

Nanocomposite-based Lignocellulosic Fibers

Zhiyuan Lin

Dissertation submitted to the faculty of the
Virginia Polytechnic Institute and State University in partial
fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

In

Forest Products

Scott H. Renneckar, Chairman

Scott W. Case

Charles E. Frazier

Joseph R. Loferski

Audrey Zink-Sharp

Dec 16, 2009
Blacksburg, Virginia

Keywords: layer-by-layer assembly, lignocellulosic fibers, fiber surface modification,

nanotechnology, polyelectrolyte adsorption

Nanocomposite-based Lignocellulosic Fibers

Zhiyuan Lin

ABSTRACT

The formation of layered nanoparticle films on the surface of wood fibers is reported in this study. The layer-by-layer (LbL) assembly technique was comprehensively investigated as a non-covalent surface modification method for lignocellulosic fiber. Nanocomposite-based lignocellulosic fibers were successfully fabricated by sequential adsorption of oppositely charged poly(diallyldimethylammonium) chloride (PDDA) and clay nanoparticles in a number of repeated deposition cycles. Nanocomposite fibers displayed layered structure as indicated by the electrokinetic potential studies and scanning electron microscopy (SEM) analysis.

Layer-by-layer films of PDDA and clay impacted the thermal stability of wood fibers. Average degradation temperature at 5 and 10% weight loss for modified fibers with 4 bi-layers increased by up to ~24 and ~15°C, respectively. Significant char residue formed for the LbL modified fibers after heating to 800°C, indicating that the clay-based coating may serve as a barrier, creating an insulating layer to prevent further decomposition of the material.

Layer-by-layer film formation on wood fibers was investigated as a function of parameters related to fiber composition and solution conditions (ie. presence of lignin, salt concentration and pH). Elemental analysis of modified fibers revealed that PDDA adsorption to the fibers was reduced for all solution conditions for the samples with the highest content of lignin. Upon

extracting the non-covalently attached lignin, the samples showed the greatest amount of PDDA adsorption, reaching to 1.5% of total mass, under neutral solution conditions without the presence of added electrolyte. Furthermore, the influence of both the amount of PDDA adsorbed onto the fiber surface and electrokinetic potential of modified fibers on subsequent multilayer formation was quantified. Under select fiber treatments, great amount of PDDA/clay (up to ~75% total mass for only 4 bi-layers) was adsorbed onto wood fibers through the LbL process, giving these high surface area fibers nanocomposite coatings.

LbL modified fibers were melt compounded with isotactic polypropylene (PP) and compression molded into test specimens. The effect of LbL modification as a function of the number of bi-layers on composite performance was tested using the tensile, flexural, dynamic mechanical and thermal properties of fiber reinforced thermoplastic composites. LbL modified fiber composites had similar modulus values but significantly lower strength values than those of unmodified fiber composites. However, composites composed of LbL modified fibers displayed increased elongation at break, increasing by more than 50%, to those of unmodified samples. DSC results indicated that crystallization behavior of PP is promoted in the presence of wood fibers. Both unmodified and LbL modified fibers are able to act as nucleating agents, which cause an increase of the crystallinity of PP. Moreover, results from tensile and flexural strength, dynamic mechanical analysis and water absorption tests revealed that the material (PDDA or clay) at the terminal (outer) layer of LbL modified fiber influences the performance of the composites.

These findings demonstrate control over the deposition of nanoparticles onto lignocellulosic fibers influencing terminal surface chemistry of the fiber. Further investigation into using renewable fibers as carriers of nanoparticle films to improve fiber durability, compounding with thermoplastics that have higher melt processing temperatures, and tailoring terminal surface chemistry to enhance adhesion is justified by this research.

Dedicated to my parents

Lamei Tang and Guohai Lin

Acknowledgements

There are many individuals without whom this dissertation would not have been possible.

Dr. Renneckar, I will never be able to express how truly grateful I am to you for everything. Your constant guidance, encouragement, dedication, trust and patience have helped me in every step of this long journey. To me, you are not only an advisor or a mentor, but also a friend. Thank you so much!

I would like to thank my committee members, Dr. Scott W. Case, Dr. Charles E. Frazier, Dr. Joseph R. Loferski and Dr. Audrey Zink-Sharp for their efforts and dedication in helping me create a work, which I can be proud of. I really appreciate your invaluable discussions, suggestions and comments throughout this process. I also wish to express my sincere gratitude to Dr. Daniel P. Hindman for bringing me to this wonderful place. Your insight and wisdom impacted me greatly.

I want to thank the extraordinary Wood Science staff. Bob Wright played an important role in steam explosion and fiber extraction. Rick Caudill, Kenny Albert, and David Jones assisted in sample preparation and mechanical testing. Debbie Garnand, Angie Riegel, Linda Caudill and William Pfeil helped with all kinds of issues related to study and daily life.

My gratitude also goes to our group members: Richard, Karthik, Qingqing, Angela, Rob, Travis and Katia. Thank you all for assistance when I needed it here and there. Dakai and Sudip from Dr. Frazier's group assisted in DMA and DSC experiments.

I also thank Dr. Richey M. Davis from the Department of Chemical Engineering, Dr. Justin Barone from the Department of Biological Systems Engineering for use of equipments in their lab.

I also wish to express my special appreciation to my former advisor, Dr. Jianxiong Lu of Chinese Academy of Forestry, I would not be where I am today without your words of encouragement.

I deeply appreciate the Sustainable Engineered Materials Institute (SEMI) for the financial support of this project.

Last but not least, I want to give my deepest gratitude to my wife, Yaru, for being everything a man could ask for in a woman. You are my biggest supporter ever since we met eight years ago. I am loving every moment with you!

Preface

This dissertation is written in manuscript format. Chapters 4, 5 and 6 of this dissertation have been prepared as manuscripts, which have been, or will be, submitted for publication. The terms like “we” and “our” refer to the authors of the manuscript. These three chapters have their own abstract, introduction, experimental section and reference citations. Apologies are made here for this inconvenience.

Attribution

Several colleagues and coworkers assisted in the research behind several chapters of this dissertation. A brief description of their background and their contributions are included here.

Dr. Scott H. Renneckar (Department of Wood science and Forest Product, Virginia Tech) is the Major Advisor and Committee Chair. Dr. Renneckar provided guidance through this research and dissertation writing.

Dr. Daniel P. Hindman (Department of Wood science and Forest Product, Virginia Tech) aided in experimental design and manuscript revision in Chapter 4.

Table of Contents

Chapter 1 Introduction and Background	1
References.....	7
Chapter 2 Literature Review	11
2.1 Lignocellulosic fibers and fiber reinforced thermoplastic composites	11
2.1.1 Lignocellulosic fibers	11
2.1.2 Lignocellulosic fiber reinforced thermoplastic composites	15
2.2 Layer-by-layer assembly.....	26
2.2.1 Introduction of layer-by-layer assembly technique	26
2.2.2 Layer-by-layer assembly in lignocellulosic fiber	29
2.2.3 Review of recent studies on layer-by-layer modification of lignocellulosic fibers	34
2.3 Steam explosion.....	37
2.3.1 Introduction of steam explosion process.....	37
2.3.2 Treatment condition affecting the steam explosion process	38
2.3.3 Effect of steam explosion treatment on lignocellulosic fibers	39
2.3.4 Recent research in steam-exploded wood fiber reinforced thermoplastic composites	40
2.4 Summary	42
References.....	43
Chapter 3 Preparation and characterization of experimental materials	56
3.1 Flow chart of experimental work.....	56
3.2 Preparation of experimental materials	57
3.2.1 Separation of wood fibers by steam explosion	57
3.2.2 Water, alkali extraction and bleaching of steam-exploded fibers	61
3.2.3. Layer-by-layer system	61
3.2.4 Preparation of composite materials	63
3.3 Characterization of experimental materials	65
3.3.1 Charge determination of steam-exploded fibers.....	65
References.....	69

Chapter 4 Layer-by-layer build-up and its effect on thermal stability of lignocellulosic wood fibers.....	70
Abstract.....	71
Introduction.....	72
Materials and Methods.....	75
Results and Discussion	80
Conclusions.....	96
Acknowledgements.....	97
References.....	99
Chapter 5 Polyelectrolyte adsorption onto heterogeneous fiber surfaces.....	104
Abstract.....	104
Introduction.....	105
Materials and Methods.....	108
Results and Discussion	112
Conclusions.....	123
Acknowledgment.....	124
References.....	125
Chapter 6 Layer-by-layer modification of wood fibers as reinforcement in thermoplastic composites .	130
Abstract.....	130
Introduction.....	131
Experimental.....	134
Results and Discussion	140
Conclusions.....	154
Acknowledgment.....	156
References.....	157
Chapter 7 Summary and Conclusions	162
Appendix.....	166

List of Figures

Figure 2.1 Constitutive polymers of wood.....	13
Figure 2.2 Diagram of effect of fiber length (l) on tensile stress within fiber	20
Figure 2.3 Schematic diagram of layer-by-layer deposition process	29
Figure 2.4 Amount of polyelectrolyte adsorption as a function of salt concentration (Cs) at various levels of the adsorption energy parameters	33
Figure 3.1 Flow chart of experimental work in the present study	57
Figure 3.2 Yellow-poplar chips used in steam explosion.....	58
Figure 3.3 Steam explosion batch reactor used in this study	59
Figure 3.4 PDDA used in our layer-by-layer system.....	63
Figure 3.5 Tensile, flexural, sorption and dynamic mechanical test specimens cutting.....	65
Figure 3.6 Conductometric titration curve for steam-exploded fibers.....	67
Figure 4.1 Average effective size of clay platelets as a function of sonication time. Inset: Size distribution for clay platelets after 6 minutes of sonication.....	81
Figure 4.2 AFM image of sonicated clay platelets deposited on cleaved mica.....	82
Figure 4.3 Real time monitoring of sequential adsorption cycles of PDDA and clay using QCM-D.....	84
Figure 4.4 Zeta potential of alkali extracted steam-exploded wood as a function of pH.....	86
Figure 4.5 Zeta potential of alkali extracted steam-exploded wood at sequential adsorption steps of polymer and clay	87
Figure 4.6 Field emission scanning electron micrographs of steam-exploded wood fiber surfaces.....	88
Figure 4.7 Thermogravimetric degradation profiles in air of extracted steam-exploded wood that is unmodified (control) or with bilayers of PDDA and clay	89
Figure 4.8 Temperature of initial fiber mass weight loss, 5% and 10%, as a function of the number of PDDA and clay bilayers	91
Figure 4.9 Residual weight for extracted steam-exploded wood samples as a function of the number of PDDA and clay bilayers	92
Figure 4.10 Photoacoustic FTIR spectrum of steam-exploded wood with 4-bilayers of PDDA and clay after TGA tests heated in air to 600°C.	92
Figure 4.11 Steam-exploded wood with 4-bilayers of PDDA and clay before (a:100x mag., c:1000x mag.) and after (b:100x mag., d:1000x mag.) TGA tests heated in air to 600°C.....	93
Figure 4.12 Maximum rate of weight loss for steam-exploded wood as a function of the number of PDDA and clay bilayers.....	94
Figure 4.13 Thermogravimetric degradation profiles in a nitrogen atmosphere of extracted steam-exploded wood that is unmodified (control) or with 4 bilayers of PDDA and clay	95
Figure 5.1 Zeta potential of WEF, AEF, and BF at different pH in ultrapure water	113

Figure 5.2 Comparison of PDDA adsorption on WEF, AEF and BF as a function of NaCl concentration	117
Figure 5.3 Zeta potential of fiber after PDDA adsorption as function of NaCl concentration and pH.....	119
Figure 5.4 Linear relationship between absorbance and clay concentration from UV Spectroscopy	121
Figure 6.1 Storage modulus and $\tan\delta$ spectra of neat PP, unmodified and LbL modified fiber composites	148
Figure 6.2 DSC cooling curves of neat PP, unmodified and LbL modified fiber composites	150
Figure 6.3 DSC 2 nd melting curves of neat PP, unmodified and LbL modified fiber composites.....	151
Figure 6.4 Percent weight gain of unmodified and LbL modified fiber composites after 24 hours water immersion	154

List of Tables

Table 2.1 Mechanical properties of lignocellulosic fibers	14
Table 3.1 Moisture content and solid content of steam-exploded fibers.....	60
Table 3.2 Acidic group content of steam-exploded fibers	68
Table 4.1 Thermal characteristics of untreated and treated steam-exploded wood.....	90
Table 5.1 Deposition parameters used in this study	110
Table 5.2 The amount of the PDDA and clay adsorption of each individual layer during layer-by-layer assembly at different deposition conditions as a percentage of fiber mass.....	121
Table 5.3 Comparison between CNS/UV-Spec method and gravimetric method for mass gain after four bi-layers	123
Table 6.1 Thermal stability of unmodified and LbL modified fibers with different number of bi-layers.....	140
Table 6.2 Tensile properties of neat PP, unmodified and LbL modified fiber composites.....	144
Table 6.3 Flexural properties of neat PP, unmodified and LbL modified fiber composites.....	145
Table 6.4 Glass transition temperature of neat PP, unmodified and LbL modified fiber composites determined from peak of both $\tan\delta$ and loss modulus curves	149
Table 6.5 Melting and cooling parameters of neat PP, unmodified and LbL modified fiber composites	152

Chapter 1 Introduction and Background

Lignocellulosic fiber offers a combination of attractive properties such as low density, high specific strength and modulus, renewability, biodegradability, wide availability, and low cost, which make it a principal material for many applications. Fibers have been used in applications related to paper such as packaging, composite materials like medium density fiberboard, and are converted into thermoplastic polymers such as cellulose acetate for coatings. For composite materials, lignocellulosic fibers have been used for more than one century (Bledzki and Gassan 1999). In the early 1900s, a commercial composite marketed under the trade name Bakelite was developed from a combination of phenol-formaldehyde and wood flour (Clemons 2002). Over the past two decades, the use of the lignocellulosic fibers has expanded in the market for reinforcement in thermoplastics. These composites have experienced a dramatic growth in North America mainly due to their applications in automobile, building materials and packaging industries (Bledzki and Gassan 1999; Clemons 2002; Morton et al. 2003).

Some limitations tend to constrain the use of these lignocellulosic fibers. The relatively low thermal stability of lignocellulosic fibers restricts the allowable processing temperature, which is generally lower than 200°C. This processing temperature limits the use of the fibers as fillers and reinforcement in thermoplastics that are not considered for many structural applications. In addition, the hydrophilic nature of lignocellulosic fibers makes them poorly compatible with commonly used non-polar and hydrophobic thermoplastics, such as polyethylene. This

incompatibility leads to poor interfacial adhesion resulting in the inefficient load transfer from thermoplastic matrix to the lignocellulosic fiber. Poor interfacial adhesion diminishes the reinforcement potential of the fiber to enhance the mechanical properties of the final composite.

Various types of surface modification methods have been attempted to alleviate the above-mentioned issues. Surface modification of lignocellulosic fiber can modify the fiber itself and the interfacial adhesion between fibers and matrices. The modification methods fall into two primary categories: physical treatments and chemical modification. Physical treatments include corona, dielectric barrier and plasma discharges, laser and γ -ray treatments to purify, oxidize and/or activate the surface of lignocellulosic fibers (Belgacem et al. 1994; Felix et al. 1994; Belgacem et al. 1995; Hedenberg and Gatenholm 1996; Simonsen et al. 1997; Belgacem and Gandini 2005). Chemical modification of lignocellulosic fibers involves various chemical treatments with the aim to reduce the number of polar groups of the fillers or to introduce cross-linking by physical and chemical bonds between the fibers and the matrix resin (Bledzki and Gassan 1999). Commonly used chemical modification methods for lignocellulosic fiber include acetylation (Rowell et al. 1993), graft copolymerization (MAPP), and other coupling agents such as polyisocyanates and silanes (Maldas et al. 1988; Maldas and Kokta 1989; Raj et al. 1990; Felix and Gatenholm 1991; Maldas and Kokta 1991; Felix et al. 1993). Most research in the area of fiber modification for enhanced adhesion for thermoplastic composites is mature and industry has adopted the use of coupling agents in materials where the expense is justified. New methods for fiber modification must justify research aims in terms of lowering costs of expensive

coupling agents, by increasing fiber loading while maintaining performance, or enhancing the durability. This latter fact is of importance as wood is susceptible to biological degradation, such as fungal decay. In certain situations, particularly exterior applications, the durability may be as equally important for wood thermoplastic materials.

New technologies can be used to wrap the plant-based fibers and fiber bundles in a nanoscale film (nanoscale coating). These nanoscale films are often referred to as layer-by-layer films. Film formation occurs by repeated exposure of a substrate to charged polymers in dilute aqueous solutions, exploiting the simple phenomenon that opposites attract. This technique involves the sequential adsorption of oppositely charged components to the fiber surfaces. The electrostatic interaction between opposite charged components serves as the main driving force for the multilayer formation. In other words, the fiber substrate is suspended in a solution that contains the charged polymer (polyelectrolyte) and the polyelectrolyte automatically assembles onto the fiber surface, becoming irreversibly adhered.

In recent years, the layer-by-layer self-assembly technique has attracted considerable attention due to the simplicity and versatility of the build-up process (Decher 1997). This layer-by-layer technique can tailor the surface chemistry of a substrate for many needs based on incorporated layered components (Decher 1997). A great variety of organic or inorganic materials has been incorporated into the layer-by-layer system to create advanced materials with controlled nanoscale architectures with desired properties (Decher and Hong 1991; Schmitt et al. 1993; Onoda and Yoshino 1995; Lvov et al. 1996; Kotov et al. 1997; Lvov et al. 1997; van

Duffel et al. 2001; Lin et al. 2008). The layer-by-layer modification method has been investigated in paper science and successfully applied to cellulosic pulp fibers to enhance the properties of paper (Wagberg et al. 2002; Eriksson et al. 2005; Lingstrom et al. 2006; Lu et al. 2007; Peng et al. 2008). However, limited research has been carried out in the area of LbL modification of non-bleached wood fibers with polyelectrolyte's and its application in composites. There has been limited work on utilizing amine containing polymers such as the use of polyethelenimine (PEI) as a priming/coupling agent (Eisenheld and Gardner 2005) or in bio-based adhesive mixtures (Li et al. 2004; Li and Geng 2005; Geng and Li 2006) resulting in a commercially available soy-based adhesive. Amine/ammonium functional groups can interact strongly with wood surfaces and have been used throughout history (amine containing proteins such as albumin), but there is a dearth of research in the area of polycation modification of wood fiber. While paper products have benefited remarkably from these amine/ammonium additives, there is large gap of work with modification non-bleached fiber substrates (i.e. mechanically isolated wood fiber, wood strands, etc.). This dissertation is aimed to fill in the missing links for woody fiber surface modification by polymer adsorption of cationic polyelectrolytes.

The goal of present study is to investigate the layer-by-layer assembly technique as a surface modification method for lignocellulosic wood fiber and its effect on properties of fiber and fiber reinforced thermoplastic composites. Poly(diallyldimethylammonium) chloride (PDDA) and montmorillonite clay are the materials that are used in the study to modify the wood fiber. Stand-alone films of these materials have been previously created with mechanical properties of

up to 11 GPa, while clay has served as barriers for gas transport and enhances thermal stability in thermoplastics. Additionally, a provisional patent was filed based on the ability for PDDA to serve as an anti-microbial agent, reducing the ability for wood surfaces to grow mold.

The specific objectives of the study are to:

- Monitor the layer-by-layer build-up of PDDA and clay onto the lignocellulosic wood fibers, including characterization of surface properties of wood fibers after modification.
- Examine the effect of layer-by-layer modification on thermal stability of wood fibers.
- Determine factors affecting polyelectrolyte adsorption onto wood fibers, such as solution deposition parameters (salt concentration and pH) and presence of lignin.
- Quantify and optimize the multilayer build-up onto the lignocellulosic wood fibers.
- Evaluate the effect of layer-by-layer modification on properties of wood fiber reinforced thermoplastic composites including tensile and flexural mechanical, dynamic mechanical, water absorption tests and thermal analysis.

This dissertation is composed of seven chapters. Chapter 1 provides an introduction and background information of entire project. Chapter 2 is the literature review on lignocellulosic fiber, fiber reinforced thermoplastic composites and layer-by-layer modification method (history and development). Chapter 3 includes the preparation and characterization of the experimental materials. Chapter 4 monitors the layer-by-layer build-up of PDDA and clay on model (gold coated quartz crystal surface) as well as wood fiber surfaces. The effect of layer-by-layer

adsorption of PDDA and clay on thermal stability of the lignocellulosic wood fibers is also investigated in this chapter (published in *cellulose*). Chapter 5 examines the parameters (presence of lignin, salt concentration and pH of solution conditions) affecting the initial PDDA layer adsorption onto the lignocellulosic fiber surfaces and relates the properties of initial PDDA layer formation to subsequent multilayer build-up of fibers. Chapter 6 applies the layer-by-layer modified fibers in thermoplastic composite application. The effect of layer-by-layer modification on thermal, static, dynamic mechanical and sorption properties of wood fiber reinforced thermoplastic composites is evaluated. Chapter 7 provides the summary and conclusions for this research.

References

- Belgacem, M. N., P. Bataille and S. Sapiha (1994). "Effect of corona modification on the mechanical properties of polypropylene/cellulose composites." *Journal of Applied Polymer Science* **53**(4): 379-85.
- Belgacem, M. N., G. Czeremuskin, S. Sapiha and A. Gandini (1995). "Surface characterization of cellulose fibers by XPS and inverse gas chromatography." *Cellulose (London)* **2**(3): 145-157.
- Belgacem, M. N. and A. Gandini (2005). "The surface modification of cellulose fibres for use as reinforcing elements in composite materials." *Composite Interfaces* **12**(1-2): 41-75.
- Bledzki, A. K. and J. Gassan (1999). "Composites reinforced with cellulose based fibres." *Progress in Polymer Science* **24**(2): 221-274.
- Clemons, C. M. (2002). "Wood-plastic composites in the United States: the interfacing of two industries." *Forest Products Journal* **52**(6): 10-18.
- Decher, G. (1997). "Fuzzy nanoassemblies: toward layered polymeric multicomposites." *Science (Washington, D. C.)* **277**(5330): 1232-1237.
- Decher, G. and J. D. Hong (1991). "Buildup of ultrathin multilayer films by a self-assembly process. 1. Consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces." *Makromolekulare Chemie, Macromolecular Symposia* **46**(Eur. Conf. Organ. Org. Thin Films, 3rd, 1990): 321-7.
- Eisenheld, L. and D. J. Gardner (2005). "Developing an industrial friendly process for hydroxymethyl resorcinol (HMR) priming of wood using a novolak-based HMR." *Forest Products Journal* **55**(9): 61-66.
- Eriksson, M., S. M. Notley and L. Wagberg (2005). "The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibers." *Journal of Colloid and Interface Science* **292**(1): 38-45.
- Felix, J., P. Gatenholm and H. P. Schreiber (1994). "Plasma modification of cellulose fibers: effects on some polymer composite properties." *Journal of Applied Polymer Science* **51**(2): 285-95.

- Felix, J. M. and P. Gatenholm (1991). "The nature of adhesion in composites of modified cellulose fibers and polypropylene." *Journal of Applied Polymer Science* **42**(3): 609-20.
- Felix, J. M., P. Gatenholm and H. P. Schreiber (1993). "Controlled interactions in cellulose-polymer composites. I: Effect on mechanical properties." *Polymer Composites* **14**(6): 449-57.
- Geng, X. and K. Li (2006). "Investigation of wood adhesives from kraft lignin and polyethylenimine." *Journal of Adhesion Science and Technology* **20**(8): 847-858.
- Hedenberg, P. and P. Gatenholm (1996). "Conversion of plastic/cellulose waste into composites. II. Improving adhesion between polyethylene and cellulose using ozone." *Journal of Applied Polymer Science* **60**(13): 2377-2385.
- Kotov, N. A., T. Haraszti, L. Turi, G. Zavala, R. E. Geer, I. Dekany and J. H. Fendler (1997). "Mechanism of and Defect Formation in the Self-Assembly of Polymeric Polycation-Montmorillonite Ultrathin Films." *Journal of the American Chemical Society* **119**(29): 6821-6832.
- Li, K. and X. Geng (2005). "Formaldehyde-free wood adhesives from decayed wood." *Macromolecular Rapid Communications* **26**(7): 529-532.
- Li, K., X. Geng, J. Simonsen and J. Karchesy (2004). "Novel wood adhesives from condensed tannins and polyethylenimine." *International Journal of Adhesion and Adhesives* **24**(4): 327-333.
- Lin, Z., S. Renneckar and D. P. Hindman (2008). "Nanocomposite-based lignocellulosic fibers 1. Thermal stability of modified fibers with clay-polyelectrolyte multilayers." *Cellulose (Dordrecht, Netherlands)* **15**(2): 333-346.
- Lingstrom, R., L. Wagberg and T. Larsson Per (2006). "Formation of polyelectrolyte multilayers on fibres: influence on wettability and fibre/fibre interaction." *Journal of Colloid and Interface Science* **296**(2): 396-408.
- Lu, Z., S. Eadula, Z. Zheng, K. Xu, G. Grozdits and Y. Lvov (2007). "Layer-by-layer nanoparticle coatings on lignocellulose wood microfibrils." *Colloids and Surfaces, A Physicochemical and Engineering Aspects* **292**(1): 56-62.
- Lvov, Y., K. Ariga, I. Ichinose and T. Kunitake (1996). "Formation of Ultrathin Multilayer and Hydrated Gel from Montmorillonite and Linear Polycations." *Langmuir* **12**(12): 3038-3044.

- Lvov, Y., K. Ariga, M. Onda, I. Ichinose and T. Kunitake (1997). "Alternate Assembly of Ordered Multilayers of SiO₂ and Other Nanoparticles and Polyions." *Langmuir* **13**(23): 6195-6203.
- Maldas, D. and B. V. Kokta (1989). "Improving adhesion of wood fiber with polystyrene by the chemical treatment of fiber with a coupling agent and the influence on the mechanical properties of composites." *Journal of Adhesion Science and Technology* **3**(7): 529-39.
- Maldas, D. and B. V. Kokta (1991). "Influence of maleic anhydride as a coupling agent on the performance of wood fiber-polystyrene composites." *Polymer Engineering and Science* **31**(18): 1351-7.
- Maldas, D., B. V. Kokta, R. G. Raj and C. Daneault (1988). "Improvement of the mechanical properties of sawdust wood fiber-polystyrene composites by chemical treatment." *Polymer* **29**(7): 1255-65.
- Morton, J., J. Quarmley and L. Rossi (2003). *Natural and Woodfiber Composites in North America and Europe*. Proc. 7th International conference on Woodfiber-plastic composites, Madison, Wis., Forest Prod. Society.
- Onoda, M. and K. Yoshino (1995). "Fabrication of self-assembled multilayer heterostructure of poly(p-phenylene vinylene) and its use for an electroluminescent diode." *Journal of Applied Physics* **78**(7): 4456-62.
- Peng, C. Q., Y. S. Thio and R. A. Gerhardt (2008). "Conductive paper fabricated by layer-by-layer assembly of polyelectrolytes and ITO nanoparticles." *Nanotechnology* **19**(50): 505603/1-505603/10.
- Raj, R. G., B. V. Kokta, G. Grouleau and C. Daneault (1990). "The influence of coupling agents on mechanical properties of composites containing cellulosic fillers." *Polymer-Plastics Technology and Engineering* **29**(4): 339-53.
- Rowell, R. M., B. A. Cleary, J. S. Rowell, C. Clemons and R. A. Young (1993). *Results of Chemical Modification of Lignocellulosic Fibers for Use in Composites*. Wood-Fiber / Polymer Composites: Fundamental Concepts, Processes, and Material Options, Madison, WI., Forest Products Society.
- Schmitt, J., T. Gruenewald, G. Decher, P. S. Pershan, K. Kjaer and M. Loesche (1993). "Internal structure of layer-by-layer adsorbed polyelectrolyte films: a neutron and x-ray reflectivity study."

Macromolecules **26**(25): 7058-63.

Simonsen, J., Z. Hong and T. G. Rials (1997). "The properties of the wood-polystyrene interphase determined by inverse gas chromatography." *Wood and Fiber Science* **29**(1): 75-84.

van Duffel, B., T. Verbiest, S. van Elshocht, A. Persoons, F. C. de Schryver and R. A. Schoonheydt (2001). "Fuzzy Assembly and Second Harmonic Generation of Clay/Polymer/Dye Monolayer Films." *Langmuir* **17**(4): 1243-1249.

Wagberg, L., S. Forsberg, A. Johansson and P. Juntti (2002). "Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept. Part I. Modification of paper strength." *Journal of Pulp and Paper Science* **28**(7): 222-228.

Chapter 2 Literature Review

2.1 Lignocellulosic fibers and fiber reinforced thermoplastic composites

2.1.1 Lignocellulosic fibers

Natural fibers can be classified based on their origins, coming from plants, animals or minerals (Bledzki and Gassan 1999). Lignocellulosic fiber refers to the plant fiber, which is composed of three major polymeric constituents: cellulose, hemicelluloses, and lignin (Figure 2.1). Jute, sisal, flax, cotton and wood represent the most commonly used lignocellulosic fibers for thermoplastic composites. Cellulose is a linear polysaccharide consisted of β -D-anhydroglucopyranose units, which are linked together by β -1-4-glycosidic bonds (Sjostrom 1993). The cellulose molecules undergo intra and inter-molecular hydrogen bonding, forming microfibrils, which have a distinct orientation in the cell wall dependent upon the location within it. The chemical structure of cellulose together with the extensive hydrogen bonding leads to a semi-crystalline polymer possessing highly ordered (crystalline) regions alternating with disordered (amorphous) regions. Unlike cellulose, hemicelluloses are branched heteropolysaccharides that usually contain more than one type of monomer; examples include a combination of D-xylose, L-arabinose, and D-glucuronic acid forming arabinoglucuronoxylan or D-glucose and D-mannose forming glucomannan. Hemicelluloses have relatively lower molecular weight with an average degree of polymerization of \sim 200 in wood. The hemicelluloses components are intimately associated with cellulose microfibrils and the third polymeric

component, lignin. Lignin is thought to be a cross-linked three-dimensional amorphous polymer that constituted of phenylpropane units (Figure 2.1). Lignocellulosic fiber itself can be considered a composite, where hemicelluloses and lignin serve as amorphous matrices in which the cellulose microfibrils are embedded. In lignocellulosic fibers, cellulose primarily provides tensile stiffness to cell wall while lignin imparts toughness and is primarily responsible for the rigidity of the plant cell wall (Haygreen and Bowyer 1989). The amorphous polysaccharides are mainly responsible for the moisture absorption behavior of lignocellulosic fibers because of their high hydroxyl content. The percentage composition of each of these components varies depending on the type of fibers. For example, the cellulose content of cotton reaches 82.7% (Bledzki and Gassan 1999), which is substantially higher than that of wood fiber.

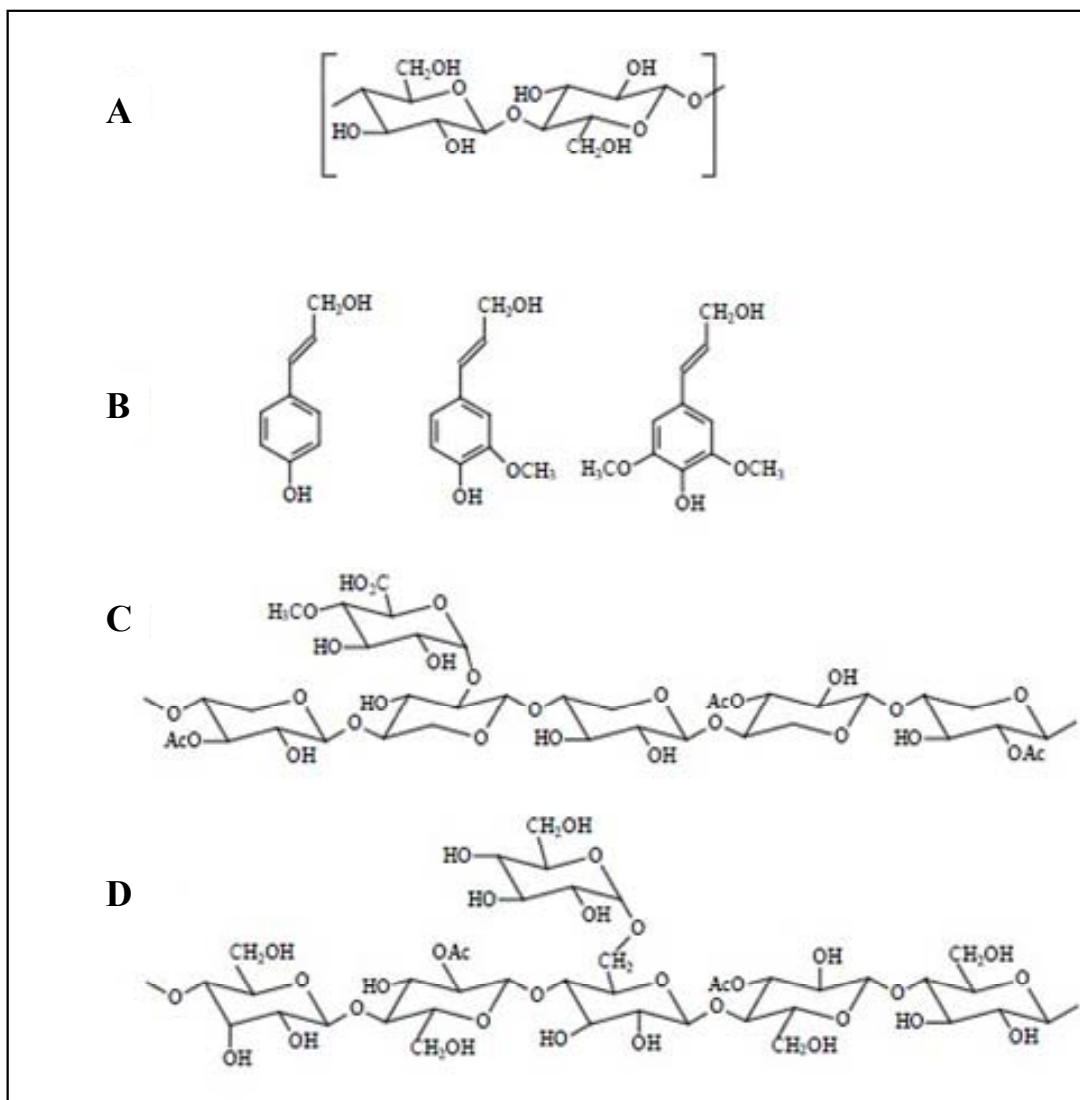


Figure 2.1 Constitutive polymers of wood

A) Cellobiose, repeating unit of cellulose, B) p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol--lignin precursor building units C) Partial structure of O-acetyl-4-O-methylglucuronoxylan, D) Partial structure of O-acetylgalactoglucomanan (Renneckar 2004, reprinted with permission from the author).

The properties of lignocellulosic fibers are presented in Table 2.1 (Rials and Wolcott 1997;

Bledzki and Gassan 1999). As shown in Table 2.1, the tensile strength of E-glass fiber is substantially greater than that of the lignocellulosic fibers even though the modulus is of the same order. However, lignocellulosic fibers exhibit comparable properties to the synthetic glass fibers in terms of specific modulus (modulus/specific gravity) due to their relative lower density. These high specific properties are one of the primary advantages lignocellulosic fibers contain over the synthetic fibers as reinforcement, particularly for applications when weight is a major concern.

Table 2.1 Mechanical properties of lignocellulosic fibers

Fiber	Specific gravity	Tensile modulus (GPa)	Tesile strength (MPa)	Specific modulus
Flax	1.5	28.5	351.6	19
Hemp	1.48	29.6	820.5	20
Jute	1.5	26.2	579.2	18
Sisal	1.45	17.2	524	12
Cotton	1.5-1.6	8.2	551.6	5.3
Softwood kraft pulp	1.5	40	1000	27
E-glass fiber	2.5	70	3400	28

Lignocellulosic fibers offer several attractive features, including (1) low density, (2) high specific properties, (3) renewable character, (4) biodegradability, (5) wide availability, and (6) low cost. These advantages make lignocellulosic fibers potential alternatives to synthetic fibers as reinforcement in the thermoplastic composites in many applications. However, lignocellulosic fibers also possess some limitations. Low thermal stability of lignocellulosic fibers restricts the

allowable processing temperature (normally less than 200°C) due to the potential thermal degradation, which limits the types of thermoplastics and manufacturing processes that can be used with these fibers (Sanadi et al. 1997). Secondly, the highly polar nature of the lignocellulosic fibers makes them poorly compatible with commonly used non-polar matrices. Moreover, another concern results from the hygroscopic nature of the lignocellulosic fibers. Moisture absorption can result in loss of mechanical properties and undesirable dimensional instability of the lignocellulosic fiber composites. Some of these challenges have been addressed as noted below, in order to commercially produce lignocellulosic fiber reinforced thermoplastic composites.

2.1.2 Lignocellulosic fiber reinforced thermoplastic composites

Lignocellulosic fiber plastic composites refer to any composites that contain lignocellulosic fiber and either thermosets or thermoplastic polymers (Clemons 2002). The difference between these two plastics arises from their varying response to temperature. Thermosets are plastics that, once cured, do not remelt by heating, while thermoplastics can be repeatedly melted when heated above their melting temperatures (or glass transition temperature if there are no crystalline portions). Lignocellulosic fibers have been involved in thermoset composites for more than one century (Bledzki and Gassan 1999). In the early 1900s, an early commercial composite marketed under the trade name Bakelite was composites of phenol-formaldehyde and wood flour (Clemons 2002). Thermoplastics offer many advantages over thermosets for lignocellulosic composites.

One of the main advantages of thermoplastic composites is their low processing costs. In addition, design flexibility and ease of molding complex parts is another merit for thermoplastics (Saheb and Jog 1999). Simple methods such as extrusion and injection molding can be used for processing of these composites. Over the past two decades, the use of the lignocellulosic fibers as reinforcement in thermoplastic composites has experienced a dramatic growth in North America. The automotive, building materials and package industries represent the fastest growing segments in demand of lignocellulosic fiber reinforced thermoplastic composites (Bledzki and Gassan 1999; Morton et al. 2003).

The lignocellulosic fiber reinforced thermoplastic composites exhibit hybrid properties of both lignocellulosic fiber and thermoplastics (Wolcott and Englund 1999). The wide variety of lignocellulosic fiber composites makes it difficult to discuss the performance of these materials. The properties of lignocellulosic fiber thermoplastic composites are also affected by various factors, which will be discussed in the next section. But in general, the addition of lignocellulosic fiber to a thermoplastic matrix may increase stiffness and sometimes strength properties of composites as compared with the neat thermoplastics, depending on the interfacial adhesion between fiber and matrix. The presence of hydrophobic thermoplastic fraction in the composites also decreases the water adsorption and undesirable dimensional instability of composites when compared to the solid wood.

2.1.2.1 Factors affecting performance of lignocellulosic fiber reinforced thermoplastic

composite

The performance of lignocellulosic fiber reinforced thermoplastic composites depends on many factors including: (1) fiber volume fraction, (2) fiber aspect ratio, (3) fiber dispersion and (4) interfacial adhesion between fiber and matrix. Understanding the effect of these variables helps to develop the high performance lignocellulosic fiber-reinforced thermoplastic composites.

Fiber volume fraction

Similar to other short fiber composites system, the fiber volume fraction in the composites is very important to the mechanical properties of lignocellulosic fiber reinforced thermoplastic composites. As indicated by the simple “rule of mixtures” model, the strength and stiffness properties of fiber composites increase as the fiber volume fraction increases. However, in practical applications, this is not always the case. For short fiber composites, at very low fiber volume fraction, the matrix is not restrained by enough fibers and highly localized strains occur in the matrix at low strains levels, causing the bond between fiber and matrix to break, leaving the matrix diluted by non-reinforcing, debonded fibers (Bigg 1996; Nando and Gupta 1996). This matrix dilution effect results in the decreased strength properties of composites at very low fiber loading. With the addition of more fibers, the matrix is sufficiently restrained and the stress is more evenly distributed. Therefore, the fiber reinforcement effect overwhelms the dilution effect (Senapati et al. 1988; Ibarra and Chamorro 1991), which results in elevated mechanical properties with increasing fiber concentration. The corresponding fiber volume fraction beyond

which the composites properties improve over the original matrix strength is known as the critical or optimum fiber volume fraction (Nando and Gupta 1996; Gatenholm 1997). Then, as the fiber volume fraction continues to increase, the strength properties of composites decrease once again as a result of insufficient wetting of the fibers by the polymer matrix and increased fiber to fiber interactions (Roe and Ansell 1985; Nando and Gupta 1996). This reduction in mechanical properties of composites has been observed by many researchers (Roe and Ansell 1985; Yam et al. 1990; Lu et al. 2005). Roe and Ansell reported that for jute/polyester composites, the modulus and strength cease to increase with the fiber volume fraction up to 60%. Further increase in volume fraction resulted in a decrease in the properties (Roe and Ansell 1985). Lu et al. also observed that the tensile strength of wood fiber reinforced high density polyethylene composites increased with increasing fiber content up to 15 wt %, after which it decreased at higher wood fiber content (Lu et al. 2005). Moreover, due to the hygroscopic nature of lignocellulosics, the water adsorption properties of thermoplastic composites also increase as the lignocellulosic fiber content increases (Ichazo et al. 2001).

Fiber aspect ratio

Fiber aspect ratio, ratio of the length to the diameter of the fiber (l/d), is an important parameter for mechanical properties of short fiber composite. The load can be carried by a fiber only if it can be effectively transferred from the matrix to the fiber. The basic mechanism used to transfer a tensile load in fiber reinforced plastic composites can be interpreted as follows (Hyer

1998): when a tensile load (F) is applied to the composites, a shear stress (τ) is induced on the outer surface of the fiber along the fiber-matrix interface. This shear stress, in turn, causes a tensile stress (σ) within the fiber. In short, the matrix transmits the load to the fiber through a shear stress. Near the ends of the fiber, the shear stress (τ) on the surface of the fiber is high and the tensile stress (σ) at the fiber end is low. As the distance from the end of the fiber increases, the shear stress decreases in magnitude and the tensile stress increases. After some length, normally referred to as the critical fiber length (l_c), the shear stress becomes very small and the tensile stress reaches a maximum value (Hyer 1998). In other word, critical fiber length (l_c) is the minimum fiber length in which the maximum allowable stress within fiber can be achieved. The corresponding aspect ratio is called critical aspect ratio (l_c/d). As shown in Figure 2.2, if the fiber length (l) is shorter than critical fiber length (l_c), the fiber never reaches the maximum stress placed upon the composite. As a result, insufficient stress will be transferred and the fiber reinforcement will be inefficient. Only when the fiber length is greater than that critical value, maximum stress transfer can be achieved within the composites.

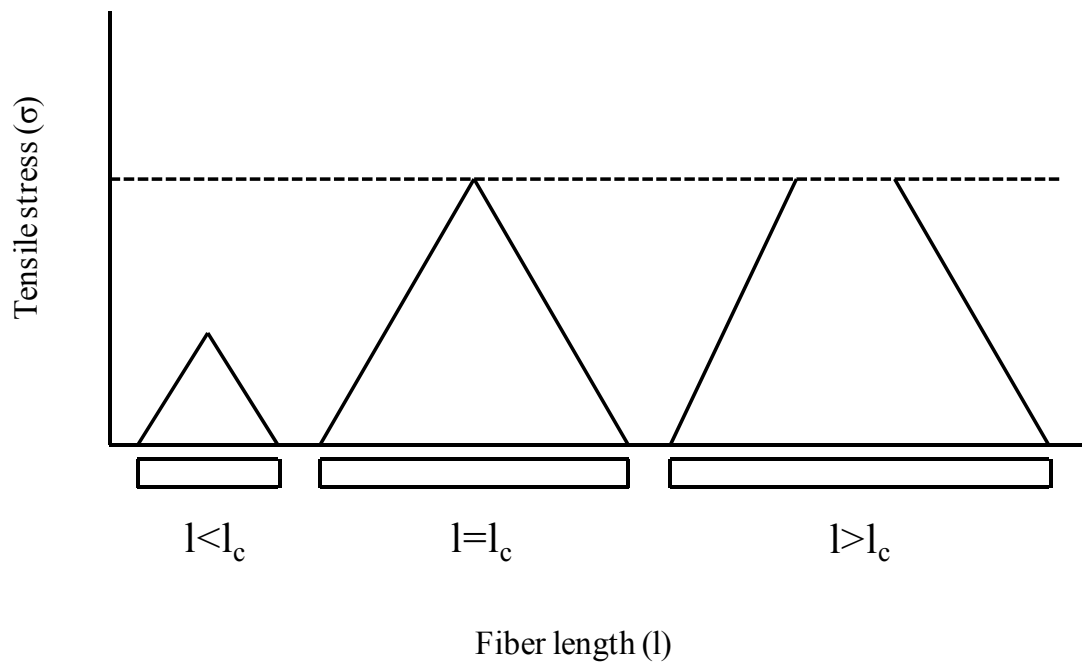


Figure 2.2 Diagram of effect of fiber length (l) on tensile stress within fiber

The ultimate fiber aspect ratios present in the composites depend on the initial fiber aspect ratios and the type of compounding and molding equipment used. Many factors including shear forces generated during compounding, residence time/temperature, levels of fiber loading and viscosity of blends, contribute to the fiber attrition, which can result in reduced fiber aspect ratio (Czarnecki and White 1980; Sanadi et al. 1997). During compounding processes such as extrusion, wood fiber is added to the thermoplastics in the melt and undergoes severe agitation and the aspect ratio of the fiber can be reduced by more than half (Yam et al. 1990; Clemons et al. 1999). In this case, lignocellulosic fibers are commonly too short to be effective as reinforcement (Felix et al. 1994). One potential strategy to overcome this problem is to improve the interfacial adhesion between lignocellulosic fibers and thermoplastic matrix. The critical aspect ratio of

fiber is determined not only by properties of fiber and matrix themselves, but also by the interface between fiber and matrix. There is an inverse relationship between critical fiber aspect ratio and interfacial shear stress (Kelly and Tyson 1965). Improved interfacial adhesion between fiber and matrix results in a smaller critical aspect ratio needed for maximum stress transfer. Many surface modification methods for lignocellulosic fibers modifies the adhesion between fiber and matrix by the use of coupling agents. Moreover, fiber reinforcement effect is not always better with increasing aspect ratio because of processing issues. If the fiber length is too high, the long fibers may entangle with each other during compounding and cause problems associated with fiber dispersion (Nando and Gupta 1996).

Fiber dispersion

Fiber dispersion is crucial to achieve high performance of short fiber composites. Good fiber dispersion indicates that the fibers are separated from each other (i.e. no fiber agglomeration and clumping), and the matrix surrounds each individual fiber. Insufficient fiber dispersion leads to an inhomogeneous mixture of matrix-rich and fiber-rich areas, which obviously contributes to inferior mechanical properties of short fiber composites (Taib 1998).

The incorporation of lignocellulosic fibers in a thermoplastic matrix has the tendency to form large aggregates, mainly due to the strong fiber-fiber interactions (Bledzki and Gassan 1999). Therefore, the dispersion of the lignocellulosic fibers in the polymer matrix is insufficient in many cases and the reinforcing ability of the fiber is decreased remarkably. Good dispersion of

lignocellulosic fiber becomes even more difficult to achieve due to the incompatibility between lignocellulosic fibers and non-polar thermoplastic matrices. The dispersion of lignocellulosic fibers can be improved by pretreatment with dispersing agents such as stearic acid (Woodhams et al. 1984; Raj et al. 1989). Raj et al. reported that addition of small amount of stearic acid (1% weight of fiber) during compounding decreased both the size and number of the fiber aggregates in polypropylene (Raj et al. 1989).

Fiber dispersion can also be improved by the compounding techniques. Woodhams et al. and Myers et al. found that use of turbine mixer (thermokinetic mixer) effectively improved the dispersing of lignocellulosic fibers in the thermoplastics due to the high shearing action produced in the mixer (Woodhams et al. 1990; Myers et al. 1992). Karmaker and co-workers also observed an increase in tensile strength of jute polypropylene composites using high shear mixer (Karmaker and Youngquist 1996). Rozman et al. investigated the effect of compounding methods on mechanical properties of oil palm empty fruit bunch reinforced polypropylene composites (Rozman et al. 1998). They concluded that the tensile strength, tensile modulus and impact strength properties of composites produced by an internal mixer were higher than those produced by extrusion. The authors attributed this improvement in mechanical properties of composites to better filler dispersion achieved by high shear rate of internal mixture. In addition, increasing mixing time can also improve the fiber dispersion (Nando and Gupta 1996) at the expense of production speed.

Interfacial adhesion between fiber and matrix

In fiber reinforced thermoplastic composites, fibers are the main source of stiffness, whereas the load is transferred from matrix to the fibers along the fiber-matrix interface. In order to achieve satisfactory performance of fiber composites, stress has to be effectively transmitted from matrix to the fibers. Therefore, interfacial adhesion between the fiber and matrix plays a critical role in mechanical properties of fiber plastic composites. As for lignocellulosic fiber reinforced thermoplastic composites, lignocellulosic fiber has high surface energy due to the presence of polar functional groups. In contrast, the surface energy of commonly used non-polar thermoplastic resins (such as polyolefins) is low. This difference in surface energy leads to the incompatibility between lignocellulosic fibers and thermoplastic matrix. The work of adhesion, defined as the strength of this interfacial interaction between the liquid and solid phases can shed light on the interfacial properties in our lignocellulosic fiber composites (Dupre 1869):

$$W_a = \gamma_s + \gamma_l - \gamma_{sl} \quad \text{Eq. 2.1}$$

Where

W_a : work of adhesion

γ_s : solid surface energy

γ_l : liquid surface energy

γ_{sl} : interfacial energy at solid-liquid interface

As can be seen from Eq. 2.1, a stronger work of adhesion between solid and liquid can be obtained by decreasing the interfacial energy (γ_{sl}) at solid-liquid interface. This Dupre equation can also be applied to our lignocellulosic fiber composites. To improve the adhesion between lignocellulosic fibers and thermoplastic matrix, one may either decrease the surface energy of the fibers or increase the surface energy of the thermoplastic matrix in order to decrease the interfacial energy between them. In other words, either the surface of the lignocellulosic fiber or the thermoplastic matrix needs to be modified in order to improve the adhesion between fibers and matrix.

Increasing the functionality of thermoplastic matrix is possible (such as through oxidation), but most often treatments are focused on the lignocellulosic fibers (Nunez et al. 2002). Several fiber modification approaches have been employed including physical treatments and chemical modification. Physical treatments include corona, dielectric barrier and plasma discharges, laser, γ -ray treatments and steam explosion (Belgacem et al. 1994; Felix et al. 1994; Belgacem et al. 1995; Hedenberg and Gatenholm 1996; Simonsen et al. 1997; Avellar and Glasser 1998; Belgacem and Gandini 2005). The main goal of physical treatments is to purify, oxidize and/or activate the surface of lignocellulosic fibers (Belgacem and Gandini 2005). Chemical modification of lignocellulosic fibers involves various chemical treatments with the aim to reduce the number of polar hydroxyl groups of the fillers or to introduce cross-linking by physical and chemical bonds between the fibers and the matrix resin (Bledzki and Gassan 1999). Commonly used chemical modification methods for lignocellulosic fiber include acetylation

(Rowell et al. 1993), or the use of different coupling agents such as isocyanates, silanes and maleic anhydride-grafted polypropylene (MAPP) (Maldas et al. 1988; Maldas and Kokta 1989; Kokta et al. 1990; Raj et al. 1990; Felix and Gatenholm 1991; Felix et al. 1993).

More than forty coupling agents have been used in wood fiber reinforced thermoplastic composites (Lu et al. 2000). Maleic anhydride-grafted polypropylene (MAPP) is among one of the most popular and commercialized coupling agents for wood based composites (Maldas and Kokta 1991; Olsen 1991). Maleic anhydride (MA) is a widely used product for modifying the polymer resins such as polypropylene and polyethylene. The MA is grafted onto these polymers by the aid of a free radical initiator to form a functional polymer, which is more compatible with lignocellulosic fibers. Maleic anhydride-grafted polypropylene has been reported to form both covalent ester linkages and hydrogen bonds when reacting with hydroxyl groups of lignocellulosic fiber (Hedenberg and Gatenholm 1995). Adding MAPP to wood composites can remarkably increase the tensile strength properties (Felix and Gatenholm 1991; Felix and Gateholm 1993; Hedenberg and Gatenholm 1995) and decrease the sorption properties (Avella et al. 1995) of lignocellulosic fiber reinforced thermoplastic composites. Moreover, isocyanates and silanes are also commonly used coupling agents to improve the mechanical properties of composites (Maldas et al. 1988; Raj et al. 1990).

Recently, the layer-by-layer self-assembly technique has attracted considerable attention to change the surface chemistry of substrates due to the simplicity and versatility of the build-up process (Decher 1997). This technique involves the sequential adsorption of oppositely charged

components to the substrate surfaces. The electrostatic interaction between opposite charged components serves as the main driving force for the multilayer adsorption. This layer-by-layer technique can tailor the surface chemistry of substrate for many needs based on incorporated layered components (Decher 1997). A great variety of organic or inorganic materials has been incorporated into the layer-by-layer system to create advanced materials with controlled nanoscale architectures with desired properties (Decher and Hong 1991; Schmitt et al. 1993; Lvov et al. 1995; Onoda and Yoshino 1995; Lvov et al. 1996; Kotov et al. 1997; van Duffel et al. 2001; Lin et al. 2008; Renneckar and Zhou 2009). The layer-by-layer modification method has been heavily investigated in paper science and successfully applied to cellulosic pulp fibers to enhance the properties of paper (Wagberg et al. 2002; Eriksson et al. 2005; Lingstrom et al. 2006; Zheng et al. 2006). In the next section, background and recent studies of this new layer-by-layer self-assembly technique will be introduced and reviewed.

2.2 Layer-by-layer assembly

2.2.1 Introduction of layer-by-layer assembly technique

For more than 60 years, fabrication of multilayer films on solid surfaces with controlled surface chemistry and architecture has been dominated by Langmuir-Blodgett technique, in which monolayers of organic compounds are deposited from a liquid surface onto a solid support (Blodgett 1934). However, the Langmuir-Blodgett technique demands special equipment and has severe limitations related to the substrate topology and size (Decher 1997). Since the early 1990s,

Decher's group has developed a technique for creation of the nanostructured multilayers by the so-called layer-by-layer assembly method (Decher and Hong 1991; Lvov et al. 1993; Decher 1997). This layer-by-layer technique involves the sequential adsorption of oppositely charged components onto the substrate surface. The electrostatic attraction between oppositely charged molecules, which represents the least steric demand of all chemical bonds, serves as the main driving force for the multilayer build-up (Decher 1997). The layer-by-layer adsorption process is very simple as illustrated in Figure 2.3 for the case of polyanion-polycation deposition onto a positively charged surface. In Figure 2.3 (a), steps 1 and 3 represent the adsorption of a polyanion and polycation, respectively, and steps 2 and 4 are washing steps, which remove reversibly adsorbed polyelectrolytes. It is important to rinse after each adsorption step to remove the loosely adsorbed polymers in order to ensure the film stability (Hoogeveen et al. 1996). These four steps are the basic build-up sequence for the simplest film architecture. Figure 2.3 (b) is the diagram of the first two adsorption steps illustrating the film deposition starting with a positively charged substrate. The electrostatic forces between polyanions and positively charged substrate pull the polyelectrolytes onto the surface and reverse the existing surface charge of the substrate (from positive to negative), subsequently the substrate is then placed into a polycation solution, which absorbs the oppositely charged polycations to form another layer. This adsorption processes can be repeated multiple times to obtain a desired number of bi-layers.

While the technique was first suggested as a strategy in the 1960's by Iler (Iler 1966), it was not until the early 1990's that the first work was published on the subject of LbL films for model

surfaces (Lvov et al. 1993). Film formation and film structure was first investigated and then quickly the work exploded in the direction of changing the composition of the films from polyelectrolytes to nanoparticles and enzymes (Lvov et al. 2002). Many components that are charged including organic or inorganic nanoparticles (Decher and Hong 1991; Kotov et al. 1995; Lvov et al. 1997; Hyde et al. 2005), macromolecules (Yoon and Kim 2000; Cheng and Cox 2001), biomacromolecules such as protein and DNA (Lvov et al. 1993; Elbert et al. 1999; Wang and Hu 2001), were incorporated into LbL films. Next, research evolved from planar surfaces to unique small diameter (colloidal) substrates for microcapsule formation (Donath et al. 1998; Moya et al. 1999; Sukhorukov et al. 1999; Sukhorukov et al. 2001). These efforts show LbL assembly as a proven technology to create nanoscale films on virtually any substrate (air bubbles (Shchukin et al. 2005), oil droplets (Grigoriev et al. 2008), wood fibers (Lin et al. 2008), cells, etc). Next, a number of groups developed novel applications of these films such as superhydrophobic surfaces (Han et al. 2005) and artificial nacre material (Tang et al. 2003). Finally, a number of studies have shown how to exploit other intermolecular interactions to build films besides ionic forces (Zhang et al. 2007). Over and over again these studies showed highly reproducible film formation and the simplicity of the process, which brought about a solid field of work by a variety of researchers across disciplines. In fact, Decher's 1997's review (Decher 1997) on the subject of LbL film formation has been cited more than 3500 times demonstrating the significance of the work across multiple disciplines.

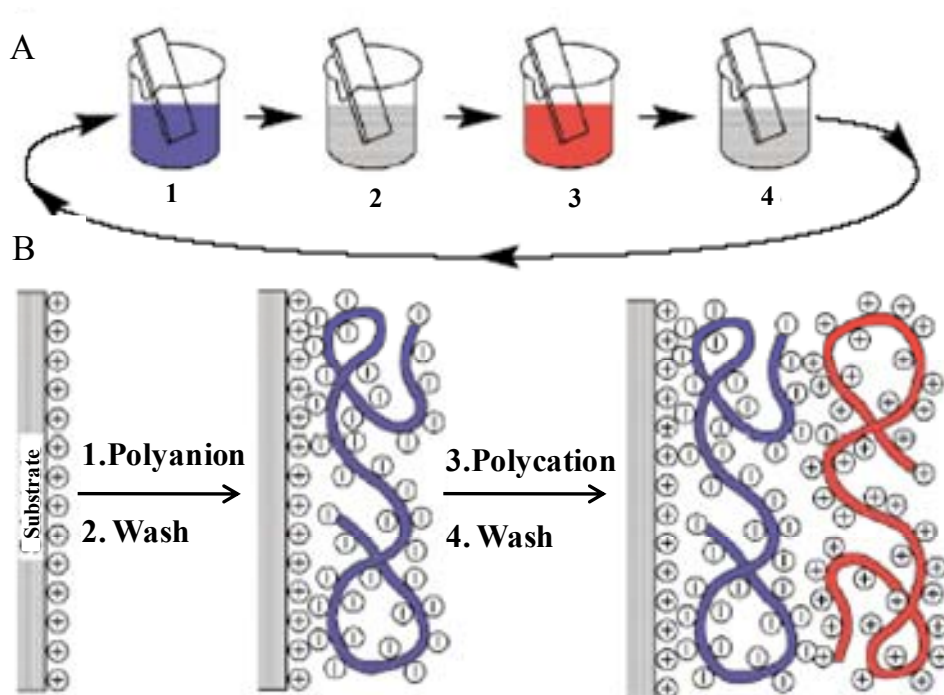


Figure 2.3 Schematic diagram of layer-by-layer deposition process

(Decher 1997, reprinted with permission from AAAS)

2.2.2 Layer-by-layer assembly in lignocellulosic fiber

As mentioned above, the layer-by-layer assembly technique is not limited on planar model surfaces. In recent years, this method has been successfully applied to the lignocellulosic pulp fibers and wood surfaces to modify their surface properties (Wagberg et al. 2002; Eriksson et al. 2005; Lingstrom et al. 2006; Zheng et al. 2006; Lin et al. 2008; Renneckar and Zhou 2009).

Lignocellulosic fibers are well suited substrate for layer-by-layer adsorption method because the fibers display an anionic character in aqueous solution as a result of the ionization of carboxylic

acid groups formed during pulping and bleaching. Under alkaline conditions, ionization of other functional groups like phenolic hydroxyls in the residual lignin also contributes to this anionic nature at elevated pH (Norgren and Lindstrom 2000).

The formation of polyelectrolyte multilayers onto pulp fibers is an extension of the surface modification method involved in the papermaking industry, where polycations have been widely used to modify the fiber-fiber interactions (Erspamer 1940; Moeller 1966; Allan and Reif 1971; Howard and Jowsey 1989; Formento et al. 1994). In part, this enormously complex body of study focuses on how additives can be applied to fiber surfaces in an efficient manner to modify the properties of paper. Adsorption of cationic polymer on lignocellulosic pulp fibers to enhance the strength properties of paper has been extensively studied for a long period of time. In 1971, Allen and co-workers investigated the effect of cationic polyamines adsorption on the strength properties of paper. The researchers reported that the dry strength of paper was improved by 60% with the polyamine additions (Allan and Reif 1971). Additionally, Allan and co-workers found that pH sensitive cationic polymers could become irreversibly attached to pulp fiber surfaces and repeated washing steps could not dislodge these polymers from the fiber (Sarkanen et al. 1966; Allan et al. 1970). The researchers developed a “Jack-in-a-box” theory, which they indicated the polymer could adsorb into the fibers’ microvoids and then become uncoiled/expanded by changing pH of the solution. The uncoiling mechanically locked the polymer into the fiber ultrastructure as the volume of the polymer expanded (changing the pH caused the amino groups on the polymers to become charged to ammonium ions through protonation; charge-charge

repulsion between polymer segments containing ammonium ions caused uncoiling of a polymer like a “Jack-in-the box”). Interestingly, Allan and co-workers proceeded to combine these positively charged pulp fibers with fibers that contained anionic charged groups and found enhanced adhesion between fibers, so much adhesion they had to move to a spray coating of the web because of severe flocculation issues (Allan and Reif 1971). Moreover, Hubbe and co-workers have shown similar ways to increase paper properties, but instead of mixed modified fibers of polyelectrolytes, they focused on a dual polyelectrolyte system where positive and negative polymers are added in sequential steps in a single batch (Hubbe et al. 2005). In this case, layered film formation does not occur on the fiber surface, but polyelectrolyte complex formation leads to the increase of dry strength of paper. These studies highlight how polyelectrolytes can be used to modify the surfaces of lignocellulosic materials to impact product applications.

Factors affecting the polyelectrolyte adsorption onto lignocellulosic fibers

Many factors such as surface charge density of fiber, polyelectrolyte segment charges, and salt concentration affect the adsorption of polyelectrolytes (Tanaka et al. 1979; Lindstrom and Wagberg 1983; van de Steeg et al. 1993; Wagberg 2000; Rojas et al. 2002; Horvath et al. 2006). Salt effect represents one of the most important parameters that control the conformation of polyelectrolyte adsorption. Horvath et al. investigated the effect of electrolyte concentration on the poly(diallyldimethylammonium) chloride (PDDA) adsorption onto the bleached kraft pulp

fibers, it was found that charge stoichiometry prevails under electrolyte free conditions, where the thickness of electric double layer (Debye length) was larger than the mean distance between the charges on the fiber surface. The surface charge overcompensation occurs via decreased Debye length at higher electrolyte concentrations, transitioning the surface from an average field of charge to islands of charges (Horvath et al. 2006). In general, polyelectrolyte adsorption exhibits two distinct adsorption regimes, a screening-reduced adsorption regime and a screening-enhanced adsorption regime upon the addition of salt, which depends on the balance between electrostatic and non-electrostatic attraction between the segment and surface (van de Steeg et al. 1992). These two adsorption regimes are illustrated in Figure 2.4, where the amount of polyelectrolyte adsorption (Γ) is plotted as a function of salt concentration (C_s) at various levels of the adsorption energy parameters (X_s), which represents the non-electrostatic affinity for the surface. If the attraction between polyelectrolyte and surface is purely electrostatic ($X_s=0$ in Figure 2.4), the adsorption decreases with the increase of salt concentration since the segment-surface attraction is screened by the added salts. A screening-enhanced adsorption regime occurs when a non-electrostatic interaction is introduced ($X_s>0$). In this case, the addition of electrolyte screens the intra-molecular repulsion between the charged segments, allowing the polyelectrolytes to be adsorbed onto the surface adopting “loops and tails” conformation, which leads to the increase in adsorption at high salt concentration. However, it is possible that competitive adsorption of the simple electrolyte will negatively impact the adsorption of the polyelectrolyte since the cations also compete with the polyelectrolytes to compensate the

surface charge (van de Steeg et al. 1992). Moreover, polyelectrolytes adsorption is also affected by the surface charge density of fiber. In general, higher surface charge of fiber results in greater amount of polyelectrolyte adsorption in the absence of salt (Horvath et al. 2006). This makes sense since greater polyelectrolyte adsorption is needed to compensate the surface charge with a high surface charge density.

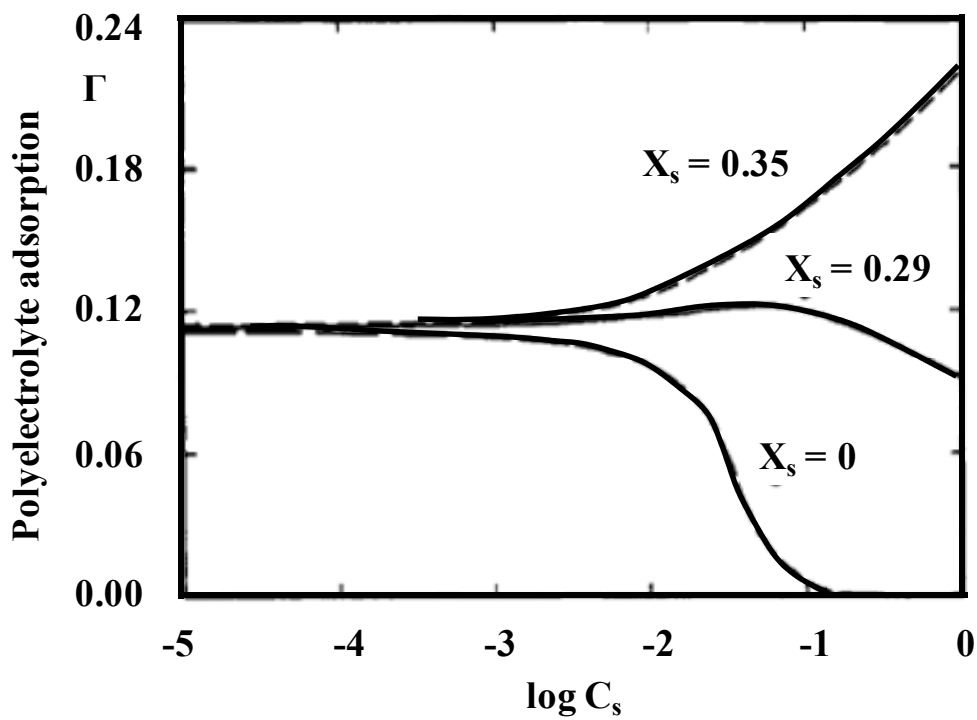


Figure 2.4 Amount of polyelectrolyte adsorption as a function of salt concentration (C_s) at various levels of the adsorption energy parameters

2.2.3 Review of recent studies on layer-by-layer modification of lignocellulosic fibers

Layer-by-layer modification of lignocellulosic pulp fibers is a continuation of polyelectrolyte adsorption. Using the layer-by-layer technique, it is possible to increase the amount of the polyelectrolytes adsorption beyond what can be obtained through a single treatment, which contributes to the enhanced fiber-fiber interactions (Lingstrom et al. 2006). With most of the layer-by-layer studies still focused on strength development of paper (Wagberg et al. 2002; Eriksson et al. 2005; Lingstrom et al. 2006; Zheng et al. 2006), its application in some other fields of lignocellulosic fibers has also been explored (Lu et al. 2007; Lin et al. 2008; Peng et al. 2008; Renneckar and Zhou 2009).

Wagberg et al. investigated the effect of the layer-by-layer adsorption of oppositely charged polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) onto softwood kraft fibers on strength properties of final paper (Wagberg et al. 2002). The authors reported that dry strength of papers from an unbeaten pulp could be increased from 20 to 56 kNm/kg and wet strength increased from 0 to 20 kNm/kg. Wagberg et al. attributed this strength improvement to the increased molecular contact area and the specific interaction between fibers as a result of the layer-by-layer polyelectrolyte adsorption (Wagberg et al. 2002).

Eriksson et al. applied the similar layer-by-layer system to the bleached softwood kraft fibers (Eriksson et al. 2005). The authors reported that the amount of PAH and PAA absorbed onto the fibers, and hence the strength properties of paper, can be changed by simply adjusting the pH of the deposition solutions. The tensile index of the paper improved up to 170% by the

multilayer loading. It should be mentioned that both PAH and PAA used in this study are weak polyelectrolytes which are sensitive to pH. The ionization levels, hence the charge densities of these polymers, are different by adjusting the background pH of deposition solutions. One interesting observation from this article is that the paper strength was also dependent on the specific polyelectrolyte in the outmost layer: having PAH as the outmost layer had a greater effect on paper strength than that of PAA as the outmost layer. This finding was supported by another study by Notley et al., in which the researchers found that the multilayer assembly with PAA as the outmost layer is much more rigid than PAH as indicated by the quartz crystal microbalance (QCM) measurements (Notley et al. 2005). Eriksson et al. ascribed the greater strength properties of paper with PAH as the terminal layer to the polyelectrolyte mobility with the assumption that high polymer mobility (less rigidity) in each layer may lead to polymer diffusion between polyelectrolyte multilayers to generate a stronger fiber-fiber joints (Eriksson et al. 2005).

Lingström et al. also confirmed the finding that the strength properties of paper are influenced by the polyelectrolyte absorbed in the outmost layer using different set of polymers (Lingstrom et al. 2006). Papers from fibers treated with PDDA in the outmost layer had a higher tensile index than did those with polystyrene sulfonate (PSS) in the outmost layer. A correlation between the adsorbed amount and the tensile index was also found. Moreover, the authors observed that the absorbed amount of the PDDA increases with the increase of the electrolyte concentration up to 0.05 M. The addition of electrolyte (NaCl) reduces the repulsion between the

charges of the strong polyelectrolyte and further increases the flexibility of the chain, which facilitates the polyelectrolyte adsorption in the polyelectrolyte multi-layer layer build-up.

Zheng et al. enhanced the paper strength by mixing the layer-by-layer modified negative and positive pulp to take advantage of increased fiber-fiber interactions (Zheng et al. 2006). Oppositely charged polyelectrolytes were alternately adsorbed onto the pulp fibers using the standard layer-by-layer assembly process. The authors reported that paper dry strength was doubled by using 50%:50% mixture of positively and negatively charged layer-by-layer coated pulp fibers. The researchers also ascribed this behavior to increase of interaction between the fibers during paper formation by adding an electrostatic interaction to traditional hydrogen bonding.

The layer-by-layer technique has also been used to develop the functional paper (Zheng et al. 2006; Lu et al. 2007; Peng et al. 2008). Conductive paper has been successfully fabricated by layer-by-layer assembly of conductive indium tin oxide (ITO) nanoparticles onto wood fibers, and manufacturing these treated fibers into paper handsheets through the conventional paper making methods (Peng et al. 2008). The conductivity of layer-by-layer modified papers remarkably increases when several bi-layers of PSS and ITO are coated onto the wood fibers. The authors reported that the conductivity of coated paper is improved by more than six orders of magnitude in both the in-plane and through-the-thickness directions as compared with plain paper made from unmodified control fibers. Lu et al. coated the inorganic TiO_2 and SiO_2 nanoparticles onto the bleached kraft softwood pulp fibers by the layer-by-layer assembly

technique (Lu et al. 2007). The authors concluded that brightness of paper increases by incorporation of the TiO₂ nanoparticles. The paper handsheets made with nanoparticle coated fibers also shows much higher porosity compared to that of virgin fibers.

Recently, Renneckar and Zhou investigated the layer-by-layer assembled film formation on solid wood surface (Rennekar and Zhou 2009). Wood samples (10*7.5*0.3 cm) were first coated with polyethylenimine (PEI) and then sequentially treated with PAA and PAH solutions. Microscopic analysis showed that layered films did not mask the micro-scale features (cut lumen walls and openings) of the wood surface. Hence, nanoscale films on wood were deposited without changing the microscopic and macroscopic texture (Rennekar and Zhou 2009).

2.3 Steam explosion

2.3.1 Introduction of steam explosion process

Steam explosion is an effective and economical method for converting the lignocellulosic biomass into cellulose-rich fibers and other lignocellulosic components such as xylan and lignin (Focher et al. 1991). The conventional mechanical methods such as disc refiner require 70% more energy than steam explosion to obtain the same particle size reduction (Holtzapple et al. 1989). Steam explosion is similar to the industrially practiced “Masonite process”, which represents the basis for fiberboard production (Glasser and Wright 1998). During steam explosion, the lignocellulosic biomass is pressurized with high steam pressure and elevated temperature, followed by a sudden decompression (Kokta and Ahmed 1998). The steam

plasticizes the wood cell wall and condenses in micro-capillaries within the wood. When the pressurized system is suddenly released to atmospheric pressure, the condensed water vaporizes, rupturing wood and causing mechanical failure (Rennekar 2004). The fibrous materials produced from steam explosion can be further fractionated into a water-soluble, an alkali-soluble, and an insoluble fraction to separate desirable products (Wallis and Wearne 1985; Overend and Chornet 1987; Beltrame et al. 1991; Montane et al. 1993; Glasser and Wright 1998). Component analysis reveals that the water soluble fraction consists primarily of mono, oligo-saccharides and water soluble lignin; the alkali soluble fraction contains most of the lignin and unidentified alkali-soluble polysaccharides; and the residual fiber is mostly cellulose (Glasser and Wright 1998). Steam explosion can be performed either in batch reactors or continuously (Schultz et al. 1983; Schultz et al. 1984; Overend and Chornet 1987). The only variation is the method of feeding and discharging (Avellar and Glasser 1998). Other than energy efficiency merit mentioned above, steam explosion also offers several advantages as compared with the alternative hydrolysis and pulping processes, such as (1) environmental friendly character, (2) lower capital investment, (3) less hazardous process chemicals and conditions, and (4) the more complete recovery of all wood biopolymers in a usable form (Focher et al. 1991).

2.3.2 Treatment condition affecting the steam explosion process

The steam explosion process is affected by several treatment condition variables including reaction temperature (T_r), retention time (t), chip size and moisture content (Wright 1988; Duff

and Murray 1996). The severity factor (R_0) is one way to characterize the exposure levels by combining the reaction temperature and retention time factors into a single parameter using the following empirical equation 2.2 (Overend and Chornet 1987). As shown from this equation, the severity factor increases with the increase of the reaction temperature and the retention time.

$$R_0 = \int_0^t \exp[(T_r - T_b)/14.75] dt \quad \text{Eq. (2.2)}$$

Where,

R_0 = severity factor

T_r = reaction temperature, °C

T_b = base temperature, °C

t = retention time, minute

2.3.3 Effect of steam explosion treatment on lignocellulosic fibers

Steam explosion is a thermo-hydrolytic-mechanical process, which affects all the constitutive polymers of wood (Tanahashi 1990). The hemicelluloses are hydrolyzed to oligosaccharides and monosaccharides, which can be removed through water and alkali extraction. The lignin is depolymerized and redistributed on the fiber surface (Donaldson et al. 1988). The amorphous cellulose was either hydrolyzed or transformed to crystalline cellulose, which leads to increased crystallinity of cellulose (Focher et al. 1991). As a result, the

hygroscopic nature of steam-exploded fibers is reduced. The steam explosion process also causes ultra-structure changes of wood fiber cell wall. Available surface area and porosity of wood fibers substantially increase after steam explosion treatment (Michalowicz et al. 1991). Therefore, steam-exploded lignocellulosic fibers exhibit superior solvent and enzyme accessibility (Focher et al. 1991; Samaranayake et al. 1994).

2.3.4 Recent research in steam-exploded wood fiber reinforced thermoplastic composites

Due to the unique properties of lignocellulosic fibers upon steam explosion, the use of steam explosion in thermoplastic composite has been gaining considerable interest (Angles et al. 1999; Glasser et al. 1999; Takatani et al. 2000; Johnson 2004; Renneckar 2004; Yin et al. 2007; Cheng et al. 2009). One approach of using steam explosion in thermoplastic composites is first to pretreat the wood materials with steam explosion and then use them as reinforcing filler in thermoplastic composites (Glasser et al. 1999; Takatani et al. 2000; Yin et al. 2007; Cheng et al. 2009). Glasser et al. investigated the thermal and mechanical properties of steam-exploded wood fibers reinforced thermoplastic cellulose acetate butyrate (CAB) composites (Glasser et al. 1999). The authors reported that the thermal stability of steam-exploded fibers substantially increases as the fibers are extracted with water and alkali. Glasser and co-workers attributed this improvement mainly to the removal of water-soluble hemicelluloses. The authors also observed that the acetylated steam-exploded fiber displays the best reinforcing effect due to the improved interfacial wetting by the CAB matrix.

Takatani et al. examined the effect of mixing steam-exploded and regular wood flours on the properties of thermoplastic composite (Takatani et al. 2000). The authors found that addition of steam-exploded wood flour increased the fracture strength and water resistance of the resulting composite board up to 105 % and 60%, respectively. The researchers concluded that the effect of the steam-exploded fiber is based on the increased contact of the components of the composite. Steam-exploded fibers were also explored as fillers for polypropylene composites (Angles et al. 1999; Yin et al. 2007). Angles and co-workers reported that steam-exploded softwood fibers were ineffective, giving similar Young's modulus and lower strengths compared to the unfilled PP matrix and to the composites with untreated softwood fibers (Angles et al. 1999). Another study by Yin et al. showed that the addition of steam-exploded wood fibers greatly increased the modulus of elasticity (MOE) of the fiber reinforced polypropylene composites. The yield stress was decreased slightly by inclusion of 50% steam-exploded wood fibers with no compatibilizer (Yin et al. 2007).

Another approach of using steam explosion in wood fiber reinforced plastic composites is to co-refine wood and plastics by steam-explosion (Brooks 1999; Johnson 1999; Brooks et al. 2002; Renneckar 2004). This process offered a unique processing technique that created a moldable composite panel with improved dimensional stability (Brooks 1999). Renneckar reported that the hygroscopic nature of the co-processed fiber decreased (Rennekar 2004). Moreover, many differences in the co-processed materials such as increased cellulose crystallinity, new covalent linkages and an alternative distribution of components on the nanoscale were also revealed by

the co-refining process (Rennekar 2004).

2.4 Summary

Layer-by-layer adsorption of oppositely charged organic and inorganic components has been successfully applied to cellulosic pulp fibers to enhance the properties of paper. The layer-by-layer assembly method appears to be a promising surface modification approach for the negatively charged lignocellulosic fibers. However, despite the similarity between bleached pulp fibers and thermomechanical isolated wood fibers, adsorption behavior of the polyelectrolyte and subsequent layer-by-layer multilayer build-up may be different between these two fibers because of the higher lignin content present in the latter fibers. Therefore, it is of interest to comprehensively investigate this layer-by-layer assembly technique as a surface modification method for lignocellulosic wood fibers. Additionally, as an important utilization aspect of lignocellulosic fiber, there is a lack of research on layer-by-layer modification of wood fibers for reinforcement in thermoplastic composites. Due to its ability to tailor the surface chemistry of substrates, the LbL fiber modification method, if properly exploited, may be able to alleviate the shortcomings encountered for wood thermoplastic composites.

References

- Allan, G. G., K. Akagane, A. N. Neogi, W. M. Reif and T. Mattila (1970). "Physical entrapment of polyelectrolytes within microporous solids: the \"jack-in-the-box\" effect." *Nature (London, United Kingdom)* **225**(5228): 175-6.
- Allan, G. G. and W. M. Reif (1971). "Fiber surface modification. 6. Jack-in-the-Box effect: new mechanism for the retention of poly(ethylenimine) and other polyelectrolytes by pulp fibers." *Svensk Papperstidning* **74**(2): 25-31.
- Allan, G. G. and W. M. Reif (1971). "Fiber surface modification. Stereotopochemistry of ionic bonding in paper." *Svensk Papperstidning* **74**(18): 563-70.
- Angles, M. N., J. Salvado and A. Dufresne (1999). "Steam-exploded residual softwood-filled polypropylene composites." *Journal of Applied Polymer Science* **74**(8): 1962-1977.
- Avella, M., C. Bozzi, R. dell'Erba, B. Focher, A. Marzetti and E. Martuscelli (1995). "Steam-exploded wheat straw fibers as reinforcing material for polypropylene-based composites. Characterization and properties." *Angewandte Makromolekulare Chemie* **233**: 149-66.
- Avellar, B. K. and W. G. Glasser (1998). "Steam-assisted biomass fractionation. I. Process considerations and economic evaluation." *Biomass and Bioenergy* **14**(3): 205-218.
- Belgacem, M. N., P. Bataille and S. Sapiuha (1994). "Effect of corona modification on the mechanical properties of polypropylene/cellulose composites." *Journal of Applied Polymer Science* **53**(4): 379-85.
- Belgacem, M. N., G. Czeremuskin, S. Sapiuha and A. Gandini (1995). "Surface characterization of cellulose fibers by XPS and inverse gas chromatography." *Cellulose (London)* **2**(3): 145-157.
- Belgacem, M. N. and A. Gandini (2005). "The surface modification of cellulose fibres for use as reinforcing elements in composite materials." *Composite Interfaces* **12**(1-2): 41-75.
- Beltrame, P. L., P. Carniti, A. Visciglio, B. Focher and A. Marzetti (1991). "Fractionation and bioconversion of steam-exploded wheat straw." *Bioresource Technology* **39**(2): 165-71.
- Bigg, D. M., Ed. (1996). *Properties and Processing of Short Metal Fiber Filled Polymer Composites.*

- Short Fiber-Polymer Composites. Cambridge, Woodhead Publishing.
- Bledzki, A. K. and J. Gassan (1999). "Composites reinforced with cellulose based fibres." *Progress in Polymer Science* **24**(2): 221-274.
- Blodgett, K. B. (1934). "Monomolecular films of fatty acids on glass." *Journal of the American Chemical Society* **56**: 495.
- Brooks, S. H. W. (1999). Steam explosion, a uniquely new method of producing a wood plastic-molding compound, Unpublished technical report to client. Brooks Associates,. Rochester Hills, MI.
- Brooks, S. H. W., C. Duranceau, W. Gallmeyer, R. Williams and G. Winslow (2002). "Stake digester process for HDPE fuel tank recycling." *Society of Automotive Engineers*: 1371:1.
- Cheng, L. and J. A. Cox (2001). "Preparation of multilayered nanocomposites of polyoxometalates and poly(amidoamine) dendrimers." *Electrochemistry Communications* **3**(6): 285-289.
- Cheng, Q., S. Wang, T. G. Rials, K. M. Kit and M. Hansen (2009). "Fabrication optimization of polypropylene composites reinforced with steam-exploded wood flour by wet process." *Holz als Roh- und Werkstoff* **67**(4): 449-455.
- Clemons, C. M. (2002). "Wood-plastic composites in the United States: the interfacing of two industries." *Forest Products Journal* **52**(6): 10-18.
- Clemons, C. M., D. F. Caulfield and A. J. Giacomini (1999). "Dynamic fracture toughness of cellulose fiber-reinforced polypropylene: Preliminary investigation of microstructural effects." *Journal of Elastomers and Plastics* **31**(4): 367-378.
- Czarnecki, L. and J. L. White (1980). "Shear flow rheological properties, fiber damage, and mastication characteristics of aramid-, glass-, and cellulose-fiber-reinforced polystyrene melts." *Journal of Applied Polymer Science* **25**(6): 1217-44.
- Decher, G. (1997). "Fuzzy nanoassemblies: toward layered polymeric multicomposites." *Science (Washington, D. C.)* **277**(5330): 1232-1237.
- Decher, G. (1997). "Fuzzy nanoassemblies: Toward layered polymeric multicomposites." *Science* **277**(5330): 1232–1237.
- Decher, G. and J. D. Hong (1991). "Buildup of ultrathin multilayer films by a self-assembly process. 1.

- Consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces." *Makromolekulare Chemie, Macromolecular Symposia* **46**(Eur. Conf. Organ. Org. Thin Films, 3rd, 1990): 321-7.
- Donaldson, L. A., K. K. Y. Wong and K. L. Mackie (1988). "Ultrastructure of steam-exploded wood." *Wood Science and Technology* **22**(2): 103-14.
- Donath, E., G. B. Sukhorukov, F. Caruso, S. A. Davis and H. Mohwald (1998). "Novel hollow polymer shells by colloid-templated assembly of polyelectrolytes." *Angewandte Chemie-International Edition* **37**(16): 2202-2205.
- Duff, S. J. B. and W. D. Murray (1996). "Bioconversion of forest products industry waste cellulose to fuel ethanol: a review." *Bioresource Technology* **55**(1): 1-33.
- Dupre, A. (1869). "Theorie mecanique de la chaleur." 368-369.
- Elbert, D. L., C. B. Herbert and J. A. Hubbell (1999). "Thin Polymer Layers Formed by Polyelectrolyte Multilayer Techniques on Biological Surfaces." *Langmuir* **15**(16): 5355-5362.
- Eriksson, M., S. M. Notley and L. Wagberg (2005). "The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibers." *Journal of Colloid and Interface Science* **292**(1): 38-45.
- Eriksson, M., G. Pettersson and L. Waagberg (2005). "Application of polymeric multilayers of starch onto wood fibres to enhance strength properties of paper." *Nordic Pulp & Paper Research Journal* **20**(3): 270-276.
- Erspamer, A. (1940). "The flocculation and dispersion of papermaking fibers." *Paper Trade Journal* **110**(No. 24): 33-8.
- Felix, J., P. Gatenholm and H. P. Schreiber (1994). "Plasma modification of cellulose fibers: effects on some polymer composite properties." *Journal of Applied Polymer Science* **51**(2): 285-95.
- Felix, J. M. and P. Gateholm (1993). "Formation of entanglements at brushlike interface in cellulose-polymer composites." *Journal of Applied Polymer Science* **50**(4): 699-708.
- Felix, J. M. and P. Gatenholm (1991). "The nature of adhesion in composites of modified cellulose fibers and polypropylene." *Journal of Applied Polymer Science* **42**(3): 609-20.

- Felix, J. M., P. Gatenholm and H. P. Schreiber (1993). "Controlled interactions in cellulose-polymer composites. I: Effect on mechanical properties." *Polymer Composites* **14**(6): 449-57.
- Focher, B., A. Marzetti and V. Crescenzi (1991). *Steam explosion Techniques: Fundamentals and Industrial Applications*, Philadelphia, Gordon and Breach Publishers.
- Formento, J. C., M. G. Maximino, L. R. Mina, M. I. Srayh and M. J. Martinez (1994). "Cationic starch in the wet end: Its contribution to interfiber bonding." *Appita Journal* **47**(4): 305-8.
- Gatenholm, P., Ed. (1997). *Interfacial adhesion and dispersion in biobased composites. Molecular interactions between cellulose and other polymers. Lignocellulosic-Plastics Composites*. Sao Paulo, Brazil, USP and UNESP
- Glasser, W. G., R. Taib, R. K. Jain and R. Kander (1999). "Fiber-reinforced cellulosic thermoplastic composites." *Journal of Applied Polymer Science* **73**(7): 1329-1340.
- Glasser, W. G. and R. S. Wright (1998). "Steam-assisted biomass fractionation. II. Fractionation behavior of various biomass resources." *Biomass and Bioenergy* **14**(3): 219-235.
- Grigoriev, D. O., T. Bukreeva, H. Moehwald and D. G. Shchukin (2008). "New Method for Fabrication of Loaded Micro- and Nanocontainers: Emulsion Encapsulation by Polyelectrolyte Layer-by-Layer Deposition on the Liquid Core." *Langmuir* **24**(3): 999-1004.
- Han, J. T., Y. Zheng, J. H. Cho, X. Xu and K. Cho (2005). "Stable Superhydrophobic Organic-Inorganic Hybrid Films by Electrostatic Self-Assembly." *Journal of Physical Chemistry B* **109**(44): 20773-20778.
- Haygreen, G. and G. L. Bowyer (1989). *Forest products and wood science : an introduction*. Ames, Iowa State University Press.
- Hedenberg, P. and P. Gatenholm (1995). "Conversion of plastic/cellulose waste into composites. I. Model of the interphase." *Journal of Applied Polymer Science* **56**(6): 641-51.
- Hedenberg, P. and P. Gatenholm (1996). "Conversion of plastic/cellulose waste into composites. II. Improving adhesion between polyethylene and cellulose using ozone." *Journal of Applied Polymer Science* **60**(13): 2377-2385.
- Holtzapple, M. T., A. E. Humphrey and J. D. Taylor (1989). "Energy requirements for the size reduction

- of poplar and aspen wood." *Biotechnology and bioengineering* **33**(2): 207-10.
- Hoogeveen, N. G., M. A. C. Stuart, G. J. Fleer and M. R. Boehmer (1996). "Formation and Stability of Multilayers of Polyelectrolytes." *Langmuir* **12**(15): 3675-3681.
- Horvath, A. E., T. Lindstrom and J. Laine (2006). "On the Indirect Polyelectrolyte Titration of Cellulosic Fibers. Conditions for Charge Stoichiometry and Comparison with ESCA." *Langmuir* **22**(2): 824-830.
- Howard, R. C. and C. J. Jowsey (1989). "The effect of cationic starch on the tensile strength of paper." *Journal of Pulp and Paper Science* **15**(6): J225-J229.
- Hubbe, M. A., S. M. Moore and S. Y. Lee (2005). "Effects of Charge Ratios and Cationic Polymer Nature on Polyelectrolyte Complex Deposition onto Cellulose." *Ind. Eng. Chem. Res.* **44**(9): 3068-3074.
- Hyde, K., M. Rusa and J. Hinestroza (2005). "Layer-by-layer deposition of polyelectrolyte nanolayers on natural fibers: Cotton." *Nanotechnology* **16**(7): 422-428.
- Hyer, M. W. (1998). *Stress analysis of fiber-reinforced composite materials*, McGraw-Hill Companies, Inc.
- Ibarra, L. and C. Chamorro (1991). "Short fiber-elastomer composites. Effects of matrix and fiber level on swelling and mechanical and dynamic properties." *Journal of applied Polymer Science* **43**(10): 1805-19.
- Ichazo, M. N., C. Albano, J. Gonzalez, R. Perera and M. V. Candal (2001). "Polypropylene / Wood Flour Composites: Treatments and Properties." *Composites Structures* **54**(2-3): 207-214.
- Iler, R. K. (1966). "Multilayers of colloidal particles." *Journal of Colloid and Interface Science* **21**(6): 569-94.
- Johnson, J. (1999). *Technology turns old bits and pieces into new parts*. Times- New River Valley Current. Roanoke: 1-3.
- Johnson, R. (2004). *Wetlaid cellulose fiber-thermoplastic hybrid composites-Effects of lyocell and steam exploded wood fiber blends*. Department of wood science and forest products. Blacksburg, Virginia Polytechnic Institute and State University. **MS. Thesis**.
- Karmaker, A. C. and J. A. Youngquist (1996). *Fiber attrition during injection molding and its effect on the*

- mechanical performance of natural fiber-reinforced polypropylene composites. Proc. Wood fiber-plastic composites: virgin and recycled wood fiber and polymers for composites. Forest Products Society, Madison, WI.
- Kelly, A. and W. R. Tyson (1965). "Tensile properties of fiber-reinforced metals: copper/tungsten and copper/molybdenum." *Journal of the Mechanics and Physics of Solids* **13**: 329-350.
- Kokta, B. V. and A. Ahmed (1998). *Steam Explosion Pulping. Environmentally Friendly Technologies for the Pulp and Paper Industry*, New York, John Wiley and Sons Incorporated.
- Kokta, B. V., D. Maldas, C. Daneault and P. Beland (1990). "Composites of poly(vinyl chloride) - wood fibers. III: Effect of silane as coupling agent." *Journal of Vinyl Technology* **12**(3): 146-53.
- Kotov, N. A., I. Dekany and J. H. Fendler (1995). "Layer-by-Layer Self-Assembly of Polyelectrolyte-Semiconductor Nanoparticle Composite Films." *Journal of Physical Chemistry* **99**(35): 13065-9.
- Kotov, N. A., T. Haraszti, L. Turi, G. Zavala, R. E. Geer, I. Dekany and J. H. Fendler (1997). "Mechanism of and Defect Formation in the Self-Assembly of Polymeric Polycation-Montmorillonite Ultrathin Films." *Journal of the American Chemical Society* **119**(29): 6821-6832.
- Lin, Z., S. Renneckar and D. P. Hindman (2008). "Nanocomposite-based lignocellulosic fibers 1. Thermal stability of modified fibers with clay-polyelectrolyte multilayers." *Cellulose (Dordrecht, Netherlands)* **15**(2): 333-346.
- Lin, Z., S. Renneckar and D. P. Hindman (2008). "Nanocomposite-based lignocellulosic fibers 1. Thermal stability of modified fibers with clay-polyelectrolyte multilayers." *Cellulose (Dordrecht, Neth.)* **15**(2): 333-346.
- Lindstrom, T. and L. Wagberg (1983). "Effects of pH and electrolyte concentration on the adsorption of cationic polyacrylamides on cellulose." *Tappi Journal* **66**(6): 83-5.
- Lingstrom, R., L. Wagberg and T. Larsson Per (2006). "Formation of polyelectrolyte multilayers on fibres: influence on wettability and fibre/fibre interaction." *Journal of Colloid and Interface Science* **296**(2): 396-408.
- Lu, J. Z., Q. Wu and H. S. McNabb, Jr. (2000). "Chemical coupling in wood fiber and polymer

- composites: a review of coupling agents and treatments." *Wood and Fiber Science* **32**(1): 88-104.
- Lu, J. Z., Q. Wu and I. I. Negulescu (2005). "Wood-fiber/high-density-polyethylene composites: coupling agent performance." *Journal of Applied Polymer Science* **96**(1): 93-102.
- Lu, Z., S. Eadula, Z. Zheng, K. Xu, G. Grozdits and Y. Lvov (2007). "Layer-by-layer nanoparticle coatings on lignocellulose wood microfibrils." *Colloids and Surfaces, A Physicochemical and Engineering Aspects* **292**(1): 56-62.
- Lvov, Y., K. Ariga, I. Ichinose and T. Kunitake (1995). "Assembly of Multicomponent Protein Films by Means of Electrostatic Layer-by-Layer Adsorption." *Journal of the American Chemical Society* **117**(22): 6117-23.
- Lvov, Y., K. Ariga, I. Ichinose and T. Kunitake (1996). "Formation of Ultrathin Multilayer and Hydrated Gel from Montmorillonite and Linear Polycations." *Langmuir* **12**(12): 3038-3044.
- Lvov, Y., K. Ariga, M. Onda, I. Ichinose and T. Kunitake (1997). "Alternate Assembly of Ordered Multilayers of SiO₂ and Other Nanoparticles and Polyions." *Langmuir* **13**(23): 6195-6203.
- Lvov, Y., G. Decher and H. Mohwald (1993). "Assembly, Structural Characterization, and Thermal-Behavior of Layer-by-Layer Deposited Ultrathin Films of Poly(Vinyl Sulfate) and Poly(Allylamine)." *Langmuir* **9**(2): 481-486.
- Lvov, Y., G. Decher and G. Sukhorukov (1993). "Assembly of thin films by means of successive deposition of alternate layers of DNA and poly(allylamine)." *Macromolecules* **26**(20): 5396-9.
- Lvov, Y., R. Price, B. Gaber and I. Ichinose (2002). "Thin film nanofabrication via layer-by-layer adsorption of tubule halloysite, spherical silica, proteins and polycations." *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* **198**: 375-382.
- Maldas, D. and B. V. Kokta (1989). "Improving adhesion of wood fiber with polystyrene by the chemical treatment of fiber with a coupling agent and the influence on the mechanical properties of composites." *Journal of Adhesion Science and Technology* **3**(7): 529-39.
- Maldas, D. and B. V. Kokta (1991). "Influence of maleic anhydride as a coupling agent on the performance of wood fiber-polystyrene composites." *Polymer Engineering and Science* **31**(18): 1351-7.

- Maldas, D., B. V. Kokta, R. G. Raj and C. Daneault (1988). "Improvement of the mechanical properties of sawdust wood fiber-polystyrene composites by chemical treatment." *Polymer* **29**(7): 1255-65.
- Michalowicz, G., B. Toussaint and M. R. Vignon (1991). "Ultrastructural changes in poplar cell wall during steam explosion treatment." *Holzforschung* **45**(3): 175-9.
- Moeller, H. W. (1966). "Cationic starch as a wet-end strength additive." *Tappi* **49**(5): 211-14.
- Montane, D., J. Salvado, X. Farriol and E. Chornet (1993). "The fractionation of almond shells by thermomechanical aqueous-phase (TM-AV) pretreatment." *Biomass and Bioenergy* **4**(6): 427-37.
- Morton, J., J. Quarmley and L. Rossi (2003). *Natural and Woodfiber Composites in North America and Europe*. Proc. 7th International conference on Woodfiber-plastic composites, Madison, Wis., Forest Prod. Society.
- Moya, S., G. B. Sukhorukov, M. Auch, E. Donath and H. Mohwald (1999). "Microencapsulation of organic solvents in polyelectrolyte multilayer micrometer-sized shells." *Journal of Colloid and Interface Science* **216**(2): 297-302.
- Myers, G. E., C. M. Clemons, J. J. Balatinez and R. T. Woodhams (1992). Effects of composition and polypropylene melt flow on polypropylene-waste newspaper composites. Proc. Annual Technical Conference. Society of Plastics Industry.
- Nando, G. B. and B. R. Gupta, Eds. (1996). *Short fiber-thermoplastic elastomer composites. Short Fibre--Polymer Composites*. Cambridge, Woodhead Publishing.
- Norgren, M. and B. Lindstrom (2000). "Dissociation of phenolic groups in kraft lignin at elevated temperatures." *Holzforschung* **54**(5): 519-527.
- Notley, S. M., M. Eriksson and L. Wagberg (2005). "Visco-elastic and adhesive properties of adsorbed polyelectrolyte multilayers determined in situ with QCM-D and AFM measurements." *Journal of Colloid and Interface Science* **292**(1): 29-37.
- Nunez, A. J., J. M. Kenny, M. M. Reboledo, M. I. Aranguren and N. E. Marcovich (2002). "Thermal and dynamic mechanical characterization of polypropylene-woodflour composites." *Polymer Engineering and Science* **42**(4): 733-742.
- Olsen, D. J. (1991). Effectiveness of maleated polypropylenes as coupling agents for wood

- flour/polypropylene composites. ANTEC Proc. of the 49th Annual Technical Conference. Society of Plastics Engineers, Brookfield, Montreal, Canada.
- Onoda, M. and K. Yoshino (1995). "Fabrication of self-assembled multilayer heterostructure of poly(p-phenylene vinylene) and its use for an electroluminescent diode." *Journal of Applied Physics* **78**(7): 4456-62.
- Overend, R. P. and E. Chornet (1987). "Fractionation of lignocellulosics by steam-aqueous pretreatments." *Philosophical Transactions of the Royal Society of London, Series A: Mathematical, Physical and Engineering Sciences* **321**(1561): 523-36.
- Peng, C. Q., Y. S. Thio and R. A. Gerhardt (2008). "Conductive paper fabricated by layer-by-layer assembly of polyelectrolytes and ITO nanoparticles." *Nanotechnology* **19**(50): 505603/1-505603/10.
- Raj, R. G., B. V. Kokta and C. Daneault (1990). "Wood flour as a low-cost reinforcing filler for polyethylene: studies on mechanical properties." *Journal of Materials Science* **25**(3): 1851-5.
- Raj, R. G., B. V. Kokta, F. Dembele and B. Sanschagrain (1989). "Compounding of cellulose fibers with polypropylene: effect of fiber treatment on dispersion in the polymer matrix." *Journal of Applied Polymer Science* **38**(11): 1987-1996.
- Raj, R. G., B. V. Kokta, G. Grouleau and C. Daneault (1990). "The influence of coupling agents on mechanical properties of composites containing cellulosic fillers." *Polymer-Plastics Technology and Engineering* **29**(4): 339-53.
- Rennekar, S. (2004). *Modification of Wood Fiber with Thermoplastics by Reactive Steam Explosion Processes*. Department of wood science and forest products. Blacksburg, Virginia Polytechnic Institute and State University. **PhD Dissertation**.
- Rennekar, S. and Y. Zhou (2009). "Nanoscale Coatings on Wood: Polyelectrolyte Adsorption and Layer-by-Layer Assembled Film Formation." *ACS Applied Materials & Interfaces* **1**(3): 559-566.
- Rials, T. G. and M. P. Wolcott (1997). *Physical and Mechanical Properties of Agro-Based Fibers. . Paper and Composites from Agro-Based Resources*, Boca Raton.
- Roe, P. J. and M. P. Ansell (1985). "Jute-reinforced polyester composites." *Journal of Materials Science*

20(11): 4015-20.

- Rojas, O. J., M. Ernstsson, R. D. Neuman and P. M. Claesson (2002). "Effect of Polyelectrolyte Charge Density on the Adsorption and Desorption Behavior on Mica." *Langmuir* **18**(5): 1604-1612.
- Rowell, R. M., B. A. Cleary, J. S. Rowell, C. Clemons and R. A. Young (1993). *Results of Chemical Modification of Lignocellulosic Fibers for Use in Composites. Wood-Fiber / Polymer Composites: Fundamental Concepts, Processes, and Material Options*, Madison, WI., Forest Products Society.
- Rozman, H. D., R. N. Kumar, M. R. M. Adlli, A. Abusamah and Z. A. M. Ishak (1998). "The effect of lignin and surface activation on the mechanical properties of rubberwood-polypropylene composites." *Journal of Wood Chemistry and Technology* **18**(4): 471-490.
- Saheb, D. N. and J. P. Jog (1999). "Natural fiber polymer composites: A review." *Advances in Polymer Technology* **18**(4): 351-363.
- Samaranayake, G., X. Li and W. G. Glasser (1994). "Solvent accessibility of steam-exploded cellulose." *Holzforschung* **48**(Suppl.): 69-71.
- Sanadi, A. R., D. F. Caulfield and R. E. Jacobson, Eds. (1997). *Agro-Fiber Thermoplastic Composites. Paper and Composites from Agro-Based Resources*. Boca Raton, Lewis Publishers.
- Sarkanen, K. V., F. Dinkler and V. Stannett (1966). "The effects of polyethylenimine on some properties of pulp and paper." *Tappi* **49**(1): 4-9.
- Schmitt, J., T. Gruenewald, G. Decher, P. S. Pershan, K. Kjaer and M. Loesche (1993). "Internal structure of layer-by-layer adsorbed polyelectrolyte films: a neutron and x-ray reflectivity study." *Macromolecules* **26**(25): 7058-63.
- Schultz, T. P., C. J. Biermann and G. D. McGinnis (1983). "Steam explosion of mixed hardwood chips as a biomass pretreatment." *Industrial & Engineering Chemistry Product Research and Development* **22**(2): 344-8.
- Schultz, T. P., M. C. Templeton, C. J. Biermann and G. D. McGinnis (1984). "Steam explosion of mixed hardwood chips, rice hulls, corn stalks, and sugar cane bagasse." *Journal of Agricultural and Food Chemistry* **32**(5): 1166-72.
- Senapati, A. K., G. B. Nando and B. Pradhan (1988). "Characterization of short nylon fiber reinforced

- natural rubber composites." *International Journal of Polymeric Materials* **12**(2): 73-92.
- Shchukin, D. G., K. Köhler, H. Möhwald and G. B. Sukhorukov (2005). "Gas-Filled Polyelectrolyte Capsules." *Angewandte Chemie International Edition* **44**(21): 3310-3314.
- Simonsen, J., Z. Hong and T. G. Rials (1997). "The properties of the wood-polystyrene interphase determined by inverse gas chromatography." *Wood and Fiber Science* **29**(1): 75-84.
- Sjostrom, E. (1993). *Wood Chemistry Fundamentals and Applications*. 2nd Edition. San Diego, Academic Press Incorporated.
- Sukhorukov, G. B., A. A. Antipov, A. Voigt, E. Donath and H. Mohwald (2001). "pH-controlled macromolecule encapsulation in and release from polyelectrolyte multilayer nanocapsules." *Macromolecular Rapid Communications* **22**(1): 44-46.
- Sukhorukov, G. B., M. Brumen, E. Donath and H. Mohwald (1999). "Hollow polyelectrolyte shells: Exclusion of polymers and donnan equilibrium." *Journal of Physical Chemistry B* **103**(31): 6434-6440.
- Taib, R. M. (1998). *Cellulose fiber-reinforced thermoplasticcomposites: processing and product characteristics*. Wood Science and Forest Products. Blacksburg, Virginia Polytechnic Institute and State University. **Master Thesis**.
- Takatani, M., O. Kato, T. Kitayama, T. Okamoto and M. Tanahashi (2000). "Effect of adding steam-exploded wood flour to thermoplastic polymer/wood composite." *Journal of Wood Science* **46**(3): 210-214.
- Tanahashi, M. (1990). "Characterization and degradation mechanisms of wood components by steam explosion and utilization of exploded wood." *Wood Research* **77**: 49-117.
- Tanaka, H., K. Tachiki and M. Sumimoto (1979). "Adsorption of cationic polymers onto bleached kraft pulp." *Tappi* **62**(1): 41-4.
- Tang, Z. Y., N. A. Kotov, S. Magonov and B. Ozturk (2003). "Nanostructured artificial nacre." *Nature Materials* **2**(6): 413-419.
- van de Steeg, H. G. M., M. A. Cohen Stuart, A. De Keizer and B. H. Bijsterbosch (1992). "Polyelectrolyte adsorption: a subtle balance of forces." *Langmuir* **8**(10): 2538-46.

- van de Steeg, H. G. M., A. de Keizer, M. A. C. Stuart and B. H. Bijsterbosch (1993). "Adsorption of cationic starches on microcrystalline cellulose." *Nordic Pulp & Paper Research Journal* **8**(1): 34-40.
- van Duffel, B., T. Verbiest, S. van Elshocht, A. Persoons, F. C. de Schryver and R. A. Schoonheydt (2001). "Fuzzy Assembly and Second Harmonic Generation of Clay/Polymer/Dye Monolayer Films." *Langmuir* **17**(4): 1243-1249.
- Wagberg, L. (2000). "Polyelectrolyte adsorption onto cellulose fibers -- a review." *Nordic Pulp & Paper Research Journal* **15**(5): 586-597.
- Wagberg, L., S. Forsberg, A. Johansson and P. Juntti (2002). "Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept. Part I. Modification of paper strength." *Journal of Pulp and Paper Science* **28**(7): 222-228.
- Wallis, A. F. A. and R. H. Wearne (1985). "Fractionation of the polymeric components of hardwoods by autohydrolysis-explosion-extraction." *Appita* **38**(6): 432-7.
- Wang, L. and N. Hu (2001). "Direct electrochemistry of hemoglobin in layer-by-layer films with poly(vinyl sulfonate) grown on pyrolytic graphite electrodes." *Bioelectrochemistry* **53**(2): 205-212.
- Wolcott, M. P. and K. Englund (1999). A technology review of wood-plastic composites. Proceedings of the Washington State University 33rd International Particleboard/Composite Materials Symposium.
- Woodhams, R. T., S. Law and J. J. Balatinecz (1990). Properties and possible applications of wood fiber-polypropylene composites. Proc. Symposium on wood adhesives, Madison, WI.
- Woodhams, R. T., G. Thomas and D. K. Rogers (1984). "Wood fibers as reinforcing fillers for polyolefins." *Polymer Engineering and Science* **24**(15): 1166-71.
- Wright, J. D. (1988). "Ethanol from biomass by enzymatic hydrolysis." *Chemical Engineering Progress* **84**(8): 62-74.
- Yam, K. L., B. K. Gogoi, C. C. Lai and S. E. Selke (1990). "Composites from compounding wood fibers with recycled high-density polyethylene." *Polymer Engineering and Science* **30**(11): 693-9.

- Yin, S., S. Wang, T. G. Rials, K. M. Kit and M. G. Hansen (2007). "Polypropylene composites filled with steam-exploded wood fibers from beetle-killed loblolly pine by compression-molding." *Wood and Fiber Science* **39**(1): 95-108.
- Yoon, H. C. and H.-S. Kim (2000). "Multilayered Assembly of Dendrimers with Enzymes on Gold: Thickness-Controlled Biosensing Interface." *Analytical Chemistry* **72**(5): 922-926.
- Zhang, X., H. Chen and H. Zhang (2007). "Layer-by-layer assembly: from conventional to unconventional methods." *Chem. Commun. (Cambridge, U. K.)*(14): 1395-1405.
- Zheng, Z., J. McDonald, R. Khillan, Y. Su, T. Shutava, G. Grozdits and Y. M. Lvov (2006). "Layer-by-layer nanocoating of lignocellulose fibers for enhanced paper properties." *Journal of Nanoscience and Nanotechnology* **6**(3): 624-632.

Chapter 3 Preparation and characterization of experimental materials

3.1 Flow chart of experimental work

Figure 3.1 shows the flow chart of the key steps of the present study. Wood veneers were cut into wafers for the steam explosion process. Steam explosion was used to separate the wood fibers (steam-exploded fibers). Optimization of the layer-by-layer (LbL) adsorption onto wood fibers was carried out by investigating the parameters including fiber characteristics and deposition conditions (salt concentration and pH). To examine the influence of fiber characteristics (presence of lignin) on the polyelectrolyte adsorption onto fibers, steam-exploded fibers (SEF) with three different levels of lignin content were obtained through water extraction (water extracted fibers), alkali extraction (alkali extracted fibers) and bleaching process (bleached fibers). Then, layer-by-layer modification was applied to the alkali extracted fibers using the optimal condition derived from the optimization process. Thermal stability of layer-by-layer modified fiber was evaluated by the thermogravimetric analysis (TGA). Moreover, the effect of layer-by-layer modification of wood fibers as reinforcement in thermoplastic composites was also investigated. The composites were prepared by melt compounding of thermoplastic matrix (isotactic polypropylene) and unmodified controls/LbL modified fibers, followed by compression molding. The tensile and flexural mechanical, thermal (DMA and DSC), and sorption properties of composite materials were determined. This chapter presents the preparation and characterization of experimental materials used throughout this research.

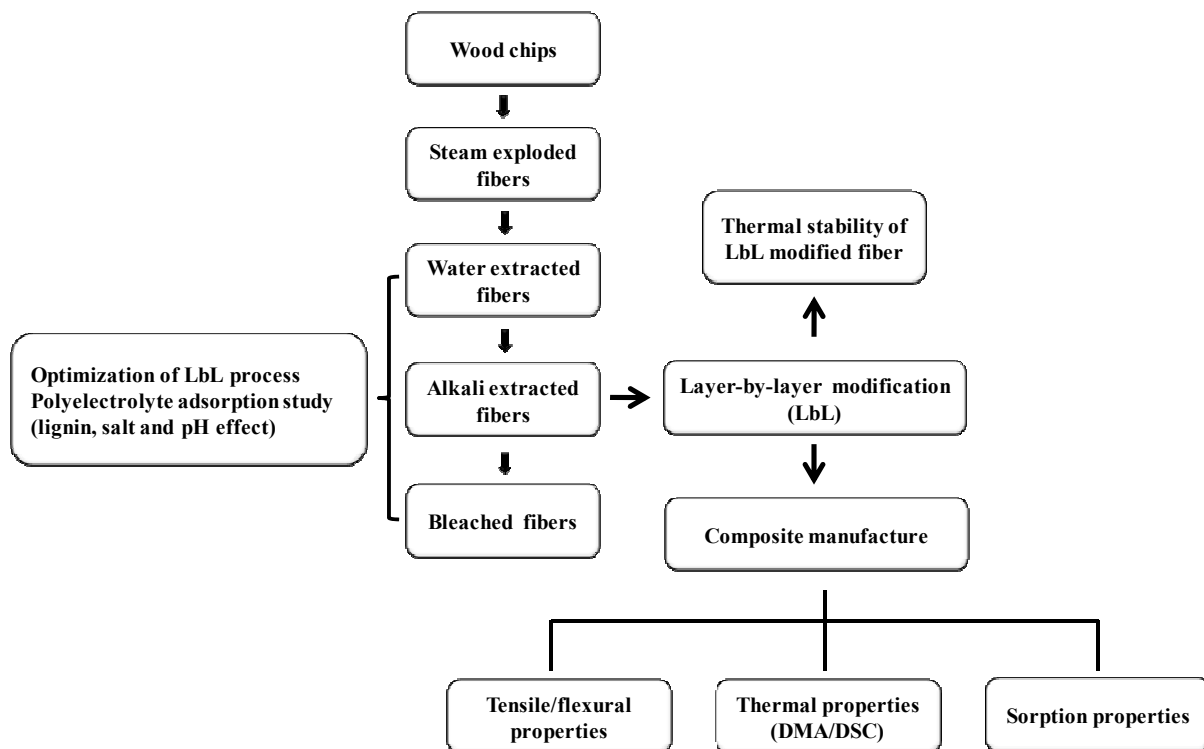


Figure 3.1 Flow chart of experimental work in the present study

3.2 Preparation of experimental materials

3.2.1 Separation of wood fibers by steam explosion

Wood fibers were separated from yellow-poplar (*Liriodendron tulipifera*) chips using the steam explosion technique. As shown in Figure 3.2, 20 kg of air-dried (6.4% MC) yellow-poplar chips with size of 25*25*4 mm were cut from wood veneers using a band saw. Yellow-poplar was chosen in this study mainly because the hardwood is relatively easier to process by steam explosion as compared to softwood (Sun and Cheng 2002). In addition, yellow-poplar fibers

have excellent fiber length (Pashin and de Zeeuw 1980), which is important as reinforcement for thermoplastic composite applications.



Figure 3.2 Yellow-poplar chips used in steam explosion

Steam explosion was performed in a two-cubic foot batch reactor. As shown in Figure 3.3, the major components of batch reactor include a reaction chamber, cyclone, funnel to guide raw materials into reactor and a steam vent to atmosphere. The steam explosion process can be generally described as below: the yellow-poplar chips were fed through funnel to the reaction chamber. Within this stainless steel reactor, wood chips were pressurized with high steam pressure and temperature for a certain period of time, followed by sudden decompression. After reducing the pressure to atmosphere pressure by open a ball valve, the solids were separated from steam through a cyclone.



Figure 3.3 Steam explosion batch reactor used in this study

(Johnson 2004, reprinted with permission from the author)

1. Reaction chamber
2. Steam duct from boiler
3. Metal pipe for transfer of steam-exploded material to collector
4. Cyclone
5. Funnel for guiding raw material into reactor
6. Steam vent (to atmosphere)
7. Collection bin

Three different steam explosion conditions were used in a preliminary study: (1) 234 °C for 2.3 min, (2) 234 °C for 3.6 min and (3) 240 °C for 3 min. The fiber separation efficiency of steam explosion processing at different conditions was investigated by examining the obtained fibers using a Zeiss microscope. It was observed that steam-exploded fibers from the first condition contained many large fiber bundles, while the third condition produced small fiber fragments.

Steam explosion at 240 °C for 3 min provided the best fiber separation results and was chosen as the final conditions in the present study. The severity factor (R_0) at this condition was 4.6 determined by Eq. 2.2 (Overend and Chornet 1987).

Two kilograms of air dried wood chips were steam-exploded at each batch. Thus, a total of eight runs were required to treat all the wood chips. After steam explosion, the moisture content (MC) and solids content of fibers for each run was determined by the gravimetric method and summarized in Table 3.1. As shown in the table, the average solids content of the steam-exploded fibers reached 89.3%, indicating that only ~10% mass loss occurred during the steam explosion process.

Table 3.1 Moisture content and solid content of steam-exploded fibers

Run No.	Moisture content (%)	Solids content (%)
1	31.6	89.2
2	57.2	87.3
3	55.9	85.9
4	43.2	90.7
5	42.0	91.2
6	36.8	89.7
7	47.0	91.1
8	56.4	89.0
Average	46.3	89.3
SD	9.6	1.8

3.2.2 Water, alkali extraction and bleaching of steam-exploded fibers

To investigate the influence of lignin on the polyelectrolyte adsorption onto fibers, steam-exploded fibers (SEF) with three different levels of lignin content were isolated through water extraction, alkali extraction and bleaching process. Glasser et al.'s method was adopted to perform the water and alkali extraction (Glasser et al. 1999). Steam-exploded fibers were first extracted with water at 60 °C for 24 hours (water extracted fibers) followed by extraction with 20% (based on fiber solids weight) aqueous alkali using an 8:1 liquor-to fiber ratio at 60 °C for 30 min (alkali extracted fibers). After water and alkali extraction, the fibers were isolated and washed multiple times with ultrapure water (Milli-Q Direct 3UV 18.2 MΩ) using a centrifuge until the supernatant pH became neutral. Alkali extracted fibers were then bleached with sodium chlorite to further remove the residual lignin from the fibers (Wise et al. 1946). The obtained fibers were called bleached fibers. The reported lignin content of water extracted fiber (WEF), alkali extracted fiber (AEF) and bleached fiber (BF) was 39, 11.4 and ~3%, respectively (Wise et al. 1946; Ibrahim and Glasser 1999).

3.2.3. Layer-by-layer system

Poly(diallyldimethylammonium) chloride (PDDA) and negatively charged inorganic montmorillonite clay were used in our layer-by-layer system. PDDA used in the study was an aqueous solution (Mw 200,000-350,000) obtained from Sigma-Aldrich Inc, USA (Figure 3.4).

Montmorillonite clay used was a high purity sodium montmorillonite donated by Kunimine industries, Japan. Montmorillonites are colloidal, layered aluminosilicates (clays) with exchangeable cations distributed over their external and internal surfaces (van Olphen 1977). Each layer consists of a sheet (typically $\sim 100 \times 100$ nm and 1 nm thick) of $\text{AlO}_4(\text{OH})_2$ octahedral sandwiched between two sheets of SiO_4 tetrahedral (Fendler 2002). The layers are then stacked parallel to one another to form plates. The clay displays an anionic nature as a result of isomorphous substitution of Al and Si atoms by atoms of lower valence. Prior to layer-by-layer adsorption, ultra-sonication was applied to the clay suspension for 6 minutes to break the clay into fine nanoscale platelets. The detailed layer-by-layer process will be introduced in Chapter 4. To investigate the potential effects of layer-by-layer modification (the number of the bi-layers and materials as the outmost layer), layer-by-layer modified fibers with five different numbers of bi-layers were prepared: 0.5, 1, 2, 3, 4 and 4.5, with 1 bi-layer designates a combination of 1 layer of PDDA and 1 layer of clay adsorbed onto the fiber. Therefore, layer number 0.5 refers to fiber that was only coated with a single layer of PDDA and 4.5 for a sample in which the final layer is PDDA.

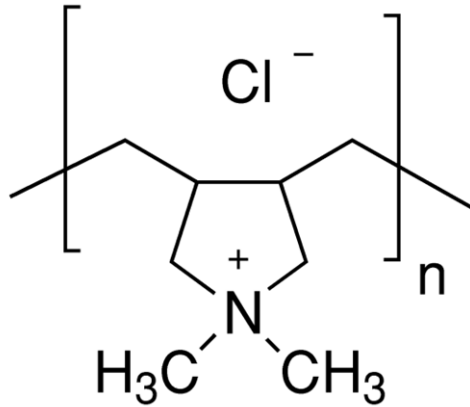


Figure 3.4 PDDA used in our layer-by-layer system

3.2.4 Preparation of composite materials

The composites were prepared by melt compounding of isotactic polypropylene (average M_w 340,000, melting index 4 g/10min, Sigma Aldridge) and unmodified control fibers/LbL modified fibers, followed by compression molding. The compounding and compression molding process will be described in detail in Chapter 6. The fiber volume fraction was kept constant at 25% for all the fiber composites. The fiber weight fraction (W_f) can be calculated from the fiber volume fraction (V_f) by the following equation:

$$W_f = \frac{V_f \rho_f}{V_f \rho_f + (1 - V_f) \rho_m} \quad \text{Eq. 3.1}$$

Where, ρ_f and ρ_m are density of fiber and matrix (polypropylene), respectively. The

density of the unmodified wood fiber used in this study is assumed to be 1.46 g/cm^3 based on the cell wall density. The density of the polypropylene is 0.9 g/cm^3 from the manufacture's data. The density of layer-by-layer modified fibers was calculated by simple "rule of mixtures" model including the adsorbed clay and PDDA fractions, which were quantified in our study.

Test specimens were cut from compression molded composite plaques with the dimensions of $152.4 \times 152.4 \text{ mm}$. Figure 3.5 illustrated how test specimens were cut from a molded plaque. The tensile specimens were 152.4 mm in length and 19.05 mm in width according to ASTM D638-03. The dimensions of specimens for flexural tests were $63 \times 12.7 \text{ mm}$ in accordance with ASTM D790-03. The sorption test specimens were in the form of a bar 76.2 mm long by 25.4 mm wide (ASTM D570-98). The specimens for dynamic mechanical analysis (DMA) are 35 mm in length and 12.7 mm in width.

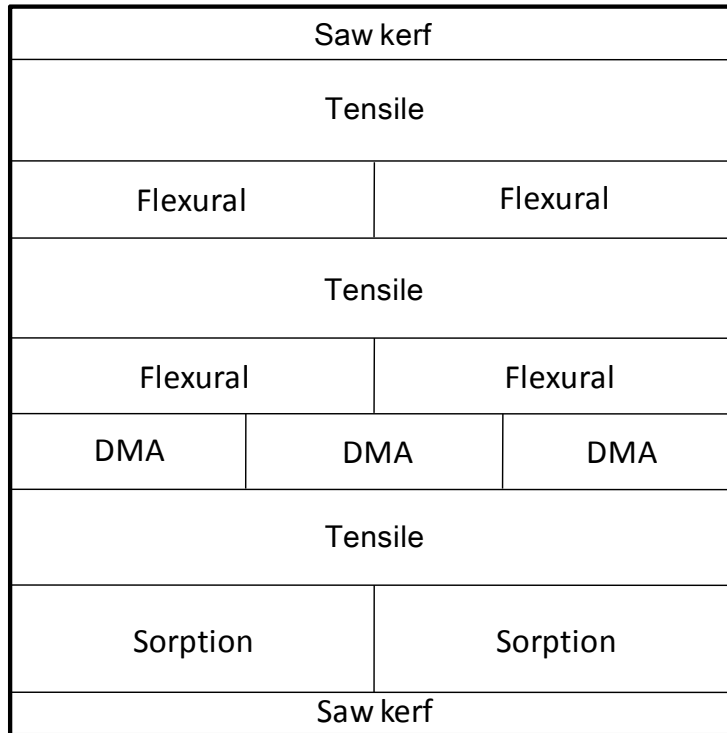


Figure 3.5 Tensile, flexural, sorption and dynamic mechanical test specimens cutting

3.3 Characterization of experimental materials

3.3.1 Charge determination of steam-exploded fibers

Conductometric titration method was used to measure the bulk charge density of the steam-exploded fibers (Katz et al. 1984). The titration was carried out in the presence of 0.001M sodium chloride, which was found optimal for the conductometric titration (Katz et al. 1984). During titration, the solution was stirred under a nitrogen atmosphere. The detailed procedures of the titration were listed as below:

1. Approximately 2g (dry weight basis) of steam-exploded fibers was converted to a fully

protonated form by soaking twice in 0.1 M hydrochloric acid for 45 min and then washing with de-ionized water to a constant conductance.

2. The fiber was drained and dispersed in 400ml of 0.001M sodium chloride prepared in de-ionized water. Prior to the titration, 3 ml of 0.1 M hydrochloric acid was added to the fiber suspension to achieve a clear titration curve.
3. Titration was carried out with 0.1 M sodium hydroxide dispersed from a digital burette while the suspension was stirred under a nitrogen atmosphere.
4. The alkali was added at a rate of 0.5ml every 5 min so as to allow sufficient time for equilibrium to be reached between readings.

Following titration, the pulp was washed with De-ionized water and oven-dried at 105°C.

The total charge density of the fiber can be calculated by the following equation (Fras et al. 2004).

$$X = \frac{C_{OH} V_t}{m_{dry}} \quad \text{Eq. 3.2}$$

Where,

X : Total acidic group content

C_{OH} : Concentration of the sodium hydroxide solution

V_t : Volume of the sodium hydroxide solution consumed during titration

m_{dry} : Oven-dry weight of the sample

Figure 3.6 shows the titration curve for the steam-exploded fibers. There are three lines in the curve. The speedy drop in conductance (Left line) was due to the neutralization of liberated protons from the added hydrochloric acid in step 2. The center line corresponded to the neutralization of weak acidic groups from wood fibers. The increase of conductance in the right line was resulted from the accumulation of excess NaOH in the suspension.

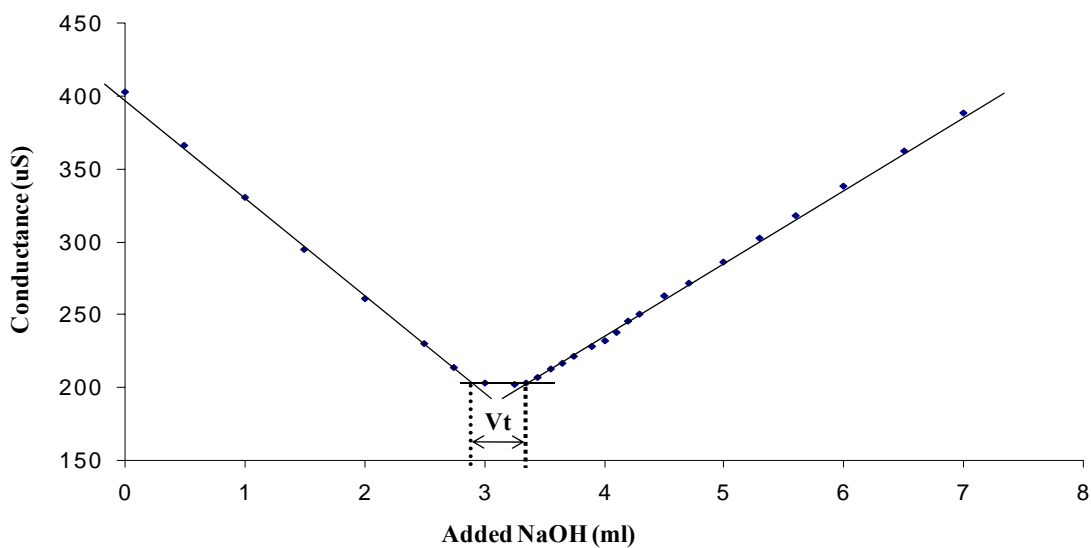


Figure 3.6 Conductometric titration curve for steam-exploded fibers

Table 3.2 lists the acidic group content of alkali extracted and bleached steam-exploded fiber determined from conductometric titration. As can be seen from Table 3.2, alkali extracted fibers have a relatively low acidic group content of 28.4 mmol/kg. The charge density (60 mmol/kg) of the bleached fibers is much greater than that of alkali extracted fibers as a result of bleaching oxidation process.

Table 3.2 Acidic group content of steam-exploded fibers

Sample	Acidic group content (mmol/kg)
Alkali extracted fibers	28.4
Bleached fibers	60

References

- Fendler, J. H., Ed. (2002). Chapter 9. Layer-by-Layer Self-assembled Polyelectrolytes and Nanoplatelets. Multilayer Thin Films, Wiley-VCH Verlag GmbH & Co.KGaA.
- Fras, L., J. Laine, P. Stenius, K. Stana-Kleinschek, V. Ribitsch and V. Dolecek (2004). "Determination of dissociable groups in natural and regenerated cellulose fibers by different titration methods." *Journal of Applied Polymer Science* **92**(5): 3186-3195.
- Glasser, W. G., R. Taib, R. K. Jain and R. Kander (1999). "Fiber-reinforced cellulosic thermoplastic composites." *Journal of Applied Polymer Science* **73**(7): 1329-1340.
- Ibrahim, M. and W. G. Glasser (1999). "Steam-assisted biomass fractionation. Part III. A quantitative evaluation of the "clean fractionation" concept." *Bioresource Technology* **70**(2): 181-192.
- Johnson, R. (2004). Wetlaid cellulose fiber-thermoplastic hybrid composites-Effects of lyocell and steam exploded wood fiber blends. Department of wood science and forest products. Blacksburg, Virginia Polytechnic Institute and State University. **MS. Thesis**.
- Katz, S., R. P. Beatson and A. M. Scallan (1984). "The determination of strong and weak acidic groups in sulfite pulps." *Svensk Papperstidning* **87**(6): R48-R53.
- Overend, R. P. and E. Chornet (1987). "Fractionation of lignocellulosics by steam-aqueous pretreatments." *Philosophical Transactions of the Royal Society of London, Series A: Mathematical, Physical and Engineering Sciences* **321**(1561): 523-36.
- Pashin, A. J. and de Zeeuw (1980). *Textbook of wood technology*. New York, NY., McGraw Hill Book Co.,.
- Sun, Y. and J. Cheng (2002). "Hydrolysis of lignocellulosic materials for ethanol production: a review." *Bioresource Technology* **83**(1): 1-11.
- van Olphen, H. (1977). *An Introduction to Clay Colloid Chemistry*. New York, Wiley.
- Wise, L. E., M. Murphy and A. A. D'Addieco (1946). "Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses." *Paper Trade Journal* **122**(No. 2): 35-43.

Chapter 4 Layer-by-layer build-up and its effect on thermal stability of lignocellulosic wood fibers.

Zhiyuan Lin¹, Scott Renneckar*², and Daniel P. Hindman²

¹ Graduate Fellow of the Sustainable Engineered Materials Institute

² Assistant Professor in the Department of Wood Science and Forest Products

T. Brooks Forest Products Center, Virginia Tech

Blacksburg, VA 24061

Phone: (540) 231-7100; Fax: (540) 231-8176; email: srenneck@vt.edu

Scott Renneckar* To whom correspondence should respond

Copyright Notice:

This chapter is reprinted from Lin et al. (2008): Nanocomposite-based lignocellulosic fibers 1. Thermal stability of modified fibers with clay-polyelectrolyte multilayers, *Cellulose* 15:333-346 with kind permission from Springer Science+Business Media.

Abstract

The layer-by-layer (LbL) assembly process of creating highly structured thin films derived from layers of polyelectrolytes and nanoparticles was adopted in this study to modify the surface of lignocellulosic fibers. Aqueous dispersions of clay nanoplatelets were created with ultrasonication and characterized with dynamic light scattering and atomic force microscopy in which confirmed the presence of individual clay nanoplatelets. Film thickness of never-dried clay and poly(diallyldimethylammonium chloride) (PDDA) multilayers was studied with a quartz crystal microbalance with dissipation monitoring (QCM-D). Using identical LbL deposition parameters, a slurry of steam-exploded wood fibers was modified by alternate adsorption of PDDA and clay with multiple rinsing steps after each adsorption cycle. Zeta potential measurements were used to characterize the fiber surface charges after each adsorption step while SEM images revealed that the LbL film masked the cellulose microfibril structure. Using a thermogravimetric analyzer, LbL modified steam-exploded wood fibers were observed to attain increased thermal stability relative to the unmodified material tested in both air and nitrogen atmospheres. Significant char for the LbL clay coated steam-exploded wood suggests the multilayer film serves as a barrier creating an insulating layer to prevent further decomposition of the material. This nanotechnology may have a positive impact on the processing of lignocellulosic fibers in thermoplastic matrices, designing of paper-based overlays for building products, and modification of cellulosic fibers for textiles.

Keywords: fiber modification, layer-by-layer, polyelectrolyte multilayers (PEM), pulp,

self-assembly, thermal degradation

Introduction

In order to expand the applications of bio-based composite materials, it is imperative that the issues related to their thermal stability be addressed. While it is possible to influence the thermal stability of lignocellulosic fibers with chemical modification, such as acetylation (Herdle and Griggs 1965; Glasser et al. 1999), currently there have been a minimal number of alternatives to address the thermal performance of biobased materials. To that end, adding silicates has shown to be a productive method of improving the thermal response of composite materials (Giannelis 1996; Shanmuganathan et al. 2007). In the 1990's Toyota developed a method of reinforcing thermoplastic nanocomposites with clay where the aggregates of clay are dispersed as single platelets throughout the matrix (Okada et al. 1987; Okada et al. 1990; Kojima et al. 1993; Usuki et al. 1993). In general, exfoliated clay nanocomposites produce an oxygen barrier within the composite, suppressing the oxidation cycle of volatile gaseous products by helping to create insulating char layers, which provides self-extinguishing characteristics (Giannelis 1996). Clay nanotechnology has been applied to thermally sensitive materials such as starch to change the thermal response (Park et al. 2003). White et al. created a nanocomposite of cellulose and exfoliated clay and showed that the decomposition temperature and char yield were significantly increased by the presence of montmorillonite clay (White 2004). However, these cellulose nanocomposites were made from dissolved cellulose, which prohibits the adoption to

naturally occurring cellulose-based fibers.

Another method of fiber modification that does not involve chemical reactions is by secondary interactions, which may provide a route towards addressing fiber performance. This route to modifying cellulose fibers has been thoroughly investigated in the field of paper science for the study of the wet strength retention modifiers such as polyethylenimine (PEI) (Sarkanen et al. 1966). A number of factors that influence polyelectrolyte entrapment on pulp fiber surfaces are solution pH, ionic strength, and temperature (Laine et al. 2000). Recently, another method adaptable for fiber modification was reported with the use of sequential adsorption of oppositely charged polyelectrolyte multilayers to the fiber surfaces. Decher and co-workers reported the layer-by-layer (LbL) technique in the early 1990's (Decher 1997). They developed a method to create nanoscale layers of polymers and nanoparticles with controlled structure (Decher 1997). The technique of using polyelectrolyte multilayer films was adopted by Wagberg and co-workers to modify pulp fibers with thin films to improve the properties of paper (Wagberg et al. 2002; Eriksson et al. 2005; Lingstrom et al. 2006). Along a similar line, Lvov and co-workers reported that the LbL method was capable of improving the strength of recycled composites (Lvov et al. 2006). In addition, a scale integrated approach of linking nanoscale multilayer structure onto microscale lignocellulosic fibers for use in the wetlay (paper) process for composite construction was developed to impact macroscale composite properties (Lvov et al. 2006). Nanoparticles and enzymes have been incorporated into these films to impact paper properties, such as strength, porosity, and brightness (Agarwal et al. 2006; Zheng et al. 2006; Lu et al. 2007).

Silicate-based clays such as montmorillonite have been used in the LbL process to form films. Lvov and co-workers found that clay multilayer films can be created and their structure was substantially different than the clay-polyelectrolyte complexes formed through direct mixing (Lvov et al. 1996). In addition, stand-alone clay polyelectrolyte films were created that had properties similar to nacre (Tang et al. 2003). Clay LbL films on pulp fiber has concentrated on tubular halloysite clay with the possibility of filling the halloysite tubes for controlled released applications (Lu et al. 2007).

Delignified and bleached pulp fibers have made up the primary source of investigation into fiber modification. An alternative method to traditional pulp fiber generation is the steam-explosion processing method, which is hydro-thermo-mechanical process of rapid decompression of steam saturated woody biomass. Steam-explosion processing has been studied for the production of pulp (Kokta 1991), animal feed (Sciaraffia and Marzetti 1991), fiber-based composites (Renneckar et al. 2006), and biomass pretreatment for biofuel production largely due to its low costs (Avellar and Glasser 1998) and increased accessibility of biomass (Samaranayake et al. 1994). Because of the growing interest in biofuel production there lies the future availability of steam-exploded lignocellulosic biomass as a low cost fiber. This fiber has a long industrial history in the area of hardboard materials (i.e. Masonite) and it may be suited for other applications if its properties can be augmented by nanoscale engineering. In this study, we report on creating nanocomposite-based wood fibers, fibers that have a controlled nanoscale surface architecture derived by the layer-by-layer process, with a clay platelet coating to determine the

influence of the amount of clay, related to the number of layers, to act as a protective shell. We followed individual layer formation, and determined the impact on the thermal stability of lignocellulosic materials.

Materials and Methods

Materials

Wood fibers were obtained through steam explosion of yellow-poplar (*Liriodendron tulipifera*) veneers of dimensions 25*25*4 mm. The wood chips were steam-exploded at 240 °C for 3 min, resulting in a steam explosion severity factor ($\log R_0$) of 4.6 (Overend and Chornet 1987). The positively charged poly(diallyldimethylammonium) chloride (PDDA) used in the experiments was an aqueous solution (Molecular weight 200,000-350,000) purchased from Sigma-Aldrich Inc, USA. Montmorillonite used was a high purity sodium montmorillonite donated by Kunimine industries, Japan.

Methods

Fiber Treatment

After steam explosion, a modified method developed by (Glasser et al. 1999) was followed to remove lignin and water soluble materials. Steam-exploded wood was first extracted with water at 60 °C for 24 hours and then extracted with 20% (based on fiber solids weight) aqueous alkali using an 8:1 liquor-to fiber ratio at 60 °C for 30 min. After extraction, the fibers were isolated and washed 12 times with ultrapure Mill-Q water using a centrifuge until the supernatant

pH became neutral. Approximately 52% of the original fiber dry mass was retained after extraction.

Fiber Coating Procedure

Positively charged PDDA and negatively charged montmorillonite clay were alternately adsorbed onto the surface of alkali extracted fibers (AEF) using the layer-by-layer (LbL) assembly process. NaCl (0.5 M) was added to PDDA solution to reduce the repulsion between the charges of the polyelectrolyte and facilitate its adsorption. Before layer adsorption, sonication (500 Watts) was applied to the clay suspension for 6 minutes to break the clay into fine nanoscale platelets. The detailed LbL deposition process can be described as follows: first, 2 g (dry weight basis) of alkali extracted fibers (AEF) were added to 200 ml of a 5 mg/ml cationic PDDA solution. The deposition time was 20 minutes with stirring. After each layer, the samples were washed with ultrapure Milli-Q water and recovered using a centrifuge. This washing process was repeated four times to remove excess polyelectrolyte. Next, 200 ml of 0.5 mg/ml montmorillonite clay suspension was added to coat the fibers with the first anionic layer and subsequently rinsed four times. The procedure was repeated multiple times to achieve the desired number of bi-layers. During the deposition of the first layer of PDDA, the pH of the solution was adjusted to 10.5. For the other layers, no pH adjustment of the solution was performed.

Zeta Potential measurements

Many methods have been used to determine the charge nature of cellulosic fibers including some titration techniques and electrokinetic methods. Among all these techniques, microelectrophoresis methods have been frequently used by many papermakers due to their established theoretic foundation and reliable data they provide (Hunter 1981; Strazdins 1995). In this study, zeta potential measurements were conducted on a Zetasizer Nano ZS (Malvern Instrument Ltd, Worcestershire, UK), which can measure a combination of the particle size (dynamic light scattering) and zeta potential (microelectrophoresis). This instrument was used to measure effective particle size of the clay platelets and zeta potential of clay, AEF, and AEF with alternating deposition of PDDA and clay. For determining clay particle size and zeta potential measurements, 0.5 mg/ml clay suspension was used. To study the pH dependence of zeta potential for AEF, the AEF samples were dispersed in the ultrapure Milli-Q water and adjusted to five pH levels by adding aqueous NaOH. Five replications were used for each treatment. Note that steam-exploded wood has a fine particulate fraction that is highly amenable for microelectrophoresis zeta potential measurements.

AFM measurements

AFM was used to measure the size of the clay nanoplatelets. A droplet of clay suspension was dispersed on a freshly cleaved mica substrate, followed by air drying prior to analysis. Very low concentration of clay suspension (0.001%) was used to obtain images of the individual clay

particles. All measurements were conducted in tapping mode on an Asylum Research MFP 3D microscope with a silicon tip.

QCM-D measurements

Real time build-up of the multilayers of PDDA and clay onto a gold coated quartz crystal was continuously monitored with a quartz crystal microbalance with dissipation monitoring (QCM-D) (Q-Sense E4 system, Gothenburg, Sweden). The principle of this technique is that the oscillation frequency of crystal decreases when additional mass is adsorbed onto the crystal surface. For rigid, uniform and sufficiently thin adsorbed layers, the Sauerbrey equation can be used to calculate the adsorbed mass, which is directly proportional to the frequency shift of the crystal (Sauerbrey 1959). However, for soft and thick layer, the Sauerbrey relationship is no longer applied due to the visco-elastic nature of the adsorbed layer and also the presence of coupled water (Höök and Kasemo 2001). In this case, layer thickness was derived by adopting the Voight model incorporated into the Q-Tools software by measuring changes in frequency and dissipation at multiple overtones. Model details are explained elsewhere (Voinova et al. 1999; Höök and Kasemo 2001). Solution conditions used in these measurements were the same as those used in LbL deposition on the fiber.

TGA

Thermogravimetric analysis (TGA) was performed to determine weight loss as a function of

temperature. The samples were vacuum-dried (40°C, gauge pressure of 85 kPa) and stored in a desiccator before tests. Samples of 7.5 mg were heated from room temperature to 600°C under air or nitrogen atmospheres with a constant heating rate of 10 °C /min. AEF (control) and LbL modified fibers with 1, 2, and 4 bi-layers samples were tested with a TA Instruments Q-500 with a platinum sample pan as sample holder. Each sample type was measured in triplicate. Independent temperature calibrations were performed for both air and nitrogen atmospheres.

SEM imaging

The surface structure of the AEF control and AEF with 2 bi-layers of PDDA and clay was characterized with a Leo 1550 field emission scanning electron microscope (FE-SEM). Samples were freeze-dried from a dilute slurry (0.5% w/v), mounted on stubs with carbon tape, and sputtered-coated with a 2 nm thick gold -palladium coating prior to analysis.

Photoacoustic FTIR

The photo-acoustic Fourier Transform infrared spectroscopy (PA-FTIR) analysis of the LbL coated fiber with 4 bi-layers after TGA experiments was performed with a helium-purged MTEC 300 photoacoustic cell in a Nicolet 8700 spectrometer. The spectra resolution was 8 cm⁻¹ with 64 scans per spectrum. Prior to analysis carbon black was used as a reference to normalize the PA signal.

Results and Discussion

Characterization of the “Nanoclay”

Adequate dispersion of nanoscale filler materials is a challenge as has been in the case for montmorillonite clay nanocomposites (Alexandre and Dubois 2000). An alternative approach of using aqueous dispersion and physical means (ultrasonic power) was used to break apart the aggregates of the montmorillonite platelets. Sonication for short times successfully reduced the size of the montmorillonite aggregates (Figure 4.1). Without sonication the aggregates had an average hydrodynamic radius of 518 nm with an upper tail distribution into the scale of microns. After sonication for 3 minutes, the average effective size reduced over 50% to 235 nm and the micron scale aggregates were significantly reduced (see Figure 4.1, inset for scattering intensity plot). Continued sonication up to 10 minutes did not cause a significant change in the average hydrodynamic radius of the clay particles (Figure 4.1). Because the calculation of the hydrodynamic radius assumes a spherical structure, the light scattering data reports an average effective size, but does not provide detail of the anisotropic structure of the clay particles.

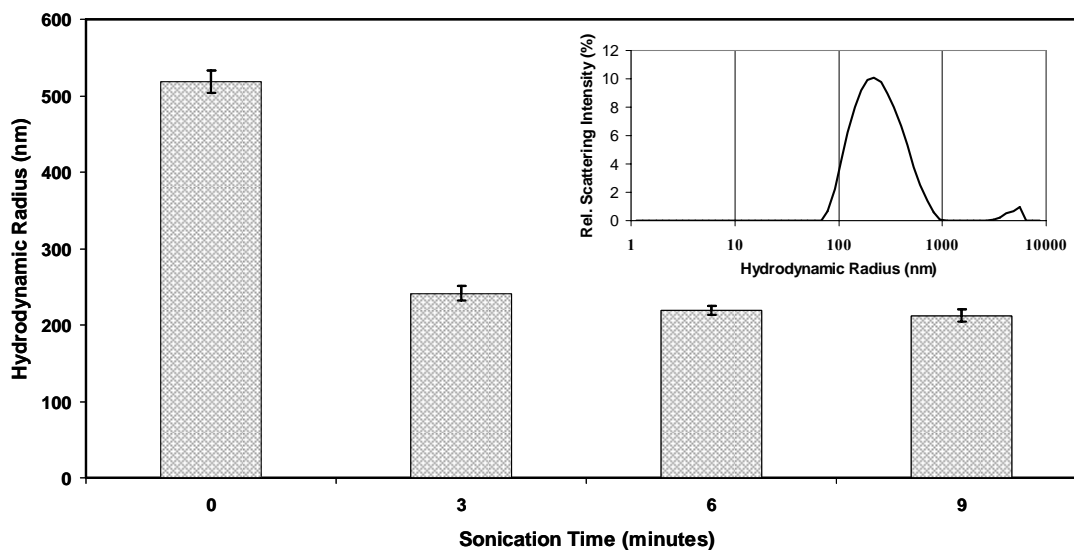


Figure 4.1 Average effective size of clay platelets as a function of sonication time. Inset: Size distribution for clay platelets after 6 minutes of sonication

In order to investigate the platelet structure, atomic force microscopy was used to determine the thickness of individual platelets (Figure 4.2). As seen in Figure 4.2a, the lateral sizes of the platelets are within the range of the hydrodynamic radii found in the distribution of sizes (Figure 4.1, inset). Based on the height data (Figure 4.2b,c), the thickness of the platelet is 1 nm in size, which corresponds to the thickness of individual platelets (Giannelis 1996). Thickness of platelets never exceeded 2 nm, which suggests that stirring and sonication is an adequate method of delaminating the clay aggregates. Once delaminated, the anionic nature of the platelet, arising from isomorphous substitution, prevents agglomeration due to electrostatic interactions. This latter point is revealed in the zeta potential measurements for the clay platelets with the average zeta potential of -44.9 ± 2.8 mV at all sonication levels.

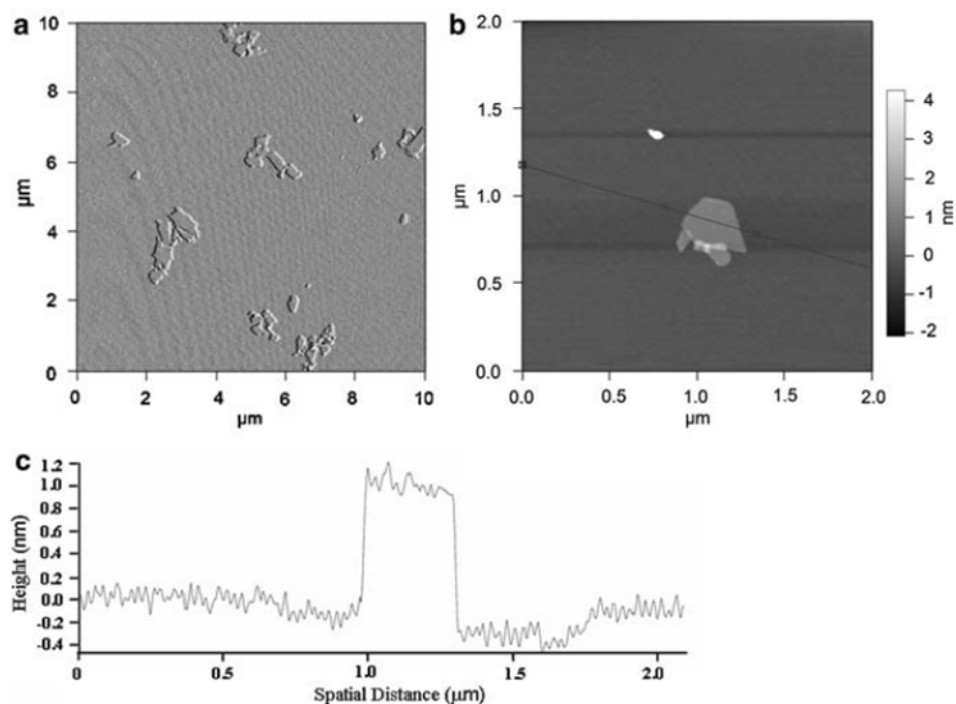


Figure 4.2 AFM image of sonicated clay platelets deposited on cleaved mica

A) amplitude mode image of clay platelets; B) height mode image of clay platelet; and C) height data from (B) indicating 1 nm clay platelet thickness.

Layer-by-layer Monitoring with QCM-D

A quartz crystal microbalance with dissipation monitoring measures both the changes in resonant frequency (and overtones) of the coated quartz crystal, along with the attenuated response of the signal. For the former a reduction in frequency occurs when material adsorbs to the surface arising from a change in response. Using QCM-D, the PDDA-clay build-up was studied in real-time in the wet state (Figure 4.3a). The first two bi-layers have a smaller change in frequency as the two subsequent layers. As evident from the figures, each bilayer remains after

rinsing with water, demonstrating the irreversible nature of bilayer formation. While the mass of the adsorbed material can be found directly with the Sauerbrey relation (Sauerbrey 1959), the contact of the crystal with the aqueous phase impacts this relationship. Using multiple overtones and the dissipation response, the thickness of the hydrated bilayers was modeled using Qtools software (Figure 4.3b). Bilayer thicknesses are 29 nm, 47 nm, 78 nm, and 83 nm, respectively for bilayers 1 through 4. Two observations can be made from this data, 1) the first two bilayers are lower in value than the subsequent layers, which may be attributed to incomplete bi-layer formation (Schoenhoff 2003) and 2) the thickness is less than the average hydrodynamic radius, indicating a planar adsorption of the clay. However, the greater than 1 nm thickness of the clay adsorption step indicates there is significant overlap of the clay platelets. In addition, the hydrated thickness of bilayers is significantly greater than reported thicknesses for clay-polyelectrolyte multilayers in the dry state (Kleinfeld and Ferguson 1994; Kotov et al. 1997). Using a similar solution conditions for layer build-up, Tang et al. found bilayers of clay and PDDA to be 25 nm in the dry state (Tang et al. 2003). Additionally, in the investigation of clay-PDDA films as humidity sensors, Kleinfeld and Ferguson (1995) reported that a multilayer film would change significantly in thickness when exposed to increases in relative humidity. Hence, the data from the model, accounting for the never-dried, hydrated state, is up to three times the size as reported for films in the dry state.

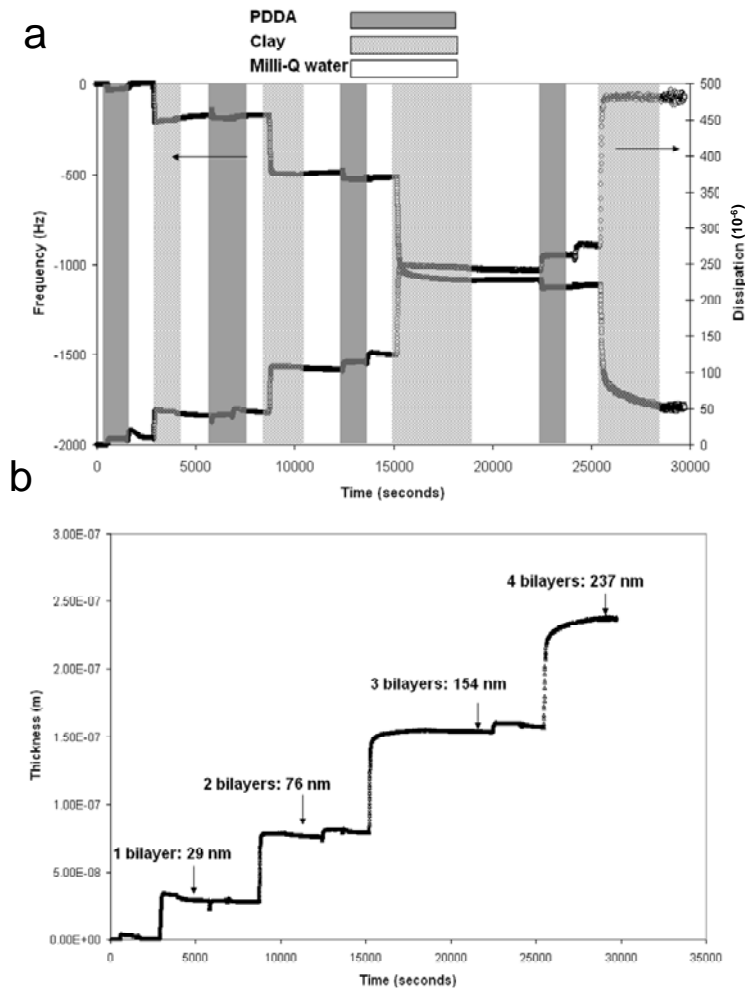


Figure 4.3 Real time monitoring of sequential adsorption cycles of PDDA and clay using QCM-D

A) Frequency and dissipation (5th overtones) response during adsorption cycles and B) Hydrated bilayer thickness derived using Voight model (3, 5, and 7 overtones).

Fiber Characterization

Steam-exploded wood fiber (delignified by alkali treatment) is found to follow the same trend of an increase in the anionic nature of the fiber as the pH is elevated (Figure 4.4). The difference in dissociation of the carboxylic groups from the cellulose of the nonbleached

steam-exploded fiber surface at various pH values contributes to the increased anionic nature at high pH. In addition, ionization of the phenolic hydroxyls in the remaining lignin starts at pH 8.5, which also contributes to this trend (Lloyd and Horne 1993). While an increase in negative surface charge has been shown to increase the adsorption of cationic surfactants (Alila et al. 2005) or polyethylenimine (Sarkanen et al. 1966), the elevated pH also impacts the structure of the cell wall by swelling the microfibril structure (Andreasson et al. 2005). This opens the possibility of trapping polyelectrolytes into the fiber surface when the pH is lowered, causing the cell wall to contract around the polyelectrolyte. The possibility of irreversibly adsorbing polyelectrolytes to cellulosic fibers was explored previously by Allan and co-workers, by adsorbing polyethylenimine above its isoelectric points and then lowering the pH by washing the fiber with acidic solutions (Allan et al. 1970; Allan and Reif 1971). Because the amine becomes protonated, the charged polymer expands from its coiled conformation locking it within the cell wall surface structure-- termed a "jack-in-box" effect.

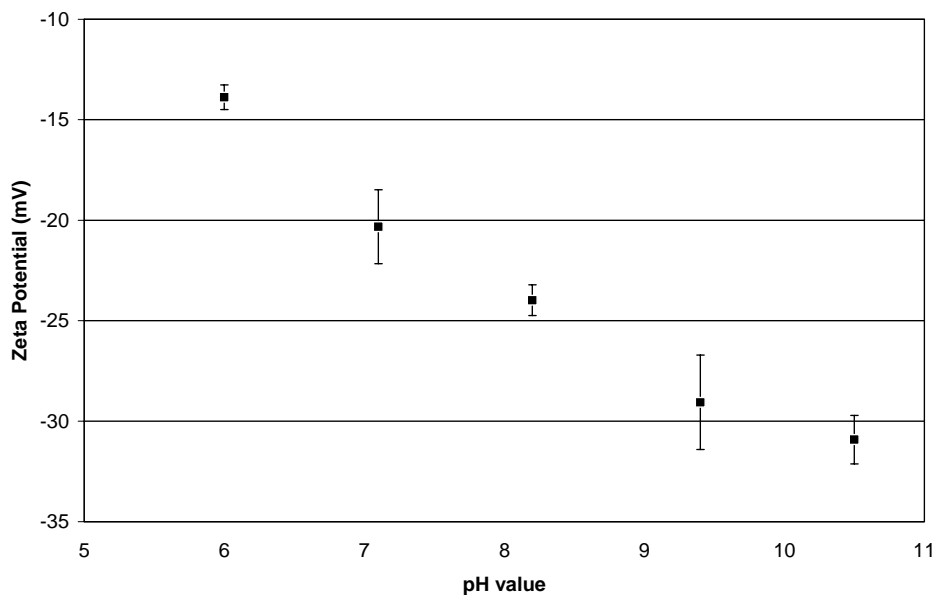


Figure 4.4 Zeta potential of alkali extracted steam-exploded wood as a function of pH

After adsorption of PDDA onto the fiber surface at an elevated pH and washing profusely with Milli-Q ultrapure water, the fiber surface is positively charged with a value of 53.2 mV (Figure 4.5). In order for layer-by-layer assembly to be realized, each new layer must saturate the surface and render it oppositely charged relative to the layer beneath (Schoenhoff 2003). Zeta potential measurements for five sequential adsorption steps from the steam-exploded fiber substrates are shown in Figure 4.5, with the reversal of surface charge after each adsorption step (~48 mV for PDDA terminal layer and -25 mV for clay terminal layers). This data strongly suggests the creation of PDDA and clay bilayers on the fiber surface, which is supported by the evidence of bi-layer build-up with the same materials on the gold coated quartz crystal substrate (Figure 4.3). Note, for 3 bilayers, with clay as the terminal surface layer, the settling of the fiber

prevented the measurement of the zeta potential. However, for 3.5 and 4.5 bilayers, where the PDDA served as the terminal layer, the zeta potential measurements were recorded for the dispersed fiber and reflected the cationic nature of the surface with zeta potentials similar to 0.5, 1.5 and 2.5 layer values. Furthermore, a modified fiber surface is revealed in SEM micrographs (Figure 4.6). Cellulose microfibrils clearly evident on the unmodified fiber surface (Figure 4.6a) are masked for fibers with only 1.5 bilayers (Figure 4.6b) or 2 bi-layers (Figure 4.6c). The modified fiber surface (Figure 4.6c) resembles clay- PEI colloidal gels as reported by Lvov and co-authors (Lvov et al. 1996).

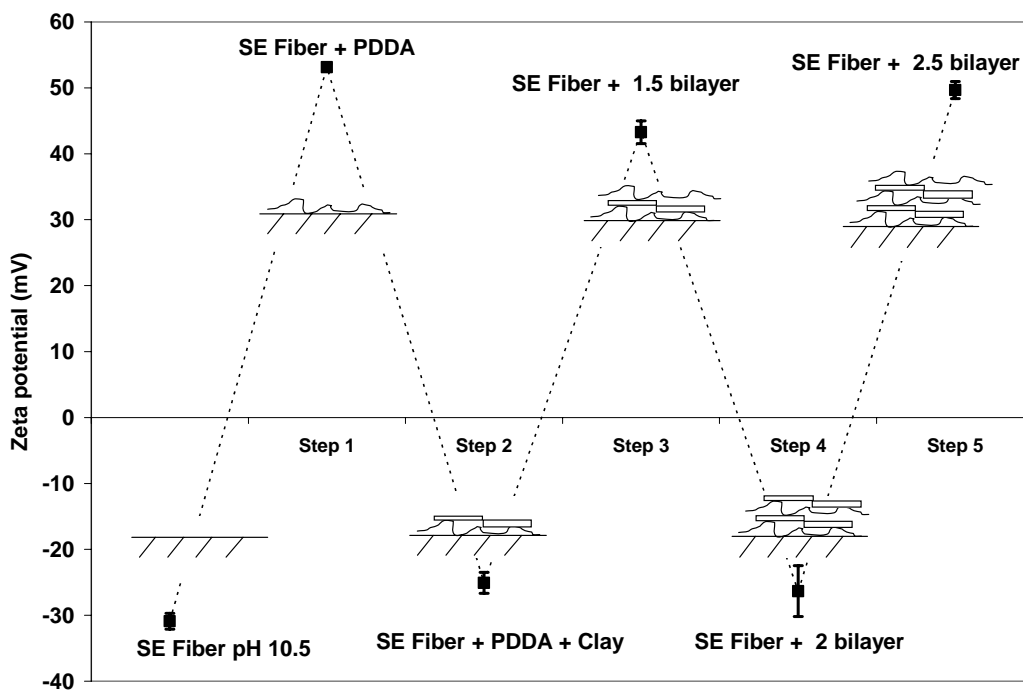


Figure 4.5 Zeta potential of alkali extracted steam-exploded wood at sequential adsorption steps of polymer and clay

Note four washing cycles after each adsorption step. The combination of (+) charged PDDA and (-)

charged clay platelets make up a single bilayer. Half bilayers indicate PDDA as the terminal coating layer.

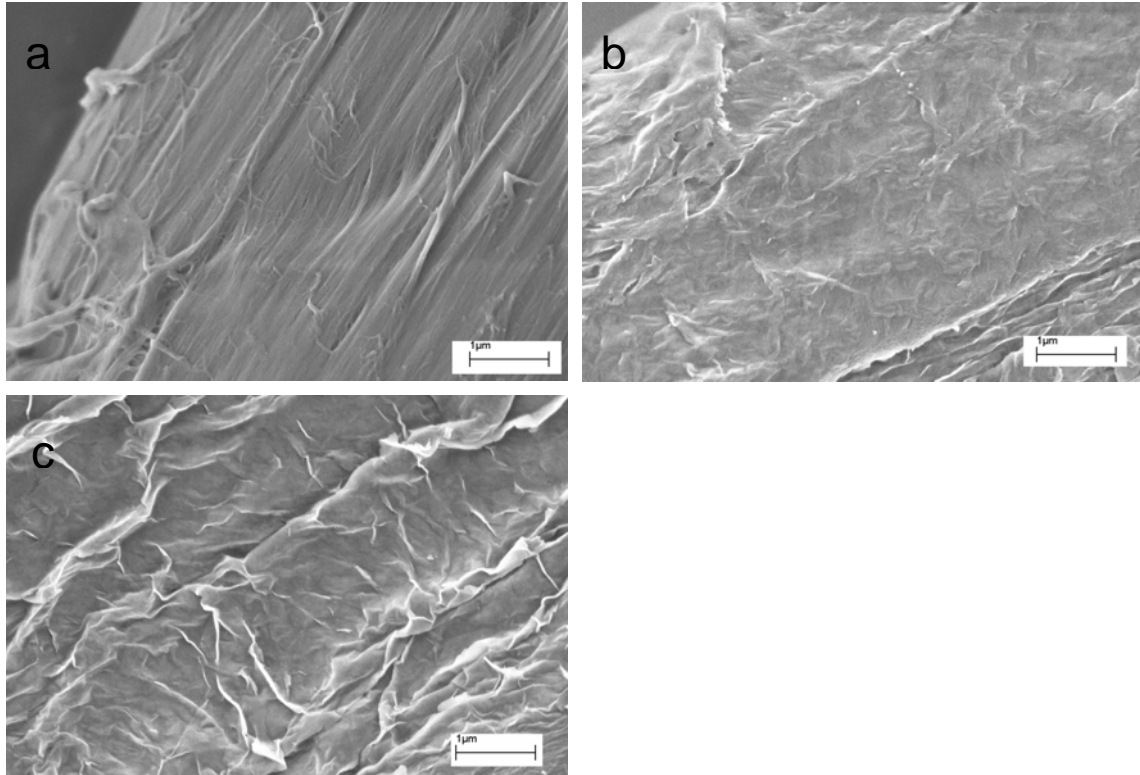


Figure 4.6 Field emission scanning electron micrographs of steam-exploded wood fiber surfaces

(a) unmodified, (b) modified with 1.5 bi-layers with the terminal surface PDDA (c) modified with 2-bilayers with the terminal surface clay. The microfibril pattern evident in (a) is masked by the PDDA-Clay coating. 50,000X magnification.

Thermal Stability

Thermal properties of delignified steam-exploded wood are shown as a function of the number of bilayers (Figure 4.7). Both the onset of decomposition and the residual mass is impacted by the bi-layer treatment. For the former, noted by the occurrence of 5% weight loss the temperature increased as a function of bilayer number (Table 4.1). Note that the 5% weight

loss is calculated after taking in account the loss of moisture and this value can be considered weight loss of dry fiber mass. While the magnitude of change is not as significant as other studies (White 2004), it is highly reproducible phenomenon that does increase the average value by almost 9°C when there are just two bilayers (Figure 4.8). The bilayers had less of an effect on limiting the mass loss for of occurrence at 10% weight loss (Figure 4.8). Average temperatures at this weight loss only increased for 2 and 4 layers by 2.5 and 3.9 °C, respectively.

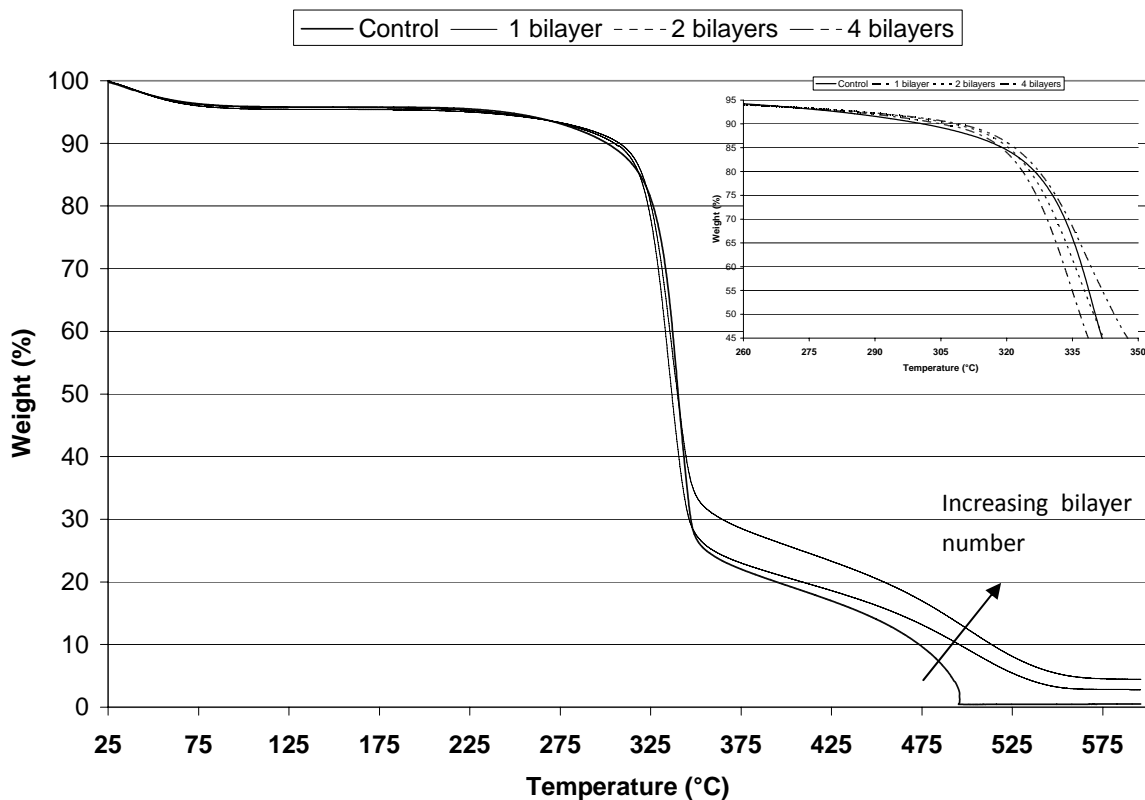


Figure 4.7 Thermogravimetric degradation profiles in air of extracted steam-exploded wood that is unmodified (control) or with bilayers of PDDA and clay

Inset: expanded view of the onset of decomposition.

Table 4.1 Thermal characteristics of untreated and treated steam-exploded wood

Sample	Temp at max deg rate (°C)	Maximum deg rate (%/°C)	Residue wt. (%)	Temp at 5% wt. loss (°C)	Temp at 10% wt. loss (°C)
Control	340.2(0.06)	3.16(0.003)	0.57(0.08)	295.9(1.73)	317.3(0.83)
1	335.2(0.54)	2.73(0.02)	2.58(0.23)	300.2(0.90)	317.5(0.38)
2	336.8(0.33)	2.35(0.03)	4.38(0.07)	305.0(0.37)	319.8(0.13)
4	338.3(0.45)	1.95(0.001)	7.29(0.11)	307.2(0.21)	321.2(0.30)

Each bilayer is composed of PDDA and clay. Standard deviations are shown in parentheses

The TGA curves display a cross over point at which the decomposition of the fibers with 1 and 2 bilayers occurs more readily until a second cross over point at which the fiber that contains no bilayers is degraded to a greater extent (Figure 4.7). The result is that there is almost no residual mass for steam-exploded fiber without bilayer treatment and an intact carbonaceous-inorganic char for the samples with bilayer treatment that corresponds linearly with the number of bilayers (Figure 4.9). The presence of this char component can be verified by the PA-FTIR of the coated fiber after exposure to 600 °C in air (Figure 4.10). The absorption bands found between the 2856 cm^{-1} and 2960 cm^{-1} are corresponded to the symmetric and asymmetric stretching of the methyl and methylene functional groups, which are not present in the spectrum of montmorillonite clay. This char layer prohibits the clay-fiber composition to be unequivocally determined. While almost no recoverable sample was obtained for the uncoated steam-exploded wood after the TGA investigation, the coated samples were intact, black in appearance, and could be used for further analysis (Figure 4.9, inset). Examination of the sample with SEM revealed distinct fiber structure similar in appearance to samples that were not heated

to 600°C in air (Figure 4.11). Samples with intact fiber structure provide evidence that the LbL coatings serve as a protective shell to the fiber structure.

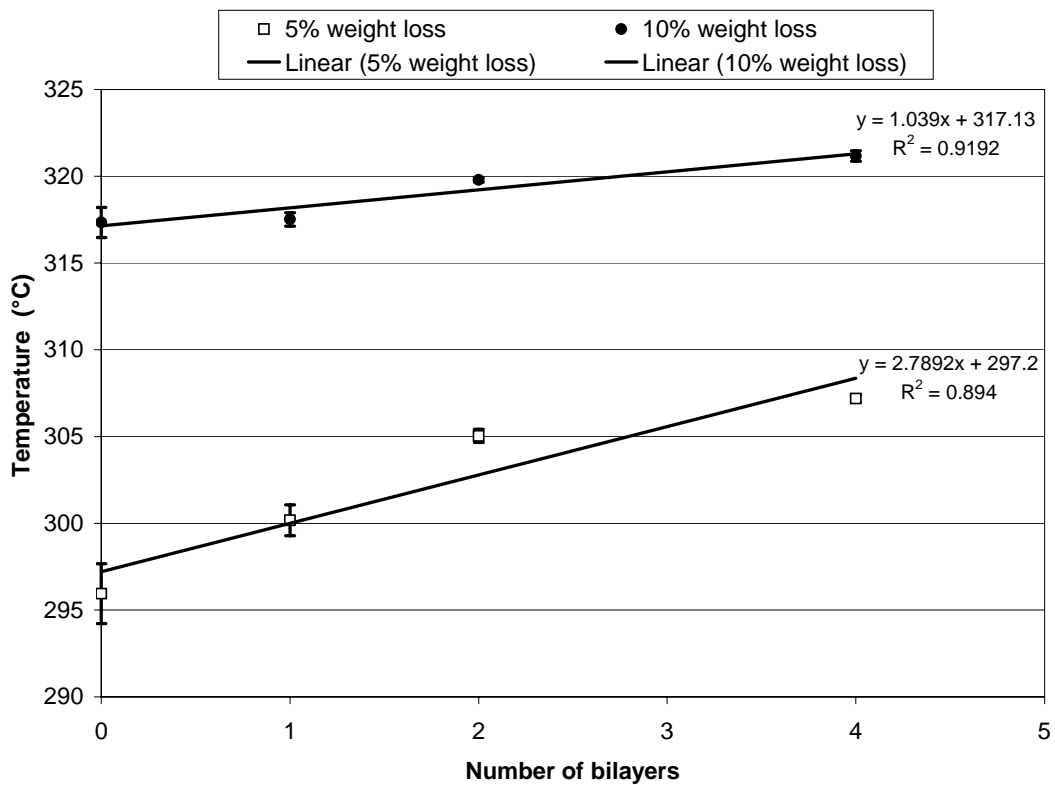


Figure 4.8 Temperature of initial fiber mass weight loss, 5% and 10%, as a function of the number of PDDA and clay bilayers

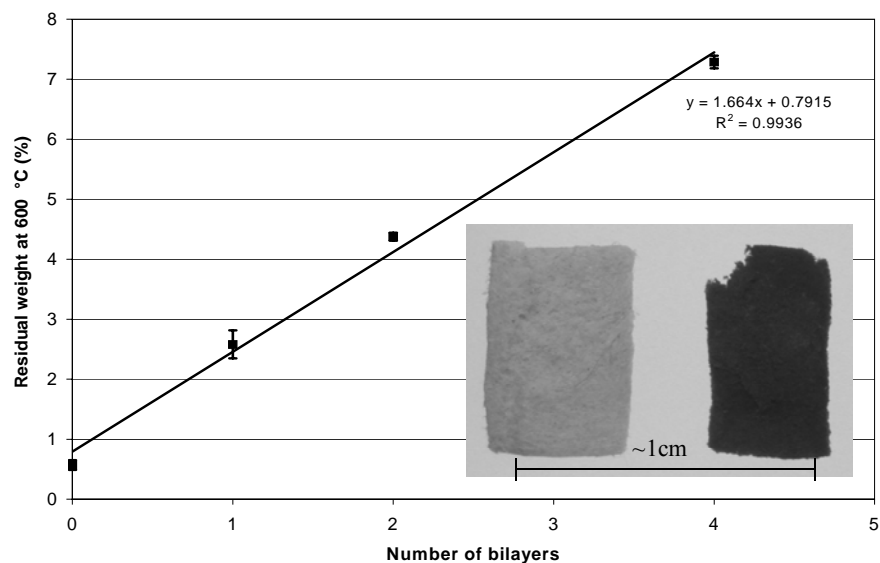


Figure 4.9 Residual weight for extracted steam-exploded wood samples as a function of the number of PDDA and clay bilayers

Inset: TGA samples before and after heat exposure (4 bilayer sample).

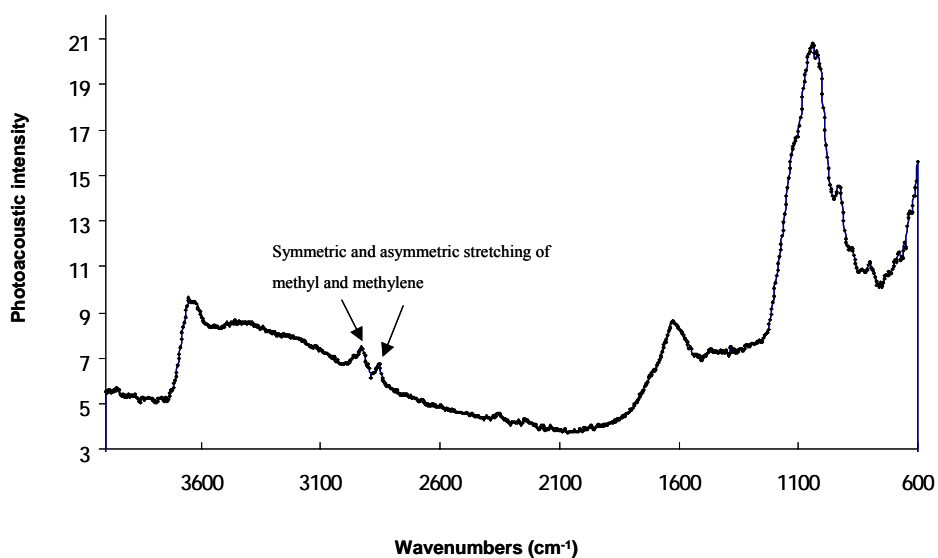


Figure 4.10 Photoacoustic FTIR spectrum of steam-exploded wood with 4-bilayers of PDDA and clay after TGA tests heated in air to 600°C.

In addition, the rate at which weight loss occurs with temperature at the maximum weight loss rate (the peak rate of the derivative of the thermogram) decreases linearly with the number of bilayers (Figure 4.12). The linearity of the relationships shed light onto the uniformity of the coating process of the steam-exploded wood, indicating a cumulative effect of more bilayers. Often surface roughness, as well as charge, influences the first bilayer build-up and this may provide reason to the differences in LbL assembly on planar substances relative to the fiber surfaces, since the first two layers detected with the QCM-D did not reflect a linear film build-up (Figure 4.3).

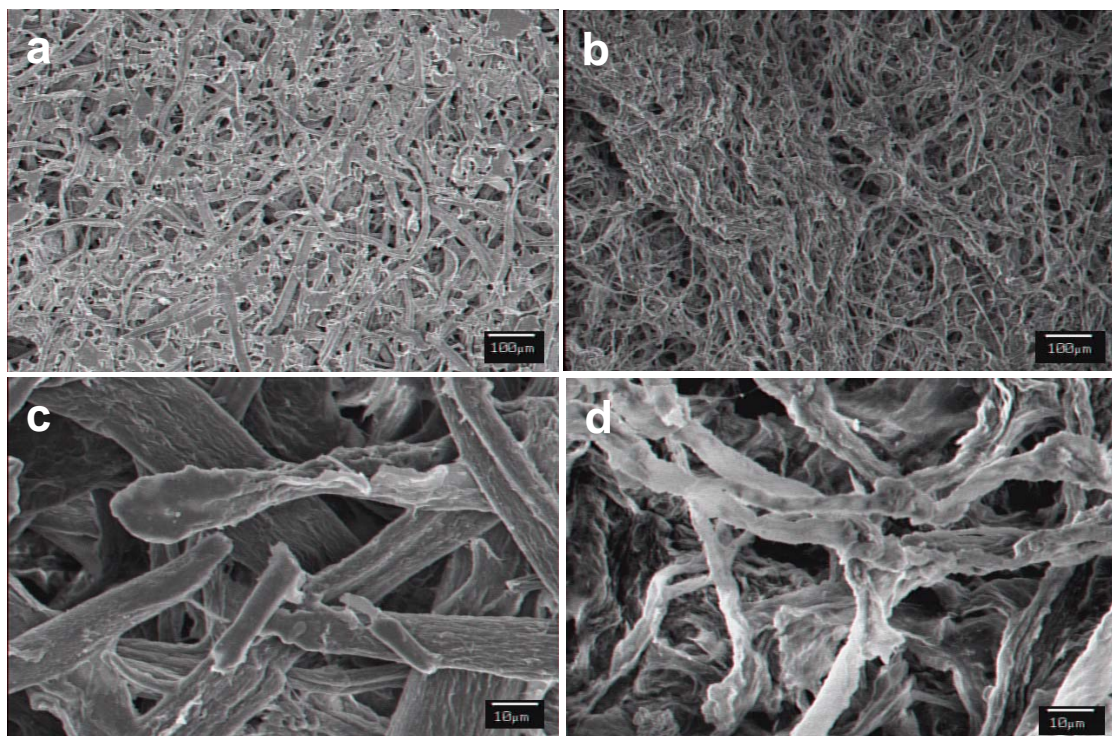


Figure 4.11 Steam-exploded wood with 4-bilayers of PDDA and clay before (a:100x mag., c:1000x mag.) and after (b:100x mag., d:1000x mag.) TGA tests heated in air to 600°C

Note for uncoated specimens there was no recoverable material in sample pan.

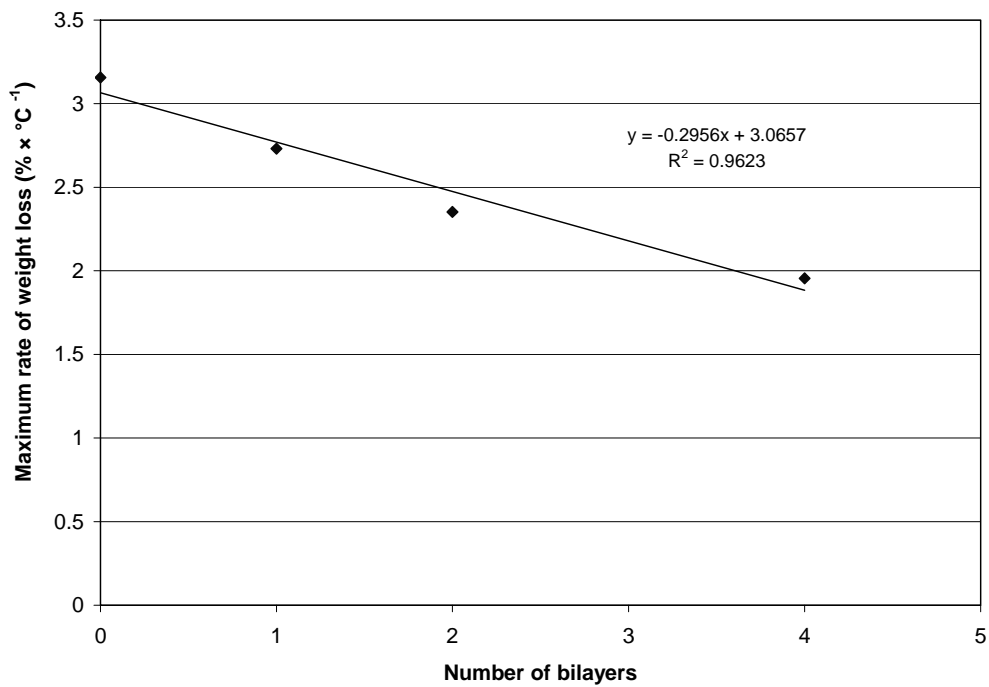


Figure 4.12 Maximum rate of weight loss for steam-exploded wood as a function of the number of PDDA and clay bilayers

Bulk fiber thermal stability is impacted by surface nanoscale coatings of clay, noted by the changes in the 5% weight loss temperature, the maximum rate of weight loss, and the residual mass. An increase of char at the end of the experiment suggests the mechanism leading to the change in residual weight is the development of a clay-char barrier which may suppress the transport of oxidative degradation products. A protective shell may limit the diffusion of oxygen to the surface of the fiber, as well as limit the escape of thermal decomposition products. If this were to happen, then the sample would degrade at a faster rate once the generation of decomposition products occurs in the initial portion of the decomposition stages. Limited

diffusion of the products out of the bulk of the sample may be related to the initial cross over point within the 1 and 2 bilayer samples (Figure 4.7). Additional tests were performed under an inert atmosphere comparing the 4 bilayer sample to the unmodified sample. The 4 bilayer sample had the onset to the main degradation step prolonged and a significant increase in the residual mass (9% change) relative to the control fiber (Figure 4.13). Within this sample there are two cross-over points, which support the theory of limited diffusion of degradation products out of the fiber. However, a second possible affect of the clay acting as a heat shield, changing thermal transport into the fiber, may cause the prolonged onset to thermal degradation of the LbL modified fiber when tested in an inert atmosphere.

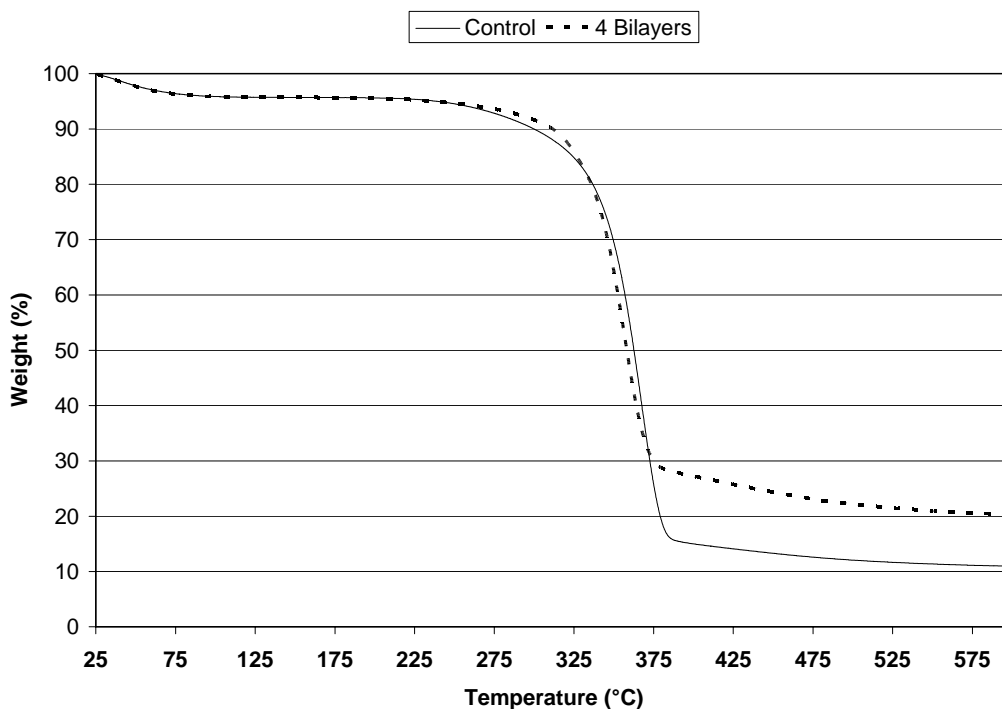


Figure 4.13 Thermogravimetric degradation profiles in a nitrogen atmosphere of extracted steam-exploded wood that is unmodified (control) or with 4 bilayers of PDDA and clay

Flame retardancy of the samples were not determined in this experiment, but other research has shown that there is a link between the decomposition region of 400-600°C during the TGA tests to flame retardant performance determined with cone calorimeter tests (Devaux et al. 2002). Research investigating the thermal stabilization of textiles with nanoclay-filled polyurethane coatings revealed a measurable effect on the surface modified fabric compared to uncoated fabric in both TGA tests and a reduction of rate of heat release (Devaux et al. 2002). It is inferred from the study, that increases of the residual mass is indicative of the increase of the flame retardancy properties of layer-by-layer modified lignocellulosic fibers. It is apparent from this study that directing nanoscale clay layers on the fiber surface has a significant impact on the thermal properties of the lignocellulosic material.

Conclusions

Lignocellulosic fiber was modified through sequential steps of exposure of the material to aqueous solutions of a cationic polymer and platelets of montmorillonite clay with rinsing in between the treatment steps. The fibrous material has a layered structure indicated by the surface charge reversal after each sequential exposure to solutions with oppositely charged species; when a cationic polymer irreversibly adsorbed onto the fiber surface it was rendered positive and subsequent exposure to montmorillonite clay left the fiber with a net negative zeta potential. This process was shown to be repeatable within the number of treatment steps and fibers with up to 4 bi-layers of PDDA and clay were created. The layered coatings veiled the fine structure of

wood fiber surfaces. To provide a relative estimation of film thickness, a model planar substrate was used to follow the adsorption process using a quartz crystal microbalance with dissipation monitoring, in which each hydrated, never-dried bi-layer was revealed to have a thickness up to 83 nm.

The effect of the nanoscale PDDA-clay films on the specimen thermal properties was significant. With only two bi-layers, the onset to decomposition noted by a 5% weight loss was shifted by 9°C. Residual mass increased as a function of the number of bilayers. After heating the samples to 600°C under air atmosphere, samples with a 9% residual mass contained complete fiber structures shown by scanning electron microscopy. In addition to the clay material, FTIR spectra of the thermally treated samples contained carbon-based stretching peaks. It is suspected that the clay-based coating serves as a barrier from oxidative degradation cycle. However, stability increased in a nitrogen atmosphere indicating heat conduction to the fiber interior may be changed as a result of the coating. LbL clay coated lignocellulosic materials may be considered nanocomposite-based wood fibers because of the controlled assembly of nanoscale materials (clay), that impacts the thermal behavior at low loading levels.

Acknowledgements

This project was supported by the USDA CSREES Special Grant No. 2006-06204 and the Sustainable Engineered Materials Institute, College of Natural Resources, Virginia Tech.

The authors wish to thank Dr. R.M. Davis of the Chemical Engineering Department for the help and discussion with regards to the zeta potential and light scattering measurements. We also greatly acknowledge Kunimine Industries for the donation of the clay material.

References

- Agarwal, M., Y. Lvov and K. Varahramyan (2006). "Conductive wood microfibrils for smart paper through layer-by-layer nanocoating." *Nanotechnology* **17**(21): 5319-5325.
- Alexandre, M. and P. Dubois (2000). "Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials." *Materials Science & Engineering, R: Reports* **R28**(1-2): 1-63.
- Alila, S., S. Boufi, M. N. Belgacem and D. Beneventi (2005). "Adsorption of a Cationic Surfactant onto Cellulosic Fibers I. Surface Charge Effects." *Langmuir* **21**(18): 8106-8113.
- Allan, G. G., K. Akagane, A. N. Neogi, W. M. Reif and T. Mattila (1970). "Physical entrapment of polyelectrolytes within microporous solids: the \"jack-in-the-box\" effect." *Nature (London, United Kingdom)* **225**(5228): 175-6.
- Allan, G. G. and W. M. Reif (1971). "Fiber surface modification. 6. Jack-in-the-Box effect: new mechanism for the retention of poly(ethylenimine) and other polyelectrolytes by pulp fibers." *Svensk Papperstidning* **74**(2): 25-31.
- Andreasson, B., J. Forsstroem and L. Wagberg (2005). "Determination of fibre pore structure: influence of salt, pH and conventional wet strength resins." *Cellulose (Dordrecht, Netherlands)* **12**(3): 253-265.
- Avellar, B. K. and W. G. Glasser (1998). "Steam-assisted biomass fractionation. I. Process considerations and economic evaluation." *Biomass and Bioenergy* **14**(3): 205-218.
- Decher, G. (1997). "Fuzzy nanoassemblies: Toward layered polymeric multicomposites." *Science* **277**(5330): 1232-1237.
- Devaux, E., M. Rochery and S. Bourbigot (2002). "Polyurethane/clay and polyurethane/POSS nanocomposites as flame retarded coating for polyester and cotton fabrics." *Fire and Materials* **26**(4-5): 149-154.
- Eriksson, M., S. M. Notley and L. Wagberg (2005). "The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibers." *Journal of Colloid and Interface*

- Science **292**(1): 38-45.
- Giannelis, E. P. (1996). "Polymer layered silicate nanocomposites." *Advanced Materials* (Weinheim, Germany) **8**(1): 29-35.
- Glasser, W. G., R. Taib, R. K. Jain and R. Kander (1999). "Fiber-reinforced cellulosic thermoplastic composites." *Journal of Applied Polymer Science* **73**(7): 1329-1340.
- Herdle, L. E. and W. H. Griggs (1965). "Partially acetylated cellulose-its properties and potential applications." *Tappi* **48**(7): 103A-107A.
- Höök, F. and B. Kasemo (2001). "Variations in coupled water, viscoelastic properties, and film thickness of a mefp-1 protein film during adsorption and cross-linking: a quartz crystal microbalance with dissipation monitoring, ellipsometry, and surface plasmon resonance study." *Anal. Chem.* **73**: 5796-5804.
- Hunter, R. J. (1981). *Zeta potential in colloid science*. London, Academic Press.
- Kleinfeld, E. R. and G. S. Ferguson (1994). "Stepwise formation of multilayered nanostructural films from macromolecular precursors." *Science* (Washington, DC, United States) **265**(5170): 370-3.
- Kojima, Y., A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi and O. Kamigaito (1993). "Synthesis of nylon 6-clay hybrid by montmorillonite intercalated with ϵ -caprolactam." *Journal of Polymer Science, Part A: Polymer Chemistry* **31**(4): 983-6.
- Kokta, B. V. (1991). *Steam-explosion pulping. Steam explosion techniques fundamentals and industrial applications*. B. Foher, A. Marzetti and V. Crescenzi. Philadelphia, Gordon and Breach Science Publishers.
- Kotov, N. A., T. Haraszti, L. Turi, G. Zavala, R. E. Geer, I. Dekany and J. H. Fendler (1997). "Mechanism of and Defect Formation in the Self-Assembly of Polymeric Polycation-Montmorillonite Ultrathin Films." *Journal of the American Chemical Society* **119**(29): 6821-6832.
- Laine, J., T. Lindstrom, G. G. Nordmark and G. Risinger (2000). "Studies on topochemical modification of cellulosic fibers. Part 1. Chemical conditions for the attachment of carboxymethyl cellulose onto fibers." *Nordic Pulp & Paper Research Journal* **15**(5): 520-526.
- Lingstrom, R., L. Wagberg and P. T. Larsson (2006). "Formation of polyelectrolyte multilayers on fibres:

- Influence on wettability and fibre/fibre interaction." *Journal of Colloid and Interface Science* **296**(2): 396-408.
- Lloyd, J. A. and C. W. Horne (1993). "The determination of fiber charge and acidic groups of radiata pine pulps." *Nordic Pulp Paper Res. J.* **8**: 48-67.
- Lu, Z. H., S. Eadula, Z. G. Zheng, K. Xu, G. Grozdits and Y. Lvov (2007). "Layer-by-layer nanoparticle coatings on lignocellulose wood microfibrils." *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **292**(1): 56-62.
- Lvov, Y., K. Ariga, I. Ichinose and T. Kunitake (1996). "Formation of Ultrathin Multilayer and Hydrated Gel from Montmorillonite and Linear Polycations." *Langmuir* **12**(12): 3038-3044.
- Lvov, Y., Q. Xing, R. Davis and S. Renneckar (2006). "Nano- Micro- Macro Integration for New Cellulose Based Materials." Abstracts, 62nd Southwest Regional Meeting of the American Chemical Society, Houston, TX, United States, October 19-22: SRM-545.
- Lvov, Y. M., G. A. Grozdits, S. Eadula, Z. G. Zheng and Z. H. Lu (2006). "Dry and wet strength of paper - Layer-by-layer nanocoating of mill broken fibers for improved paper." *Nordic Pulp & Paper Research Journal* **21**(5): 552-557.
- Okada, A., M. Kawasumi, T. Kurauchi and O. Kamigaito (1987). "Synthesis and characterization of a nylon 6-clay hybrid." *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* **28**(2): 447-8.
- Okada, A., M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi and O. Kamigaito (1990). "Nylon 6-clay hybrid." *Materials Research Society Symposium Proceedings* **171**(Polym. Based Mol. Compos.): 45-50.
- Park, H.-M., W.-K. Lee, C.-Y. Park, W.-J. Cho and C.-S. Ha (2003). "Environmentally friendly polymer hybrids. Part I. Mechanical, thermal, and barrier properties of thermoplastic starch/clay nanocomposites." *Journal of Materials Science* **38**(5): 909-915.
- Renneckar, S., A. Zink-Sharp, A. R. Esker, R. K. Johnson and W. G. Glasser (2006). Novel methods for interfacial modification of cellulose-reinforced composites. *Cellulose Nanocomposites: Processing, Characterization, and Properties*. Washington, Amer Chemical Soc. **938**: 78-96.

- Samaranayake, G., X. M. Li and W. G. Glasser (1994). "Solvent accessibility of steam exploded cellulose." *Holzforschung* **48**: 69-71.
- Sarkanen, K. V., F. Dinkler and V. Stannett (1966). "The effects of polyethylenimine on some properties of pulp and paper." *Tappi* **49**(1): 4-9.
- Sauerbrey, G. Z. (1959). "The use of quartz crystaloscillators for weighing thin layers and for microweighing." *Zeitschrift fuer Physic* **155**: 206-222.
- Schoenhoff, M. (2003). "Layered polyelectrolyte complexes: Physics of formation and molecular properties." *Journal of Physics: Condensed Matter* **15**(49): R1781-R1808.
- Sciaraffia, F. and A. Marzetti (1991). Enhancement of wheat straw digestability by steam-explosion pretreatment. *Steam explosion techniques fundamentals and industrial applications*. B. Focher, A. Marzetti and V. Crescenzi. Philadelphia, Gordon and Breach Science Publishers: 365-374.
- Shanmuganathan, K., S. Deodhar, N. Dembsey, Q. Fan, P. D. Calvert, S. B. Warner and P. K. Patra (2007). "Flame retardancy and char microstructure of nylon-6/layered silicate nanocomposites." *Journal of Applied Polymer Science* **104**(3): 1540-1550.
- Strazdins, E. (1995). "Critical issues in applying electrokinetics to papermaking." *Tappi J* **78**: 115-119.
- Tang, Z. Y., N. A. Kotov, S. Magonov and B. Ozturk (2003). "Nanostructured artificial nacre." *Nature Materials* **2**(6): 413-419.
- Usuki, A., Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito (1993). "Synthesis of nylon 6-clay hybrid." *Journal of Materials Research* **8**(5): 1179-84.
- Voinova, M. V., M. Rodahl, M. Jonson and B. Kasemo (1999). "Viscoelastic acoustic response of layered polymer films at fluid-solid interfaces: continuum mechanics approach." *Physica Scripta* **59**: 391-396.
- Wagberg, L., S. Forsberg, A. Johansson and P. Juntti (2002). "Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept. Part I: Modification of paper strength." *Journal of Pulp and Paper Science* **28**(7): 222-228.
- White, L. A. (2004). "Preparation and thermal analysis of cotton-clay nanocomposites." *Journal of Applied Polymer Science* **92**(4): 2125-2131.

Zheng, Z. G., J. McDonald, R. Killan, Y. Su, T. Shutava, G. Grozdits and Y. M. Lvov (2006).
"Layer-by-layer nanocoating of lignocellulose fibers for enhanced paper properties." *Journal of
Nanoscience and Nanotechnology* **6**(3): 624-632.

Chapter 5 Polyelectrolyte adsorption onto heterogeneous fiber surfaces

Zhiyuan Lin¹ and Scott Renneckar^{*2}

¹ Sustainable Engineered Materials Institute, Virginia Tech, Blacksburg, VA 24061

² Department of Wood Science and Forest Products, Virginia Tech, Blacksburg, VA 24061

* To whom correspondence should be addressed. Phone: (540) 231-7100. Fax: (540) 231-8176.

Email: srenneck@vt.edu.

Abstract

Wood and natural fibers are composed of multiple polymeric components. Lignin, one primary component, is typically removed to various degrees during paper making, but is present on thermomechanically isolated fibers. The effect of the residual lignin on the adsorption of poly(diallyldimethylammonium) chloride (PDDA) onto lignocellulosic fibers was investigated under varying solution conditions (ionic strength and pH). Using nitrogen elemental analysis it was shown for the samples with the highest concentration of lignin, PDDA adsorption to the fibers was reduced for all solution conditions. However, upon extracting of the non-covalently attached lignin, the samples showed the greatest amount of PDDA adsorption, reaching to 1.5%, under neutral solution conditions without the presence of added electrolyte. Furthermore, the influence of polyelectrolyte loading and electrokinetic potential on subsequent multilayer formation of PDDA and montmorillonite clay was quantified. It was revealed that electrokinetic

potential of fiber after PDDA adsorption, rather than the amount of adsorbed PDDA layer, controlled the subsequent clay adsorption layers. Significant mass of PDDA/clay (up to ~75% of starting dry fiber mass for only 4 bi-layers) can be adsorbed onto wood fibers through the multilayer assembly process. This paper provides insight into how non-covalent modification of heterogeneous fibrous substrates offers a novel route for the creation of organic/inorganic fiber materials.

Introduction

The layer-by-layer (LbL) assembly technique has attracted considerable interest over past decades due to the simplicity and versatility of the build-up process (Decher 1997). A great variety of components, including organic or inorganic compounds (Decher and Hong 1991; Lvov et al. 1996; Kotov et al. 1997; Lvov et al. 1997; van Duffel et al. 2001; Hyde et al. 2005), macromolecules (Schmitt et al. 1993; Onoda and Yoshino 1995; Yoon and Kim 2000; Cheng and Cox 2001), biomacromolecules such as protein and DNA (Lvov et al. 1993; Elbert et al. 1999; Wang and Hu 2001), has been incorporated into the LbL system to create advanced materials with nanoscale architectures with desired properties. The electrostatic attraction between oppositely charged macromolecules, coupled with counter-ion release during the adsorption process serves as the main driving forces for the multilayer assembly process (Ariga et al. 2007). Because substrate shape has little impact on this mechanism, LbL films have been successfully applied to cellulosic pulp fibers to enhance the properties of paper (Wagberg et al. 2002;

Eriksson et al. 2005; Lingstrom et al. 2006; Lu et al. 2007; Peng et al. 2008).

The study of polyelectrolyte adsorption onto pulp fibers to enhance fiber-fiber interactions goes back many decades (Erspamer 1940; Allan and Reif 1971; Allan and Reif 1971; Formento et al. 1994), and has been the subject to many reviews (Wagberg and Odberg 1989; Odberg et al. 1993; Wagberg 2000). A number of factors such as segment charge, surface charge density and salt concentration affect the adsorption of polyelectrolytes (Tanaka et al. 1979; Lindstrom and Wagberg 1983; van de Steeg et al. 1992; Wagberg 2000; Rojas et al. 2002; Horvath et al. 2006). Horvath et al. investigated the effect of salt concentration during poly(diallyldimethylammonium) chloride (PDDA) adsorption onto the bleached kraft pulp fibers. The authors found that charge stoichiometry prevailed under electrolyte free conditions, where the range of electrostatic force fields was larger than the mean distance between the charges on the fiber surface. For this phenomenon there is a continuous charged layer emanating from the surface. However, surface charge overcompensation occurred at higher electrolyte concentrations because of the salt influence on the Debye length, transitioning the pulp surface from an average field of charge to islands of point charges (Horvath et al. 2006). As this transition occurs, less expanded polyelectrolytes neutralize islands and adsorption increases as multiple chains interact with multiple islands. In general, polyelectrolyte adsorption onto surfaces exhibits two distinct adsorption regimes, a screening-reduced adsorption regime and a screening-enhanced adsorption regime upon the addition of salt, which depends on the balance between electrostatic and non-electrostatic attraction between the segment and surface (van de Steeg et al. 1992). If the

attraction between polyelectrolyte and surface is purely electrostatic, the adsorption decreases with increasing salt concentration since the segment-surface attraction is screened by the added salt. A screening-enhanced adsorption regime occurs when non-electrostatic interactions are present. In this case, the addition of electrolyte screens the intramolecular repulsion between the charged segments, allowing the polyelectrolytes to be adsorbed in a more coiled conformation, which leads to the increase in adsorption. However, it is possible that competitive adsorption of the simple electrolyte will negatively impact the adsorption of the polyelectrolyte if there is a preferred interaction, since the ions also compete with the polyelectrolytes to compensate the surface charge (van de Steeg et al. 1992).

Despite similarity between bleached pulp fibers and thermomechanical treated fibers, adsorption behavior of the polyelectrolyte onto the latter fibers may be different because of the higher lignin content present. Lignin composes 20 to 30% of the mass within the stem of a tree and is removed to various degrees based upon the pulping process. This aromatic biopolymer has structure arising from the polymerization of substituted phenolic monomers such as coniferyl and sinapyl alcohol units. Furthermore, as lignin remains on the fibers other interactions may influence polyelectrolyte adsorption. Cation- π interactions were recently reported to assist in the adsorption between PDDA and isolated lignins (Pillai and Renneckar 2009). Therefore, it is of interest to examine the potential effect of residual lignin contained within the fiber on PDDA adsorption under a variety of deposition solution conditions (ionic strength and pH). Moreover, we investigated the influence of the initial PDDA layer on the subsequent multilayer build-up of

PDDA and montmorillonite clay. The inorganic montmorillonite clay component is used as the negatively charged material in this study because of its unique physical and mechanical properties (Okada et al. 1987; Okada et al. 1990; Messersmith and Giannelis 1994; LeBaron et al. 1999). For this study, elemental analysis and spectrophotometry methods were used in conjunction with microelectrophoresis to show the influence of residual lignin on polyelectrolyte adsorption to fiber surfaces and on multilayer build-up.

Materials and Methods

Materials

Wood fibers were obtained through steam explosion of yellow-poplar (*Liriodendron tulipifera*) veneers of dimensions 25*25*4 mm. This treatment is similar to the Masonite method that involves rapid release of pressure from a vessel containing steam-saturated wood chips. The wood chips were steam-exploded after exposure to 240 °C steam for 3 min, resulting in a steam explosion severity factor of 4.6 (Overend and Chornet 1987). Poly(diallyldimethylammonium) chloride (PDDA) used in the study was an aqueous solution (Mw 200,000-350,000) obtained from Sigma-Aldrich Inc, USA. The ionic strength and pH of solutions were adjusted by adding NaCl and NaOH. Montmorillonite clay used was a high purity sodium montmorillonite donated by Kunimine industries, Japan.

Methods

Fiber Treatment

Steam-exploded fibers (SEF) with three different levels of lignin content were isolated through water extraction, alkali extraction and bleaching process. SEF were first extracted with water at 60 °C for 24 hours and then extracted with 20 % (based on fiber solids weight) aqueous alkali using an 8:1 liquor-to fiber ratio at 60 °C for 30 min (Glasser et al. 1999; Lin et al. 2008). After water and alkali extraction, the fibers were isolated and washed multiple times with ultrapure water (Milli-Q Direct 3UV 18.2 M Ω) using a centrifuge until the supernatant pH was neutral. Alkali extracted fibers were then bleached with sodium chlorite to further remove the residual lignin from the wood (Wise et al. 1946). The fibers obtained from these steps were called water extracted fibers (WEF), alkali extracted fibers (AEF) and bleached fibers (BF), respectively. The reported lignin content of WEF, AEF and BF is 39, 11.4 and 3%, respectively (Wise et al. 1946; Ibrahim and Glasser 1999).

Polyelectrolyte adsorption and layer-by-layer assembly

Adsorption experiments were performed to investigate the effect of the deposition conditions (ionic strength and pH) and lignin contents (WEF, AEF, and BF) on the multilayer build-up of PDDA and clay. Table 5.1 summarizes the deposition parameters used in this study. PDDA solutions were adjusted to a series of salt concentrations at 0, 0.1M, 0.5M, and 1M and pH at 6.7, 8.5 and 10.7. Polyelectrolyte adsorption were performed by adding 2g (dry weight

basis) of wood fibers (WEF, AEF, and BF) into 200 ml PDDA solutions (5 mg/ml), adjusted to each set of conditions listed above. After 20 min of stirring, the samples were centrifuged and rinsed with ultrapure water and recovered using a centrifuge. To determine the influence of the initial PDDA layer on subsequent multilayer assembly, the alternate adsorption of positively charged PDDA and negatively charged montmorillonite clay were compared at four selected initial PDDA layer deposition conditions: AEF without any salt and pH adjustment; AEF at 0.1M salt, pH 10.7; AEF at 1M salt, pH 10.7; and WEF at 0.1M, pH 10.7. Note that pH adjustment for LbL adsorption was only performed during the initial PDDA layer adsorption. Before layer adsorption, ultrasonication (medium intensity horn up to 500 Watts) was applied to the clay suspension for 6 minutes to break the clay into fine nanoscale platelets (Lin et al. 2008). The detailed LbL deposition process has been described elsewhere (Lin et al. 2008). A greater concentration of clay suspension (1 mg/ml) was used in this study relative to a previous study (Lin et al. 2008) to ensure that clay was not totally depleted from the solution after adsorption.

Table 5.1 Deposition parameters used in this study

Parameters	Levels
Fiber	WEF, AEF and BF
pH	6.7, 8.5 and 10.7
Ionic strength	0, 0.1, 0.5 and 1M

Zeta Potential measurements

WEF, AEF, and BF were dispersed in the ultrapure water adjusted to a series of pH ranging

from 6.1 to 10.7. After sedimentation of large particles, the supernatant of fine fiber suspension were used to measure the zeta potential, which was conducted on a Zetasizer Nano ZS (Malvern Instrument Ltd, Worcestershire, UK). The same instrument was used to measure the zeta potential of particles after the initial PDDA layer adsorption, measured in ultrapure water. Five replications were used for each set of conditions. Note that SEW has a fine particulate fraction that is highly amenable for microelectrophoresis measurements.

Carbon-Nitrogen-Sulfur (CNS) Elemental Analysis

Bulk nitrogen content of PDDA adsorbed fibers was measured with a Vario Max CNS analyzer (Elementar). Samples are converted into gases in a dry combustion process and the amount of nitrogen is determined by a thermal conductivity detector (sensitivity of 10 ppm nitrogen in helium carrier gas). All the samples were dried in a vacuum oven at 40 °C for 48 h (0.1 mm Hg), ground into particles (60 mesh), and kept dry in a conventional oven at 60 °C until measurements. Samples of 300 mg were used in the experiments.

UV-VIS Depletion Analysis

The clay concentrations before and after adsorption were measured using an UV-VIS Spectrometer (Milton Roy Spectronic 601) monitoring the absorbance. The UV-Spectrometer (UV-Spec) was used to determine the amount of clay concentration in solution after the creation of a linear calibration curve between clay concentration and absorbance (Figure 5.4). The

concentration of clay was monitored as a function of absorbance with monochromatic light of 250 nm.

Gravimetric method

The total amount of adsorbed PDDA and clay on the fibers was measured gravimetrically. The LbL modified fibers were dried in a vacuum oven at 40 °C for 48 h (0.1 mm Hg) and weighed.

Results and Discussion

Surface charge of WEF, AEF and BF at different pH

Microelectrophoresis methods have been frequently used to describe the surface potential of cellulosic fibers due to their established theoretic foundation and reliable data they provide (Hunter and Editor 1981; Strazdins 1995). The zeta potential of WEF, AEF and BF at different pH was measured in this study (Figure 5.1). The anionic nature of both WEF and AEF increases in magnitude with elevated pH, similar to the reported results using ground wood samples (Rennekar and Zhou 2009). Ionization of phenolic hydroxyls in the lignin under alkaline condition contributes to this increased anionic nature at high pH (Norgren and Lindstrom 2000). The difference in dissociation level of the carboxylic acid groups (0.0284 mmol /g) of the cellulosic fibers also contributes to this trend. The zeta potential of BF increases slightly in magnitude with increasing pH, which is attributed to low lignin content present in BF. The zeta potential of BF is significantly greater than those of WEF and AEF, which has increased

carboxylic acid groups from partial degradation of the cellulose in the bleaching process (approximately twice that of SEF and AEF). The zeta potential of WEF and AEF is comparable, which indicates similar surface potential of the WEF and AEF at various pH.

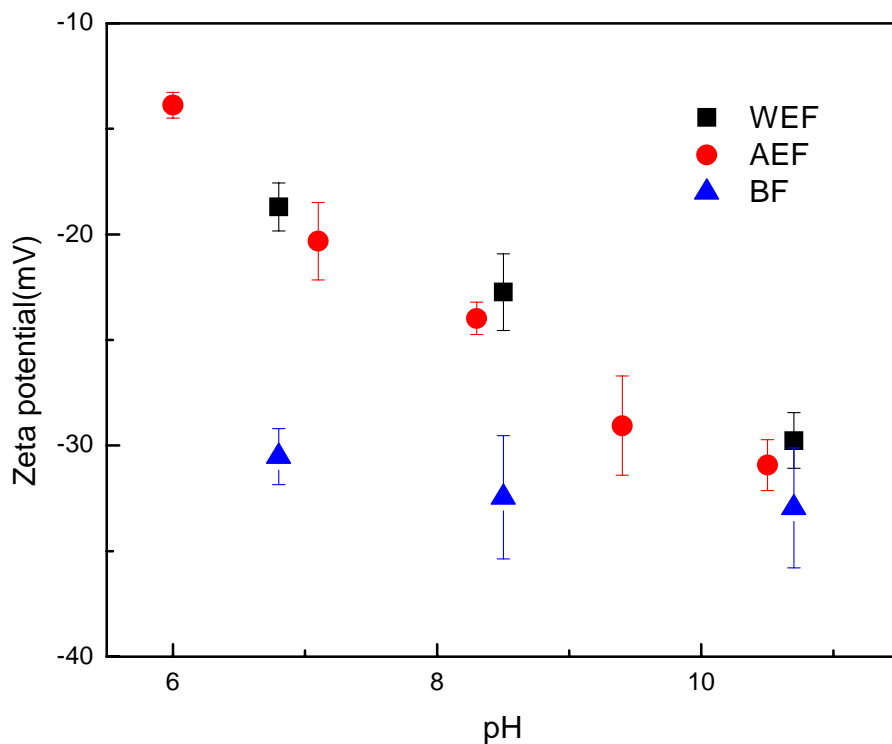


Figure 5.1 Zeta potential of WEF, AEF, and BF at different pH in ultrapure water

Adsorption of PDDA to lignocellulosic fibers

Adsorption behavior of PDDA onto fiber treated surfaces at varying salt concentrations and pH was studied by elemental analysis relating the nitrogen content of the modified fiber to the amount of polymer adsorbed (Figure 5.2). The differences in adsorbed amounts of PDDA

amongst WEF and the other samples indicate that lignin content disparities must play a significant role in polyelectrolyte adsorption. The zeta potentials of WEF and AEF are comparable at all pH conditions, while values for BF are greater in magnitude (Figure 5.1). Increased requirements for charge neutralization of BF, relative to the WEF, enhanced the adsorption of PDDA to the fiber surface. A similar finding was observed by Horvath et al., following PDDA adsorption to bleached pulp surfaces with different surface charge densities obtained through surface carboxymethylation (Horvath et al. 2006). This phenomenon is seen for the effect of pH on adsorption; higher pH solutions enhance the deprotonation of acidic groups on the fiber surfaces making them more negatively charged. However, zeta potential data cannot be used to discriminate the dramatic difference between the AEF and WEF. A second mechanism, either related to the fiber porosity or surface chemistry must influence the adsorption. It has been shown that extraction of lignin, physically adsorbed to the surface after steam-explosion treatment, changes the available surface area (Michalowicz et al. 1991), providing for more adsorption spots upon its removal. Other studies have shown that PDDA adsorption to lignin surfaces forms very thin layers, as small as 0.5 nm (Notley and Norgren 2008). A cation- π interaction has been implicated as an adsorption mechanism between PDDA and technical lignins (Pillai and Rennekar 2009). Short range nature of cation- π interactions between PDDA and phenolic groups in the lignin requires the polymer to be adsorbed within a very small effective thickness (Pillai and Rennekar 2009), which contributes to reduced adsorption of PDDA on WEF since loops and tails are minimized. This mechanism provides basis to the

decreased PDDA adsorption on WEF under all the pH conditions. A competitive ion adsorption mechanism may play a role in this lignin-containing system for decreased adsorption with added salt; based on computational studies of cation- π interactions, binding energy of a phenol-sodium ion pair is greater than that of phenol-ammonium ion pair (Ma and Dougherty 1997). This data indicates with the addition of the sodium chloride salt, sodium ions dominate the adsorption process over PDDA ammonium segments for the lignin-rich WEF. Considering its high lignin content, this competitive ion adsorption effect is significant for PDDA adsorption on WEF.

PDDA adsorption on BF does not follow the same trend as the WEF. PDDA adsorption was increased for the electrolyte concentration of 0.1M NaCl, after which it decreases at high electrolyte concentrations. Similar adsorption behavior was reported, where PDDA was adsorbed to bleached wood pulps (Horvath et al. 2006). In that study, the initial increase in adsorption is due to a deviation from a 1:1 charge stoichiometry in the presence of electrolyte. Additional increase in the salt concentration to 0.5 M NaCl decreases the adsorption as the attraction between segment and surface is also screened by these ions (Horvath et al. 2006). An increase in adsorption for salt concentration of 1.0 M occurs for all three pH levels. Because total mass is measured (and not surface mass), it is plausible that PDDA is able to penetrate into the fiber cell wall for BF at high electrolyte concentration. Polyelectrolyte chains become more flexible and able to penetrate at very high electrolyte conditions (Horvath et al. 2008; Gimaker and Wagberg 2009). The hydrodynamic diameter of PDDA was reported to be reduced by two-thirds from an increased salt concentration of 10^{-4} to 1M (Horvath et al. 2008). Moreover, the removal of lignin

during bleaching process opens the channels within the cell wall (Michalowicz et al. 1991), which may also facilitate the PDDA penetration.

Polymer adsorption onto AEF has differing responses to increased salt concentrations dependent upon pH. The fiber surface charge (0.0284 mmol /g), can only be considered as a series of point charges instead of mean field charges below pH 8.5 (as supported by zeta potential values in Figure 5.1) under electrolyte-free conditions. Therefore, the added salt ions tend to screen the surface-segment attraction rather than segment-segment repulsion, which results in the decrease of the polyelectrolyte adsorption at neutral pH. At higher pH, PDDA adsorption of AEF is very similar to that of BF, except at the very high electrolyte concentration (1.0 M NaCl) adsorption continues to decrease (Figure 5.2). PDDA adsorption is maximized under neutral pH for conditions when the surface potential is similar to that of WEF. Hence charge neutralization is not the dominate interaction for this adsorption regime. The arrangement of deprotonated acidic groups and aromatic moieties facilitates the adsorption of PDDA in arrangements that minimize the energy of the system. Release of chloride counter-ions of PDDA upon adsorption of the polymer to the lignin and/or conformations that are extended away from the surface (maximizing conformational entropy of the chain) would minimize the energy of the system. This system is different from the adsorption of PDDA onto cellulosic fibers, which depends upon the surface charge density of the fiber without additional interactions with PDDA (Horvath et al. 2006). Interestingly the highest adsorption level at pH 10.7 and 0.1 M NaCl for AEF approach the AEF neutral value within a tenth of a percent. At the high pH values the

available free phenolics are deprotonated on the lignin and the Debye length is shortened by the presence of the added electrolyte, giving credence that the lignin plays an important role in both its neutral and charged form when attached to cellulose surfaces.

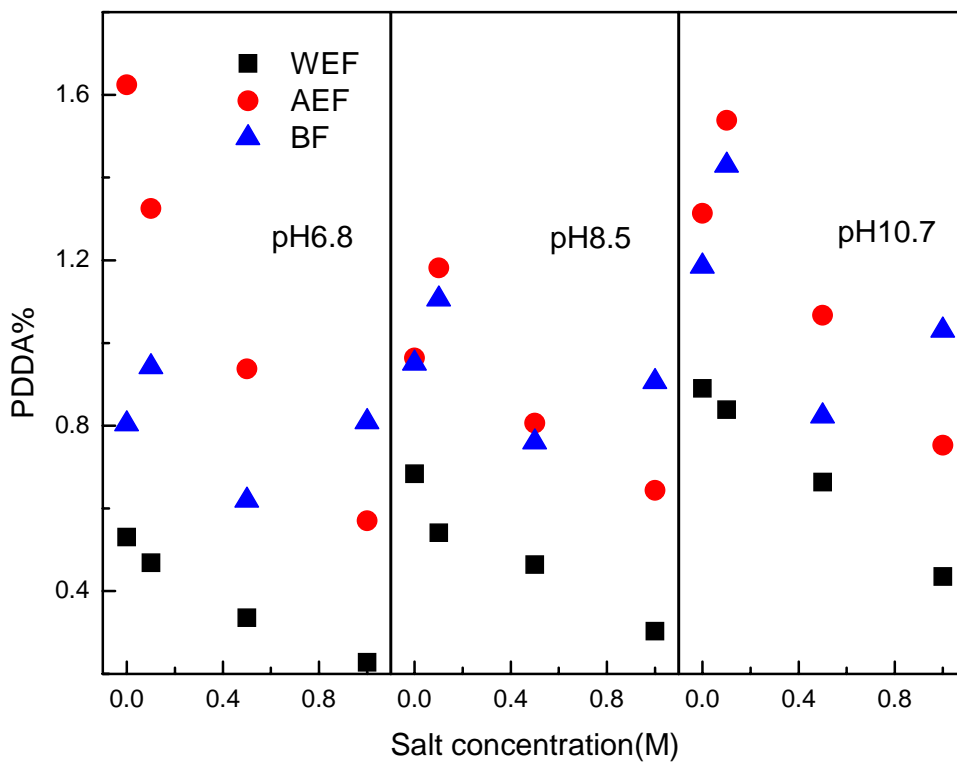


Figure 5.2 Comparison of PDDA adsorption on WEF, AEF and BF as a function of NaCl concentration

Zeta potential of fibers after PDDA adsorption

The zeta potential of steam-exploded fibers after PDDA adsorption is summarized in Figure 5.3. The reversal of the surface charge occurs for all three types of fibers at almost all conditions, which indicates a PDDA layer adsorbed onto the fiber surface. The zeta potential of WEF is

significantly lower than those of AEF and BF under all conditions, which agrees well with the corresponding PDDA adsorption results from Figure 5.2. However, even under conditions when WEF and AEF contain similar amount of adsorbed PDDA, their zeta potential values are significantly different (e.g. WEF at pH 10.7, 0.1M vs. AEF at pH 8.5, 0.5M). This disparity implicates that conformation and organization of adsorbed PDDA must be different between WEF and AEF. One clue for this difference is that short range distance of cation- π interactions requires the polymer to minimize its loops and tails (Pillai and Rennekar 2009), which may contribute to the lower surface potential of PDDA in the presence of the lignin. In other words, the ammonium groups of PDDA are tightly associated with the aromatic groups of the lignin, which limits the build-up of the double layer surrounding the polymer.

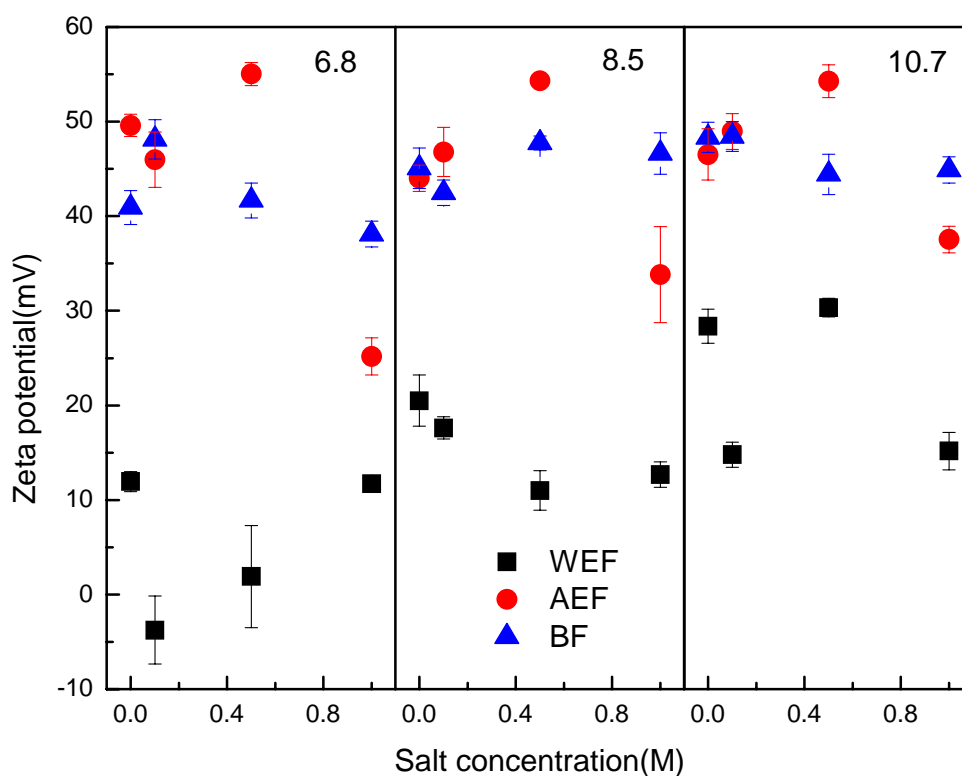


Figure 5.3 Zeta potential of fiber after PDDA adsorption as function of NaCl concentration and pH

Comparison of LbL build-up at different deposition conditions

The LbL build-up of PDDA/clay on the steam-exploded fibers was compared at four selected PDDA deposition conditions: AEF without any salt and pH adjustment; AEF at 0.1M salt, pH 10.7; AEF at 1M salt, pH 10.7; and WEF at 0.1M, pH 10.7. The pH adjustment was only performed at the 1st PDDA layer adsorption. These conditions were selected due to the quantity of PDDA adsorbed and resulting zeta potential values. The values chosen provided a range where the influence of PDDA loading and zeta potential on film build-up can be distinguished. The

amount of the PDDA and clay adsorption of each individual layer during LbL adsorption at different deposition conditions is summarized in Table 5.2. The UV-Spec method can be used to determine the amount of clay adsorption due to the fact that there is a linear relationship between clay concentration and absorbance (Figure 5.4).

As shown in Table 5.2, the amount of initial clay adsorption of WEF at 0.1M, pH 10.7 is significantly lower than that of AEF at 1M, pH 10.7 (2.8 vs. 6.6) despite WEF's slightly higher amount of PDDA content in the initial layer (0.9 vs. 0.8%). This discrepancy suggests that the amount of the initial PDDA layer is not the only factor that impacts the subsequent clay adsorption. Moreover, a strong correlation is found between the amount of the initial clay adsorption and the surface charge (zeta potential) of fiber after the first PDDA layer. Taken all this together, the zeta potential of fiber after PDDA adsorption, rather than the amount of adsorbed PDDA is related to the amount of clay adsorption onto the PDDA. This observation is supported by the first layer clay adsorption and zeta potential data from the other conditions (AEF no salt and pH adjustment; AEF at 0.1M salt, pH 10.7; and AEF at 1M salt, pH 10.7).

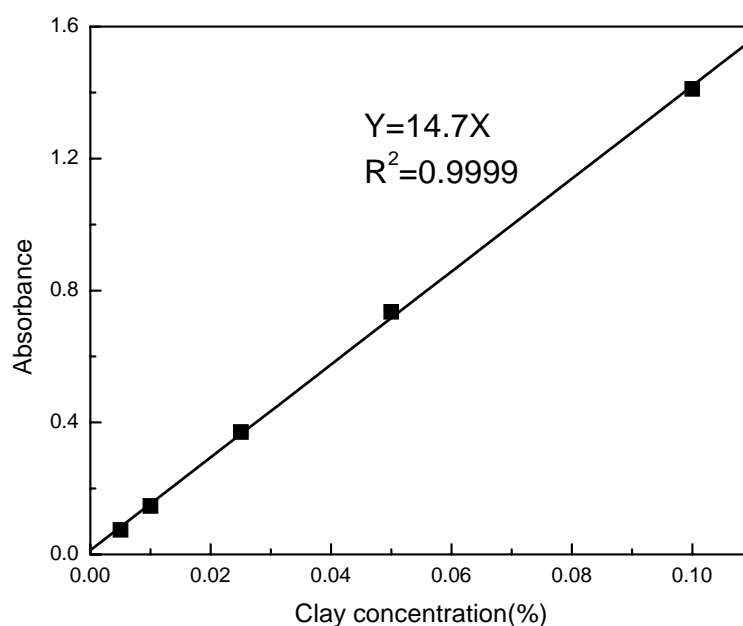


Figure 5.4 Linear relationship between absorbance and clay concentration from UV Spectroscopy

Table 5.2 The amount of the PDDA and clay adsorption of each individual layer during layer-by-layer assembly at different deposition conditions as a percentage of fiber mass

Bi-layers #	AEF, no adjustment		AEF 0.1M, pH 10.7		AEF 1M, pH 10.7		WEF 0.1M, pH 10.7	
	PDDA ^a (ZP) ^b	Clay ^a	PDDA(ZP)	Clay	PDDA(ZP)	Clay	PDDA(ZP)	Clay
1	1.7 (49.6)	7.9	1.6 (49.0)	7.8	0.8 (37.5)	6.6	0.9 (14.8)	2.8
2	1.9	12.5	4.8	12.4	5.2	11.3	3.9	8.0
3	3.4	17.7	4.6	17.8	6.3	16.4	4.5	11.4
4	3.7	23.6	3.0	23.3	4.2	21.4	0.5	14.6
Total	10.7	61.7	13.9	61.4	16.4	55.7	9.8	39.1

Note: pH adjustments were only performed in the initial PDDA layer adsorption.

^a The amount of PDDA and clay adsorption is a percentage of starting dry fiber mass.

^b ZP denotes zeta potential (mV) of fiber after initial PDDA layer adsorption.

The 2nd, 3rd and 4th layer PDDA adsorption cycles on AEF increased with the increase of salt concentration from 0 to 1M (Table 5.2). The increase is ascribed to a more coiled conformation of PDDA adopted at the clay surface in the presence of electrolyte. Similar finding was reported by Lvov et al., where thickness of PDDA layer formed on colloidal SiO₂ particles increased at elevated salt concentrations (Lvov et al. 1997). The total amount of clay adsorption of AEF after 4 layer adsorption at three deposition conditions is 61.7, 61.4, and 55.7%, respectively. Considering the difference in their first layer PDDA adsorption, there is minimum difference in layer-by-layer build-up for AEF. The total amount of clay adsorption of WEF after 4 layer adsorption is 39.1%, which is much lower than that of AEF at the same deposition conditions (61.4%). This data reflects the lower zeta potential of WEF after PDDA adsorption, which significantly impacts LbL film assembly.

The total amount of PDDA/clay after 4 bi-layers adsorption data measured from the gravimetric method was compared to those from CNS/UV-Spec method (Table 5.3). Consistent data is found for both methods at all deposition conditions. Also, evident is the overall level of fiber modification (Table 5.3), a significant amount of PDDA/clay can be adsorbed to wood fibers through LbL process, more than 75% total for AEF at 0.1M salt after only four bi-layers. This LbL assembly method provides a facile route for creation of inorganic/organic fiber materials.

Table 5.3 Comparison between CNS/UV-Spec method and gravimetric method for mass gain after four bi-layers

Deposition Conditions	Controls(g)	LbL fibers (4 bi-layers)		Mass gain ^a after 4 bi-layers (%)
		CNS/UV-Spec(g)	Gravimetric(g)	
AEF, 0.1M, pH 10.7	3.32	5.82	5.81	75.3
AEF, 1M, pH 10.7	5.04	8.67	8.66	72.0
WEF, 0.1M pH 10.7	7.17	10.5	10.17	46.4

^a Weight gain value is calculated based on CNS/UV-Spec data

Conclusions

The presence of lignin impacts PDDA adsorption onto lignocellulosic fibers. PDDA adsorption of WEF is significantly lower than that of AEF and BF at all conditions. Considering their comparable electrokinetic potential of the fibers prior to adsorption for AEF and WEF, lignin content disparities between these fibers is a significant factor for polyelectrolyte adsorption to non-bleached fibers. In addition to total mass adsorbed, differences are found in the electrokinetic properties of the modified fibers after adsorption of PDDA; WEF fibers with high lignin contents consistently have lower zeta potential values. However, the presence of lignin was not always detrimental to polyelectrolyte adsorption, as maximum polymer adsorption occurred for AEF at neutral conditions. The role of a secondary mechanism, besides charge compensation, was discussed in terms of facilitating polyelectrolyte adsorption to a surface containing aromatic moieties.

CNS/UV-Spectroscopy method was used to quantify the amount of PDDA/clay adsorption onto the wood fibers. Great amount of PDDA/clay (up to ~75% total mass for only 4 bi-layers)

can be adsorbed onto wood fibers through LbL process. The electrokinetic potential of fiber after PDDA adsorption, rather than the amount of adsorbed PDDA layer, impacted the subsequent clay adsorption on PDDA. Moreover, despite the difference in the quantity of the initial PDDA layer, minimum difference in multilayer build-up is found for subsequent bi-layers for the AEF. This study revealed the parameters that control initial polyelectrolyte deposition onto lignocellulosic fibers and the subsequent impact it has on multilayer assembly.

Acknowledgment

We acknowledge the Sustainable Engineered Materials Institute, College of Natural Resources, and the Department of Wood Science and Forest Products of Virginia Tech for financial support.

References

- Allan, G. G. and W. M. Reif (1971). "Fiber surface modification. 6. Jack-in-the-Box effect: new mechanism for the retention of poly(ethylenimine) and other polyelectrolytes by pulp fibers." *Svensk Papperstidning* **74**(2): 25-31.
- Allan, G. G. and W. M. Reif (1971). "Fiber surface modification. Stereotopochemistry of ionic bonding in paper." *Svensk Papperstidning* **74**(18): 563-70.
- Ariga, K., J. P. Hill and Q. Ji (2007). "Layer-by-layer assembly as a versatile bottom-up nanofabrication technique for exploratory research and realistic application." *Physical Chemistry Chemical Physics* **9**(19): 2319-2340.
- Cheng, L. and J. A. Cox (2001). "Preparation of multilayered nanocomposites of polyoxometalates and poly(amidoamine) dendrimers." *Electrochemistry Communications* **3**(6): 285-289.
- Decher, G. (1997). "Fuzzy nanoassemblies: toward layered polymeric multicomposites." *Science* (Washington, D. C.) **277**(5330): 1232-1237.
- Decher, G. and J. D. Hong (1991). "Buildup of ultrathin multilayer films by a self-assembly process. 1. Consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces." *Makromolekulare Chemie, Macromolecular Symposia* **46**(Eur. Conf. Organ. Org. Thin Films, 3rd, 1990): 321-7.
- Elbert, D. L., C. B. Herbert and J. A. Hubbell (1999). "Thin Polymer Layers Formed by Polyelectrolyte Multilayer Techniques on Biological Surfaces." *Langmuir* **15**(16): 5355-5362.
- Eriksson, M., S. M. Notley and L. Wagberg (2005). "The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibers." *Journal of Colloid and Interface Science* **292**(1): 38-45.
- Erspamer, A. (1940). "The flocculation and dispersion of papermaking fibers." *Paper Trade Journal* **110**(No. 24): 33-8.
- Formento, J. C., M. G. Maximino, L. R. Mina, M. I. Srayh and M. J. Martinez (1994). "Cationic starch in the wet end: Its contribution to interfiber bonding." *Appita Journal* **47**(4): 305-8.

- Gimaker, M. and L. Wagberg (2009). "Adsorption of polyallylamine to lignocellulosic fibres: effect of adsorption conditions on localisation of adsorbed polyelectrolyte and mechanical properties of resulting paper sheets." *Cellulose (Dordrecht, Netherlands)* **16**(1): 87-101.
- Glasser, W. G., R. Taib, R. K. Jain and R. Kander (1999). "Fiber-reinforced cellulosic thermoplastic composites." *Journal of Applied Polymer Science* **73**(7): 1329-1340.
- Horvath, A. E., T. Lindstrom and J. Laine (2006). "On the Indirect Polyelectrolyte Titration of Cellulosic Fibers. Conditions for Charge Stoichiometry and Comparison with ESCA." *Langmuir* **22**(2): 824-830.
- Horvath, A. T., A. E. Horvath, T. Lindstrom and L. Wagberg (2008). "Adsorption of Highly Charged Polyelectrolytes onto an Oppositely Charged Porous Substrate." *Langmuir* **24**(15): 7857-7866.
- Horvath, A. T., A. E. Horvath, T. Lindstrom and L. Wagberg (2008). "Diffusion of cationic polyelectrolytes into cellulosic fibers." *Langmuir* **24**(19): 10797-10806.
- Hunter, R. J. and Editor (1981). *Colloid Science: Zeta Potential in Colloid Science: Principles and Applications*.
- Hyde, K., M. Rusa and J. Hinestroza (2005). "Layer-by-layer deposition of polyelectrolyte nanolayers on natural fibers: Cotton." *Nanotechnology* **16**(7): 422-428.
- Ibrahim, M. and W. G. Glasser (1999). "Steam-assisted biomass fractionation. Part III. A quantitative evaluation of the "clean fractionation" concept." *Bioresource Technology* **70**(2): 181-192.
- Kotov, N. A., T. Haraszti, L. Turi, G. Zavala, R. E. Geer, I. Dekany and J. H. Fendler (1997). "Mechanism of and Defect Formation in the Self-Assembly of Polymeric Polycation-Montmorillonite Ultrathin Films." *Journal of the American Chemical Society* **119**(29): 6821-6832.
- LeBaron, P. C., Z. Wang and T. J. Pinnavaia (1999). "Polymer-layered silicate nanocomposites: an overview." *Applied Clay Science* **15**(1-2): 11-29.
- Lin, Z., S. Rennecker and D. P. Hindman (2008). "Nanocomposite-based lignocellulosic fibers 1. Thermal stability of modified fibers with clay-polyelectrolyte multilayers." *Cellulose (Dordrecht, Netherlands)* **15**(2): 333-346.
- Lindstrom, T. and L. Wagberg (1983). "Effects of pH and electrolyte concentration on the adsorption of

- cationic polyacrylamides on cellulose." *Tappi Journal* **66**(6): 83-5.
- Lingstrom, R., L. Wagberg and T. Larsson Per (2006). "Formation of polyelectrolyte multilayers on fibres: influence on wettability and fibre/fibre interaction." *Journal of Colloid and Interface Science* **296**(2): 396-408.
- Lu, Z., S. Eadula, Z. Zheng, K. Xu, G. Grozdits and Y. Lvov (2007). "Layer-by-layer nanoparticle coatings on lignocellulose wood microfibrils." *Colloids and Surfaces, A Physicochemical and Engineering Aspects* **292**(1): 56-62.
- Lvov, Y., K. Ariga, I. Ichinose and T. Kunitake (1996). "Formation of Ultrathin Multilayer and Hydrated Gel from Montmorillonite and Linear Polycations." *Langmuir* **12**(12): 3038-3044.
- Lvov, Y., K. Ariga, M. Onda, I. Ichinose and T. Kunitake (1997). "Alternate Assembly of Ordered Multilayers of SiO₂ and Other Nanoparticles and Polyions." *Langmuir* **13**(23): 6195-6203.
- Lvov, Y., G. Decher and G. Sukhorukov (1993). "Assembly of thin films by means of successive deposition of alternate layers of DNA and poly(allylamine)." *Macromolecules* **26**(20): 5396-9.
- Ma, J. C. and D. A. Dougherty (1997). "The Cation- π Interaction." *Chemical Reviews* (Washington, D. C.) **97**(5): 1303-1324.
- Messersmith, P. B. and E. P. Giannelis (1994). "Synthesis and Characterization of Layered Silicate-Epoxy Nanocomposites." *Chemistry of Materials* **6**(10): 1719-25.
- Michalowicz, G., B. Toussaint and M. R. Vignon (1991). "Ultrastructural changes in poplar cell wall during steam explosion treatment." *Holzforschung* **45**(3): 175-9.
- Norgren, M. and B. Lindstrom (2000). "Dissociation of phenolic groups in kraft lignin at elevated temperatures." *Holzforschung* **54**(5): 519-527.
- Notley, S. M. and M. Norgren (2008). "Adsorption of a Strong Polyelectrolyte To Model Lignin Surfaces." *Biomacromolecules* **9**(7): 2081-2086.
- Odberg, L., H. Tanaka and A. Swerin (1993). "Kinetic aspects of the adsorption of polymers on cellulosic fibers." *Nordic Pulp & Paper Research Journal* **8**(1): 6-9, 47.
- Okada, A., M. Kawasumi, T. Kurauchi and O. Kamigaito (1987). "Synthesis and characterization of a nylon 6-clay hybrid." *Polymer Preprints* (American Chemical Society, Division of Polymer

- Chemistry) **28**(2): 447-8.
- Okada, A., M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi and O. Kamigaito (1990). "Nylon 6-clay hybrid." *Materials Research Society Symposium Proceedings* **171**(Polym. Based Mol. Compos.): 45-50.
- Onoda, M. and K. Yoshino (1995). "Fabrication of self-assembled multilayer heterostructure of poly(p-phenylene vinylene) and its use for an electroluminescent diode." *Journal of Applied Physics* **78**(7): 4456-62.
- Overend, R. P. and E. Chornet (1987). "Fractionation of lignocellulosics by steam-aqueous pretreatments." *Philosophical Transactions of the Royal Society of London, Series A Mathematical, Physical and Engineering Sciences* **321**(1561): 523-36.
- Peng, C. Q., Y. S. Thio and R. A. Gerhardt (2008). "Conductive paper fabricated by layer-by-layer assembly of polyelectrolytes and ITO nanoparticles." *Nanotechnology* **19**(50): 505603/1-505603/10.
- Pillai, K. V. and S. Rennekar (2009). "Cation- π Interactions as a Mechanism in Technical Lignin Adsorption to Cationic Surfaces." *Biomacromolecules* **10**(4): 798-804.
- Rennekar, S. and Y. Zhou (2009). "Nanoscale Coatings on Wood: Polyelectrolyte Adsorption and Layer-by-Layer Assembled Film Formation." *ACS Applied Materials & Interfaces* **1**(3): 559-566.
- Rojas, O. J., M. Ernstsson, R. D. Neuman and P. M. Claesson (2002). "Effect of Polyelectrolyte Charge Density on the Adsorption and Desorption Behavior on Mica." *Langmuir* **18**(5): 1604-1612.
- Schmitt, J., T. Gruenewald, G. Decher, P. S. Pershan, K. Kjaer and M. Loesche (1993). "Internal structure of layer-by-layer adsorbed polyelectrolyte films: a neutron and x-ray reflectivity study." *Macromolecules* **26**(25): 7058-63.
- Strazdins, E. (1995). "Critical issues in applying electrokinetics to papermaking." *Tappi Journal* **78**(8): 115-19.
- Tanaka, H., K. Tachiki and M. Sumimoto (1979). "Adsorption of cationic polymers onto bleached kraft pulp." *Tappi* **62**(1): 41-4.
- van de Steeg, H. G. M., M. A. Cohen Stuart, A. De Keizer and B. H. Bijsterbosch (1992). "Polyelectrolyte

- adsorption: a subtle balance of forces." *Langmuir* **8**(10): 2538-46.
- van Duffel, B., T. Verbiest, S. van Elshocht, A. Persoons, F. C. de Schryver and R. A. Schoonheydt (2001). "Fuzzy Assembly and Second Harmonic Generation of Clay/Polymer/Dye Monolayer Films." *Langmuir* **17**(4): 1243-1249.
- Wagberg, L. (2000). "Polyelectrolyte adsorption onto cellulose fibers -- a review." *Nordic Pulp & Paper Research Journal* **15**(5): 586-597.
- Wagberg, L., S. Forsberg, A. Johansson and P. Juntti (2002). "Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept. Part I. Modification of paper strength." *Journal of Pulp and Paper Science* **28**(7): 222-228.
- Wagberg, L. and L. Odberg (1989). "Polymer adsorption on cellulosic fibers." *Nordic Pulp & Paper Research Journal* **4**(2): 135-40.
- Wang, L. and N. Hu (2001). "Direct electrochemistry of hemoglobin in layer-by-layer films with poly(vinyl sulfonate) grown on pyrolytic graphite electrodes." *Bioelectrochemistry* **53**(2): 205-212.
- Wise, L. E., M. Murphy and A. A. D'Addieco (1946). "Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses." *Paper Trade Journal* **122**(No. 2): 35-43.
- Yoon, H. C. and H.-S. Kim (2000). "Multilayered Assembly of Dendrimers with Enzymes on Gold: Thickness-Controlled Biosensing Interface." *Analytical Chemistry* **72**(5): 922-926.

Chapter 6 Layer-by-layer modification of wood fibers as reinforcement in thermoplastic composites

Zhiyuan Lin¹ and Scott Renneckar^{*2}

¹ Sustainable Engineered Materials Institute, Virginia Tech, Blacksburg, VA 24061

² Department of Wood Science and Forest Products, Virginia Tech, Blacksburg, VA 24061

* To whom correspondence should be addressed. Phone: (540) 231-7100. Fax: (540) 231-8176.

Email: srenneck@vt.edu.

Abstract

The present study investigated the layer-by-layer (LbL) modification of wood fibers for reinforcement in thermoplastic composites. The LbL system used in this study involved the sequential adsorption of oppositely charged poly(diallyldimethylammonium) chloride and montmorillonite clay onto the wood fiber surface. The composites were prepared by melt compounding of polypropylene and unmodified/LbL modified fibers, followed by compression molding. The thermal properties of the composites were characterized by differential scanning calorimetry and dynamic mechanical analysis, while mechanical properties were tested in tensile and flexural test modes. LbL modified fibers exhibited enhanced thermal stability as compared with the unmodified control fibers. Average degradation temperatures, at 5 and 10% weight loss for the 4 bi-layer modified fiber, increased by ~24 and ~15°C, respectively, compared to the

unmodified fibers. LbL modified fiber composites have similar modulus values but significantly lower strength values than those of unmodified fiber composites. However, composites composed of LbL modified fibers display enhanced elongation at break, increasing by more than 50%, to those of unmodified samples. DSC results indicated that crystallization behavior of PP is promoted in the presence of wood fibers. Both unmodified and LbL modified wood fibers are able to act as nucleation agents, which cause an increase of the crystallinity of PP by the presence of wood fiber. Moreover, results from tensile and flexural strength, dynamic mechanical analysis and water absorption tests reveal that the material (PDDA or clay) at the terminal (outer) layer of LbL modified fiber influences the performance of the composites.

Keywords: layer-by-layer, clay, polypropylene, nanocomposites, steam-exploded wood fibers

Introduction

Over the past two decades, the use of lignocellulosic fibers as reinforcing elements for thermoplastic composites has experienced a dramatic growth in North America in applications for automobiles, building materials and packaging industries (Bledzki and Gassan 1999; Clemons 2002; Morton et al. 2004). The lignocellulosic fibers offer a combination of attractive properties such as low density, high specific strength and modulus, renewability, biodegradability, wide availability, and low cost, which make them alternatives to traditional synthetic fibers in many applications. However, some constraints do exist for the use of lignocellulosic fibers in

thermoplastic composites. The low thermal stability of lignocellulosic fibers restricts the allowable processing temperature, which is generally lower than 200°C. The hydrophilic nature of lignocellulosic fibers makes them incompatible with commonly used hydrophobic thermoplastics, such as polyethylene and polypropylene.

Many efforts have been made to overcome these limitations including a variety of surface modification methods for lignocellulosic fiber (Maldas and Kokta 1989; Raj et al. 1990; Felix et al. 1993; Hedenberg and Gatenholm 1996; Matuana et al. 1999). In recent years, the layer-by-layer (LbL) self-assembly technique has gained a rising interest because it can modify substrate surface chemistry with a simple process of adsorption (Decher 1997). This technique involves the sequential adsorption of oppositely charged polyelectrolytes to the fiber surfaces. A great variety of organic or inorganic components have been incorporated into the LbL system to create advanced materials with nanoscale architectures with desired properties (Decher and Hong 1991; Schmitt et al. 1993; Onoda and Yoshino 1995; Lvov et al. 1996; Kotov et al. 1997; Lvov et al. 1997; van Duffel et al. 2001; Lin et al. 2008). The electrostatic interaction between opposite charged components serves as the main driving force for the polyelectrolyte adsorption. The LbL modification method has been investigated in the field of paper science and successfully applied to cellulosic pulp fibers to enhance the properties of paper (Wagberg et al. 2002; Eriksson et al. 2005; Lingstrom et al. 2006; Lu et al. 2007; Peng et al. 2008). Limited research has been carried out on LbL modification of wood fibers for reinforcement in thermoplastic composites. However, due to its ability to tailor the surface chemistry of substrates, the LbL fiber modification method,

if properly exploited, may be able to alleviate the above-mentioned issues encountered for wood thermoplastic composites.

Steam explosion is an economical fiber separation method as compared with the traditional “disc refiner” approach (Avellar and Glasser 1998; Kokta and Ahmed 1998). Steam explosion is a thermo-hydrolytic-mechanical process, where wood biomass are pressurized with high steam pressure and elevated temperature, followed by a sudden decompression. This biomass treatment process is very similar to the industrially practiced “Masonite process”, which represents was developed for fiberboard production (Glasser and Wright 1998). The steam explosion affects all the constitutive polymers of wood (Tanahashi 1990). The hemicelluloses are hydrolyzed to oligosaccharides and monosaccharides, which can be removed through water and alkali extraction. The molecular weight of lignin is reduced and the amorphous cellulose is either hydrolyzed or transformed to crystalline cellulose. Moreover, available surface area of wood fibers increases after steam explosion treatment (Michalowicz et al. 1991), which favors the subsequent LbL polyelectrolyte adsorption since it is a surface modification technique.

In this study, we investigated the layer-by-layer technique as a modification method for lignocellulosic wood fibers as reinforcement in thermoplastic composites. The inorganic montmorillonite clay nanoparticles were incorporated in the LbL system as the negatively charged components because of its unique physical and mechanical properties. Adding clays to organic polymers has shown to be a productive method to improve the mechanical, barrier and thermal properties of thermoplastics and elastomers (Okada et al. 1987; Okada et al. 1990;

Messersmith and Giannelis 1994; LeBaron et al. 1999). Additionally, poly(diallyldimethylammonium) chloride (PDDA) was used as the positively charged component, which has been shown to have antimicrobial properties. The thermal, mechanical and sorption properties of composites were characterized by static tensile and flexural tests, dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and 24 hours water immersion tests to determine the effect of the coating as a function of the number of deposited.

Experimental

Materials

Wood fibers were obtained through steam explosion of yellow-poplar (*Liriodendron tulipifera*) veneers of dimensions 25*25*4 mm. The wood chips were steam-exploded at 240°C for 3 min, resulting in a steam explosion severity factor ($\log R_0$) of 4.6 (Overend and Chornet 1987). Positively charged Poly(diallyldimethylammonium) chloride (PDDA) used in the study was an aqueous solution (M_w 200,000-350,000) obtained from Sigma-Aldrich Inc, USA. Montmorillonite clay used was a high purity sodium montmorillonite donated by Kunimine industries, Japan. Isotactic polypropylene (PP) pellets (average M_w 340,000, density 0.9 g/mL, melting index 4 g/10min, Sigma Aldrich) was the thermoplastic matrix used in this study.

Fiber treatment and layer-by-layer modification

Both the extraction and layer-by-layer adsorption process were performed using a stirred and jacketed Pfaudler reactor (60L) with a large anchor-type agitator to prevent large shear to the fibers while mixing. Prior to the layer-by-layer modification, steam-exploded fibers (SEF) were first extracted with water at 60°C for 24 hours followed by alkali extraction with 20% (based on fiber solids weight) aqueous sodium hydroxide using an 8:1 liquor-to fiber ratio at 60 °C for 30 min (Glasser et al. 1999; Lin et al. 2008). After water and alkali extraction, the fibers were isolated and washed multiple times with ultrapure Mill-Q water using a centrifuge until the supernatant pH became neutral. Positively charged PDDA and negatively charged montmorillonite clay were alternately adsorbed onto the fiber surface using the layer-by-layer assembly process. Before the layer adsorption, ultrasonication (750 Watts, VC 750 Sonics & Materials, Inc.) was applied to the clay suspension for 6 minutes to break the clay into nanoscale platelets (Lin et al. 2008). The concentrations of PDDA and clay suspension used in this study were 5 mg/ml and 1 mg/ml, respectively. No salt and pH adjustment was performed during the PDDA adsorption, which was the optimal condition for PDDA and LbL adsorption determined from the previous study (Chapter 5). The detailed LbL deposition process has been described elsewhere (Lin et al. 2008). To investigate the potential effects of LbL modification (the number of the bi-layers and the outmost adsorption layer) on the performance of final composites, LbL modified fibers with five different numbers of bi-layers were prepared: 0.5, 1, 2, 3, 4 and 4.5, with 1 bi-layer designates a combination of 1 layer of PDDA and 1 layer of clay adsorbed onto

the fiber. Therefore, layer number 0.5 refers to fiber that was only coated with a single layer of PDDA. The unmodified alkali extracted SEF were used as control fibers. After fiber treatment and LbL modification, wood fibers were air-dried and ground with a Thomas-Wiley mill to pass through a 10-mesh screen.

Compounding of PP and wood fibers

Compounding of wood fibers and polypropylene pellets was performed in a Brabender compounder (CW Brabender Prep-Center) with an internal mixer. Prior to compounding, all the fibers were oven dried at 80°C for 24h to further remove the moisture. The mixing was carried out at 180°C with a rotation speed of 60 rpm. The blending time was 15 min. For each batch, the total mass of materials was 45g. The fiber volume fraction was kept constant at 25% for all the fiber composites. Following compounding, all the blends were cooled to room temperature and ground into 10-mesh powder with a Thomas-Wiley mill.

Preparation of composites

The wood polypropylene composites were prepared by compression molding process using a square steel mold with dimensions of 152.4*152.4 mm. The platens of a 6x6" Carver hot press were preheated to 185°C for wood polypropylene composites. A minimum pressure was applied during the preheating step to maintain the contact between the platens and mold. The pressure was then increased slowly to 2 MPa in 2 min and held at 2 Mpa for an additional 10 min. The

mold was then removed from the hot press and cooled to room temperature in a separate cold press under the same pressure (2 MPa). The target thickness of plaques was 3.18 mm.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed on the fiber samples to determine the weight loss as a function of temperature. Thermal stability of unmodified and LbL modified (1, 2, 3, and 4 bi-layers) fibers were analyzed using a TA Instruments Q-500 with a platinum sample pan. All the samples were vacuum-dried and stored in desiccators prior to tests. Samples of ca.10mg were ramp heated from room temperature to 800°C with a constant heating rate of 10 °C /min under air atmospheres. Each sample type was measured in triplicate.

Mechanical Tests

The tensile and flexural mechanical properties of the composites were measured in accordance with the ASTM D638-03 and ASTM D790-03, respectively. The tensile tests were carried out on a MTS testing machine equipped with a 50,000 N load cell. The length and width of the Type I test specimens (dumbbell-shaped, cut on a router table) were 152.4 and 19.05 mm with a gauge length of 50.8 mm. The width and length of the narrow section was 12.7 and 50.8 mm, respectively. The constant crosshead speed was 0.25 mm/minute. An extensometer was used to measure the displacement within the gauge length of test specimens. The dimensions of specimens for flexural tests were 63*12.7*3.18 mm with the span-to-depth ratio of 16:1. The

three point bending tests were performed at a constant crosshead (midspan deflection) speed of 0.64 mm/min. The midspan deflection was determined by a linear variable differential transformer (LVDT) under the specimen in contact with it at the center of the support span. The specimens were deflected until rupture occurred in the outer surface of the test specimens or until a maximum midspan deflection of 5.08 mm was reached, whichever occurred first. At least ten and twelve replications of each sample type were tested for tensile and flexural tests, respectively.

Dynamic mechanical analysis

The dynamic mechanical properties of unfilled neat polypropylene, unmodified and LbL (4, and 4.5 bi-layers) modified fiber composites were determined by a TA instruments Q800 dynamic mechanical analyzer using a single cantilever mode. DMA specimens, 35*12.7*3.18 mm, were heated from -70 to 150°C with a heating rate of 3 °C/min and a frequency of 1Hz in dry air atmosphere. The constant strain of 0.03% determined by the strain sweep tests was used in DMA. At least eight specimens were tested for each formulation.

DSC analysis

All DSC experiments were conducted on a Q100 DSC from TA instruments. Sample sizes of ca 10mg were sealed in aluminum crimped pans. The DSC temperature program consisted of 1) ramp from -80 to 200°C at 10 °C/min, 2) cool from 200 to -80°C at 5 °C/min, and then 3)

ramp from -80 to 200°C at 10 °C/min. The first heating cycle was intended to remove any prior thermal history resulted from the compression molding and cooling process in the composite manufacture. The crystallinity (X_c) of the each polymer and composite was calculated using the following equation:

$$X_c = \frac{\Delta H_f \times 100}{\Delta H_f^0 W_p} \quad \text{Eq. 6.1}$$

Where, ΔH_f is the heat of fusion of PP and composites, ΔH_f^0 is the theoretical heat of fusion of 100% crystalline PP (138 J/g) (Joseph et al. 2003), and W_p is the mass fraction of PP in the composites.

Water absorption test

The sorption properties of unmodified and LbL (0.5, 1, 2, 3, 4, and 4.5 bi-layers) modified fiber composite materials were evaluated in accordance with ASTM D570-98. Twenty-four hours water immersion tests were performed to assess the water absorption behavior of composites. The test specimens were in the form of a bar 76.2 mm by 25.4 mm with a thickness of 3.18 mm. The specimens were entirely immersed in distilled water at 25°C for 24 h. The weights of the specimens before and after soaking were recorded. Prior to the test, the specimens were dried in an oven for 24h at $50 \pm 3^\circ\text{C}$, cooled in desiccators and immediately weighed. Percent weight gain (%) after water adsorption was calculated by the following equation.

$$\text{Percent weight gain} = \frac{W_w - W_c}{W_c} \times 100 \quad \text{Eq. 6.2}$$

Where, W_w represents the wet weight of specimen, W_c is the conditioned weight of specimen before water immersion. Eight replications of each sample type were tested.

Results and Discussion

TGA

Thermal stability properties of unmodified and LbL modified fibers are summarized as a function of the number of bi-layers (Table 6.1). Temperature at 5% and 10% weight loss, maximum degradation rate and residue weight at 800°C were listed. Note that the 5 and 10% thermal degradation is calculated after taking in account the loss of moisture and this value can be considered weight loss of dry fiber mass.

Table 6.1 Thermal stability of unmodified and LbL modified fibers with different number of bi-layers

Bi-layer #	Temp at 5% wt. loss (°C)	Temp at 10% wt. loss (°C)	Maximum deg rate (%/°C)	Residue wt. after heated to 800°C (%)
0	296	317	3.16	0.6
1	307	324	2.57	6.0
2	310	327	2.09	17.0
3	314	329	2.02	21.0
4	320	332	1.78	27.4

LbL modified fibers show enhanced thermal stability relative to the unmodified fibers. As can be seen from Table 6.1, the temperatures at 5 and 10% thermal degradation increase as the

number of bi-layers increases; average temperature at 5 and 10% weight loss after 4 bi-layers modification increases by ~24 and ~15°C, respectively. The maximum degradation rate also decreases by the LbL modification. The value is reduced by ~44% (from 3.16 to 1.78%) for 4 bi-layer coating. In addition, significant char residue formed for the LbL modified wood fibers (27.4% for 4 bi-layers) suggests this clay-based coating serves as a barrier creating an insulating layer to prevent further decomposition of the material (Lin et al. 2008). It should be noted that improvements in thermal stability of LbL modified fibers in this study are greater than previously reported values in Chapter 4 because the optimal deposition conditions were used in this study, which resulted in higher PDDA/clay adsorption.

Tensile and flexural mechanical properties of composites

Table 6.2 and 6.3 summarize the tensile (modulus of elasticity (MOE), tensile strength and percent elongation at break) and flexural (MOE, flexural strength (MOR) and midspan deflection at break) mechanical properties of neat PP, unmodified and LbL modified fiber composites. Tukey's Honestly Significant Difference (HSD) multiple comparison analysis was performed to determine the statistical significance of the means among different treatments and Turkey grouping letter is presented in both Table 6.2 and 6.3 ($\alpha=0.05$). Means with the same letter are not significantly different. As shown in Table 6.2 and 6.3, the addition of unmodified wood fibers to the neat PP significantly increases both tensile and flexural modulus of composites. MOE of unmodified fiber composites (sample 0) increases by 87% (1.31 to 2.45 GPa from

tensile tests) and 139% (0.95 to 2.27 GPa for flexural tests) as compared with the neat PP. This increase in modulus demonstrates that high modulus wood fibers can stiffen the thermoplastic PP matrix as noted in basic composite textbooks. The LbL adsorption of PDDA and clay has marginal influence on the modulus properties of composites, which can be attributed to the comparable MOE values between steam-exploded fiber and PDDA/clay bi-layers. The reported MOE of PDDA/clay multilayers is 11 GPa (Tang et al. 2003), which is very similar to that of unmodified steam-exploded fibers (also 11 GPa) back-calculated from the semi-empirical Tsai-Pagano micromechanical model (Tsai and Pagano 1968):

$$E_c = \frac{3}{8}E_{11} + \frac{5}{8}E_{22} \quad \text{Eq. 6.3}$$

Where E_c is the modulus of random fiber reinforced thermoplastic composites, which we assumed our composites to be. E_{11} and E_{22} are longitudinal and transverse tensile moduli of corresponding unidirectional fiber composites, which can be estimated by the simple “rule of the mixtures” models (Eq. 6.4 and 6.5):

$$E_{11} = E_f V_f + E_m V_m \quad \text{Eq. 6.4}$$

$$E_{22} = \frac{E_f E_m}{E_f V_m + E_m V_f} \quad \text{Eq. 6.5}$$

Where E_f and E_m are modulus of fiber and matrix, respectively. V_f and V_m are volume fractions of fiber and matrix, respectively. In this study, fiber volume fraction is 25%; tensile modulus of polypropylene and unmodified fiber composites are 1.31 and 2.45 GPa, respectively, as measured in Table 6.2. In combination with Eq. 6.3, 6.4 and 6.5, the tensile modulus of unmodified steam-exploded wood fiber can be back-calculated (11 GPa).

The inclusion of unmodified fibers to PP significantly decreases the strength properties of composites. Tensile strength of composites reduces from 23.99 to 21.92 MPa by the unmodified wood fibers loading. The MOR of the unmodified fiber composites in our study is 41.3 MPa which is substantially higher than the result from Yin et al.'s work. Yin et al. reported a MOR of 27.86 MPa for steam-exploded fiber reinforced polypropylene composites in a similar study, in which fiber weight fraction was 50% (Yin et al. 2007). The lower strength values obtained from Yin et al.'s study can be attributed to insufficient wetting of the fibers and increased fiber to fiber interactions in the case of high fiber content (Nando and Gupta 1996). The LbL modification of fibers has a significant influence on strength properties of composites. Both tensile strength and MOR of all LbL modified fiber composites are significantly lower than those of unmodified fiber composites (Table 6.2 and 6.3). For short fiber reinforced thermoplastic composites, strength is impacted by stress transfer efficiency from matrix to fibers. Therefore, these reductions in strength after LbL modification may suggest that the interfacial adhesion between LbL modified fiber and matrix is decreased as compared to the unmodified one. More specifically, the strength properties of composites with LbL fiber after only 0.5 bi-layer adsorption (PDDA as the outmost

layer) are significantly lower than those of unmodified fiber composites. This observation suggests that PDDA covered fiber surfaces have reduced interfacial adhesion with PP as compared with untreated fibers despite the hydrophobic methyl groups contained in the PDDA. Moreover, one consistent finding from both tensile and flexural tests is that composites with LbL modified fiber after 4.5 bi-layers modification (PDDA as the outmost layer) shows reduced strength properties to that of 4 bi-layers (clay as the outmost layer). The material as the outmost layer (PDDA or clay) plays an important role in strength properties of LbL modified composites. LbL fiber with clay as the terminal layer displays a better interfacial interaction with PP than PDDA covered fiber.

Table 6.2 Tensile properties of neat PP, unmodified and LbL modified fiber composites

Samples	MOE(GPa)	Tukey grouping	Strength(MPa)	Tukey grouping	Percent EAB ^a (%)	Tukey grouping
PP	1.31±0.05	C	23.99±1.03	A	did not break	did not break
0	2.45±0.12	B	21.92±1.10	B	1.37±0.10	D
0.5	2.54±0.09	AB	19.04±0.92	C	2.12±0.13	A
1	2.64±0.08	A	19.08±0.39	C	1.57±0.19	CD
2	2.58±0.10	AB	18.00±0.50	C	1.72±0.15	C
3	2.64±0.13	A	17.98±0.85	C	1.82±0.22	BC
4	2.61±0.16	A	18.45±0.12	C	2.05±0.21	AB
4.5	2.40±0.12	B	17.31±0.43	D	2.09±0.22	A

a. EAB refers to elongation at break.

Table 6.3 Flexural properties of neat PP, unmodified and LbL modified fiber composites

Samples	MOE(GPa)	Tukey grouping	MOR(MPa) ^a	Tukey grouping	Deflection ^b at break(mm)
PP	0.95±0.09	C	N/A	N/A	did not break
0	2.27±0.14	A	41.30±1.57	A	4.32±0.41
0.5	2.23±0.09	A	38.45±1.10	B	did not break
1	2.27±0.08	A	38.50±0.82	B	did not break
2	2.18±0.09	AB	36.83±0.79	C	did not break
3	2.19±0.11	A	36.26±0.99	CD	did not break
4	2.22±0.08	A	36.94±0.82	C	did not break
4.5	2.07±0.08	B	35.19±0.70	D	did not break

- a. MOR was calculated based on the peak load up to maximum midspan deflection of 5.08 mm.
- b. Deflection designates midspan deflection in bending.

Elongation at break of fiber composites are significantly increased by the LbL modification. After 4 bi-layers of PDDA and clay, percent elongation at break of composites increases by 50% (from 1.37 to 2.05%) as compared with the unmodified fiber composites, which indicates that fiber composites become more ductile after LbL modification. Similar to strength properties, elongation properties of modified fiber composites are also influenced by the terminal layer of LbL adsorption which directly contacts PP matrix. The LbL modified fiber composites exhibit the greatest elongation responses at only 0.5 layer modification, where PDDA is the terminal layer on the fiber surface. This finding further confirmed that the interfacial adhesion between fiber and PP is diminished after PDDA adsorption. The reduced interfacial adhesion between PDDA coated fiber and PP leads to decreased restraint of the PP matrix by the fibers, allowing the matrix to behave more like a neat PP under the tensile stress. This phenomenon ultimately

contributes to the elevated elongation properties of PDDA modified fiber composites (the neat PP specimens did not break under the test parameters). Percent elongation at break of composites also increases with increasing number of bi-layers, which could be attributed to potential parallel slippage of multilayered structure of PDDA and clay when extending the specimens because the surface is under considerable shear stress (Tang et al. 2003). Moreover, this improvement in ductility of materials can also be observed from the flexural tests. As shown in Table 6.3, all the unmodified fiber composite samples broke before midspan deflection of 5.08 mm with an average midspan break deflection of 4.32 mm. As a comparison, all the LbL modified fiber composite samples did not break before that midspan deflection.

DMA

The temperature dependence of storage modulus and $\tan \delta$ of neat PP, unmodified and LbL modified fiber composites are shown in Figure 6.1. A considerable increase in the storage modulus of all composites over neat PP is observed throughout the entire temperature range, which is consistent with results from our static mechanical testing. Storage modulus curves of both PP and composite samples display three different distinct regions with the increase of temperature: a fairly flat glassy region, a rapidly drop glass to rubber transition region, and a slower declining rubbery region. From $\tan \delta$ data, neat PP exhibits a clear thermal transition in the vicinity of 10°C. This transition corresponds to β relaxation of unrestricted amorphous portion, which often refers to the glass transition temperature (T_g) of PP. Table 6.4 summarizes the glass

transition temperature of neat PP, unmodified and LbL modified fiber composites determined from peak of both $\tan\delta$ and loss modulus curves. As seen in Table 6.4, T_g is slightly shifted to lower temperature for unmodified composites as compared to the neat PP. T_g decreases from 14.5 to 11.8°C and 10.6 to 8.8°C as determined from $\tan \delta$ and loss modulus, respectively. This reduction in T_g implies that the addition of the wood fibers alters the response of the polymer chains. Similar finding has also been reported in other studies (Nunez et al. 2002; Tajvidi et al. 2006; Yin et al. 2006). Nunez et al. concluded that the nucleating effect of the wood fibers accelerated the crystallization process of PP. This crystallization led to an amorphous zone with altered mobility, which resulted in a lower T_g value (Nunez et al. 2002). The observation is confirmed in our DSC data in the subsequent section.

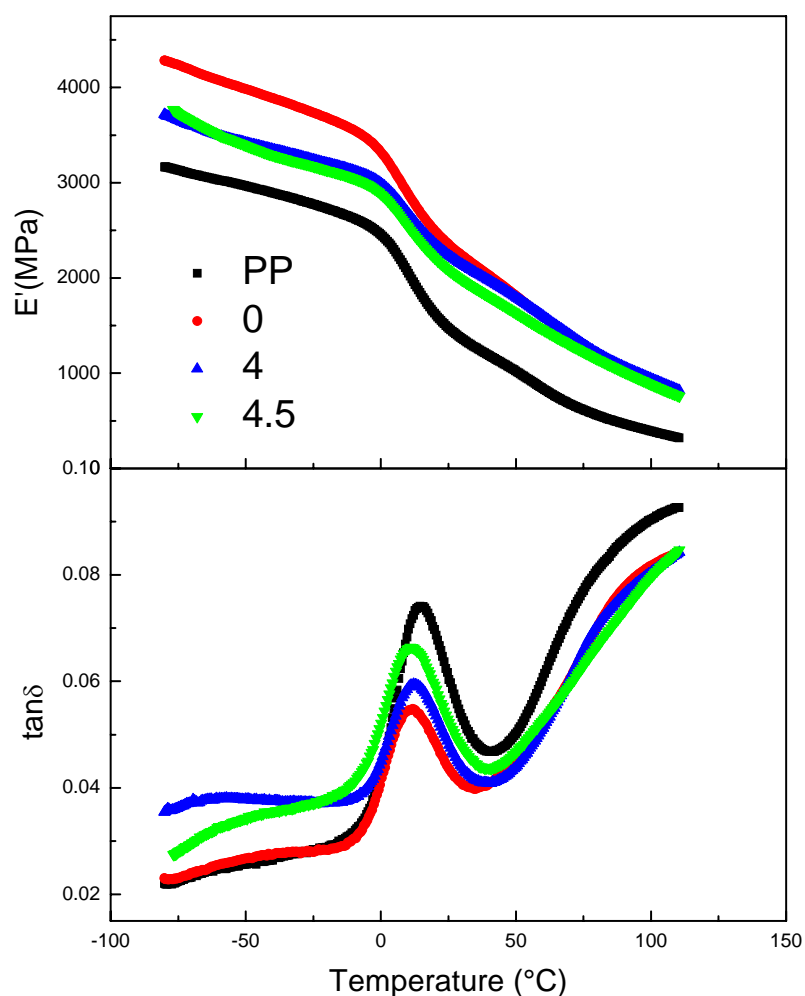


Figure 6.1 Storage modulus and $\tan\delta$ spectra of neat PP, unmodified and LbL modified fiber composites

No evident change in glass transition temperature of PP is observed between composites reinforced by unmodified fibers and LbL modified fibers with 4 bi-layers of adsorption. However, as shown in Table 6.4, glass transition temperature shows a slight but statistically significant decrease from modified composites with 4 bi-layers modification to those with 4.5 bi-layers; T_g determined from $\tan\delta$ and loss modulus curves decrease by 1.9°C (from 12.5 to 10.6°C) and

1.7°C (from 8.8 to 7.1°C), respectively. The main difference between those two fibers is whether PDDA or clay serves as the outmost layer. This finding is consistent with strength properties of LbL modified fiber composites in the previous section. The LbL modified fiber with PDDA as the outmost layer (4.5 bi-layers) shows reduced interfacial adhesion between fiber and matrix as compared to fiber with clay as the outmost layer (4 bi-layers). As a result, PP polymer chains are able to move more freely when PDDA is the terminal layer for fiber modification, which leads to the drop in T_g for 4.5 bi-layer modified fiber composites. Moreover, as illustrated in Figure 6.1, the magnitude of $\tan \delta$ peak drops by the addition of wood fibers in the transition region. Lower $\tan \delta$ value suggests that the composites display more elastic (spring-like) than viscous (dashpot-like) behavior as compared with pure PP, as the volume fraction of PP decreases in the case of composites. In addition, composites with fibers after 4.5 bi-layers modification displayed higher $\tan \delta$ values than those of fibers with 4 bi-layer and unmodified fibers. Again, this suggests a relative weaker interfacial adhesion for the fibers with PDDA as the terminal layer as compared to the fiber with clay as the terminal layer and the unmodified fiber.

Table 6.4 Glass transition temperature of neat PP, unmodified and LbL modified fiber composites determined from peak of both $\tan \delta$ and loss modulus curves

Sample	T_g from $\tan \delta$ (°C)	T_g from loss modulus (°C)
PP	14.5±0.8	10.6±0.6
0	11.8±0.3	8.8±0.5
4	12.5±0.4	8.8±0.6
4.5	10.6±0.8	7.1±0.5

DSC

Figure 6.2 and 6.3 show the cooling and 2nd melting curves of neat PP, unmodified and modified fiber composites. The melting temperature (T_m), crystallization temperature, heat of fusion (ΔH_f) and calculated crystallinity (X_c) for the neat PP, unmodified and, LbL modified composites determined from cooling and second heating cycles of DSC experiments are summarized in Table 6.5. T_{os} is the crystallization onset temperature, which represents the beginning point of the crystallization process. T_c represents the temperature at the crystallization peak. Therefore, $T_{os}-T_c$ can serve as an indicator of crystallization rate of materials; a small $T_{os}-T_c$ value refers to a fast crystallization process.

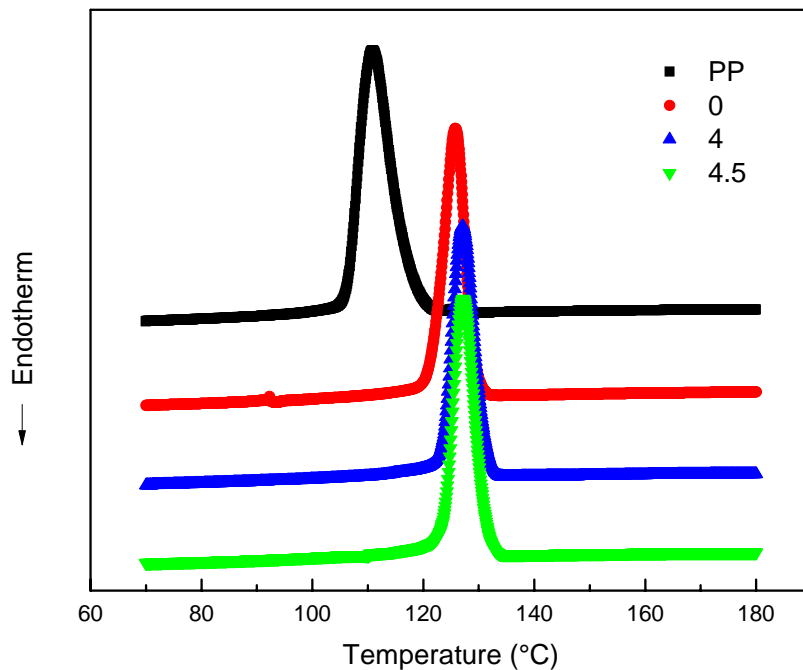


Figure 6.2 DSC cooling curves of neat PP, unmodified and LbL modified fiber composites

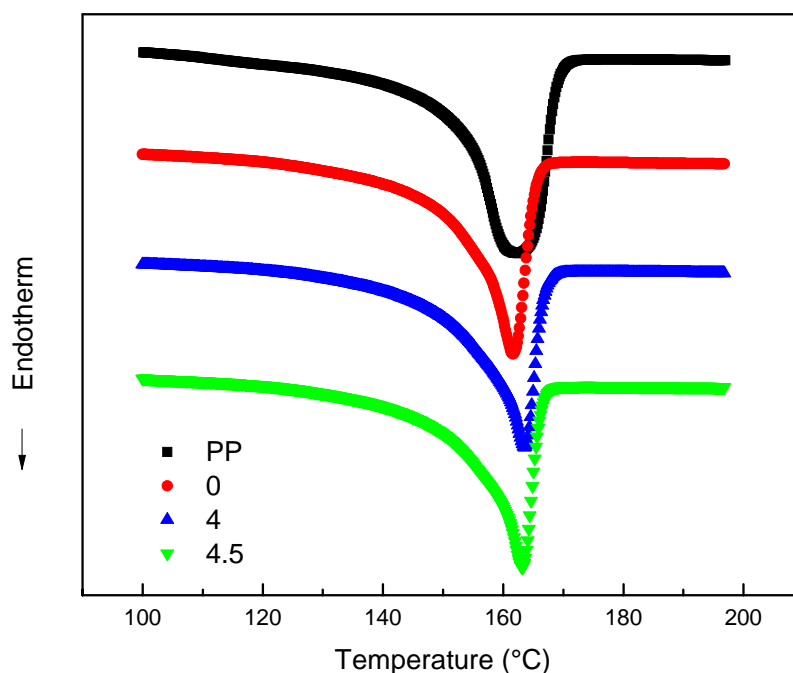


Figure 6.3 DSC 2nd melting curves of neat PP, unmodified and LbL modified fiber composites

An increase of the crystallinity of PP is observed by the adding wood fibers to the composites (Table 6.5). The crystallinity of PP increases from 59.9 to 66.9 with the inclusion of unmodified fibers, which is due to the fact that wood fibers are able to act as nucleating agents during crystallization of PP (Gray 1974; Nunez et al. 2002; Yin et al. 2006). The crystallization peak temperature of PP (T_c) also increases in the presence of wood as shown in Figure 6.2. For the neat PP, the exothermic peak occurs at $T_c = 111.3^\circ\text{C}$. These exothermic peaks shift to higher temperature of $T_c = 125.7$ for unmodified wood composites. Moreover, the crystallization rate ($T_{os} - T_c$) also increases as wood fibers are incorporated, from 5.7 to 3.2 $^\circ\text{C}$ (Table 6.5). This

increase in crystallization rate, in combination with the higher crystallization peak temperature (T_c), indicates that the crystallization is favored in the presence of wood fibers (Nunez et al. 2002; Hristov and Vasileva 2003). This phenomenon further supports the role of wood fibers as nucleating sites inducing the crystallization of the matrix. The accelerated crystallization rate by wood fiber loading leads to an inhomogeneous amorphous phase with greater mobility in the unmodified wood fiber-PP composites, which supports the lower T_g value detected by the DMA measurements.

Table 6.5 Melting and cooling parameters of neat PP, unmodified and LbL modified fiber composites

Sample	Cooling			Second heating		
	T_{os} (°C)	T_c (°C)	$T_{os}-T_c$ (°C)	T_m (°C)	ΔH_f (J/g)	X_c (%)
PP	117.0	111.3	5.7	161.8	83.3	59.9±0.7
0	128.9	125.7	3.2	161.5	59.9	66.9±1.5
4	131.0	127.1	3.9	163.6	56.4	66.2±0.7
4.5	131.0	127.1	3.9	163.3	56.4	66.3±0.7

LbL modified fiber induces the crystallization of PP at higher temperature as compared with the unmodified fiber. Both the crystallization onset and peak temperature (T_{os} and T_c) is moved upwards, ca 1.5-2°C, by incorporation of PDDA/clay. The crystallization rate of LbL modified fiber composites is slower compared with the unmodified one, as indicated by $T_{os}-T_c$ values (from 3.2 to 3.9°C). This result implies that larger spherulites may be obtained close to the LbL coated fiber surface than those in the unmodified fiber composites (Hristov and Vasileva 2003). The crystallinity of composites does not significantly change upon LbL modification (Table 6.5). However, the melting temperature of LbL modified fiber composite does increase from 161.5 to

163.6°C as compared to the unmodified one. This increment in melting temperature could be attributed to the formation of different crystalline phases in PP matrix (Mi et al. 1997; Harper and Wolcott 2004). It has been reported that both α and β crystalline phases, which have varying melting temperature, can be formed in PP in the presence of heterogeneous lignocellulosic fibers (Mi et al. 1997). The higher melting temperature of LbL modified fiber composites may imply that lower portion of β crystalline phases (with lower melting temperature) is present in these materials. No evident difference in melting and crystallization behavior (T_{os} , T_c , T_m , X_c) of modified fiber composites is observed between PDDA and clay as the terminal layer of adsorption (4 vs. 4.5 bi-layers), indicating that interfacial adhesion between fiber and matrix has marginal influence on melting and crystallization behavior of LbL modified composites.

Water absorption tests

The percent weight gain values of unmodified and LbL modified fiber composites after 24 hours water immersion are presented in Figure 6.4. Both unmodified and modified fiber composites show excellent water resistant properties due to the high volume fraction of hydrophobic PP matrix in the composites. As illustrated in Figure 6.4, percent weight gain of all the composites are less than 0.5%. The water sorption properties of composites slightly increase with increasing number of bi-layers, which is attributed to increased weight fraction of total LbL modified fiber components. The composites made of modified fiber with PDDA as terminal layer (both 0.5 and 4.5 bi-layers) show significantly higher water absorption properties than those of

unmodified fiber and modified fiber with clay as terminal layer. Relatively weaker interfacial adhesion between PDDA coated fiber and PP may provide more access along the interfaces for water absorption, which results in the higher water absorption values for composites reinforced by fibers with PDDA as the terminal layer (Lee and Kim 2009).

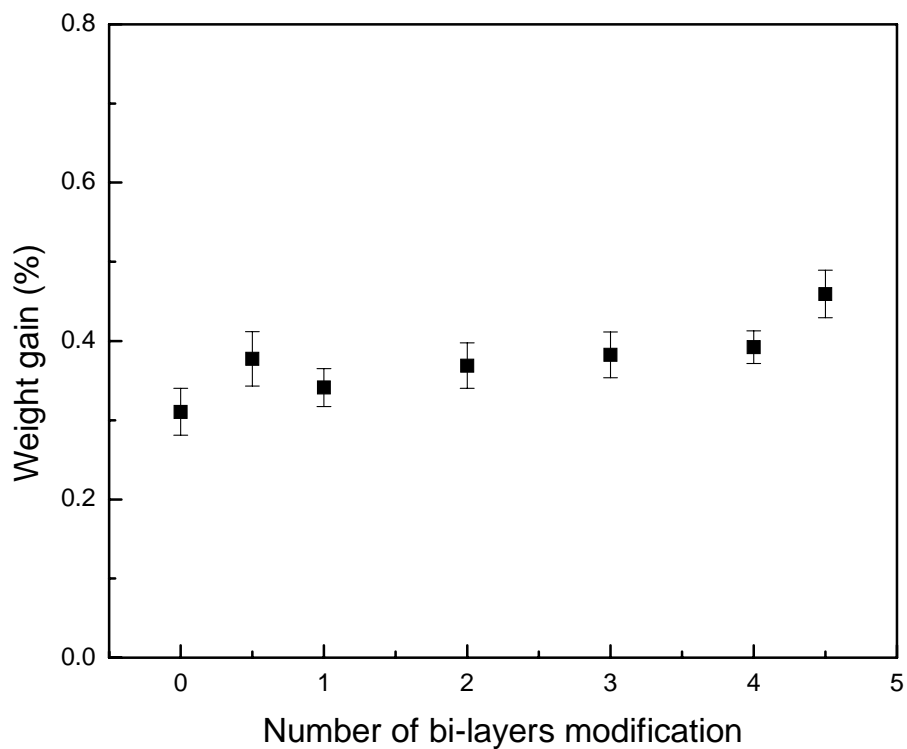


Figure 6.4 Percent weight gain of unmodified and LbL modified fiber composites after 24 hours water immersion

Conclusions

Layer-by-layer adsorption of PDDA and clay can enhance the thermal stability of wood fibers. Average temperature at 5 and 10% thermal degradation after 4 bi-layers of modification

increases by ~24 and ~15°C, respectively. Significant char residue formed for the LbL modified wood fibers after heating to 800°C indicates that the clay-based coating may serve as a barrier creating an insulating layer to prevent further decomposition of the material.

LbL modification of fibers affected the strength properties of composites. Both tensile strength and MOR of all LbL modified fiber composites are significantly lower than those of unmodified fiber composites. In addition, composites with LbL modified fibers show increased elongation properties to that of unmodified fibers. After 4 bi-layers, percent elongation at break of composites increased by 50%. Percent elongation at break of composites increases as the number of bi-layers increases.

Addition of wood fibers to neat PP results in a reduction in glass transition temperature. Crystallization behavior of PP is promoted in the presence of wood fibers. Both unmodified and LbL modified wood fibers are able to act as nucleating agents, which cause an increase of the crystallinity of PP by the wood fiber loading. No further evident change in the crystallinity of composites is observed upon LbL modification. The melting temperature of LbL modified fiber composite increased as compared to that of unmodified one, implying that different crystalline phases may be formed in the PP matrix by LbL modification.

Results from tensile and flexural strength, dynamic mechanical analysis and water absorption tests all reveal that the component at the outermost layer of LbL modified fibers impacts the performance of the composites. Composites reinforced by LbL modified fibers with PDDA as the outermost layer display lower tensile and flexural strength, higher elongation at break,

lower glass transition temperature and greater water absorption than those with clay as the terminal layer. Because the terminal surface layer can be tuned dependent on coating sequence, future work should concentrate on terminal components that may serve to enhance adhesion to the matrix.

Acknowledgment

We acknowledge the Sustainable Engineered Materials Institute, College of Natural Resources, and the Department of Wood Science and Forest Products of Virginia Tech for financial support.

References

- Avellar, B. K. and W. G. Glasser (1998). "Steam-assisted biomass fractionation. I. Process considerations and economic evaluation." *Biomass and Bioenergy* **14**(3): 205-218.
- Bledzki, A. K. and J. Gassan (1999). "Composites reinforced with cellulose based fibres." *Progress in Polymer Science* **24**(2): 221-274.
- Clemons, C. M. (2002). "Wood-plastic composites in the United States: the interfacing of two industries." *Forest Products Journal* **52**(6): 10-18.
- Decher, G. (1997). "Fuzzy nanoassemblies: toward layered polymeric multicomposites." *Science* (Washington, D. C.) **277**(5330): 1232-1237.
- Decher, G. and J. D. Hong (1991). "Buildup of ultrathin multilayer films by a self-assembly process. 1. Consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces." *Makromolekulare Chemie, Macromolecular Symposia* **46**(Eur. Conf. Organ. Org. Thin Films, 3rd, 1990): 321-7.
- Eriksson, M., S. M. Notley and L. Wagberg (2005). "The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibers." *Journal of Colloid and Interface Science* **292**(1): 38-45.
- Felix, J. M., P. Gatenholm and H. P. Schreiber (1993). "Controlled interactions in cellulose-polymer composites. I: Effect on mechanical properties." *Polymer Composites* **14**(6): 449-57.
- Glasser, W. G., R. Taib, R. K. Jain and R. Kander (1999). "Fiber-reinforced cellulosic thermoplastic composites." *Journal of Applied Polymer Science* **73**(7): 1329-1340.
- Glasser, W. G. and R. S. Wright (1998). "Steam-assisted biomass fractionation. II. Fractionation behavior of various biomass resources." *Biomass and Bioenergy* **14**(3): 219-235.
- Gray, D. G. (1974). "Polypropylene transcrystallization at the surface of cellulose fibers." *Journal of Polymer Science, Polymer Letters Edition* **12**(9): 509-15.
- Harper, D. and M. Wolcott (2004). "Interaction between coupling agent and lubricants in wood-polypropylene composites." *Composites, Part A Applied Science and Manufacturing* **35A**(3): 385-394.

- Hedenberg, P. and P. Gatenholm (1996). "Conversion of plastic/cellulose waste into composites. II. Improving adhesion between polyethylene and cellulose using ozone." *Journal of Applied Polymer Science* **60**(13): 2377-2385.
- Hristov, V. and S. Vasileva (2003). "Dynamic mechanical and thermal properties of modified poly(propylene) wood fiber composites." *Macromolecular Materials and Engineering* **288**(10): 798-806.
- Joseph, P. V., G. Mathew, K. Joseph, G. Groeninckx and S. Thomas (2003). "Dynamic mechanical properties of short sisal fibre reinforced polypropylene composites." *Composites, Part A Applied Science and Manufacturing* **34A**(3): 275-290.
- Kokta, B. V. and A. Ahmed (1998). *Steam Explosion Pulping. Environmentally Friendly Technologies for the Pulp and Paper Industry*, New York, John Wiley and Sons Incorporated.
- Kotov, N. A., T. Haraszti, L. Turi, G. Zavala, R. E. Geer, I. Dekany and J. H. Fendler (1997). "Mechanism of and Defect Formation in the Self-Assembly of Polymeric Polycation-Montmorillonite Ultrathin Films." *Journal of the American Chemical Society* **119**(29): 6821-6832.
- LeBaron, P. C., Z. Wang and T. J. Pinnavaia (1999). "Polymer-layered silicate nanocomposites: an overview." *Applied Clay Science* **15**(1-2): 11-29.
- Lee, H. and D. S. Kim (2009). "Preparation and physical properties of wood/polypropylene/clay nanocomposites." *Journal of Applied Polymer Science* **111**(6): 2769-2776.
- Lin, Z., S. Renneckar and D. P. Hindman (2008). "Nanocomposite-based lignocellulosic fibers 1. Thermal stability of modified fibers with clay-polyelectrolyte multilayers." *Cellulose (Dordrecht, Netherlands)* **15**(2): 333-346.
- Lingstrom, R., L. Wagberg and T. Larsson Per (2006). "Formation of polyelectrolyte multilayers on fibres: influence on wettability and fibre/fibre interaction." *Journal of Colloid and Interface Science* **296**(2): 396-408.
- Lu, Z., S. Eadula, Z. Zheng, K. Xu, G. Grozdits and Y. Lvov (2007). "Layer-by-layer nanoparticle coatings on lignocellulose wood microfibers." *Colloids and Surfaces, A Physicochemical and Engineering Aspects* **292**(1): 56-62.

- Lvov, Y., K. Ariga, I. Ichinose and T. Kunitake (1996). "Formation of Ultrathin Multilayer and Hydrated Gel from Montmorillonite and Linear Polycations." *Langmuir* **12**(12): 3038-3044.
- Lvov, Y., K. Ariga, M. Onda, I. Ichinose and T. Kunitake (1997). "Alternate Assembly of Ordered Multilayers of SiO₂ and Other Nanoparticles and Polyions." *Langmuir* **13**(23): 6195-6203.
- Maldas, D. and B. V. Kokta (1989). "Improving adhesion of wood fiber with polystyrene by the chemical treatment of fiber with a coupling agent and the influence on the mechanical properties of composites." *Journal of Adhesion Science and Technology* **3**(7): 529-39.
- Matuana, L. M., J. J. Balatinecz, C. B. Park and R. T. Woodhams (1999). "Surface characteristics of chemically modified newsprint fibers determined by inverse gas chromatography." *Wood and Fiber Science* **31**(2): 116-127.
- Messersmith, P. B. and E. P. Giannelis (1994). "Synthesis and Characterization of Layered Silicate-Epoxy Nanocomposites." *Chemistry of Materials* **6**(10): 1719-25.
- Mi, Y., X. Chen and Q. Guo (1997). "Bamboo fiber-reinforced polypropylene composites: crystallization and interfacial morphology." *Journal of Applied Polymer Science* **64**(7): 1267-1273.
- Michalowicz, G., B. Toussaint and M. R. Vignon (1991). "Ultrastructural changes in poplar cell wall during steam explosion treatment." *Holzforschung* **45**(3): 175-9.
- Morton, J., J. Quarmley and L. Rossi (2004). "Current and emerging applications for natural and woodfiber-plastic composites." *International Conference on Woodfiber-Plastic Composites, 7th, Madison, WI, United States, May 19-20, 2003*: 3-6.
- Nando, G. B. and B. R. Gupta, Eds. (1996). *Short fiber-thermoplastic elastomer composites. Short Fibre--Polymer Composites*. Cambridge, Woodhead Publishing.
- Nunez, A. J., J. M. Kenny, M. M. Reboredo, M. I. Aranguren and N. E. Marcovich (2002). "Thermal and dynamic mechanical characterization of polypropylene-woodflour composites." *Polymer Engineering and Science* **42**(4): 733-742.
- Okada, A., M. Kawasumi, T. Kurauchi and O. Kamigaito (1987). "Synthesis and characterization of a nylon 6-clay hybrid." *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* **28**(2): 447-8.

- Okada, A., M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi and O. Kamigaito (1990). "Nylon 6-clay hybrid." *Materials Research Society Symposium Proceedings* **171**(Polym. Based Mol. Compos.): 45-50.
- Onoda, M. and K. Yoshino (1995). "Fabrication of self-assembled multilayer heterostructure of poly(p-phenylene vinylene) and its use for an electroluminescent diode." *Journal of Applied Physics* **78**(7): 4456-62.
- Overend, R. P. and E. Chornet (1987). "Fractionation of lignocellulosics by steam-aqueous pretreatments." *Philosophical Transactions of the Royal Society of London, Series A Mathematical, Physical and Engineering Sciences* **321**(1561): 523-36.
- Peng, C. Q., Y. S. Thio and R. A. Gerhardt (2008). "Conductive paper fabricated by layer-by-layer assembly of polyelectrolytes and ITO nanoparticles." *Nanotechnology* **19**(50): 505603/1-505603/10.
- Raj, R. G., B. V. Kokta and C. Daneault (1990). "Wood flour as a low-cost reinforcing filler for polyethylene: studies on mechanical properties." *Journal of Materials Science* **25**(3): 1851-5.
- Schmitt, J., T. Gruenewald, G. Decher, P. S. Pershan, K. Kjaer and M. Loesche (1993). "Internal structure of layer-by-layer adsorbed polyelectrolyte films: a neutron and x-ray reflectivity study." *Macromolecules* **26**(25): 7058-63.
- Tajvidi, M., R. H. Falk and J. C. Hermanson (2006). "Effect of natural fibers on thermal and mechanical properties of natural fiber polypropylene composites studied by dynamic mechanical analysis." *Journal of Applied Polymer Science* **101**(6): 4341-4349.
- Tanahashi, M. (1990). "Characterization and degradation mechanisms of wood components by steam explosion and utilization of exploded wood." *Wood Research* **77**: 49-117.
- Tang, Z., N. A. Kotov, S. Magonov and B. Ozturk (2003). "Nanostructured artificial nacre." *Nature Materials* **2**(6): 413-418.
- Tsai, S. W., and N. J. Pagano (1968). "Invariant properties of composite materials." In *Composite Materials Workshop*, S. W. Tsai, J. C. Halpin, and N. J. Pagano, eds., Technomic Publishing Co., Lancaster, Pa., 233-253.

- van Duffel, B., T. Verbiest, S. van Elshocht, A. Persoons, F. C. de Schryver and R. A. Schoonheydt (2001). "Fuzzy Assembly and Second Harmonic Generation of Clay/Polymer/Dye Monolayer Films." *Langmuir* **17**(4): 1243-1249.
- Wagberg, L., S. Forsberg, A. Johansson and P. Juntti (2002). "Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept. Part I. Modification of paper strength." *Journal of Pulp and Paper Science* **28**(7): 222-228.
- Yin, S., S. Wang, T. G. Rials, K. M. Kit and M. G. Hansen (2006). "Polypropylene composites filled with steam-exploded wood fibers from beetle-killed loblolly pine by compression-molding." *Wood and Fiber Science* **39**(1): 95-108.
- Yin, S., S. Wang, T. G. Rials, K. M. Kit and M. G. Hansen (2007). "Polypropylene composites filled with steam-exploded wood fibers from beetle-killed loblolly pine by compression-molding." *Wood and Fiber Science* **39**(1): 95-108.

Chapter 7 Summary and Conclusions

Nanocomposite-based lignocellulosic fibers with controlled surface chemistry and structure were successfully fabricated by alternate adsorption of oppositely charged poly(diallyldimethylammonium) chloride (PDDA) and clay nanoparticles. The PDDA-clay multilayer build-up was examined on lignocellulosic fiber as well as model surface (gold coated quartz crystal). Optimization of the layer-by-layer (LbL) adsorption onto wood fibers was performed by investigating the parameters including fiber characteristics (presence of lignin) and deposition conditions (salt concentration and pH). In addition, the effect of LbL modification on thermal stability and surface properties of wood fiber as well as tensile, flexural, dynamic mechanical and thermal properties fiber reinforced thermoplastic composites was also investigated in this study. The conclusions of this study are summarized as below:

Layer-by-layer build-up of PDDA and clay

On a gold coated quartz crystal model surface, PDDA/clay bi-layers were formed that reached a hydrated thickness of 235 nm for 4 bi-layers. The method demonstrated that sequential adsorption increased film thickness with greater amounts of clay deposited during the third and fourth deposition cycle. A similar response was found for the layer-by-layer assembly on the fiber substrate with the amount of clay deposited increasing with layer number. Dependent upon deposition conditions, large amount of PDDA/clay (up to ~75% total mass for only 4 bi-layers)

can be adsorbed onto wood fibers through the LbL process. Electrokinetic potential of the fiber were reversed after each deposition cycle during the LbL process, indicating that a layered structure was formed on the fiber surface.

Optimization of layer-by-layer process

The presence of lignin impacted PDDA adsorption onto lignocellulosic wood fibers. PDDA adsorption to the fibers was reduced for all solution conditions for the samples with the highest content of lignin. In addition to total mass adsorbed, differences were also found in the electrokinetic properties of the modified fibers after adsorption of PDDA. Fibers with high lignin contents consistently had lower zeta potential values. However, the presence of lignin was not always detrimental to polyelectrolyte adsorption. Upon extracting the non-covalently attached lignin, the samples showed the greatest amount of PDDA adsorption, reaching to 1.5%, under neutral solution conditions without the presence of added electrolyte. A secondary mechanism, besides charge compensation, was discussed in terms of facilitating polyelectrolyte adsorption to a surface bearing aromatic moieties.

The electrokinetic potential of fiber after PDDA adsorption, rather than the amount of adsorbed PDDA layer, controlled the subsequent clay adsorption on PDDA. Moreover, despite the difference in the quantity of the initial PDDA layer, minimum difference in multilayer build-up was found for subsequent bi-layers for the alkali extracted fiber.

Thermal stability of layer-by-layer modified fiber

Layer-by-layer adsorption of PDDA and clay impacted the thermal stability of wood fibers as a function of the number of deposited layers. Average degradation temperature at 5 and 10% weight loss for 4 bi-layer modified fibers increased by ~24 and ~15°C, respectively. The maximum degradation rate of LbL modified fibers was reduced by ~44% for 4 bilayer coating. Scanning electron microscopy images showed that layer-by-layer modified fiber contained complete fiber structures after heating the samples to 600°C under air atmosphere. FTIR spectra of heated samples contained carbon-based stretching peaks indicating residual carbon in the sample. Significant char residue formed for the layer-by-layer modified wood fibers after heating to 800°C indicated that the clay-based coating may serve as a barrier creating an insulating layer to prevent further decomposition of the material.

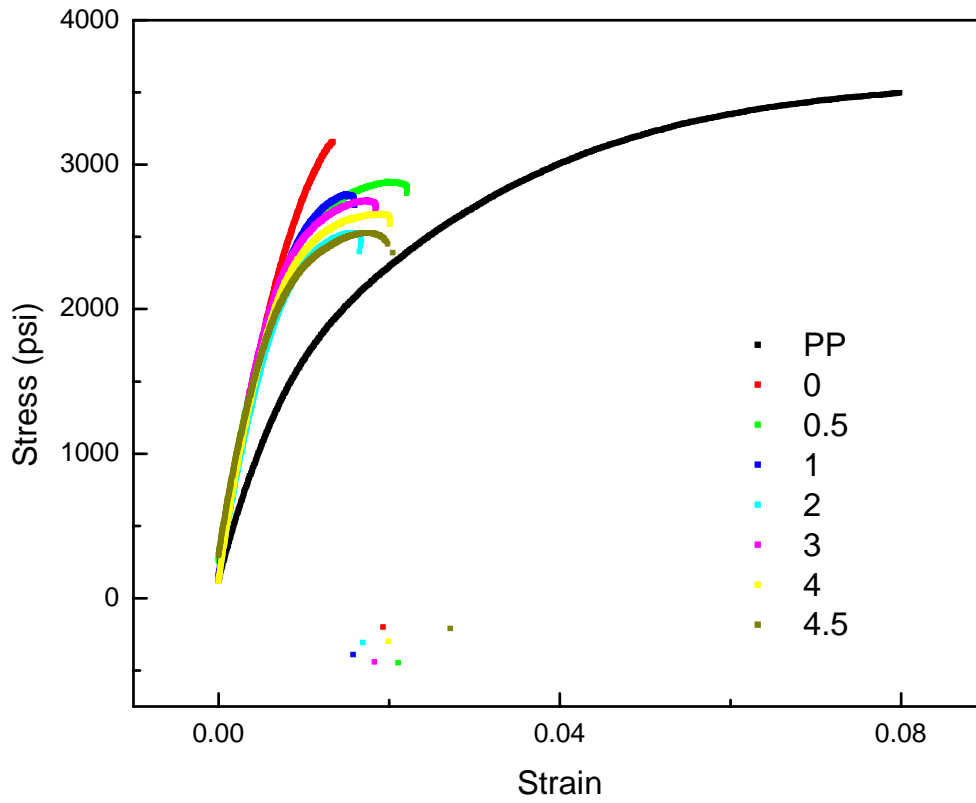
Performance of layer-by-layer modified fiber reinforced thermoplastic composite

Layer-by-layer modification of fibers does not impact the Young's modulus, but negatively affects the strength properties of fiber reinforced polypropylene (PP) composites. Both tensile strength and MOR of all LbL modified fiber composites were significantly lower than those of unmodified fiber composites. Composites with LbL modified fibers showed increased elongation properties to that of unmodified fibers; percent elongation at break of composites increased with the increase in the number of bilayers. After modification with 4 bilayers, percent elongation at break of composites increased by 50%.

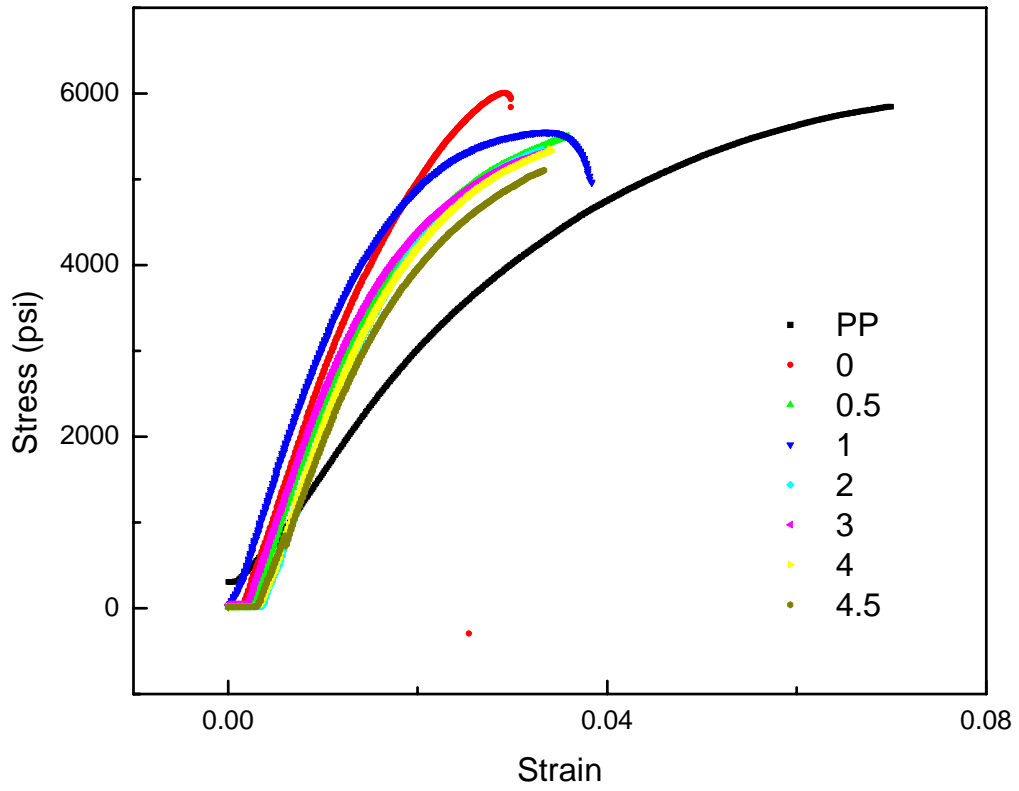
Crystallization behavior of PP was promoted in the presence of wood fibers. Both unmodified and LbL modified wood fibers are able to act as nucleating agents, which cause an increase of the crystallinity of PP by the wood fiber loading. Additionally, the presence of the wood fibers resulted in a reduction in glass transition temperature of the PP matrix.

Results from tensile and flexural strength, dynamic mechanical analysis and water absorption tests all revealed that the component at the outermost layer of LbL modified fibers impacts the performance of the composites. Composites reinforced by LbL modified fibers with PDDA as the outermost layer displayed lower tensile and flexural strength, higher elongation at break, lower glass transition temperature and greater water absorption than those with clay as the terminal layer. Future work with this unique system should comprise evaluation of terminal surface chemistries that enhance adhesion with the matrix, further modification of LbL films to enhance the mechanical properties, and evaluation of fiber and composite durability.

Appendix



Stress-strain curves of PP, unmodified and LbL modified fiber composites from tensile tests



Stress-strain curves of PP, unmodified and LbL modified fiber composites from flexural tests

Tensile properties of PP, unmodified and LbL modified fiber composites

Sample	#	Slope	Peak load	Elongation at break	Thickness	Width
		(lbf/in.)	(lbs)	(in.)	(in.)	(in.)
PP	1	5730.4	206.7	did not break	0.126	0.497
	2	6516.6	232.1	did not break	0.127	0.504
	3	7045.6	245.9	did not break	0.141	0.504
	4	5969.7	237.8	did not break	0.127	0.502
	5	5809.2	207.2	did not break	0.124	0.510
	6	6157.6	208.4	did not break	0.124	0.511
	7	6283	221.7	did not break	0.128	0.505
	8	6034.3	216.8	did not break	0.128	0.500
	9	6832.3	246.4	did not break	0.138	0.506
	10	5831.7	219.4	did not break	0.126	0.500
	11	6230.4	241.3	did not break	0.135	0.507
	12	5912.9	230.1	did not break	0.125	0.504
0	1	9600.2	160.8	0.024	0.114	0.498
	2	11418.7	205.3	0.027	0.135	0.498
	3	9071.3	179.3	0.030	0.109	0.501
	4	12300.2	224.0	0.029	0.138	0.500
	5	10043.9	189.7	0.026	0.120	0.500
	6	10572.8	173.3	0.025	0.117	0.498
	7	12161.2	208.5	0.027	0.131	0.503
	8	12323.8	215.6	0.028	0.131	0.502
	9	11008.8	198.4	0.030	0.121	0.498
	10	11361.4	209.7	0.026	0.129	0.499
	11	12199.9	217.9	0.031	0.127	0.505
0.5	1	12087.1	171.0	0.041	0.126	0.500
	2	12157	183.7	0.046	0.126	0.499
	3	11216.5	154.6	0.042	0.123	0.503
	4	12033.5	171.7	0.041	0.125	0.500
	5	11939.2	181.0	0.044	0.126	0.501
	6	10473.3	169.0	0.046	0.118	0.500
	7	10845.8	160.2	0.038	0.123	0.501
	8	11421.7	172.3	0.041	0.126	0.501
	9	11578.1	174.9	0.042	0.126	0.500
	10	10877.9	176.0	0.044	0.122	0.502
1	1	11747.7	176.5	0.035	0.126	0.500
	2	13252.8	184.0	0.028	0.133	0.504
	3	12438.3	187.8	0.032	0.134	0.503
	4	12038.3	174.7	0.029	0.122	0.503
	5	12654.7	173.8	0.030	0.126	0.502
	6	12271.1	175.6	0.040	0.128	0.501
	7	12280.2	176.8	0.027	0.128	0.507
	8	11668.7	175.8	0.032	0.124	0.502
	9	11999.8	166.1	0.030	0.124	0.501

(Continued table)

2	1	10685.3	150.7	0.033	0.119	0.500
	2	11680.4	148.3	0.034	0.118	0.503
	3	10986.6	153.0	0.031	0.121	0.500
	4	11315.8	152.7	0.036	0.117	0.498
	5	11519.3	158.0	0.033	0.121	0.502
	6	12253.6	165.7	0.032	0.125	0.501
	7	10957.2	161.2	0.039	0.123	0.501
	8	11097.6	160.0	0.035	0.121	0.503
	9	11232.7	167.5	0.031	0.122	0.501
	10	11712.4	166.7	0.040	0.125	0.499
3	1	10949.3	145.1	0.039	0.114	0.497
	2	11646.1	161.2	0.036	0.118	0.497
	3	10946.2	146.2	0.032	0.119	0.502
	4	10494.1	152.0	0.035	0.115	0.495
	5	11268.9	141.1	0.039	0.113	0.498
	6	12130.7	161.7	0.035	0.118	0.502
	7	10356	148.7	0.033	0.119	0.499
	8	10926.2	157.1	0.038	0.117	0.500
	9	11321.9	144.8	0.030	0.118	0.499
	10	11610	161.3	0.045	0.118	0.501
4	1	11865.2	162.9	0.047	0.121	0.497
	2	10919.2	154.2	0.040	0.117	0.496
	3	11282.2	150.4	0.036	0.113	0.495
	4	12011.5	163.2	0.036	0.122	0.501
	5	10549.8	155.8	0.045	0.118	0.498
	6	12199.7	157.5	0.039	0.117	0.501
	7	11321.2	164.5	0.039	0.123	0.501
	8	10690.9	159.8	0.046	0.118	0.499
	9	10382.1	159.7	0.038	0.120	0.500
	10	10910.3	159.7	0.044	0.119	0.500
4.5	1	11252	154.5	0.048	0.122	0.501
	2	10793.9	153.9	0.039	0.121	0.495
	3	10908.7	142.1	0.039	0.117	0.503
	4	10650.9	157.2	0.038	0.123	0.498
	5	10314.7	147.2	0.036	0.121	0.499
	6	10370.1	152.7	0.041	0.121	0.499
	7	10176.1	158.2	0.045	0.124	0.502
	8	9820.1	151.2	0.047	0.122	0.499

Flexural properties of PP, unmodified and LbL modified fiber composites

Sample	#	Slope	Peak load	Depth	Width
		(lbf/in.)	(lbs)	(in.)	(in.)
PP	1	82.2	17.1	0.130	0.501
	2	80.5	18.2	0.134	0.501
	3	83.6	18.3	0.133	0.502
	4	65.5	17.2	0.131	0.503
	5	83.3	17.6	0.130	0.501
	6	71.9	17.1	0.131	0.506
	7	97.2	20.0	0.141	0.504
	8	82.5	19.6	0.140	0.506
	9	85.8	16.6	0.129	0.506
	10	95.3	19.4	0.139	0.504
	11	73.7	16.5	0.129	0.504
	12	105.7	20.2	0.143	0.503
	13	76.7	15.6	0.126	0.503
0	1	133.3	14.2	0.117	0.501
	2	159.1	16.0	0.123	0.504
	3	133.7	14.0	0.118	0.507
	4	149.3	15.3	0.125	0.507
	5	177.9	15.3	0.127	0.507
	6	189.7	16.2	0.130	0.502
	7	175.5	16.6	0.128	0.506
	8	181.9	19.0	0.134	0.502
	9	132.5	12.8	0.114	0.505
	10	135.4	13.0	0.115	0.506
	11	143.9	14.2	0.121	0.501
	12	119.4	13.5	0.117	0.497
	13	132.7	15.3	0.122	0.493
	14	139.7	13.7	0.119	0.501
0.5	1	142.5	13.8	0.123	0.511
	2	134.3	13.0	0.120	0.509
	3	138.9	13.7	0.118	0.510
	4	153.1	15.0	0.124	0.510
	5	165.5	14.9	0.124	0.508
	6	153.9	15.3	0.125	0.507
	7	134.3	12.7	0.118	0.507
	8	152.5	13.5	0.121	0.510
	9	156.3	14.8	0.125	0.508
	10	156.1	14.2	0.123	0.506
	11	158.6	14.2	0.123	0.509
	12	164.1	15.3	0.128	0.509

(Continued table)

1	1	182.1	15.7	0.131	0.508
	2	167.2	14.7	0.125	0.511
	3	159.2	13.9	0.123	0.508
	4	130.1	12.7	0.115	0.506
	5	138.4	13.7	0.120	0.506
	6	145.6	13.6	0.119	0.505
	7	187.1	16.2	0.131	0.508
	8	175.4	16.5	0.131	0.510
	9	163.7	14.5	0.125	0.510
	10	128.8	12.9	0.118	0.507
	11	128.2	12.6	0.114	0.509
	12	128.0	12.4	0.115	0.508
2	1	162.8	14.1	0.127	0.508
	2	157.8	14.7	0.127	0.508
	3	127.3	12.6	0.117	0.510
	4	129.4	12.3	0.116	0.511
	5	125.1	12.5	0.118	0.507
	6	165.4	14.3	0.126	0.507
	7	178.7	14.4	0.129	0.506
	8	190.7	15.7	0.130	0.506
	9	150.2	14.5	0.126	0.508
	10	123.7	12.3	0.117	0.509
	11	121.3	12.0	0.114	0.509
	12	121.9	11.8	0.115	0.507
3	1	145.4	13.6	0.121	0.507
	2	144.0	13.5	0.124	0.506
	3	115.2	11.5	0.116	0.503
	4	123.1	12.0	0.115	0.511
	5	116.7	11.3	0.116	0.499
	6	115.9	11.4	0.111	0.506
	7	146.5	13.0	0.122	0.509
	8	159.4	13.9	0.124	0.508
	9	145.4	13.3	0.123	0.509
	10	186.4	14.7	0.130	0.510
	11	124.0	12.0	0.117	0.507
	12	125.2	11.7	0.113	0.509

(Continued table)

4	1	162.5	14.2	0.124	0.507
	2	149.9	13.4	0.122	0.506
	3	152.8	14.4	0.124	0.503
	4	119.6	11.8	0.113	0.510
	5	115.9	11.9	0.114	0.510
	6	117.6	12.2	0.114	0.510
	7	168.5	15.1	0.128	0.510
	8	164.0	14.1	0.125	0.509
	9	153.7	13.4	0.124	0.510
	10	160.0	14.0	0.126	0.510
	11	126.8	11.6	0.113	0.509
	12	119.8	11.8	0.116	0.510
	13	129.3	12.1	0.117	0.511
	14	125.0	12.1	0.115	0.511
4.5	1	141.4	13.4	0.125	0.510
	2	146.6	13.6	0.124	0.507
	3	140.7	13.2	0.124	0.509
	4	118.7	11.6	0.115	0.508
	5	117.8	11.8	0.115	0.507
	6	117.4	11.7	0.116	0.508
	7	147.2	13.5	0.126	0.510
	8	144.1	13.0	0.123	0.502
	9	149.1	13.0	0.123	0.508
	10	126.5	11.3	0.116	0.510
	11	116.5	11.4	0.115	0.509
	12	112.6	11.4	0.116	0.510