two acid anhydride modifiers for a lignocellulose wood pulp. The influence of extrusion conditions is studied on the thermoplasticity and physical properties of the modified lignocellulose.

4.3 Experimental

4.3.1 Materials

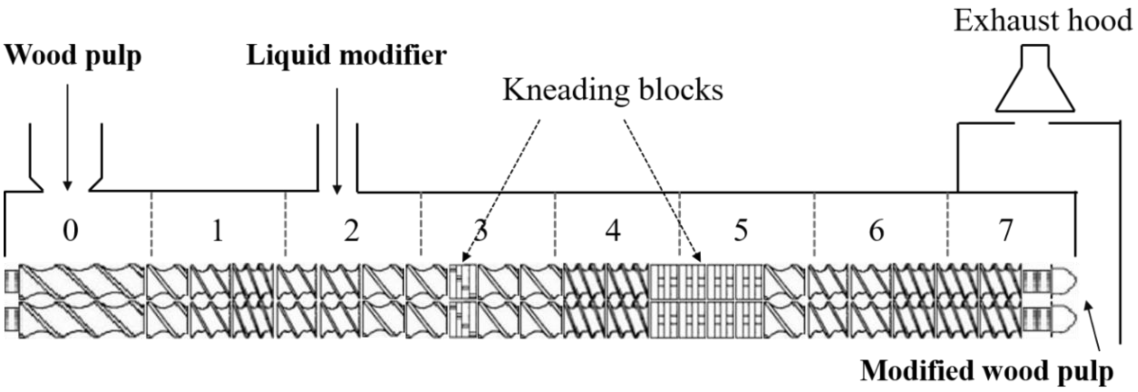
Lignocellulosic wood pulp containing 8.16 wt% Klason lignin (determined by TAPPI-T method 222 om-02) was received from Tembec (Montreal, Canada) as a high-yield

Aspen mechanical pulp. The received pulp was mechanically defibrillated in a 27 mm 40 L/D corotating twin-screw extruder (Leistritz, USA) according to a previously established method [10]. By this method, the fluffy lignocellulosic wood pulp received was converted into partially fibrillated fine granules, which made the wood pulp convenient for feeding into the process. Benzethonium chloride (hyamine, HPLC grade), sodium bicarbonate and phenolphthalein (ACS grade), and butyric anhydride (reagent grade) were purchased from Sigma Aldrich (Oakville, Canada). Acetic anhydride (reagent grade), sulfuric acid (trace metal grade), dimethyl sulfoxide (DMSO), anhydrous ethanol (reagent grade), and 1.0 M sodium hydroxide and hydrochloric acid solutions were obtained from Caledon Laboratory Ltd. (Georgetown, Canada).

4.3.2 Chemical modification of lignocellulosic wood pulp by reactive extrusion

For convenience of handling the reaction, reactive extrusion of partially defibrillated wood pulp was done used an 18 mm 40 L/D corotating twin-screw extruder (Leistritz, USA) rather than the pilot-scale 27 mm twin-screw extruder that was used in Chapter 2. Scheme 4.1 shows the extrusion process for wood pulp. The screw configuration contained one 30° offset kneading block early in the process followed by four 90° offset kneading blocks in a row later to supply sufficient mixing for the modification. The two kneading sections were put in zones with lids above for the ease of cleaning the machine in case of the lignocellulosic fibers jamming the extruder. Putting the larger kneading section at the end of the screw was for avoiding jamming the extruder, as lignocellulosic fibers had became soften after modification in the previous zones before entering the larger kneading section. Air-dried defibrillated pulp was fed by a gravimetric feeder (Coperion, Germany) at a rate of 500 g/h. The temperature of the feeding zone was maintained at 25 °C by chilled water, while the other zones were all heated. Table 4.1 presents the series of experiments that were conducted, based on the boiling point of the main chemical, extrusion temperature was set to 120 or 140 °C for the butyric anhydride series (Table 4.1a), and only considered at 120 °C for the acetic anhydride series (Table 4.2b). The liquid esterification modifier (acetic anhydride or butyric anhydride) and functionalizing agent were injected together into the second barrel zone with an Optos Series metering pump (Eldex, USA). The liquid mixture was pre-made by dissolving 30 g hyamine per 100 mL anhydride under constant agitation at 120 °C, and then adding sulfuric acid dropwise to the solution until the molar ratio of sulfuric acid/hyamine was either 0.95 or 1.2. The screw speed of the extruder was set to either 100 rpm or 300 rpm based on the chosen experimental conditions (Table 4.1). The DOE presented in Table 4.1 was set up using Origin software (OriginLab, USA).

The modified pulp was collected, and first cooled by suspended it in distilled water. Cleaning the modified pulp began by neutralization with 1 M sodium bicarbonate solution. Subsequently, a sample was repeatedly washed with distilled water until the conductivity of the filtrate determined by a Mettler Toledo S230 conductivity meter was close to that of distilled water. Finally, the modified pulp was vacuum-oven dried at 75 °C for 24 hours prior to storage and characterization.



Scheme 4.1. Reactive extrusion of lignocellulosic wood pulp by an 18 mm Leistritz twin-screw extruder.

Table 4.1. DOE layout for studying the effects of extrusion conditions on the chemical modifications of wood pulps, (a): butyric anhydride series, (b): acetic anhydride series.

(a)

Run No.	**Liquid injection rate (mL/min)**	**Temperature (°C)**	**Screw speed (rpm)**	**Molar ratio (sulfuric acid/hyamine)**
	A	**B**	**C**	**D**
B1	32	120	100	0.95
B2	32	120	300	1.2
B3	32	140	100	1.2
B4	32	140	300	0.95
B5	48	120	100	1.2
B6	48	120	300	0.95
B7	48	140	100	0.95
B8	48	140	300	1.2

(b)

Run No.	Liquid injection rate (mL/min)	Screw speed (rpm)	Molar ratio (sulfuric acid/hyamine)
	A	**B**	**C**
A1	32	100	0.95
A2	32	100	1.2
A3	32	300	0.95
A4	32	300	1.2
A5	48	100	0.95
A6	48	100	1.2
A7	48	300	0.95
A8	48	300	1.2

4.3.3 Compression molding of the modified pulps

Specimens with different dimensions (D1: 50 mm × 50 mm × 0.26 mm; D2: 50 mm × 13 mm × 0.45 mm; D3: 55 mm × 15 mm × 2 mm) were compression molded to test the thermal moldability of the modified wood pulp. Molding was done in a Carver 4389 benchtop hydraulic press with heated platens under 3 metric tons force for 3 mins and then 7 metric tons for another 12 mins. Molding temperatures for butyric anhydride modified series and acetic anhydride modified series were 150 and 180 °C, respectively.

4.3.4 Characterizations

Residence time

The residence time of the twin-screw extruder was measured by using a carbon black tracer. The carbon black was introduced as a pulse into the feed zone of the twin-screw extruder along with lignocellulosic wood pulp and timed until it first appeared at the exit. This characterization represents the minimum time allowed for the reaction.

Chemical characterization

Infrared spectra (FTIR) were collected for the powder samples on a Nicolet 6700 spectrometer with a Smart iTRTM attenuated total reflectance (ATR) sampling accessory. A spectrum was generated from 32 scans in the range of 4000-500 cm^{-1} with a 4 cm^{-1} resolution. Solution state ^{13}C nuclear magnetic resonance (NMR) spectroscopy of modified samples were performed in DMSO-d6 solvent with a Bruker AVIII 700 MHz spectrometer at ambient temperature.

Acyl and benzethonium sulfate contents of the modified pulp were determined by colorimetric titration and elemental analysis (Supporting Information). Dried modified pulp, 0.05 g, was put into a 25-mL glass vial, to which was added 5 mL of 0.25 M NaOH and 5 mL anhydrous ethanol. The mixture was left to stand for 24 h before 10 mL 0.25 M HCl was added to the system. After 30 mins, the mixture was titrated using 0.25 M NaOH with a phenolphthalein indicator. The total hydrolyzed ester content (TEC) was calculated by:

$$TEC\ \left(\frac{mmol}{g}\right) = \frac{(V_1 +\ V_2)C_1 - V_3C_2}{m} \qquad (1)$$

where V_1 (mL) is the volume of NaOH added to the system before the titration, V_2 (mL) is the volume of NaOH consumed in the titration, C_1 (M) is the NaOH concentration, V_3 (mL) is the volume of HCl added to the system before the titration, C_2 (M) is the concentration of HCl, and m is the weight of the sample.

Elemental nitrogen (N) and sulfur (S) contents were determined with an UNICUBE elemental analyzer (Elementar). Approximately 2 mg powder sample was sealed in Tin foil and loaded into the analyzer for the testing.

Inherent and intrinsic viscosity were used to assess the extent of degradation for the modified pulp samples with a Cannon Fenske viscometer (25 tube size). 40 mg dried sample was added to 40 mL DMSO solvent and stirring overnight to dissolve the pulp; the insoluble part was separated by filtering and dried to determine the concentration (c) of the solution. The solvent or pulp solution flowed through the viscometer held at 25 °C, and its flow times through the graduated region were recorded. Inherent viscosity (η_{inh}) was determined from the flow times of the DMSO solvent(t_0) and pulp solution (t), according to:

$$\eta_{inh} = \mathrm{In}\left(\frac{t}{t_0}/c\right) \qquad (2)$$

Intrinsic viscosity was estimated as the intercept of inherent viscosity curves versus concentration.

Thermal properties

Thermal transitions were analyzed using a Q200 differential scanning calorimeter (DSC; TA Instruments, USA) operating in modulated mode. Modified pulp, 9 mg, was loaded and sealed into a Tzero aluminum pan. A hole was punched into the lid to allow the release of water vapor during the test. Samples were equilibrated at -20 ˚C, then heated to 220 ˚C at the ramp rate of 5 ˚C/min, with an oscillation of 1.00 ˚C every 60 seconds. The glass transition temperatures (T_g) of modified samples were estimated from the reversible heat flow separated from the total heat flow by the Universal Analysis software (TA Instruments, USA).

Thermoplasticity of the modified pulps was quantified by its flowability with a Discovery HR-2 hybrid rheometer (TA Instruments, USA) by conducting a temperature sweep after first discovering the linear response region by a strain sweep. Testing disk for the rheometer were 1.50 mm thick and 25 mm in diameter, prepared by the compression molding. The testing was performed with a heating-cooling-heating sweep cycle over a temperature range of 90 to 200 °C at a rate of 5 °C/min, and under a constant shear rate of 0.1 s^{-1}.

Mechanical properties

Tensile and 3-point flexural properties of the D2 compression-molded specimens were measured on an Instron universal mechanical testing system (Model 3366). The tensile testing was performed at a crosshead speed of 0.085 mm/min, and force was recorded with a 0.5 kN load cell. The 3-point flexural testing was conducted at a crosshead speed of 2.5 mm/min, and the force was recorded with a 0.05 kN load cell. The length of the support span for the flexural testing was 26 mm. Mechanical properties were reported as the average of three repeats.

4.4 Results and discussion

4.4.1 Chemical structure of modified wood pulp

The FTIR spectra (see Figure S4.1) indicated that compared to the original material, the modified pulp presented a strong peak at 1740 cm^{-1} corresponding to ester species (-

COO-)[5]. Correspondingly, there was considered to be a decrease in the hydroxyl functionality of both cellulose and lignin based on the decreasing intensity of the broad peak centered at 3330 cm^{-1}. A sulfate functionality was detected in the modified pulp at 837 cm^{-1} (-C-O-S- symmetrical vibration) and 602 cm^{-1} (bending mode of sulfate).[25,26] Sulfate groups along the cellulose chain are not uncommon in the presence of sulfuric acid, but due to its molar equivalence to the benzethonium cation (shown in the subsequent elemental analysis) leads the authors to believe their presence is attributed to the benzethonium sulfate used as a functionalizing agent in the modification.

Figure 4.1 shows solution-state ^{13}C NMR spectra of the modified pulp produced by reactive extrusion using acetic and butyric anhydride. Labelled with solid arrows in plot (a), the chemical shifts at 170-174 ppm of the butyric anhydride series of modified pulp were assigned to the butyryl carbonyl group; three shifts at 13, 18 and 35 ppm corresponded to the three carbons of butyryl.[14,27] Similarly, for the acetic anhydride series in plot (b), shifts at 169-171 ppm and 21 ppm were assigned to carbonyl and methyl carbons of the acetyl functionality, respectively.[28,29] Despite the short reaction time in the extruder, both reactions with the acid anhydrides were effective; the minimum residence time inside the extruder was 90 or 45 s, respectively when a screw speed of 100 or 300 rpm was used. Additionally, the NMR technique shows that the modified pulp included chemical shifts in plot (c) similar to hyamine, as highlighted with rectangular symbols, which were assigned to the grafted benzethonium cation. The attached cation could not be clearly observed by FTIR due to its weaker signal and interfering peaks by lignocellulose.

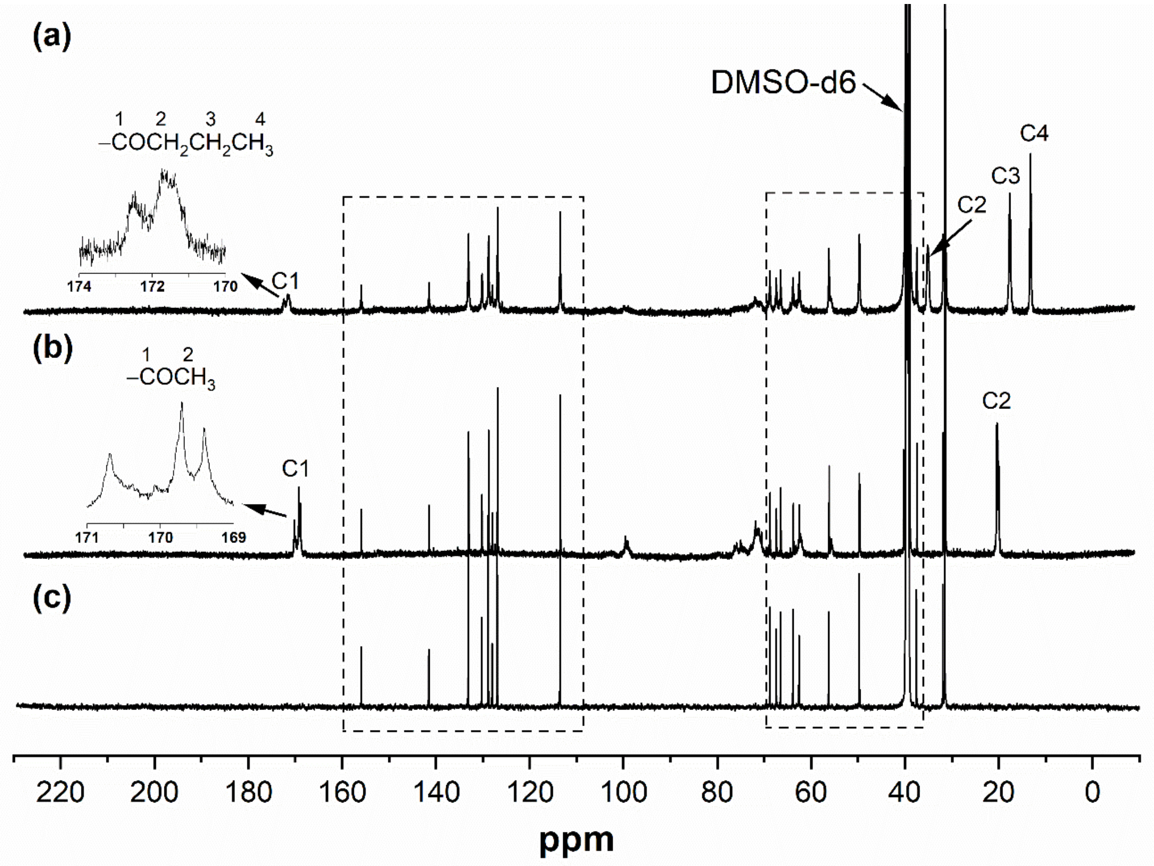


Figure 4.1. Solution-state ^{13}C NMR spectra of representative modified lignocellulose from (a): butyric anhydride series (B2, Table 4.1a), (b): acetic anhydride series (A7, Table 4.1b) and (c): pure hyamine. Rectangular boxes highlight the chemical shifts in the modified samples similar to those found with hyamine.

Understanding the manner by which benzethonium cation attached was considerably clearer by elemental analysis, with those results given in Figure 4.2. As-received lignocellulosic wood pulp had a small but detectable elemental N content, which was considered to be trace contaminants in the supplied material (though consistently present). Compared with the original material, all modified pulp from both butyric and acetic anhydride experimental series, showed a substantial increase in N content that can only be attributed to the hyamine at such relatively high values; additionally, the S content of the modified pulps was significantly increased, which was detected as sulfate groups by FTIR analysis. The molar ratio (R) of N to S elements was analyzed using the definition of:

$$R = \frac{(N - N_i)/14}{(S - S_i)/32} \qquad (3)$$

where assuming concentrations of the trace N and S unchanged in modified wood pulps, N and S corresponded to a modified pulp while N_i, and S_i corresponded to the original material. The R values for the butyric anhydride series was 1.01 ± 0.02 and while it was 1.00 ± 0.04 for the acetic anhydride series. R values of the two extrusion series are near unity, indicating the hyamine likely formed attachments to the pulp as benzethonium sulfate ($[C_{27}H_{42}NO_2]^+[\text{-}OSO_3]^-$). Differences in N and S content based on run conditions are discussed in a later section.

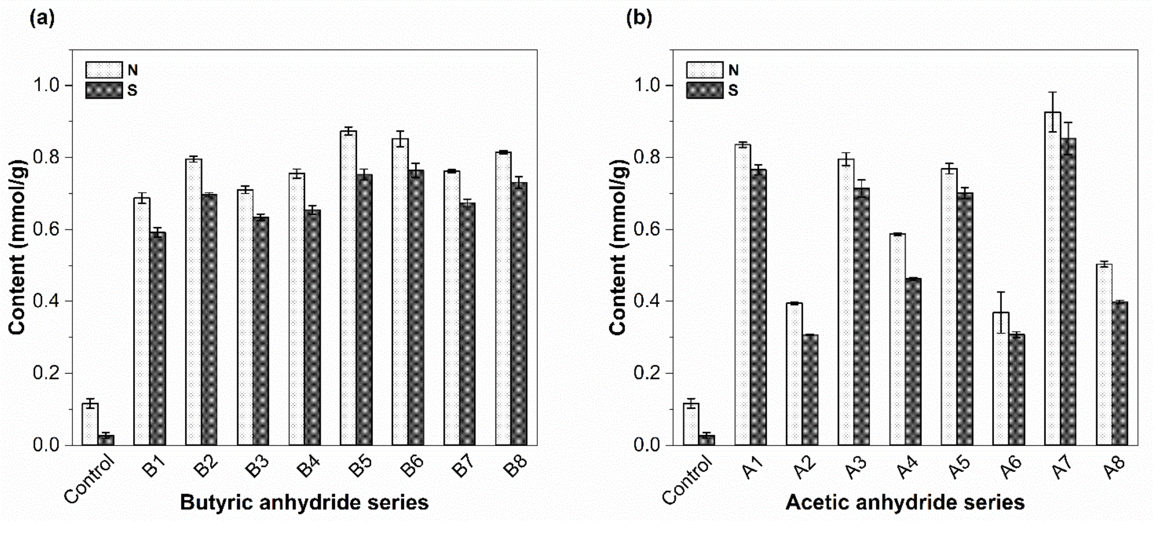


Figure 4.2. N and S elemental analysis of raw material and modified lignocellulose by reactive extrusion in (a) butyric anhydride, and (b) acetic anhydride series.

4.4.2 Thermoplasticity of the modified wood pulps

Figure 4.3 shows thermograms of the original material and modified pulp. The original wood pulp (labelled in plot(a)) did not display any noticeable thermal transition in the tested temperature range, which is consistent with its non-thermoplastic nature. After modification by reactive extrusion, the modified pulp showed distinctive glass transitions. Depending on the experimental conditions, T_g values for butyric anhydride series (Figure 4.3a, b) varied between 47-67 ℃ whereas T_g values for the acetic anhydride series varied between 87-121 ℃. The longer acyl attachment of the butyryl ester afforded greater mobility of the lignocellulosic thermoplastic at lower temperatures, which will be discussed further in a later section.

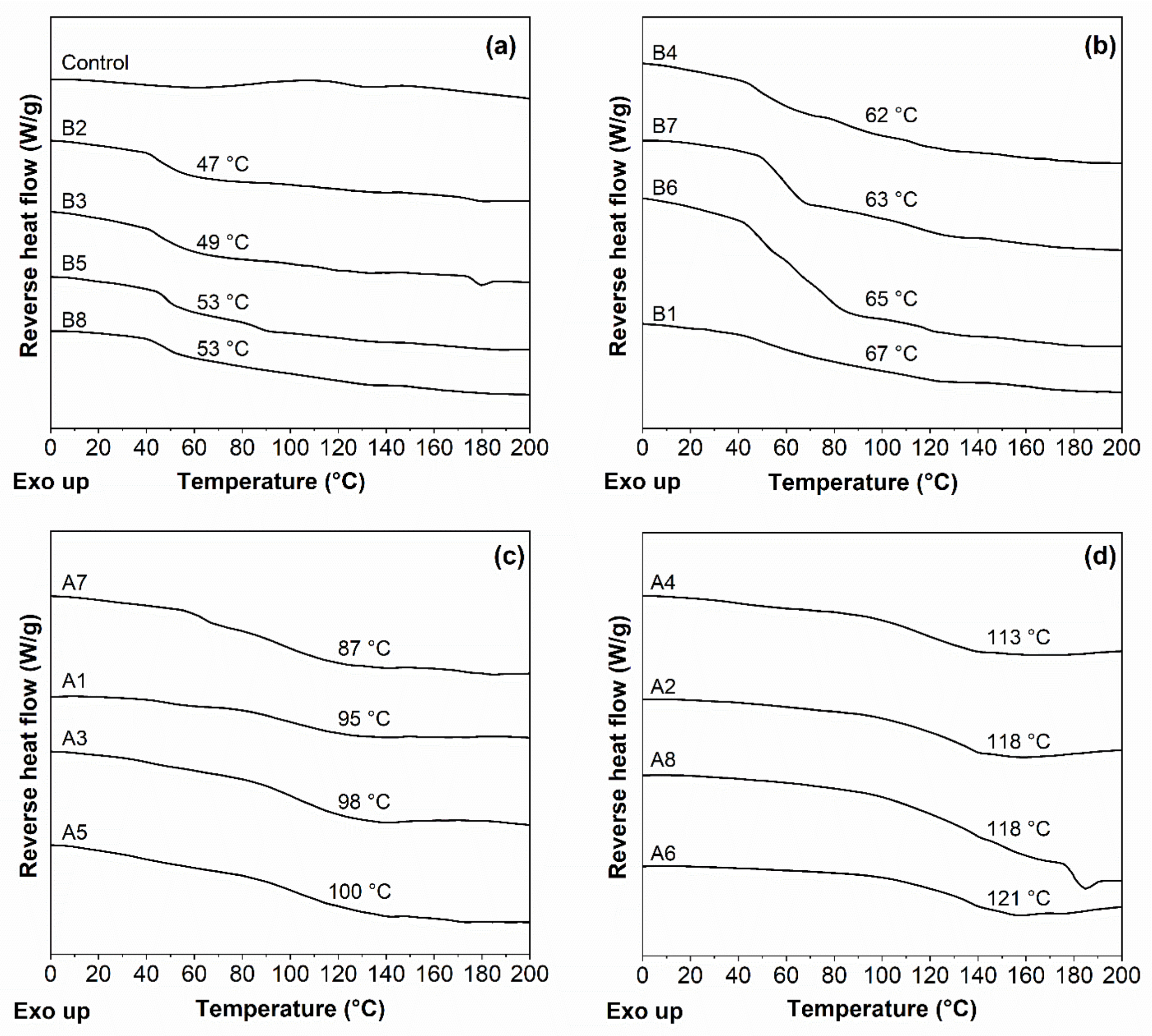


Figure 4.3. DSC thermograms of the (a, b) modified wood pulps for the butyric anhydride series and (c, d) acetic anhydride series. Results of original material were included in plot (a).

Dynamic rheological characterization can be considered as additional evidence of thermoplasticity for the modified pulp. Figure 4.4 shows complex viscosity-temperature curves for the modified pulp with differing T_g based on the run conditions for the butyric anhydride series and acetic anhydride series. For test temperatures above the corresponding

T_g of a material, samples with a lower T_g generally had better thermoplasticity, as noted by displaying a transition region response with temperature and generally lower viscosities. For the butyric anhydride series, this definition of thermoplasticity corresponded to all samples with a T_g = 47-65 °C, and in the case of the acetic anhydride series, it corresponded to samples with a T_g = 98-113 °C. The materials with higher T_g = 121 °C from the acetic anhydride series showed insignificant decline in viscosity (torque) across the range of tested temperatures, giving a more solid-like response above 160 °C.

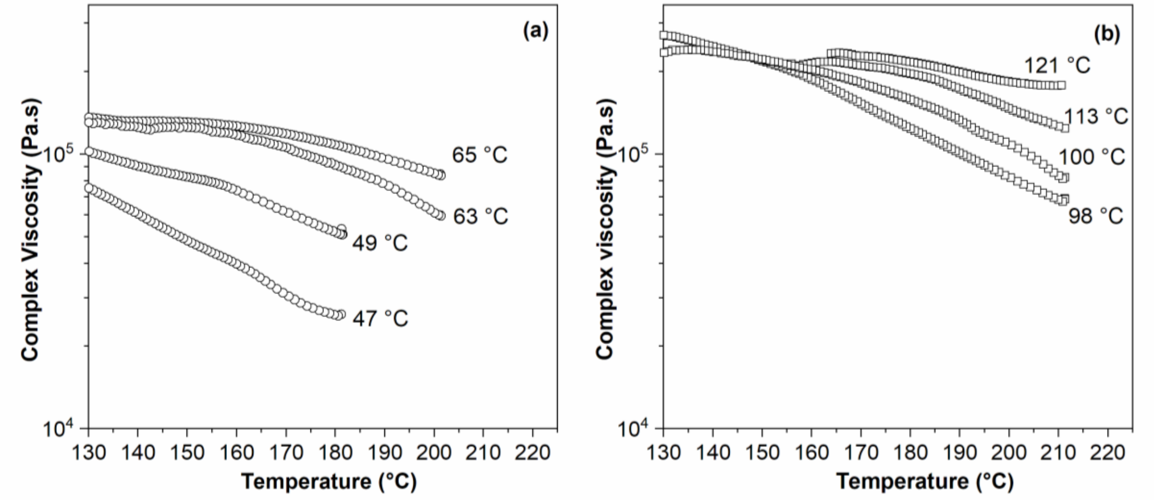


Figure 4.4. Comparison of flowability of modified wood pulps with different T_g in butyric anhydride series (a) and acetic anhydride series (b).

Owing to the displayed thermoplasticity, the resulting modified pulp from both butyric anhydride and acetic anhydride series were qualitatively evaluated for their compression-moldability. Figure 4.5 shows the molded samples of the (a) butyric anhydride series and (b) acetic anhydride series. All molded samples had smooth surfaces and well defined edges, indicating the flowability of the modified wood pulps was sufficient enough to enter into all areas of the mold. Molding changed the color of the modified samples from light brown to uniform black, probably because of thermal oxidation of lignocellulose, but this was not be considered a problem since many plastics are coloured black for parts in sectors such as the automotive industry or food packaging industry. The molding conditions were probably too long for the biopolymer, but as the mechanical testing will show, strength was not significantly deteriorated relative to literature-quoted properties for cellulose.

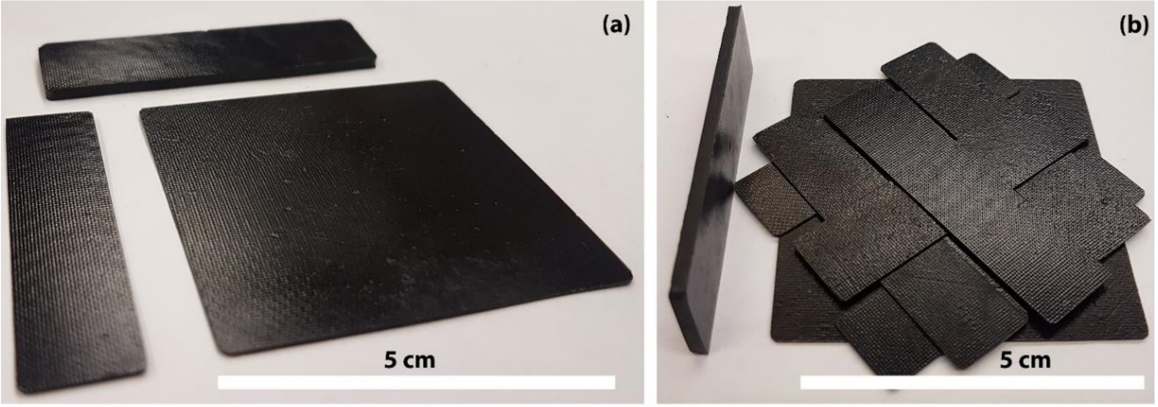


Figure 4.5. Images of compression-molded wood pulps from the (a) butyric anhydride series and (b) acetic anhydride series, prepared in molds of different dimensions (50 mm × 50 mm × 0.26 mm; 50 mm × 13 mm × 0.45 mm; 55 mm × 15 mm × 2 mm).

4.4.3 Influence of esterification on the thermoplasticity of modified wood pulp

Table 4.2 presents three groups of samples from the butyric anhydride series and acetic anhydride series. The two samples in each group were selected for having similar content of grafted benzethonium sulfate and intrinsic viscosity but differed in their acyl content. The table shows that in the three groups, sample from the acetic anhydride series had a degree of acylation nearly double the butyric anhydride series, while the samples of the butyric anhydride series had lower T_g values. This analysis is showing that the T_g of the sample was more strongly influenced by the size of the acyl side chain rather than its content; the butyryl group contributed more effectively to matrix mobility than the acetyl group and hence, yielded better thermoplasticity in the lignocellulose.

Table 4.2. Comparison of degree of modification, intrinsic viscosity and T_g among modified wood pulps in butyric anhydride series and acetic anhydride series.

Sample	Acyl (mmol/g)	Sulfate benzethonium (mmol/g)	Intrinsic viscosity (mL/g)	T_g (°C)
B5	1.68 ± 0.01	0.75 ± 0.02	140	53
A1	3.66 ± 0.01	0.75 ± 0.01	158	95
B2	1.76 ± 0.02	0.68 ± 0	168	47
A3	4.30 ± 0.03	0.70 ± 0.02	174	98
B7	1.24 ± 0.01	0.66 ± 0.01	171	63
A5	3.75 ± 0.01	0.69 ± 0.01	147	100

4.4.4 Influence of extrusion conditions on butyric anhydride modified wood pulp

DOE analysis of the series listed in Table 4.1 was conducted for the butyric anhydride series, considering factor influences on the responses of T_g (for thermoplasticity) and the grafted content of both acyl and benzethonium groups (for reaction effectiveness). Figure 4.6 shows the corresponding main effects plot of the four factors. Plot (a) shows the analysis for T_g where the molar ratio of sulfuric acid/hyamine (factor D) was the only main factor found to significantly impact the modified wood pulp (p-value = 0.025); a plot of coefficients of the significance of each factor in the regression analysis is provided in the Supplementary section, Figure S4.4. Increasing the sulfuric acid/hyamine ratio was beneficial for better thermoplasticity, the T_g of butyric anhydride-modified wood pulps based on the use of a molar ratio of 0.95 versus 1.2, was 62-67 °C versus 47-53 °C, respectively. Increasing the liquid injection rate (factor A) had a negative effect on thermoplasticity, though its effect on T_g was generally negligible (16.4 % of the significance of factor D (Figure S4.4a) and p-value = 0.47). However, liquid injection rate was worth noting because it had correlated interactions with the factors of molar ratio and screw speed (Figure S4.4a). Temperature and screw speed, as main factors, also had no significant effect on T_g (10% of the significance of factor D (Figure S4.4a) and p-value = 0.67).

Plot (b) shows factor D was the only main factor (p-value = 0.001) to significantly affected the butyrylation of wood pulp. Reactions with butyric anhydride favored the more highly acidic environment as the molar ratio reached 1.2. The other three main factors had no significant effect on butyrylation of wood pulp (p-value > 0.05). Increasing the ratio of sulfuric acid/hyamine seemed to improve the grafting of benzethonium as well (plot (c)) but statistically it was not significant (p-value = 0.42). When the liquid injection rate increased, more benzethonium was grafted onto wood pulps, but it simultaneously slightly decreased the butyryl content. Plot (a) had shown that higher liquid injection rate reduced the thermoplasticity of the modified wood pulps, which indicated that butyryl groups contributed more thermoplasticity to modified wood pulps than the grafted benzethonium.

None of the factors had a significant effect (p-value > 0.05) on benzethonium attachment, though influences were more clearly seen in plot (c).

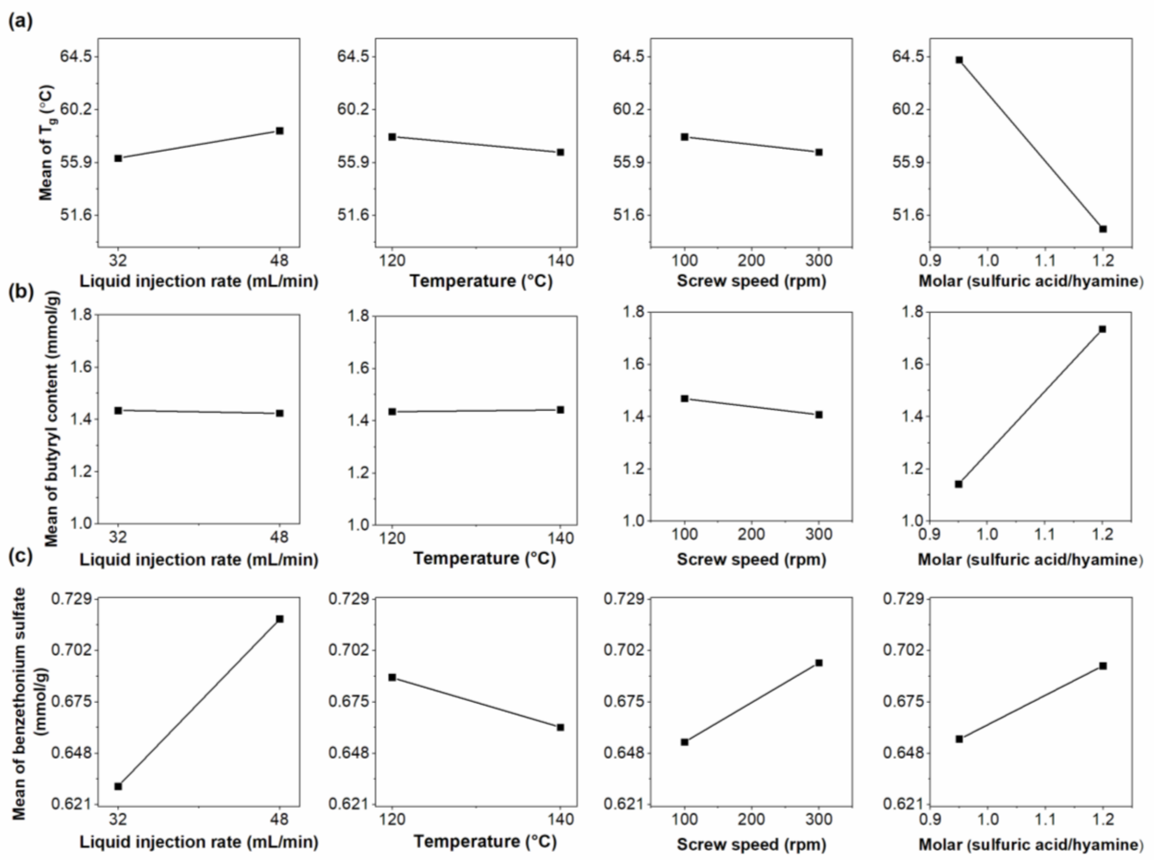


Figure 4.6. Main effects plot of the extrusion conditions on (a) T_g, (b) butyryl content and (c) benzethonium sulfate content of modified pulp in butyric anhydride series.

4.4.5 Influence of extrusion conditions on acetic anhydride modified wood pulp

Similar to butyric anhydride series, Figure 4.7 shows the main effects plot of the four extrusion factors on T_g (for thermoplasticity) and the grafted content of both acetyl and benzethonium groups (for reaction effectiveness). Whereas the supplementary Figure S4.5 shows coefficients of the significance of the four factors. In plot (a), the molar ratio of sulfuric acid/hyamine (factor C) was once again the only main factor (p-value = 0.038) to affect the thermoplasticity of modified wood pulp, in this case for acetic anhydride series. Unlike butyric anhydride, a more highly acidic extrusion environment had a negative influence on thermoplasticity. Liquid injection rate had no significant effect (p-value = 0.93) on the thermoplasticity of modified wood pulps. Screw speed had no significance as well but was determined to be the next most relevant factor to affect T_g after factor C (Figure S4.5a), with higher screw speed yielded better thermoplasticity.

Plots (b) and (c) shows factor C was also the only main factor to significantly (p-value = 0.01) affect the acetylation and graft of benzethonium sulfate to wood pulps. More sulfuric acid increased the extent of acetylation but decreased bound benzethonium sulfate content. This trend was not seen with butyrylation. It is possible the high degree of acetylation (4.2-7.0 mmol/g) as the molar ratio increased from 0.95 to 1.2 consumed hydroxyl functional groups to the detriment of sites for benzethonium sulfate grafting. For the butyric anhydride series, even when a higher molar ratio was used, butyrylation still took place at a relatively low degree (1.6-2.3 mmol/g) and thus, competition for sites with benzethonium sulfate was not significantly affecting the final product. A previous research in benchtop method demonstrated that benzethonium sulfate was more effective than acetyl in adding thermoplasticity to wood pulps, which explained why the thermoplasticity of modified wood pulps decreased when more sulfuric acid was used in extrusion. According to the study of chapter 4, the modified lignocellulose prepared from a bench-top process by acetic anhydride-liquid modifier had a lowest T_g of 159 ℃, which was significantly higher than the 87-121 ℃ of samples prepared by the reactive extrusion. Figure 4.2b shows that more benzethonium sulfate was grafted onto lignocellulose by reactive extrusion than that by a bench-top process, which explained the better thermoplasticity of modified lignocellulose prepared by reactive extrusion. The short reaction time of reactive extrusion might reduce the transesterification between sulfate ester and acetyl ester of modified lignocellulose. Higher screw speed decreased the acetylation, and as a result, increased the benzethonium attachment, which was consistent with the results that increasing screw speed had a positive effective on the thermoplasticity of modified wood pulps.

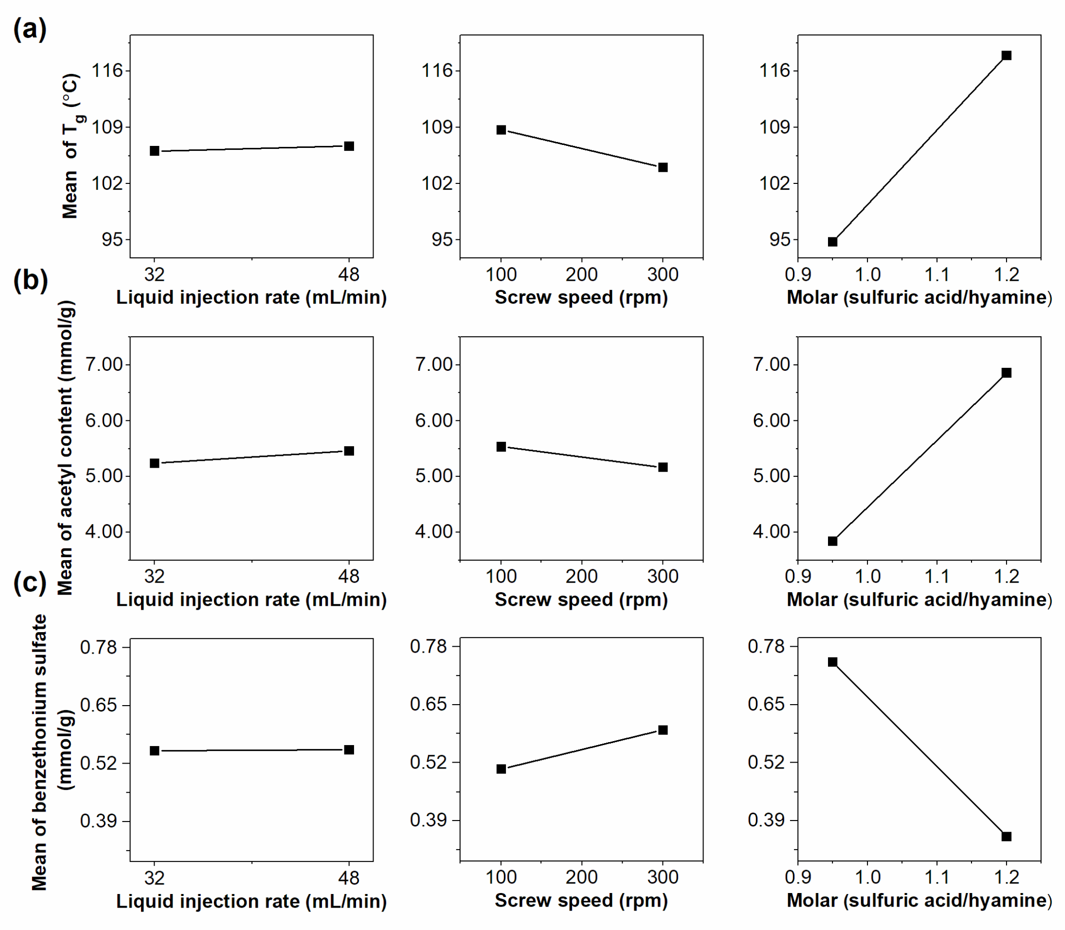


Figure 4.7. DOE analysis of the influence of extrusion conditions on thermoplasticity of modified wood pulps in acetic anhydride series.

4.4.6 Mechanical properties of the modified wood pulp-thermoplastics

Figure 4.8 shows the tensile and flexural properties of the molded specimens from the butyric anhydride and acetic anhydride series. The tensile and flexural moduli of the acetic anhydride series were 1.4-1.8 GPa and 3.5-5.4 GPa, respectively, whereas the tensile and flexural modulus of the butyric anhydride series were 1.2-1.6 GPa and 3.1-4.6 GPa, respectively. Thermoplastics from the acetic anhydride series possessed a higher flexural yield strengths of 35-46 MPa compared to the butyric anhydride series at 23-32 MPa. In comparison, the original aspen wood pulp has a reported flexural modulus of 5.79 GPa and flexural yield strength of 20.0 MPa,[30] showing the modified wood pulp-based thermoplastics were comparable in mechanical properties. The reactive extrusion converted wood pulp into thermally flowable material, which significantly improved the processability of this sustainable material-lignocellulose, simultaneously maintained the high stiffness of wood.

Thermoplastics of the butyric anhydride series with a higher T_g temperature had higher mechanical properties. In comparison, thermoplastics in acetic anhydride series with lower T_g temperature tended to have higher mechanical properties. Among all the wood pulps in acetic anhydride series, the modified wood pulp with the lowest T_g of 95 °C had the highest flexural modulus, flexural strength, and tensile modulus, which were 5.4 GPa, 46 MPa, and 1.8 GPa, respectively. Among wood pulps in the butyric anhydride series, the modified wood pulp with the most top T_g of 67 °C had the highest flexural modulus, flexural strength, and tensile modulus which were 4.6 GPa, 32 MPa, and 1.6 GPa, respectively. The stiffness of the thermoplastics in butyric anhydride series mainly related to the molecular chains of the modified wood pulp, hence the stiffness being highly matched with their T_g. For the acetic anhydride series, the modified wood pulps of higher T_g did not melt completely, and as a result, the trend seemed different. In this case, the density of the molded samples mattered. Only the modified wood pulp in acetic anhydride series with lower T_g temperature formed dense (i.e. non-porous) molded specimens, necessary to display the best mechanical properties.

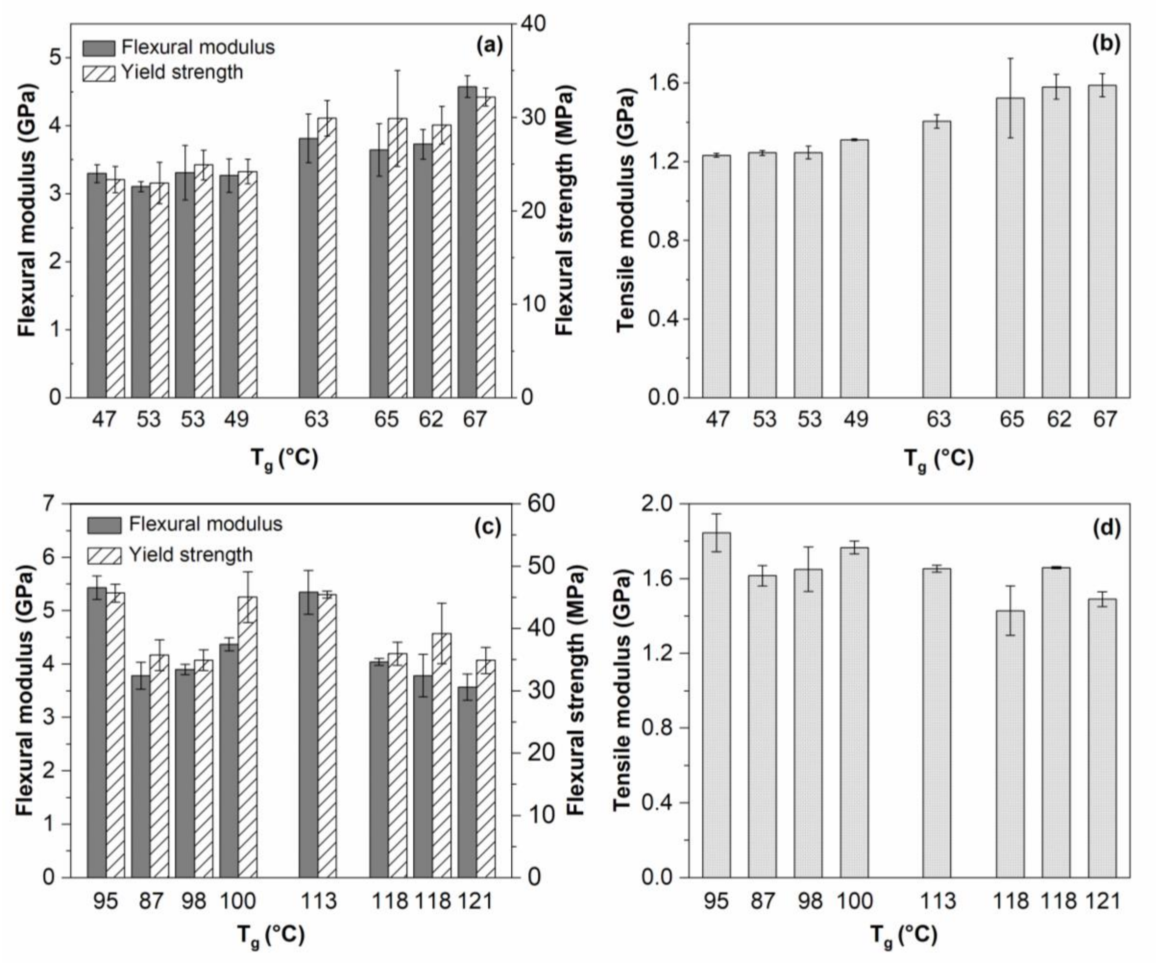


Figure 4.8. Mechanical properties of the butyric anhydride series determined by (a) flexural and (b) tensile testing; of the acetic anhydride series determined by (c) flexural and (d) tensile testing.

4.5 Conclusions

Modification of lignocellulosic wood pulp by grafting acyl and benzethonium sulfate species was achieved by reactive extrusion to prepare a new bioplastic. The modification was found to take place at an acceptable degree to afford thermoplasticity sufficient for molding, despite the short residence time in the extruder of 45-90 s. Modified polymers displayed distinctive glass transitions based on the acid anhydride modifier used, with butyric anhydride proving superior to acetic anhydride in term of the plasticization of the natural biopolymer relative to the degree of acyl group attachment. DOE analysis revealed that the molar ratio of sulfuric acid to hyamine, as a functionalizing agent to aid the reaction, was the only significant factor to impact the thermoplasticity of modified wood pulps. In addition to displaying good moldabiity, the modification showed a capacity to maintain the high mechanical strength of the original wood pulp.

4.6 References

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4.7 Supporting information

4.7.1 FTIR spectra of modified wood pulp

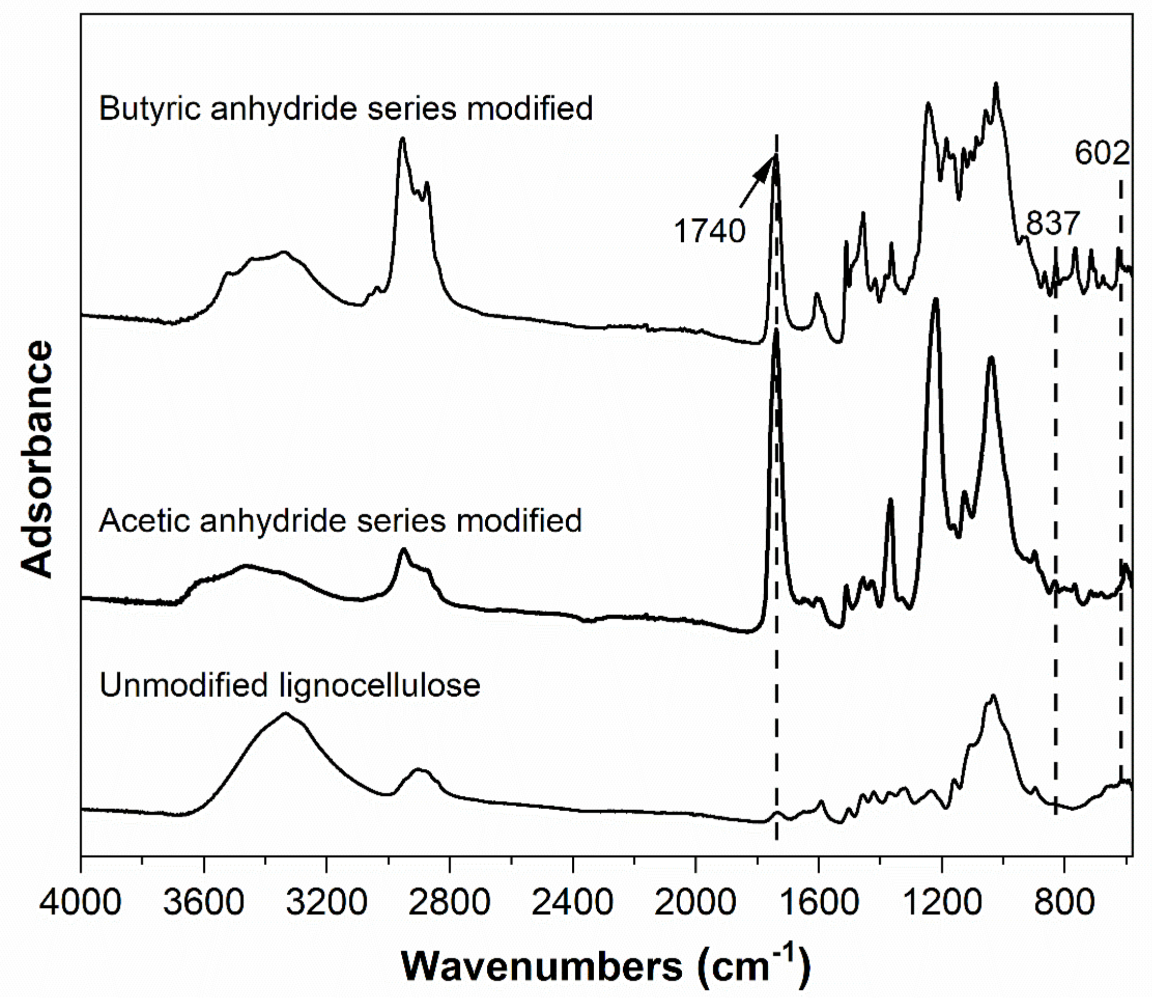

Figure S4.1. FTIR spectra of unmodified and representative modified lignocellulosic wood pulps by reactive extrusion from butyric anhydride (A2, Table 4.1a) and acetic anhydride series (A7, Table 4.1b). Dashed lines highlight the ester and sulfate groups attached during the modification.

4.7.2 Calculation of acyl group content from titration and elemental analysis results

1 g unmodified lignocellulosic wood pulp naturally contains 0.1 mmol ester species as determined by titration of the raw material. Elemental analysis shows that the 1 g raw material also has 0.027 mmol S element. After modification by the reactive extrusion, x mmol acyl and y mmol benzethonium sulfate species were attached to the 1 g lignocellulosic wood pulp. The attachment of free hyamine was neglectable as the molar ratios of N to S were near unity. When the modified wood pulp was hydrolyzed by 0.125 M NaOH water/ethanol (1:1 (v/v) solution, FTIR spectra of the hydrolyzed samples (Figure S4.2) shows the characteristic peak of ester group at 1740 cm^{-1} completely disappeared, indicating that the hydrolysis treatment removed all the acyl species. Elemental analysis of the hydrolyzed samples (Figure S4.3) shows that part of the benzethonium sulfate were also eliminated. The remaining benzethonium sulfate on modified wood pulps after the alkaline treatment was still almost in the form of benzethonium sulfate as the R values were unity.

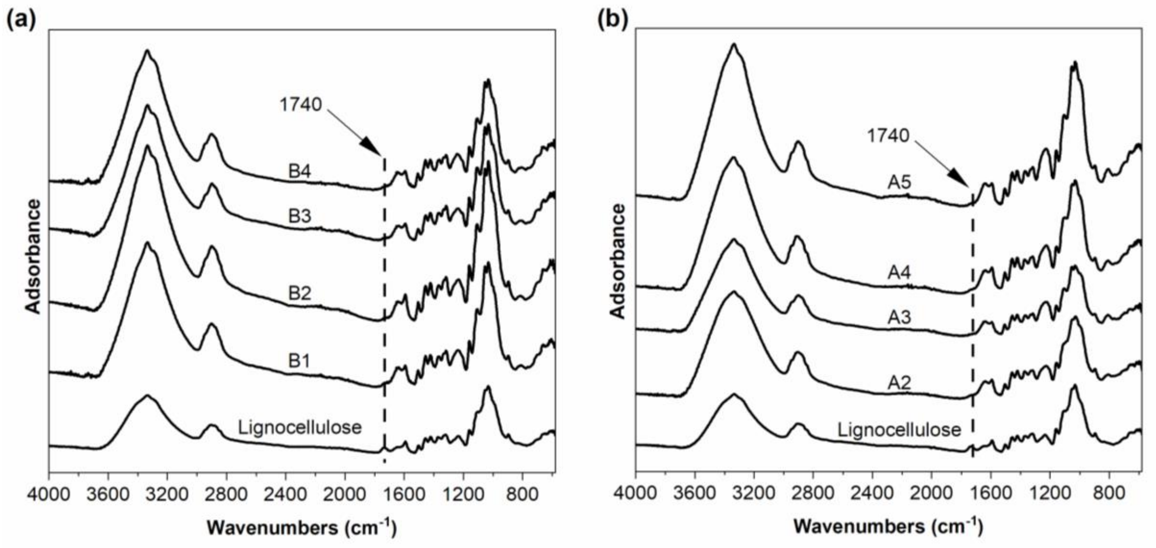

Figure S4.2. FTIR spectra modified lignocellulosic wood pulps, (a): butyric anhydride series, (b) acetic anhydride series, after being hydrolyzed by 0.125 M NaOH water/ethanol (1:1 (v/v) solution. The spectrum of the unmodified lignocellulose was also included in plots (a) and (b).

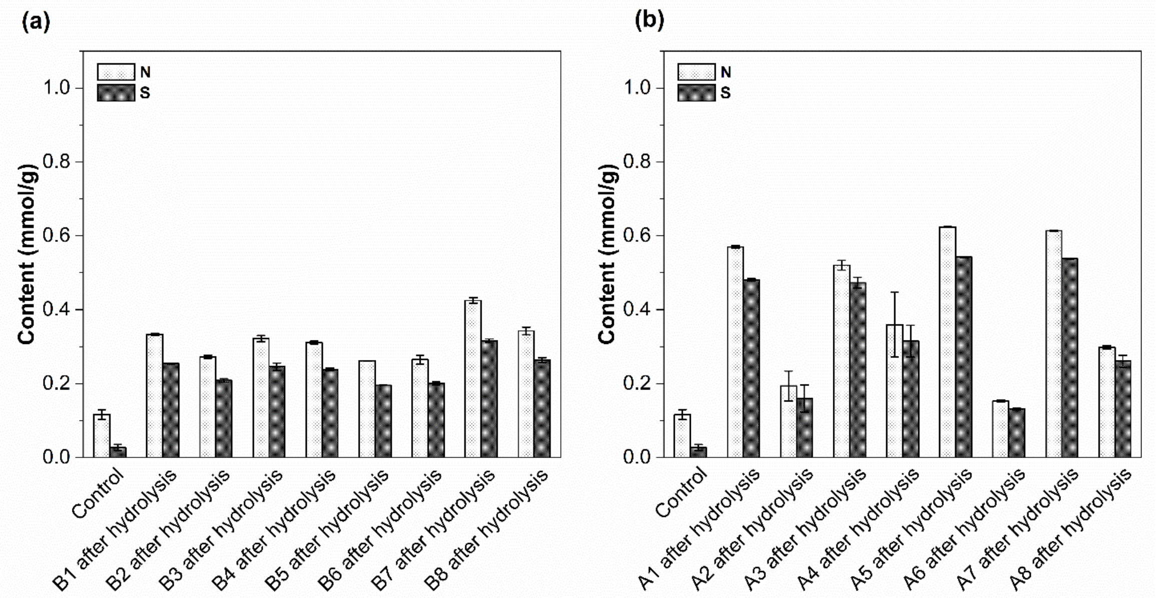

Figure S4.3. N and S elemental analysis of modified lignocellulose by reactive extrusion after being hydrolyzed by 0.125 M NaOH water/ethanol (1:1 (v/v) solution, (a) butyric anhydride and (b) acetic anhydride series.

4.7.3 Influence of extrusion conditions on Tg and degree of modification

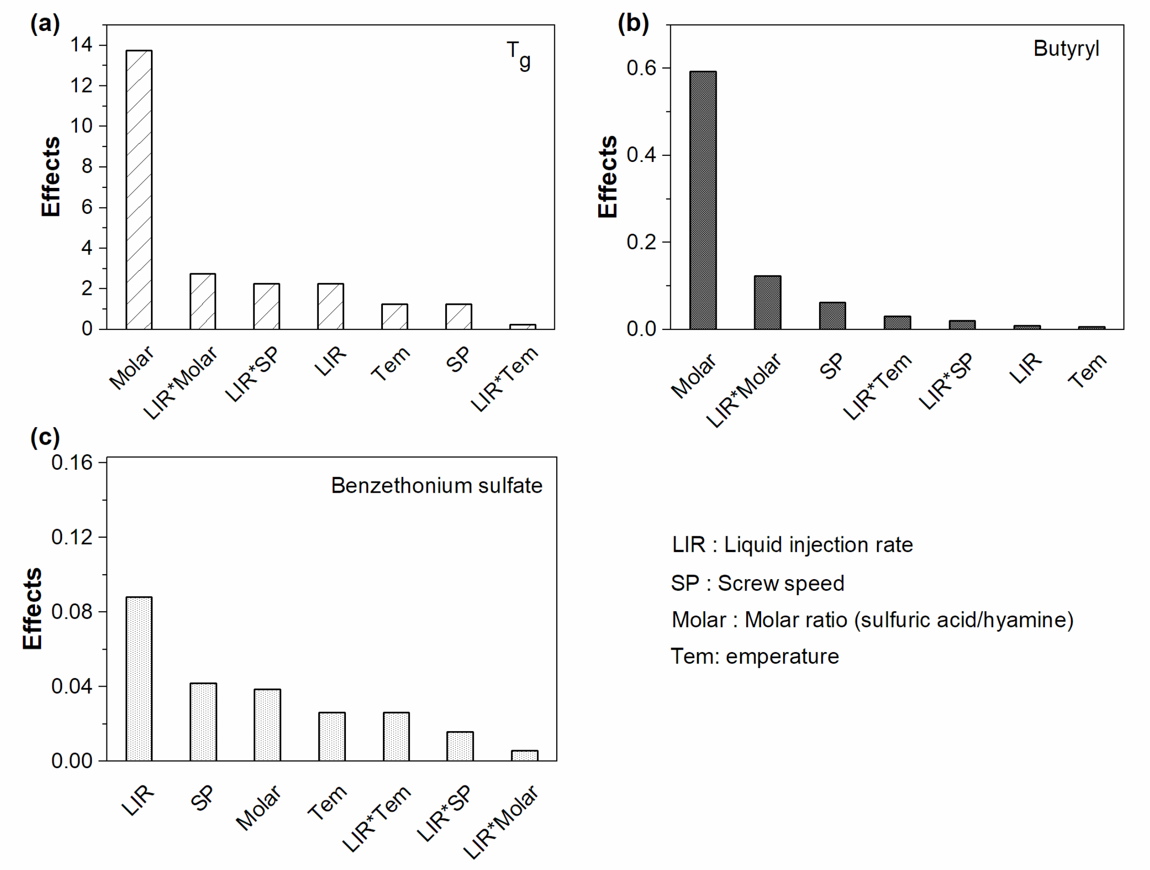

Figure S4.4. Effect coefficients of extrusion conditions for (a) T_g, (b) butyryl content and (c) benzethonium sulfate content of modified pulp in butyric anhydride series.

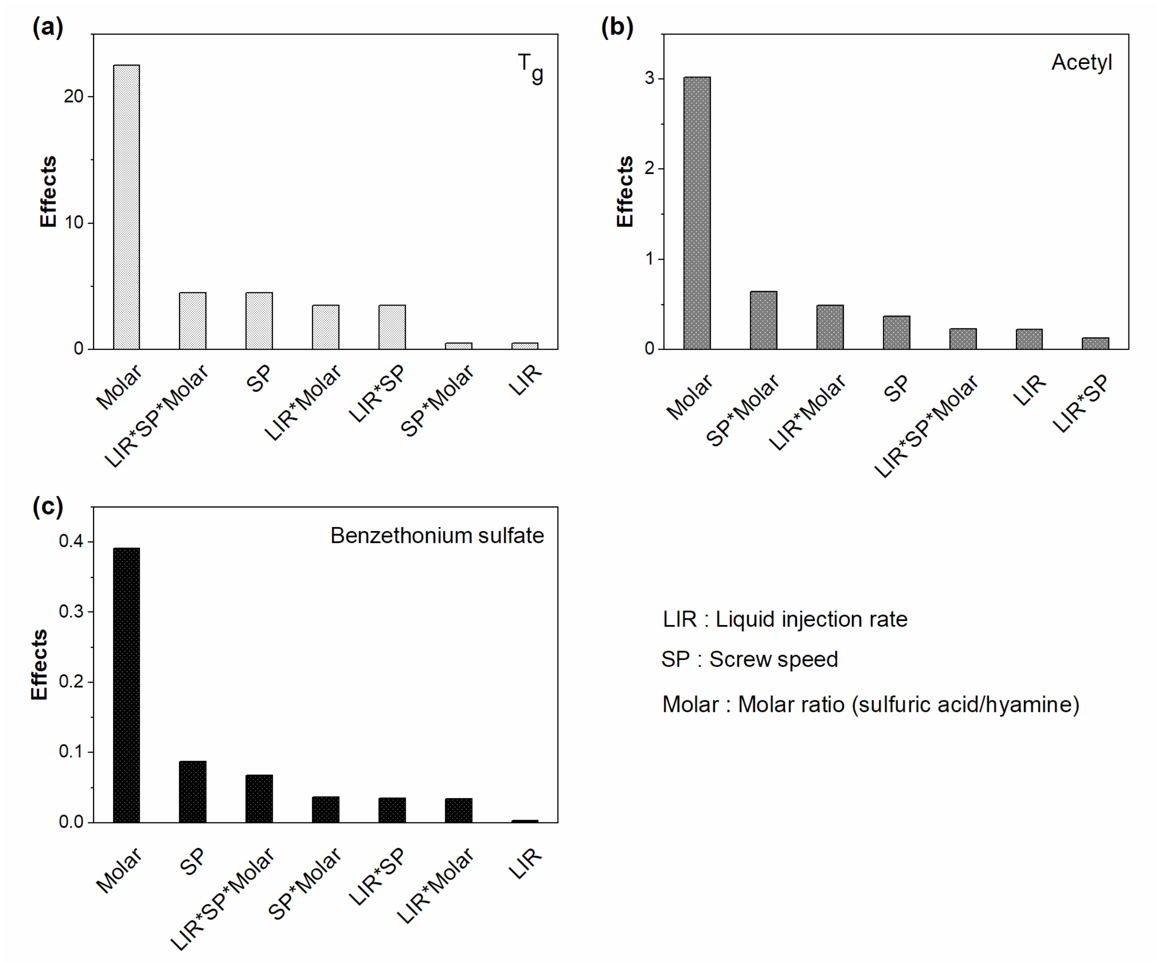

Figure S4.5. Effect coefficients of extrusion conditions for (a) T_g, (b) acetyl content and (c) benzethonium sulfate content of modified pulp in acetic anhydride series.

Chapter 5 Exploring the concept of a recycle stream for producing a thermoplastic lignocellulosic polymer from wood pulp by reactive extrusion

Based on the reactive extrusion described in chapter 4, this chapter introduces a newly conceived recycle stream method into the reactive extrusion process and significantly reduces the excessive amount of reactant needed to convert the lignocellulose into a moldable thermoplastic. The manuscript of this chapter is under preparation for publication.

Jinlei Li conducted all the experiments and wrote the draft of the manuscript. Dr. Sacripante and David Lawton provide technical guidance on the experimental design and results analysis. Heera Marway helped with the extrusion experiment. Dr. Thompson revised the draft to the final version.

5.1 Abstract

This study explores the unique concept of a recycle stream in a reactive extrusion process to reduce the excess reactant used to convert lignocellulose into a moldable thermoplastic meant for structural uses. The reactive process, reported elsewhere, employs an inexpensive functionalizing agent that mimics the wetting behaviour of an ionic liquid but becomes incorporated in the polymer to improve its flowability. Modified pulp from the first pass was recycled back to the start of the process as a lubricant, allowing a higher solids content in the subsequent pass, which avoids the need of costly plasticizing additives or use of solvents that would need to be recovered afterwards; the recycled mass had excess reactant removed prior to returning to the process in order to study its lubricating influence rather than being a source of reactant as well. A 25% recycle of the output was found to be optimal for reducing the reactant concentration in the process without significantly impacting the degree of modification. The thermoplastic nature of the modified lignocellulose was characterized by thermal and rheological analysis and demonstrated by its ability to be compression molded.

5.2 Introduction

The abundance and renewability of forestry biomass have attracted intense research interest in its use for producing various bio-polymeric products, *e.g.,* textile and packaging films.[1,2] However, the conversion of forestry biomass into polymeric products requires more complicated processes than those from fossil fuel, which decreases competitiveness in commercial applications. Hence, scalable technologies to process forestry biomass are necessary from the point of sustainable development. Extrusion technology can be considered as promising in this regard owing to its easy scale-up, cost-effectiveness and capacity for simultaneously defibrillating wood fibers.[3–5]

Direct screw extrusion of forestry biomass is challenging since the lignocellulosic fibers have low deformability and no melting point below their decomposition temperature, thus lacking the necessary flowability for most polymer processes. The most common solution currently is compounding wood fibers with a thermoplastic matrix to generate wood-plastic products.[6–8] With typically high fiber loadings (60% or higher is not uncommon), the thermoplastic melt serves as a binder and lubricant in the process.[9,10] Besides thermoplastic lubricants, use of an excessive amount of liquid is another way to aid the extrusion of lignocellulosic fibers for preparing bio-based products, *e.g.*, preparation of cellulose nanofibers by twin-screw extrusion usually uses high-percent of water to assist the convey of fibers inside the extruder.[11–13] In some cases, soluble sugars or polymers are added along with the liquid to act as a lubricant for the fibers, thereby allowing extrusion at higher solids contents.[14–17] In cases of reactive extrusion, an excess of reactants, if liquid, or added solvents are ideal for assisting conveyance of lignocellulose inside the twin-screw extruder, since many added lubricants can produce undesirable side reactions. However, using large excesses of reactants will also increase costs and mandate the complex separation of the product from residual reactant at the end of the reactive extrusion process. Inspired by the chemical engineering practice of a recycle stream in processes, this paper considers the benefits of returning a portion of the prepared thermoplastic lignocellulose to the feedstock stream of its reactive extrusion process to act as a lubricant, thus avoiding the use of costly additives and minimizing the amount of liquid reactant used. Surprisingly, the concept of a recycle stream has not been studied until now for reactive extrusion processes. For this study, the focus will be on the lubricating benefits of recycling the thermoplastic lignocellulose while the future study will consider the return of unused reactants as well, with the final goal to ultimately identify an operating state where the exiting polymer requires no post-modification cleaning before use.

Based on a reactive extrusion method described in a previous paper by the same authors, the present study considers a high solids content reactive extrusion for modifying lignocellulosic pulp from wood with a recycle stream. The investigation looks at the percent of recycled material relative to the amount of reactant added to the process on the extent of reaction and properties of the produced biopolymer. The effectiveness of this reactive extrusion process with a recycle stream was studied by examining the degree of modification and thermoplasticity of the resulting modified samples.

5.3 Experimental

5.3.1 Materials

Lignocellulosic fibers received as a high-yield Aspen mechanical pulp was supplied by Tembec (Montreal, Canada), which contains 8.2 wt% Klason lignin as determined by the TAPPI-T method 222 om-02. Before reactive extrusion, the received lignocellulosic fibers were mechanically pre-treated with a 27 mm 40 L/D twin-screw extruder (Leistritz, USA) according to a previously established method.[18] After the treatment, the fluffy received lignocellulosic wood pulp was compacted and partially micro-fibrillated into fine granules, which made the wood pulp convenient for feeding into the extrusion process and improved its chemical accessibility. Benzethonium chloride (hyamine, HPLC grade), sodium bicarbonate and phenolphthalein (ACS grade) were purchased from Sigma Aldrich (Oakville, Canada). Acetic anhydride (reagent grade), sulfuric acid (trace metal grade), anhydrous ethanol (reagent grade), and 1.0 M sodium hydroxide and hydrochloric acid solutions were obtained from Caledon Laboratory Ltd. (Georgetown, Canada).

5.3.2 Reactive extrusion of lignocellulosic fibers with a recycle stream

All reactive extrusion processing was conducted in an 18 mm (40 L/D) twin-screw extruder (Leistritz, USA) configured for solids to enter at the feed port and liquids to be metered at the second barrel zone (Figure 5.1a). For the reactive extrusion process with a recycle stream, as shown in Figure 5.1b, the first step was preparing thermoplastic for the recycling. Air-dried pre-treated lignocellulosic fibers were fed by a gravimetric feeder (Coperion, Germany) at a rate of 500 g/h. In this case, liquid modifier comprised of acetic anhydride, benzethonium chloride and sulfuric acid with a molar ratio of 13:1:0.95 was injected using an Optos Series metering pump (Eldex, USA) at a liquid rate of 32 mL/min was used corresponding to a 3.8 mL/g liquid/solid ratio. The temperature of the feeding zone was water-cooled to 25 ℃ while other zones were all heated to 120 ℃; the screw speed was set to 100 rpm. According to the study in Chapter 4, the extrusion conditions used above in the first step could prepare modified lignocellulose with the best thermoplasticity by acetic anhydride-based liquid modifier. The extruded mass, in this case, was referred to as wet-modified lignocellulose, and after it was collected, it was air-dried to constant weight in a fumehood for 1 week. Although air-drying of the modified lignocellulose was used in present study for the convenience of handling the smelly extrudate, this step can be skipped in future study by a tandem extruder or longer extruder with side feeder. The solids were ground into fine particles with size that can pass through a 20-mesh sieve and used as the recycle stream for the next step of reactive extrusion without further cleaning.

The thermoplastic lignocellulose produced in this step was meant to replace the lubricating nature of the excess liquid modifier, otherwise necessary to extrude at high solids content. Removal of the residual reactant was meant to control the lubricating contributions of the recycled thermoplastic versus liquid modifier in the second step of the process and consequently allow the study to assess how much liquid modifier was necessary for the thermoplasticization of lignocellulose. The persistence of hyamine/sulfuric acid functionalizing agent as well as its intermediates (benzethonium bisulfate) in the recycled material that was not already bound to the lignocellulose needed to be corrected for the second step below.

In the second step, the recycled thermoplastic was dry blended with defibrillated wood pulp in a high shear mixer, at either 25 wt% (R-25%) or 50 wt% (R-50%) of the lignocellulosic feedstock. The same twin-screw extruder set-up was used as previously described in the first step. For the 25% recycle series, liquid injection rates were either 18, 15, 12, 9 or 6 mL/min, corresponding to a liquid/solids ratio of 2.16, 1.80, 1.44, 1.08 or 0.72 mL/g, respectively. For the 50% recycle series, the liquid injection rate was either 12, 10, 8, 6 or 4 mL/min, with a corresponding liquid/solid (wood pulp and the lubricant) ratio of 1.44, 1.20, 0.96, 0.72 or 0.48 mL/g, respectively. For each series, baseline conditions (B-25% and B-50%) were determined by attempting to extrude 100% lignocellulose at the same liquid/solid ratios; the recycle stream contained a known amount of unbounded benzethonium sulfate, and it was decided to compare each recycle condition against its own baseline condition rather than trying to adjust all conditions to the same total amount of benzethonium sulfate due to the sensitivity of the reaction and final properties of the material to this ingredient.

The extrudate was collected, cooled in distilled water, and neutralized with 1 M sodium bicarbonate solution before repeated washed with distilled water until the conductivity of the filtrate (determined by a Mettler Toledo S230 conductivity meter) was similar to the distilled water. The modified pulp samples were then vacuum-oven dried at 75 °C for 24 hours prior to storage and characterization.

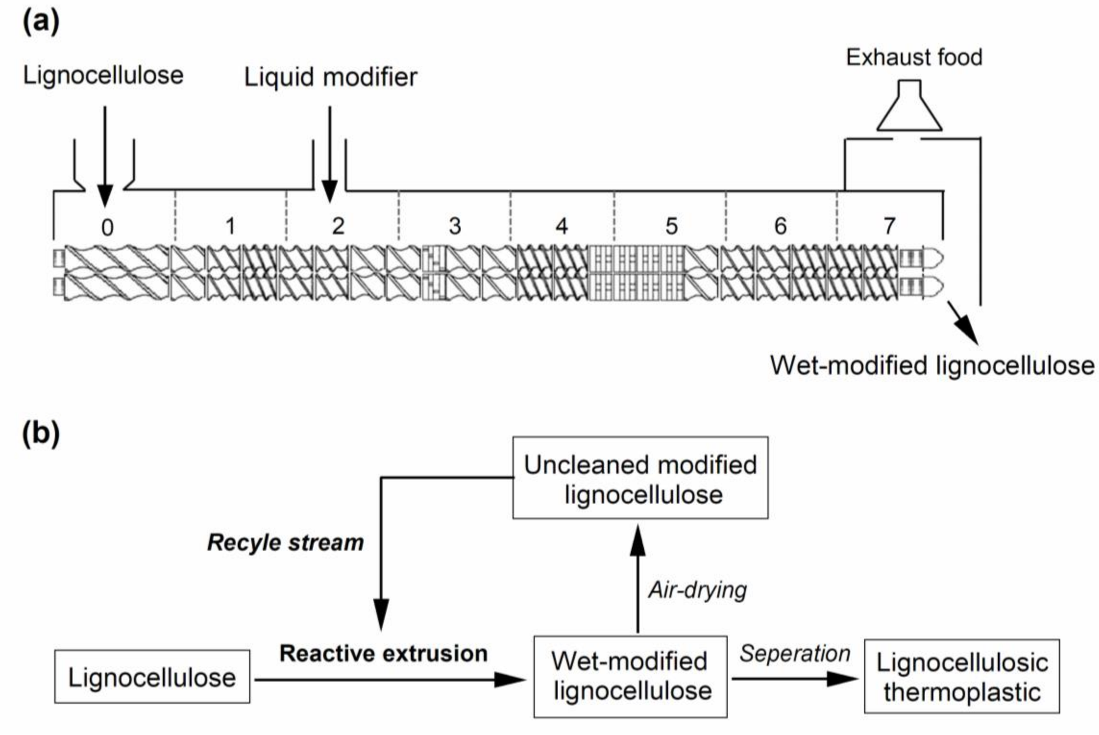

Figure 5.1. (a) Configuration of an 18 mm Leistritz twin-screw extruder for the reactive extrusion of lignocellulosic fibers, (b) flow diagram of the reactive extrusion process with a recycle stream.

5.3.3 Characterizations

Gravimetric analysis

After air-drying, the residual acetic anhydride/acid in the lubricant was estimated by vacuum drying. Five air-dried samples of the thermoplastic lignocellulose from the first step were dried under a 30 Hg vacuum until at constant weight. The weight change was used to determine the residual acetic anhydride/acid in the recycle stream. After vacuum drying, the thermoplastic was cleaned with water until the conductivity of the filtrate was close to that of distilled water. The weight change after the washing was counted as unreacted benzethonium chloride/sulfuric acid.

Degree of chemical modification and reaction effectiveness

Acetyl and benzethonium sulfate contents of the modified pulp were determined by colorimetric titration and elemental analysis, following a previously established approach in Chapter 4. Dried modified pulp, 0.05 g, was put into a 25-mL glass vial, to which was added 5 mL of 0.25 M NaOH and 5 mL anhydrous ethanol. The mixture was left to stand for 24 h for hydrolysis of the ester species in modified lignocellulose. According to a previous study, the NaOH treatment removed all acetyl groups and part of the benzethonium sulfate. The total amount of the hydrolyzed ester was then estimated by back titration by adding 10 mL 0.25 M HCl to the system and titrating the mixture with 0.25 M NaOH and a phenolphthalein indicator. The amount of benzethonium sulfate species in the modified pulp before and after NaOH treatment was determined by elemental analysis.

Elemental nitrogen (N) and sulfur (S) contents were determined with a UNICUBE elemental analyzer (Elementar). Approximately 2 mg powder sample was sealed in Tinfoil and loaded into the analyzer for testing.

Based on the estimated acetyl and benzethonium sulfate content in the modified wood pulp by titration and elemental analysis, the reaction effectiveness (mmol/g) of the extrusion process was evaluated by examining the amount of acetyl and benzethonium sulfate species incorporated onto the fed raw material. For the baseline conditions, the fed raw material was neat lignocellulose, while for the recycle series, it was neat lignocellulose and the pre-modified pulp from the recycle stream.

Thermal properties

Glass transition temperature (T_g) was determined by a Q200 differential scanning calorimeter (DSC; TA Instruments, USA) operating in modulated mode. Modified lignocellulose, 9 mg, was loaded and sealed into a Tzero aluminum pan. A hole was punched into the lid to allow moisture evaporation during the test. Samples were equilibrated at -20 °C, then scanned till 220 °C at the ramp rate of 5 °C/min, with an oscillation of 1.00 °C every 60 seconds. The reversible heat flow component was separated from the total heat flow was by the Universal Analysis software (TA Instruments, USA) and used to determine the T_g of modified samples.

The flowability of the recycled pulp and the final modified samples were quantified by a Discovery HR-2 hybrid rheometer (TA Instruments, USA) by conducting a temperature sweep after first discovering the linear response region by a strain sweep. A disk prepared by compression molding with a 1.50 mm thick and 25 mm diameter was used for the rheology testing. The testing was performed under a heating-cooling-heating model over a temperature range of 90 to 200 °C at a rate of 5 °C/min and under a constant shear rate of 0.1 s^{-1}.

Compression molding of the modified wood pulp was done with a Carver 4389 benchtop hydraulic press with heated platens. A stainless steel mold with a dimension of 50 mm × 13 mm × 0.45 mm was used for the compression molding. Molding was done at 180 °C, a 3 metric tons force was applied for 3 mins and then 7 metric tons for another 12 mins.

5.4 Results and discussion

5.4.1 Influence of recycle stream on processing of the wood pulp by twin-screw extrusion

Insights into the processability of lignocellulose based on recycle operations was determined by analysis of the torque on the machine. Figure 5.2 shows the torque (as a percentage of maximum torque capacity) for the 18 mm twin-screw extruder with different lubrication schemes. For the same liquid/solids ratio, the torque was lower for both R-25% series and R-50% series in comparison to B-25% and B-50% series, showing the thermoplastic contributed to the lubricity of the process, as hoped. For the 25% recycle stream, extruder torque of the R-25% and B-25% series were comparable to one another while the liquid/solid ratio remained above 1.8 mL/g. However, below this ratio, the two series deviated significantly, with the torque of the R-25% series only slightly increasing from 16% to 18% for ratios going from 1.44 to 1.08 mL/g. In contrast, the torque for the B-25% series dramatically jumped from 20% to 50.5% for ratios of 1.44 mL/g decreasing to 1.08 mL/g. The R-25% series could be processed at a very low liquid/solid ratio of 0.72 mL/g, but the B-25% series halted the motor at this ratio. The torque for the R-50% series shows a similar trend to the R-25% series and yet R-50% always experienced lower torque than B-50%. In this case, ratios below 1.2 mL/g, the torque of the B-50% series rapidly increased when the thermoplastic recycled material was not present, whereas the R-50% series could be operated at a much lower liquid/solid ratio of 0.48 mL/g without causing a significant increase in extruder torque. The torque of the B-50% series was slightly lower than that of the B-25% series because the liquid modifier used for B-50% contained more hyamine/sulfuric acid to correct for the unbounded benzethonium sulfate in the R-50% series. Overall, the results are showing that recycling a portion of the thermoplastic lignocellulose back to the feed stream was much more effective in lowering the motor demand than using the liquid modifier, and reactive extrusion at a very low reactant content became processible when the thermoplastic was present.

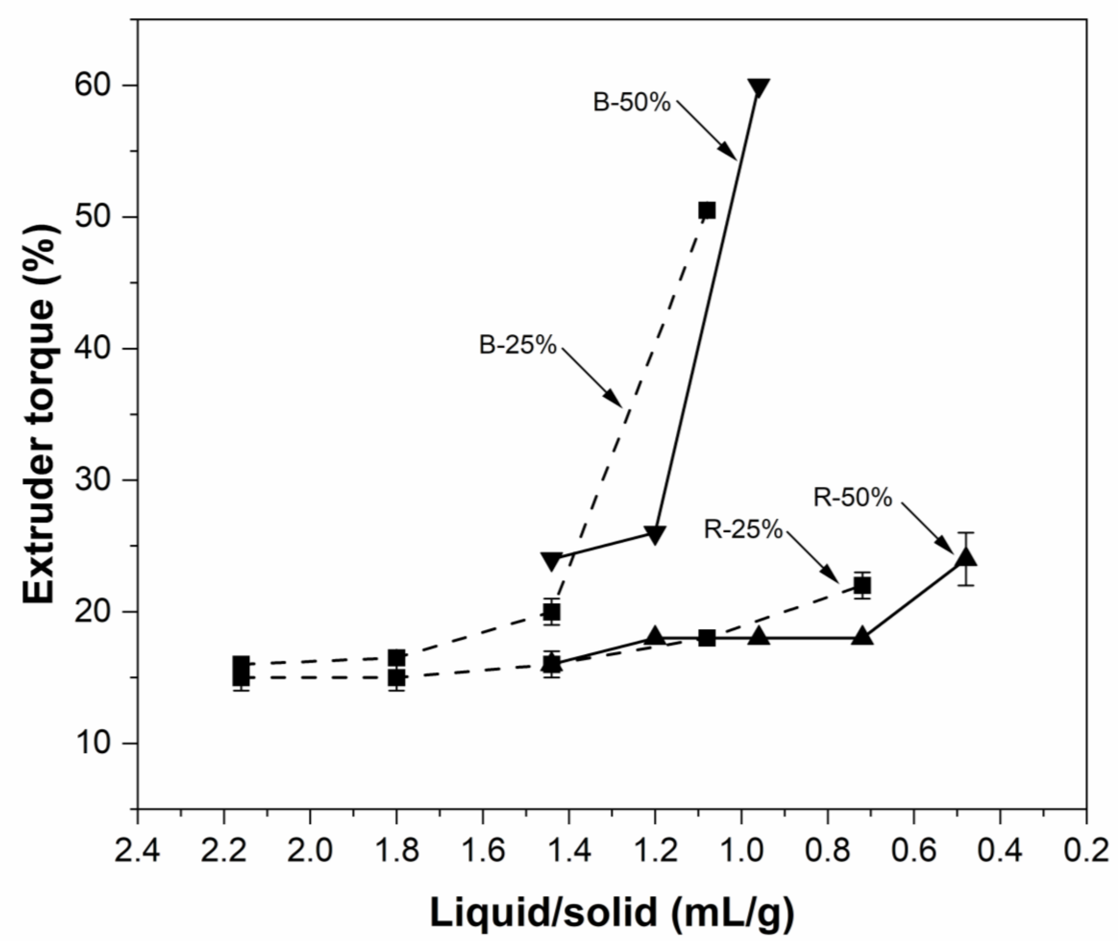

Figure 5.2. Extruder torque during reactive extrusion of wood pulp based on different liquid/solids ratios in the process and different percent recycle content in the feedstock.

To consider the rheology of the thermoplastic lignocellulose being recycled, Figure 5.3 presents its complex viscosity curves versus temperature and shear rate (i.e. angular frequency). Plot (a) shows that system temperatures above 105 ℃ are necessary to transition from a solid-like response to an increasingly viscous response. For an extrusion temperature of 120 ℃ used in the experiments, its viscosity had already dropped from 3×10^5 Pa-s to 1.5×10^5 Pa-s, and this was seen at very low shear rates of 0.1 s^{-1}. Gravimetric analysis showed that this thermoplastic retained approximately 3.5 wt% acetic anhydride/acid residuals and 30 wt% unbounded benzethonium sulfate in its air-dried state, which contributed to the thermal flowability found in this analysis. Plot (b) shows shear dependency at 120 ℃, with the thermoplastic showing significant thinning over the three decades of shear rate and displaying no plateau. At a shear rate of 10 s^{-1}, the complex viscosity of the thermoplastic had dropped to around 1000 Pa-s, and extrusion conditions are normally well above 50 s^{-1}, suggesting this modified lignocellulose had comparable flowability to many commercial extrusion-grade synthetic polymers. The flowable nature of this thermoplastic can readily be understood to be promoting the convey of wood pulp inside twin-screw extruder based on these results.

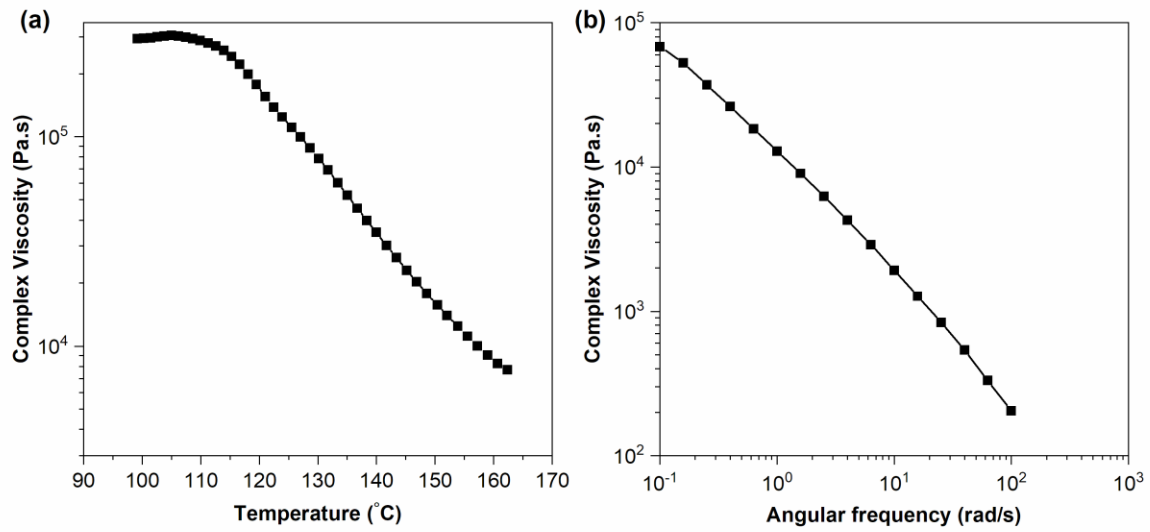

Figure 5.3. Complex viscosity of the recycled thermoplastic verse (a) temperature at 0.1 s^{-1}, (b) angular frequency at 120 ^{o}C.

5.4.2 Reaction effectiveness of the extrusion process with a recycle stream

A previous study has demonstrated that the modified pulp by this reaction exhibits grafted acetyl group and, to a lesser degree, grafted benzethonium sulfate groups, with both being important to the flowable nature of the biopolymer. Figure 5.4 shows the reaction effectiveness based on the amounts of acetyl and benzethonium sulfate groups grafted onto the original lignocellulose for the different recycle stream series and varying liquid/solid ratios, corrected to represent only new attachments during the second step of extrusion. Because the recycle series included some mass fraction of the thermoplastic pulp, to observe the effect of the different lubrication schemes on the reaction, the pre-existing acetyl and benzethonium sulfates groups in the pulp from the first step of processing were deducted from the calculation and the new groups content was normalized based only on the mass of lignocellulose pulp fed into the second step of extrusion. Additionally, since the unbounded benzethonium sulfate in the recycled thermoplastics did not react with the liquid modifier during the reactive extrusion, the reaction effectiveness was plotted versus liquid/pulp rather than liquid/solid for the convenience of comparison.

For the B-25% series, reaction effectiveness for the lignocellulose pulp declined with lower liquid/pulp ratios, with decreasing graft attachments for both acetyl and benzethonium sulfate. However, reaction effectiveness for the R-25% series showed a significant increase as new grafted content increased with decreasing liquid/pulp ratios and reached a maximum in the mid-range of examined liquid/pulp ratios. When the liquid/pulp ratio was below 1.96 mL/g, the reaction effectiveness of R-25% significantly improved compared to higher ratios, and reached a maximum at 1.57 mL/g. Only at very low liquid/pulp ratios around 0.8-1.0 mL/g did the reaction effectiveness dropped to match the other series. The maximum reaction effectiveness of the R-25% series occurring at 1.57 mL/g was 9.3 mmol/g for acetylation and 1.6 mmol/g for benzethonium sulfate attachment, surprisingly, which were even higher than that of the first-step extrusion used for preparing the recycled thermoplastic. As a matter of reference, the first-step extrusion had a 7.7 mmol/g acetylation effectiveness and 1.6 mmol/g benzethonium sulfate attachment effectiveness, respectively, but also used a much higher liquid/pulp ratio of 3.84 mL/g. That is to say, using a 25 wt% recycle stream, the reaction extrusion could be operated with high modification effectiveness without the need of a large excess of reactants for pulp conveyance.

Between the two baseline series, B-25% and B-50%, the extent of acetylation was the same, but the new benzethonium sulfate grafted content was slightly greater for B-50%, possibly because of the higher total benzethonium sulfate in the R-50% series. Comparison between B-50% and R-50% series for reaction effectiveness showed that use of the thermoplastic in the feedstock was beneficial for increased acetylation over just having the liquid modifier as a lubricant but not to the significant extent as seen with the R-25% series and at lower liquid/pulp ratios than found with the R-25% series. The higher recycle stream content (R-50%) had a negative influence on reaction effectiveness, with a lower benzethonium sulfate content grafted onto neat pulp and the pre-modified pulp in the recycled thermoplastic than seen with the B-50% series.

Several possible factors could contribute to the low reaction effectiveness of the R-50% series: (1) the pre-modified wood pulp was less reactive as a recycled stream in the second step compared to neat pulp and being in higher content at 50% recycle, it had a more noticeable effect; (2) the pre-modified wood pulp was more effective in mixing with the unreacted neat pulp than the reactant and consequently decreased accessibility to reactive sites; and (3) the recycled thermoplastic was much more effective as lubrication than the liquid modifier, which meant less mechanical stresses were supplied to the pulp fibers and reduced defibrillation which diminished the reactive surface area as a result. The last factor seems the most feasible explanation for the reduced reaction effectiveness.

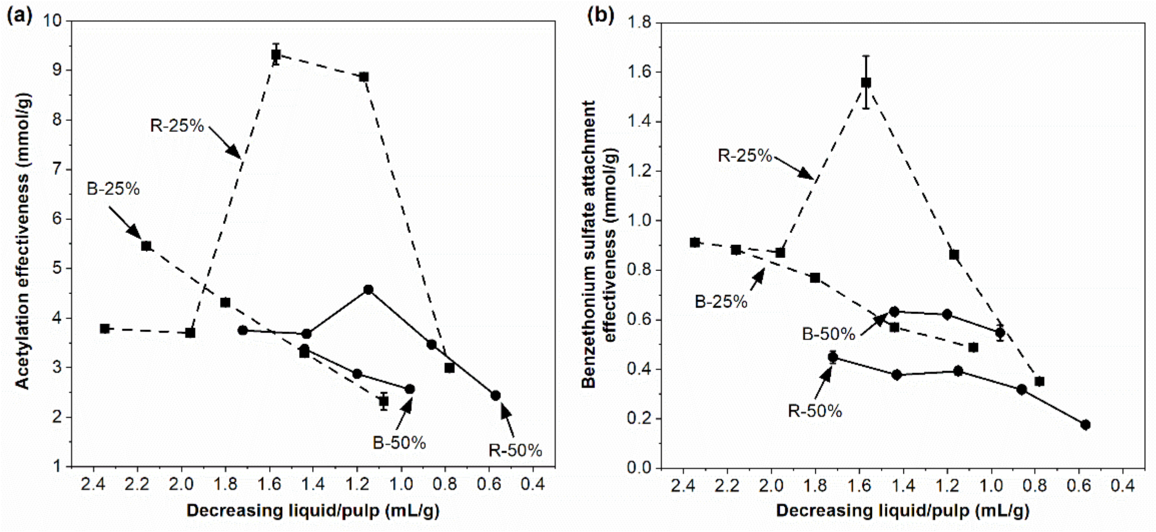

Figure 5.4. Reaction effectiveness of (a) acetylation, (b) benzethonium sulfate attachment of the reactive extrusion processes with and without a recycle stream.

5.4.3 Thermoplasticity of the modified wood pulp from the recycle series

Owing to the grafted acetyl and benzethonium sulfate, the resulting lignocellulose showed thermoplasticity after chemical modification that was displayed by now possessing a T_g well below the decomposition temperature of the pulp. Figure 5.5 shows the T_g of the modified pulp for varying liquid/pulp ratios and for the different recycle series. As a baseline for this discussion, a cleaned sample of the recycled thermoplastic from the first step had a T_g = 105 °C (based on its preparation with a liquid/pulp ratio of 3.84 mL/g, far higher than used in the recycle series). Only one sample in either recycle series, at a 1.57

mL/g liquid/pulp ratio in the R-25% series, showed a lower T_g (103 °C) and hence by the definition being used in this paper, it displayed improved thermoplasticity over the recycled thermoplastic. However, considering that this condition is using less than half the amount of reactant in the process compared to when the thermoplastic recycle was made, this lower T_g was considered a monumental improvement for the process.

For B-25% and B-50% series, their T_g was between 120-135 °C, which was higher than the series with the thermoplastic recycle, and both showed a trend of increasing with lower liquid/pulp ratios. Samples in the B-25% series below a liquid/pulp ratio of 1.44 mL/g had no T_g that could be detected by DSC. The added thermoplastic had notable benefits on the T_g, since even though the R-50% series had a similar reaction efficiency to its corresponding B-50% series, the thermoplasticity of the former modified pulp had much lower T_g and hence better, which will be explained in the following section. The R-25% series showed T_g varying between 104-124 ℃ while the R-50% series showed T_g varying between 114-126 °C. The lower reaction efficiency at 50% recycle compared to 25% (R-25% versus R-50%, Figure 5.4) was offset by the more effective plasticization of the lignocellulose by the higher recycle content in the feed stream of the process.

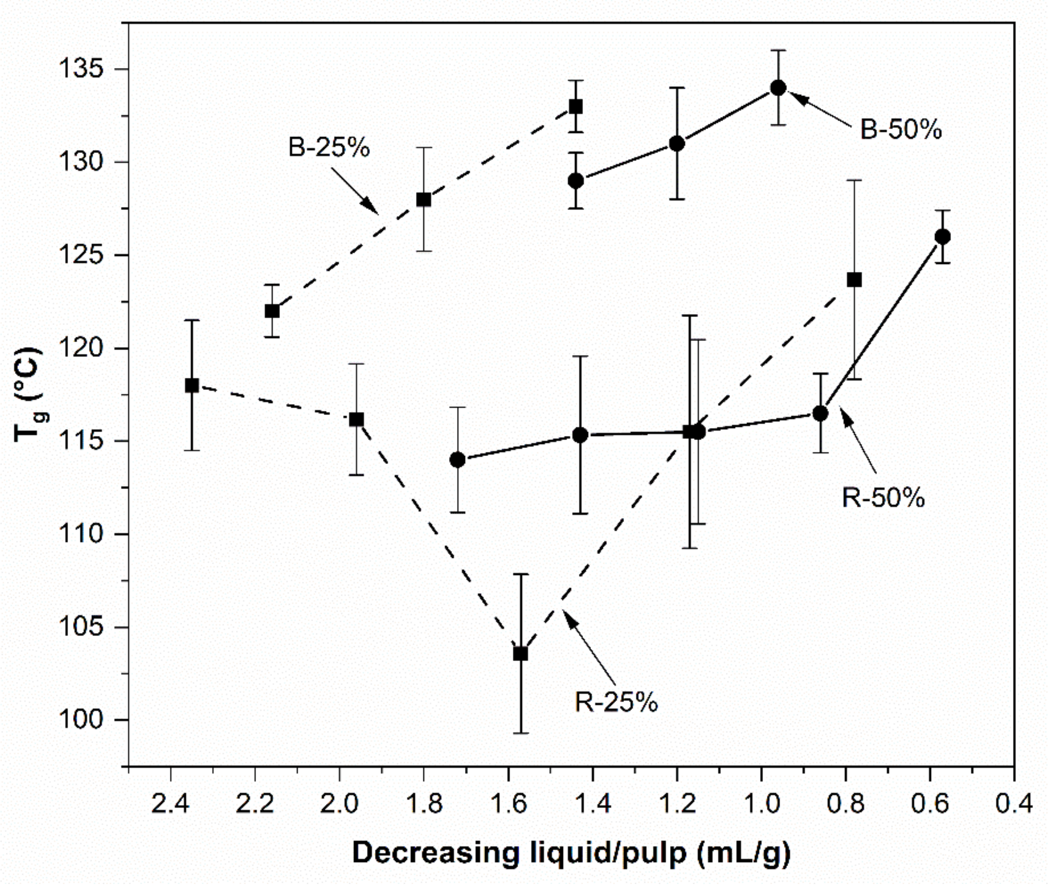

Figure 5.5. T_g temperatures of the modified wood pulp prepared by reactive extrusion with or without a recycle stream.

In our previous study, one of the other favoured methods for demonstrating thermoplasticity was to visually consider the compression-moldability of the samples, though in that case, the liquid/pulp ratios were quite high (3.84-5.76 mL/g) versus 0.57-2.35 mL/g in the present recycle stream series. The qualitative evaluation is concerned with the nature of the biopolymer to flow into all areas of the mold, such that it accurately reflects the mold shape, as well as displays smooth surfaces. Modified pulp samples at the lowest, medium and highest T_g of each series were compression molded for this evaluation and are shown in Figure 5.6. Samples of any T_g in the R-25% or R-50% series showed good compression moldable behaviour; however, not all samples of the B-25% or B-50% series showed good thermoplasticity. The two samples with T_g of 133 and 134 °C showed poor performance, with only about half of the pulp melting into the shape of the mold.

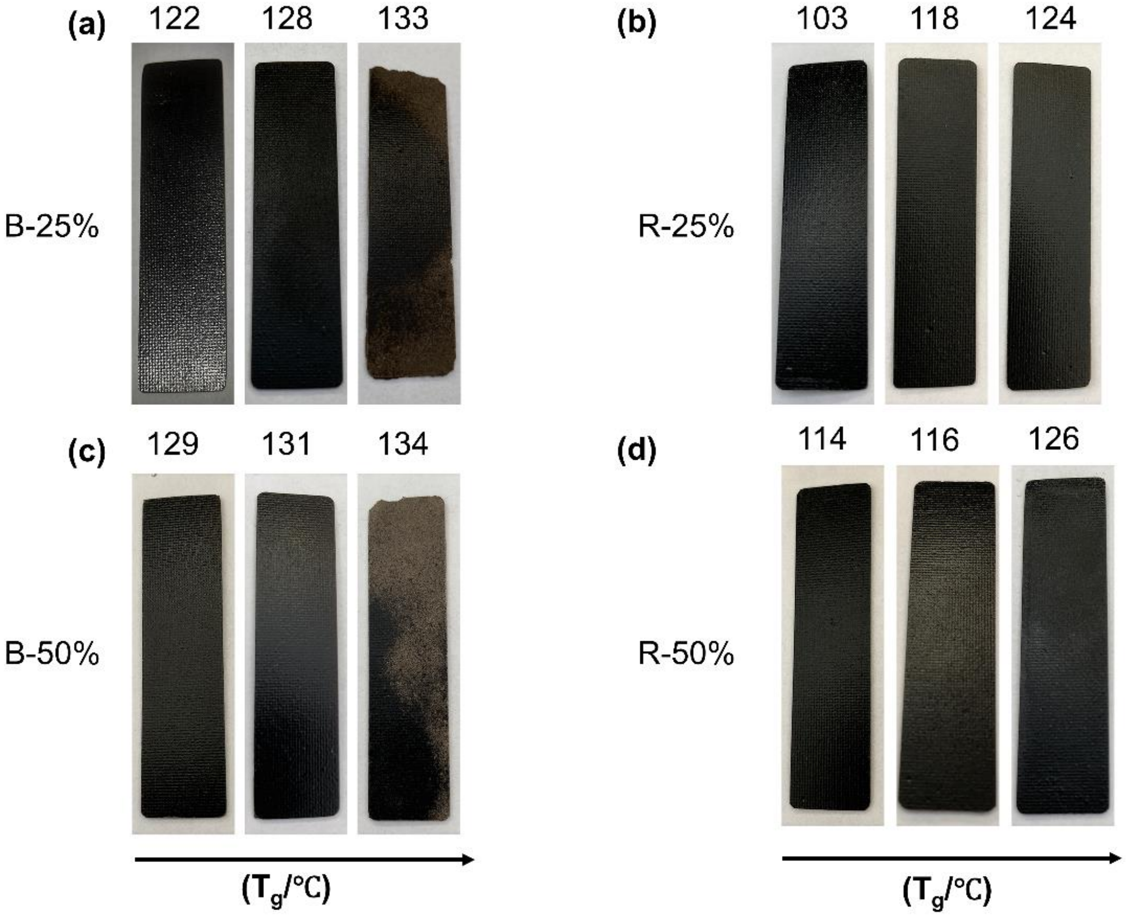

Figure 5.6. Images of the compression-molded parts of the three modified wood pulps with different T_g (stated above each part) from (a) B-25%, (b) R-25%, (c) B-50% and (d) R-50% series.

Figure 5.7 shows the complex viscosity curves from the study, examining three samples from each of the four recycle series. Significant transition behavior, shown by a steep decline in complex viscosity with increasing temperature, was observed for modified wood pulp that displayed good moldability. Good moldability corresponded to samples with a T_g below 131 °C. Generally, samples with lower T_g presented a more significant transition, which was particularly noteworthy for the sample from the R-25% series with the lowest T_g of 103 °C. Rheologically, the sample with a T_g of 103 °C from the R-25% series displayed similar flow behavior to the recycled thermoplastic (shown in Figure 5.3a), meaning that it would be equally suitable for the recycle stream but now prepared at a much lower liquid/pulp ratio. For the two samples with T_g of 133 and 134 °C from the baseline series, there was no apparent transition behavior observed in their complex viscosity curves, as highlighted with dash arrows in Figure 5.7 (a,c), and was consistent with their poor performance in compression molding.

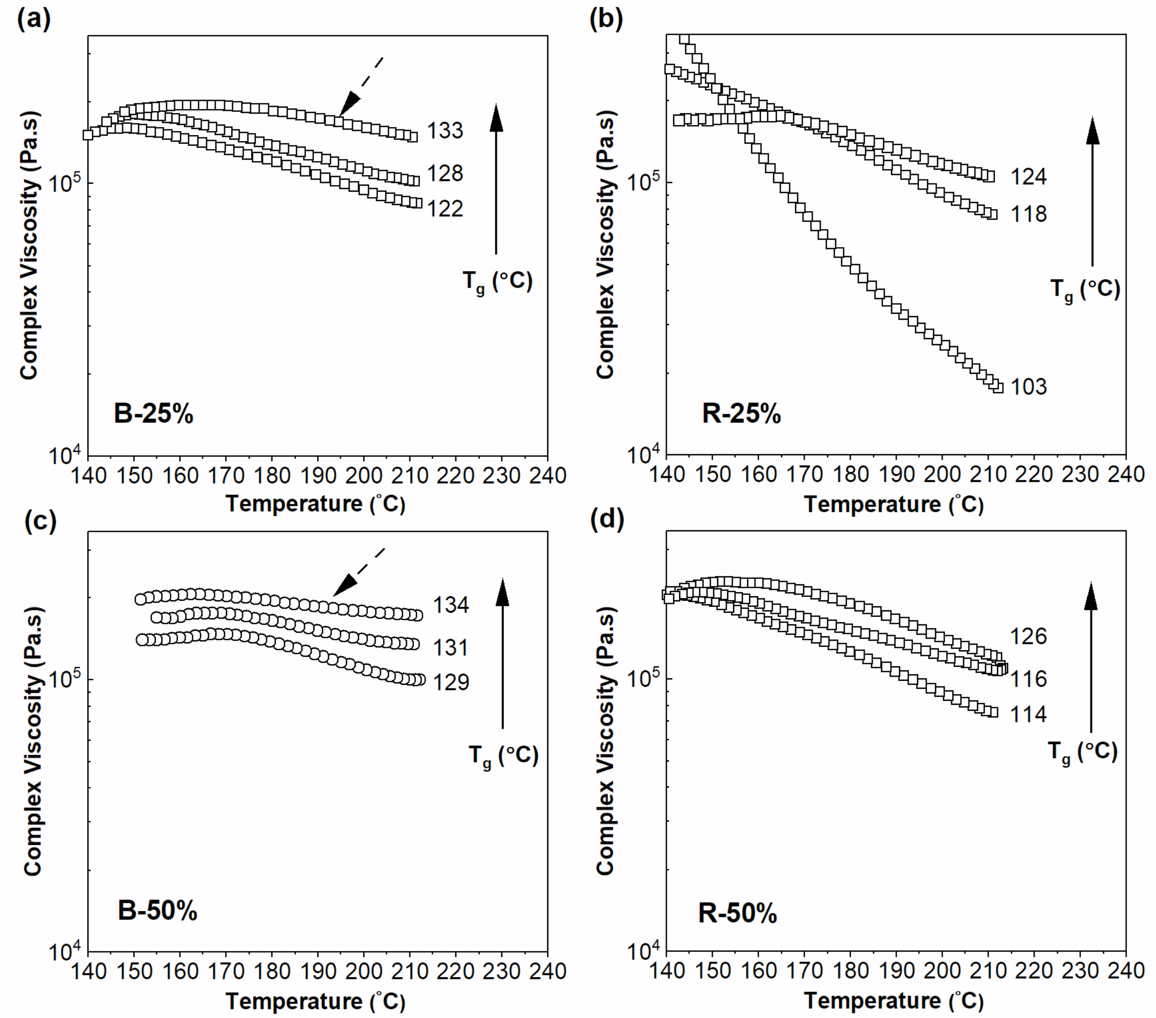

Figure 5.7. Complex viscosity curves for three samples (with their T_g listed) corresponding to the (a) B-25%, (b) R-25%, (c) B-50% and (d) R-50% series.

5.4.4 Total liquid usage of the reactive extrusion with a recycle stream

Process efficiency of a reactive extrusion process with recycle stream can be evaluated by considering the total amount of liquid modifier used in the two steps of operations to afford wood pulp thermoplasticity. Figure 5.8 (a, b) shows the liquid usage for the reactive extrusion process with and without a recycle stream, considering all samples from R-25% and R-50% series, and two samples from both B-25% and B-50% series.

Immediately, it was noticed in the plot that acetylation and benzethonium sulfate attachments for the R-25% series could be completed with lower liquid usage compared to the other three series. Comparably, the R-50% series required total liquid usage, which was higher than the R-25% series but also higher than the baseline B-50% series. Figure 5.8 (c,d) shows that 24-37% of the acetyl groups and 40-63% of bound benzethonium sulfate groups in the final modified wood pulp for the R-50% series, and 7-17% of the acetyl groups and 8-28% of bound benzethonium sulfate groups in the final modified wood pulp for the R-25% series originated from the recycled thermoplastics. Although the second step of reactive extrusion of the R-50% series used low liquid injection rates (0.57-1.72 mL/g) for the modification, less grafting of acetyl and benzethonium sulfate occurred onto the wood pulp to determine final thermoplasticity. The thermoplasticity/compression moldability of the final modified wood pulps of the R-50% series relied more heavily on the contribution by the pre-existing acetyl and benzethonium sulfate in the recycle stream. Consequently, the process efficiency was deemed lower since using such a high amount (50 wt%) of recycled thermoplastics meant the R-50% series had a high total liquid consumption (based on first step preparation at the high liquid/pulp ratio of 3.84 mL/g). On the other hand, the majority of the modification for the wood pulp for the R-25% series was finished by the second step of reactive extrusion using relatively low liquid injection rates (0.78-2.35 mL/g).

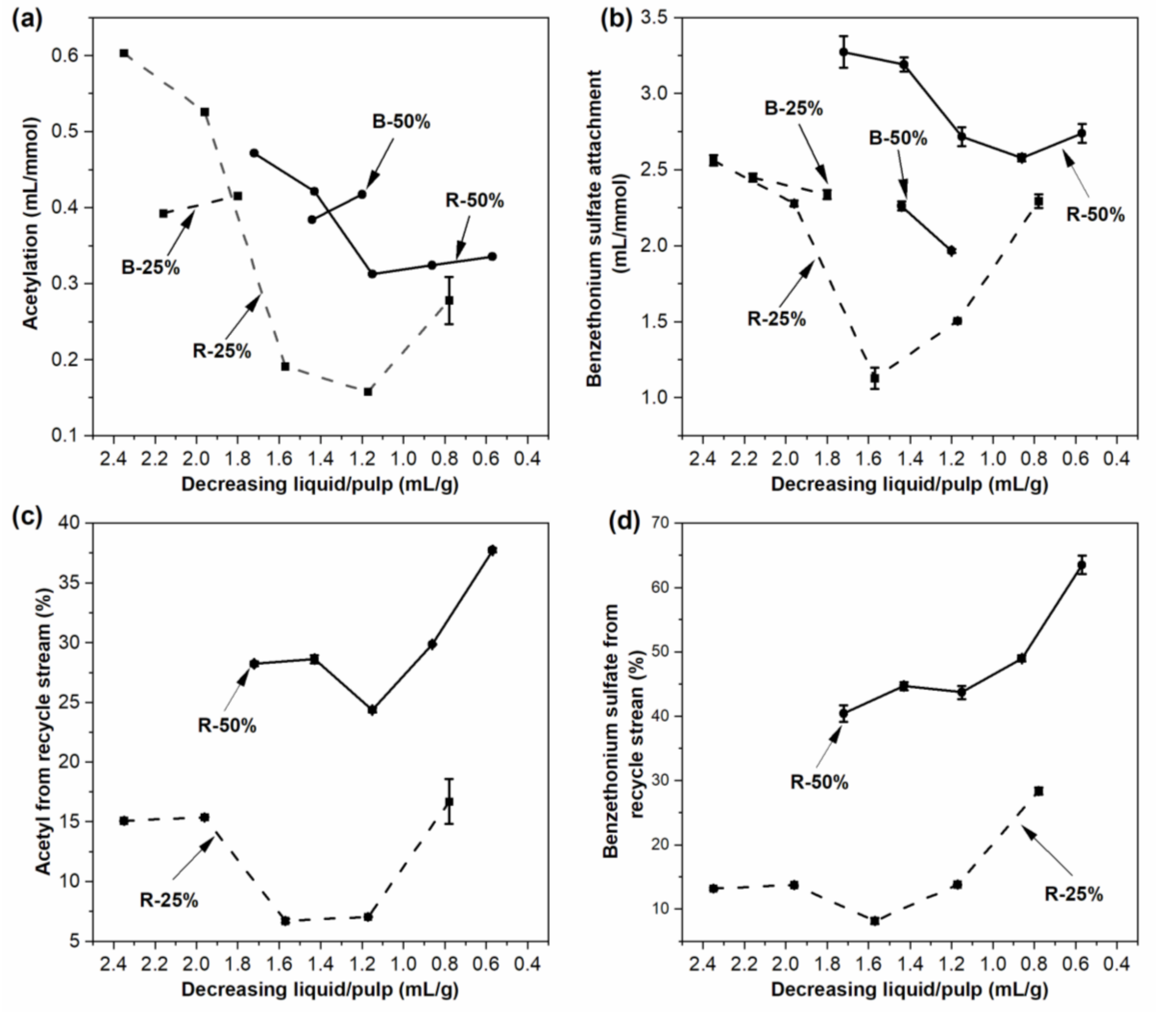

Figure 5.8. Liquid usage for (a) acetylation and (b) benzethonium sulfate attachment for reactive extrusion processes with and without a recycle stream. Plots of (c) acetyl and (d) benzethonium sulfate that originated from the recycle stream in the final modified wood pulp are displayed for the R-25% and R-50% series.

5.5 Conclusions

The concept of a recycle stream was proven feasible for lubricating lignocellulosic fibers in a reactive extrusion process for making a flowable thermoplastic, and consequently, it was possible to significantly reduce the amount of liquid reactant that was necessary inside the twin-screw extruder. Ultimately, a modified wood pulp thermoplastic with similar flowability was produced at a liquid/solid ratio of 1.57 mL/g using 25% recycled content compared to 3.84 mL/g, meaning that more than 50% of the liquid in the original reactive process was actually being included for lubrication rather than as reactant. The optimal recycle content (25 wt%) found among the conditions examined in the study gave the highest reaction effectiveness, even slightly better compared to the extrusion process operated without recycle content and relying upon a high liquid/pulp ratio. Too much recycled content (50 wt%) was seen to negatively effect the reaction, and actually needed more liquid modifier than the unlubricated process to prepare thermoplastic lignocellulose with similar grafted content.

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Chapter 6 Contributions and recommendations

6.1 Contributions

In this thesis, lignocellulosic wood pulp, rather than the more expensive purified cellulose, was modified to prepare a bio-thermoplastic, which added difficulty to designing methods for the chemical thermoplasticization because of the more recalcitrant structure of lignocellulose. Based on a new reaction method and inclusion of a recycle stream, a rapid high solids content reactive extrusion process was designed for the thermoplasticization of the pretreated lignocellulose. Key major contributions of the thesis are:

1. A new high-solids content method was developed to defibrillate lignocellulosic fibers by twin-screw extrusion, balancing wetting and friction effects on the biomass. This new method supplies an economical and clean way for the industry to prepare lignocellulosic biomass for further chemical modification.
2. For the first time, an inexpensive additive was derived from commonly used industrial chemicals, sulfuric acid and hyamine, to be used as an alternative to expensive solvents for the wetting of lignocellulose. The additive can also be described as a reactant for the thermoplasticization of lignocellulose. With the additive, a new chemical thermoplasticization strategy based on esterification was studied in detail.
3. For the first time, a continuous high-solids content modification process was designed and demonstrated for lignocellulose based on reactive extrusion. Effective acylation with acetic anhydride and butyric anhydride was found within 2 minutes,

with the thermoplasticized lignocellulose demonstrating moldability without plasticizers.

4. For the first time, a recycle stream was incorporated into a high-solids content reactive extrusion process. Its inclusion in the case of modifying lignocellulose allowed the reduction of liquid reactants which were otherwise necessary for lubrication in the conveyance of biomass within the extruder during the reaction.

6.2 Recommendations for future work

This thesis has focused on designing methods to prepare lignocellulose thermoplastics. More future works are recommended to investigate the properties and applications of the new bioplastic.

1. The new thermoplastic lignocellulose introduced by this thesis is a stiff material and lacks sufficient toughness for some possible applications, such as packaging. Investigation of adding plasticizer or blending with other polymers to improve the toughness of the lignocellulose thermoplastic is recommended. Some bio-based plasticizers such as triethyl citrate, sunflower oil and poly(ethylene glutarate) are recommended to try.
2. The thermoplastic lignocellulose contains benzethonium cation species, which is considered to have antiseptic and anti-infective properties. Investigation of whether these properties are incorporated into the lignocellulose thermoplastic is recommended.

3. Although cellulose carboxylic acid esters, such as cellulose acetate, have been reported to be biodegradable to certain bacteria, the biodegradability of lignocellulose carboxylic ester is unknown and recommended for investigation.