

**Modification of Wood Fiber with Thermoplastics
by Reactive Steam-Explosion Processing**

by

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A dissertation submitted to the faculty of
Virginia Polytechnic Institute & State University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy
in
Wood Science and Forest Products
Blacksburg, VA

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Keywords: cellulose, fractionation, confocal laser scanning microscopy, biopolymer,
thermogravimetric analysis, ¹³C solid state NMR

June 18, 2004

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(ABSTRACT)

For the first time, a novel processing method of co-refining wood and polyolefin (PO) by steam-explosion was scientifically explored for wood-thermoplastic composites without a coupling agent. Traditional studies have addressed the improvement of adhesion between components of wood thermoplastic composites through the use of coupling agents such as maleated PO. The objective of this study was to increase adhesion between wood and PO through reactive processing conditions of steam-explosion. PO characteristics, such as type (polyethylene or polypropylene), form (pellet, fiber, or powder) and melt viscosity were studied along with oxygen gas content of the steam-explosion reactor vessel. Modification of co-processed wood fiber was characterized in four studies: microscopy analysis of dispersion of PO with wood fiber, sorption properties of co-processed material, chemical analysis of fractionated components, and morphological investigation of co-processed material. Two additional studies are listed in the appendices that relate to adsorption of amphiphilic polymers to the cellulose fiber surface, which is one hypothesis of fiber surface modification by co-steam-explosion.

Microscopy studies revealed that PO melt viscosity was found to influence the degree of dispersion and uniformity of the steam-exploded material. The hygroscopic nature of the co-processed fiber declined as shown by sorption isotherm data. Furthermore, a water vapor kinetics study found that all co-refined material had increased initial diffusion coefficients compared to the control fiber. Chemical changes in fractionated components were PO-type dependent. Lignin extracted from co-processed wood and polyethylene showed PO enrichment determined from an increase of methylene stretching in the Fourier Transform infrared subtraction spectra, while lignin from co-processed wood and polypropylene did not. Additionally, extracted PO showed indirect signs of oxidation as reflected by fluorescence

studies. Solid state nuclear magnetic resonance spectroscopy revealed a number of differences in the co-processed materials such as increased cellulose crystallinity, new covalent linkages and an alternative distribution of components on the nanoscale reflected in the $T_{1\rho}$ relaxation parameter.

Steam-explosion was shown to modify wood fiber through the addition of “non-reactive” polyolefins without the need for coupling agents. In light of these findings, co-refining by steam-explosion should be viewed as a new reactive processing method for wood thermoplastic composites.

Dedicated to ***Team Renneckar***

ACKNOWLEDGEMENTS

I wish to acknowledge a number of people that contributed in many different forms to this research.

My co-advisors Wolfgang Glasser and Audrey Zink-Sharp have been amazing in all aspects of my education and research. Their guidance, encouragement, excitement, dedication, and trust have helped create this dissertation. Furthermore, they have provided me with vision for my future career to what can be accomplished with wood-based materials.

I would like to thank my committee members, William Ducker, Chip Frazier, Paul Gatenholm, Geza Ifju, and Timothy Rials, for their time and contributions. I would like to specifically thank Paul Gatenholm for providing molecular weight analysis and Timothy Rials for use of the IR microscopy equipment.

Bob Wright has been central to the development (design and manufacture) of the steam-explosion processing equipment that was used in this research. I appreciate all the time he put into the creation of the equipment and the numerous days he spent running experiments with me.

A number of fellow graduate students have spent considerable time training me and showing me how to use various lab equipment. Members (current and past) of the Wood Adhesion Group: Nikki Brown, Jun Zheng, Sudipto Das, Marie Laborie, Darren Riedlinger, have patiently answered all of my numerous questions. In addition post doctoral scientists in the Wood Adhesion group, Subiman Ghosh, “Fuco” Lopes-Suevos, Nanjian Sun have also helped me with many experiments. I would like to specifically thank Nanjian for the time he spent running my NMR samples.

There have been a number of students that I worked closely with on projects together. Richard Johnson, my joint partner in steam-explosion and wetlay, has contributed to both the brains and brawn of the project by numerous long discussions and many hours of work (in both hot and freezing conditions). Richard also provided some of the testing for the dynamic mechanical analysis tests. I would specifically like to recognize Sheila Gradwell, Sylvie Jamin, and Shinji Beppu who have helped with my

“lab education” and also substantially contributed to the work on cellulose modification through adsorption, listed in the appendix.

I wish to acknowledge the contribution of Alan Esker to the cellulose adsorption studies.

I also would like to thank the wonderful Wood Science staff. Debbie Garnand, Angie Riegel, David Jones, Harrison Sizemore, and Carlile Price.

I wish to express my gratitude to the funding agencies of my research. The USDA- NRI competitive grants program and Eastman Chemical Company for my Fellowship. I also wish to acknowledge the Wood Based Composite Center who accepted me as an Honorary Fellow.

Finally, I wish to thank my family (Renneckars and Kellys) for their support and patience. I would especially like to express my utmost gratitude to my wife Patricia.

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GLOSSARY OF SYMBOLS AND TERMS

α	significance level
ATR	attenuated total reflectance
CLSM	confocal laser scanning microscopy
co-stex	co-steam-explosion
Δ	difference in weight gain for sorption isotherm
D_1	Initial Diffusion Coefficient
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
DTG	derivative of thermogram
FE-SEM	field emission scanning electron microscopy
FT-IR	Fourier transform infrared
GPC	gel permeation chromatography
HDPE	high density polyethylene
I^*	relative peak intensity
iPP	isotactic polypropylene
K_1	initial rate of sorption
K_1^*	normalized initial rate of sorption
K_c	change in initial rate of sorption
λ_{em}	emission wavelength
λ_{ex}	excitation wavelength
LSD	least significant difference
MAPP	polypropylene-graft maleic anhydride
M_n	number average molecular weight
M_w	weight average molecular weight
MW	molecular weight
nm	nanometer
NMR	nuclear magnetic resonance
O_2	diatomic oxygen
PE	polyethylene
PO	polyolefin
RH	relative humidity
stex	steam-explosion
$T_{1\rho}$	proton rotating frame relaxation time
T_{CH}	cross polarization transfer rate constant
T_g	glass transition
TGA	thermogravimetric analysis
THF	tetrahydrofuran
T_m	melting temperature
UV-Vis	ultraviolet-visible
w_∞	weight gain at equilibrium

CHAPTER 1

INTRODUCTION AND BACKGROUND

Introduction

Wood is a complex material that is a hierarchical assembly of immiscible components. Cellulose (Figure 1.1a) and lignin (Figure 1.1b) are two cell wall constitutive polymers that have differing surface energetics, which cause the two components to phase separate [1]. Within the wood cell wall, however, cellulose and lignin are intimately associated and the suggested cause of this association is due to hemicelluloses (Figure 1.1c,d) that act as compatibilizing agents (Figure 1.2). Furthermore, there is a transition between components across a nanometer scale. This gradual transition gives the constitutive polymers of wood the ability to maintain association under stress helping to create the material's remarkable strength, modulus, and toughness that is characteristic of many materials found in nature.

The above mentioned properties are sought in synthetic composite materials, many of which are derived from non-renewable materials. With increases in population, consumption and environmental awareness, renewable materials like wood are growing in acceptance to replace materials derived from non-renewable sources. A method of reducing the amount of synthetic materials consumed is by using natural fillers. Filler materials are additives for thermoplastics or thermosets, which include glass, sand, clay and wood fiber that will either lower cost or improve material performance.

In North America, agrofiber-thermoplastic composites have developed into an annual market consisting of 400 million pounds per year [2]. Wood fiber is used as an additive for thermoplastics to improve aesthetics, lower costs, reduce weight, and increase mechanical properties like stiffness [3]. Plastic lumber (thermoplastics with wood fiber filler up to 50% by weight) has increased its market share of exterior decking to compete with wood and other products [4]. Future bans on preservative treated wood will open up the market for increased use of fiber reinforced thermoplastic materials. However, one problem with using wood fiber as a filler for thermoplastics is that polyolefins (PO) have poor interaction with the wood cell wall surface, which lowers the overall strength of the composite material.

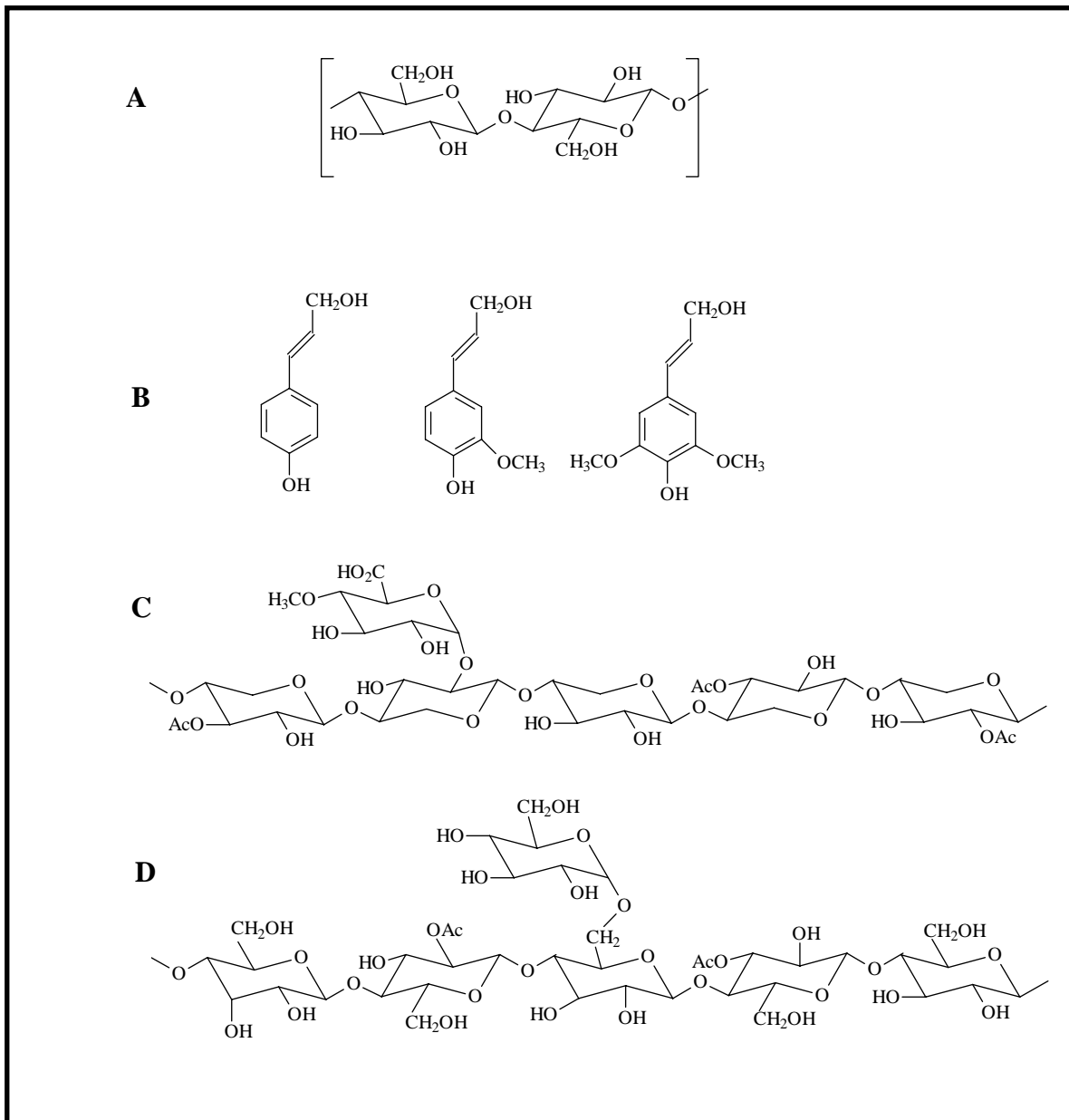


Figure 1.1 Constitutive polymers of wood. A) Cellobiose, repeating unit of cellulose, B) p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol--lignin precursor building units C) Partial structure of O-acetyl-4-O-methylglucuronoxylan, D) Partial structure of O-acetyl-galactoglucomannan.

Application of nature's technique of maintaining a gradient on the nanoscale between components would improve the performance of synthetic-natural composite materials. Thermoplastics used in fiber-reinforced plastic lumber or wood-filled thermoplastic composites are polyolefins. Due to a difference in surface free energy (the high surface energy of the cellulose fiber surface is not satisfied by the low surface energy of the PO) there is a large interaction surface energy that leads to a low work of adhesion. This gives rise to a distinct interface between the thermoplastic and reinforcing cellulose fiber because the cellulose interacts with itself or with water more than it interacts with the PO. The interface does not allow for intimate association of wood fiber and thermoplastic and the result is a product that does not have toughness, durability or dimensional stability. The thermoplastic matrix holds the wood but there is poor adhesion between wood and thermoplastic so stresses do not transfer across the interface between the wood and thermoplastic.

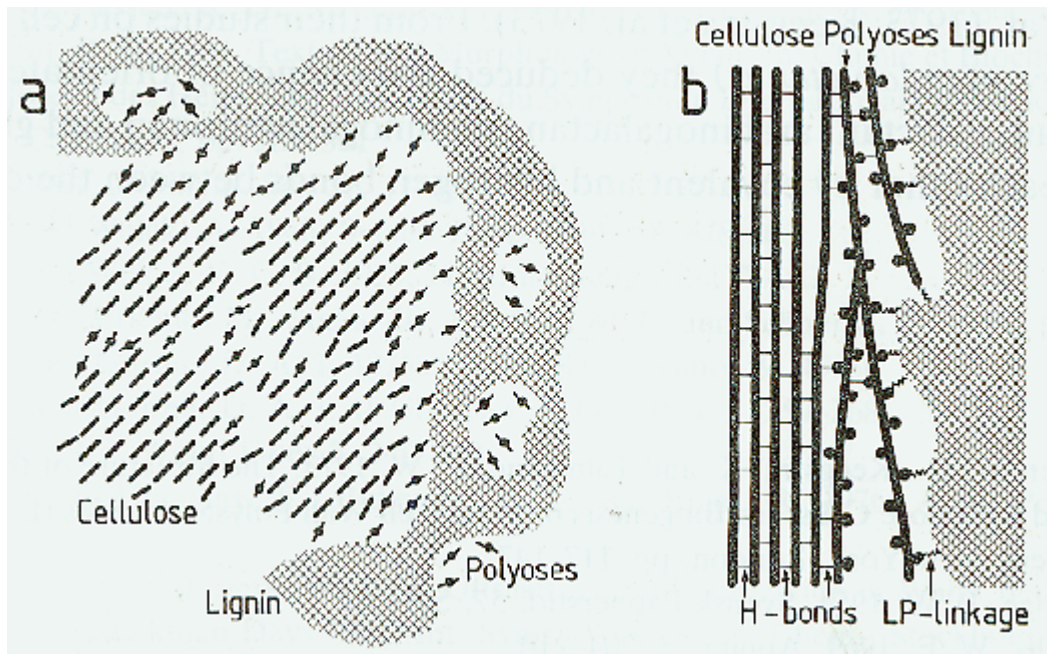


Figure 1.2. Model of hemicelluloses (polyose) at the cellulose- lignin interface serving as a compatibilizing agent. *From Fengel and Wegener 1989. [6]*

A material's toughness can be improved by creating an interphase between the two materials [5] where multiple components remain molecularly intertwined as seen in wood, bone, and insect cuticle. One technique to create an interphase region, improving toughness of wood/plastic composites, is by bridging the interface with a compatibilizer. Other options of improving product performance of composite materials are chemical modification and surface pretreatments. For wood and fiber composites, esterification or etherification of cellulose can achieve the former; corona discharge, oxygen-fluorine gas exposure, and cold plasma treatment perform the latter. These options are further reviewed in Chapter 2.

Improvement in the performance of wood-fiber filled thermoplastics will increase the possibility of competing with other materials for market acceptance and market growth [7]. A novel method was introduced by Brooks and Associates to co-refine wood and thermoplastics by steam-explosion [8-10]. This process offered a unique processing technique that created a moldable composite panel that had improved dimensional stability compared to medium density fiberboard. Specifically, the steam-explosion process exposes the materials to a water vapor-saturated environment under high temperature and pressure. The steam plasticizes the wood cell wall and condenses in micro-capillaries within the wood. The pressurized system is released to atmospheric pressure and the condensed water immediately vaporizes, rupturing wood, causing mechanical failure (Figure 1.3). Chornet and Overend report that steam-explosion is a thermo-hydrolytic-mechanical process [11].

Furthermore, there is opportunity to use post-consumer recycled materials as a component in the steam-explosion process. Because the severity of the steam-explosion process is great, slight impurities in the materials do not have a large impact. The use of recycled materials in the steam explosion process would create a market for thermoplastics and wood at the end of their normal product life. Recycling has been explored for non steam-exploded wood filled thermoplastics. Only a slight decrease in mechanical properties for wood-thermoplastic composites occurred for repeated recycling tests [12-14].

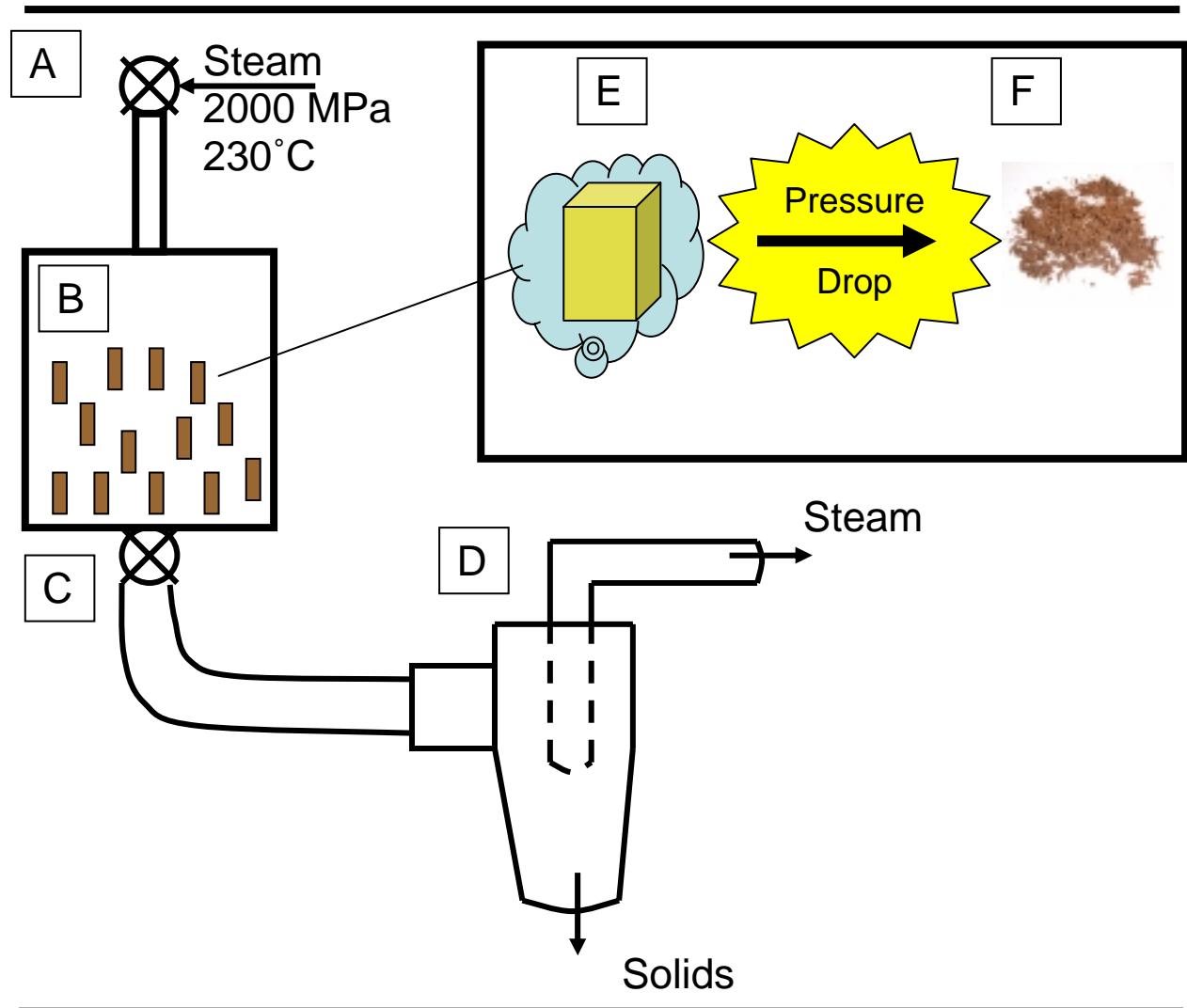


Figure 1.3. Diagram of steam-explosion batch processing equipment. A) Inlet valve for steam, B) stainless steel reactor containing wood chips (water is condensed within cell wall and biopolymers are plasticized), C) exit valve for decompression step, D) cyclone to separate solids from steam, E) wood chip in reactor immersed in steam, and F) fiberized wood chip after ejection from reactor.

Background

As further research is performed on material-property relationships, the ability to tailor properties for specific end-uses increases. Some examples of materials that are tailored for specific applications include the use of high strength polyaramides for space-suits and bulletproof vests, high refractive index polycarbonates for eyeglass lenses, and ordered liquid crystalline polymers for computer screens. However, the building units (chemical structures) of materials do not have to be vastly different to obtain unique properties. Materials found in nature have similar building blocks with vastly different properties. Intestine, bone, tendon and eye are made of the same building block, but with minute changes that affect the order and hierarchical structure. The various building blocks found in nature are listed in Figure 1.4.

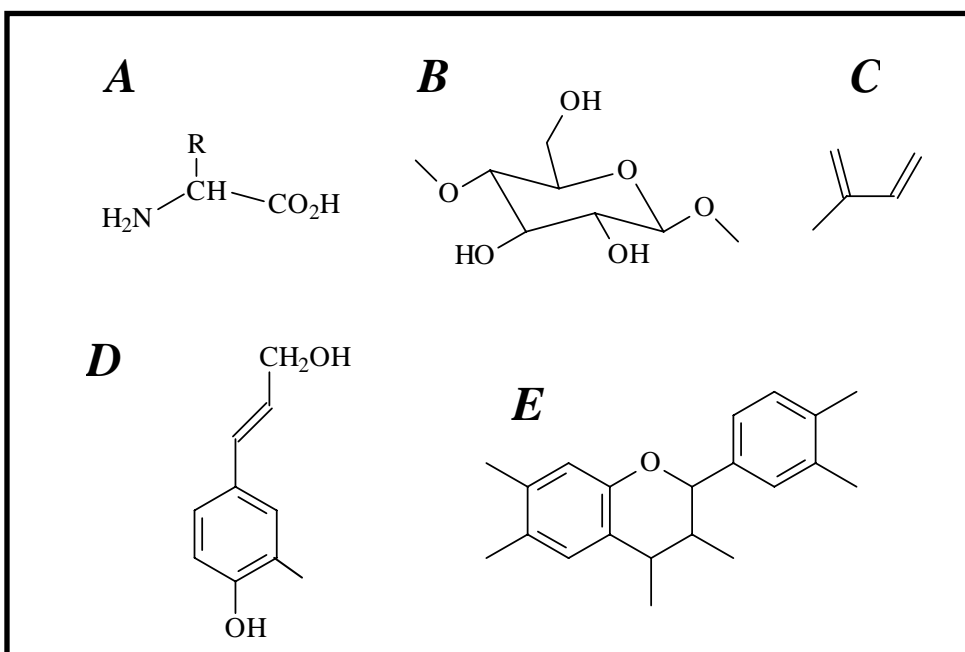


Figure 1.4. Chemical building blocks found in nature A) amino acid, B) polysaccharide, C) isoprene, D) p-hydroxy phenyl propene-ol, E) flavanoid (from Glasser 2000). [15]

Within particular environments, certain polymers demonstrate self-assembly, a method by which molecules organize into exact patterns [16]. An example by Becker and co-workers, who used fluorinated cellulose derivatives, demonstrated the effects of minute changes on the self-assembly of solvent-cast films [17]. Substitution at the terminus of the cellulose derivative

from a trifluorocarbon to a difluorocarbon changed the ordering of the polymer within the film and also the surface energy of the film. Moreover, creating new properties from the same materials can be accomplished by the orientation of components without modifying the chemistry. For example, Spectra 1000™ is a highly ordered polyethylene that has a normalized (by density) tensile modulus and a normalized tensile strength greater than steel and glass fibers [18]. Furthermore, Figure 1.5 shows an empirical compliance surface map for a polyethylene crystallite demonstrating its anisotropy. Note that slight deviation from the z-axis (crystallite C axis plane) drastically increases the reported compliance. For this reason, highly ordered polymer chains within a composite material have a large influence on macroscopic properties.

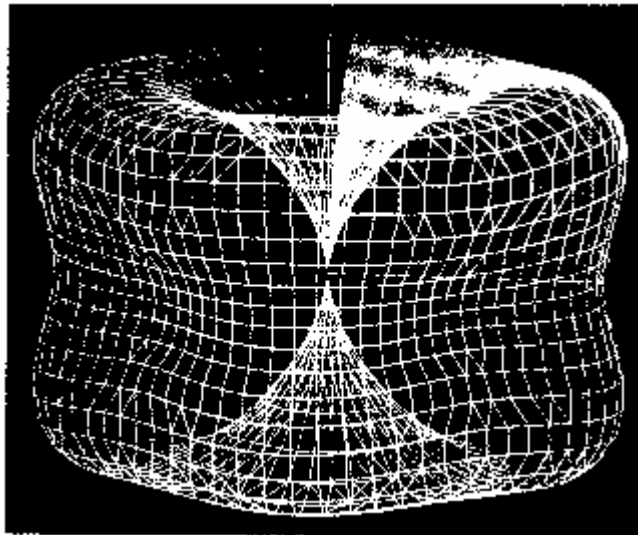


Figure 1.5. Empirically estimated compliance surface of a polyethylene crystallite. From Janzen 1992.[19]

From the above discussion it is evident that orientation of the components and/or slight changes in the polymers impact material properties and interactions. It is expected that the chemical changes and arrangement of the steam-exploded thermoplastics that are spread on the wood fiber surface will influence the final properties (sorption, durability and compatibility) of the material.

Another important aspect of the fiber modification is the interfacial properties between the thermoplastic and wood fibers. There are five proposed mechanisms accepted for adhesive like behavior that influence the interfacial properties. Two of the five mechanisms, electrostatic forces and diffusion, would not be applicable for the co-steam-exploded wood-thermoplastic interface. The neat thermoplastics used in this study do not have ionic force components, eliminating the possibility for electrostatic forces. Diffusion is unlikely in hetero-component systems containing large molecular weight polymers. The other three mechanisms that should be considered in this study are mechanical interlock, adsorption and chemical bonding.

Mechanical interlock can be visualized as a dovetail joint; the two components do not interact or react with each other but are held in position by geometric constraints. This method of adhering two components together is the technique used in attaching dental fillings to teeth. Mechanical interlock has a limitation that the two components have a distinct interface.

Another possible method of adhering two components is by intermolecular forces. Because of the short-range distance wherein these forces are prevalent, there must be intimate association between components. From an adhesive standpoint there must be wetting of the adherend. This would allow for the various possible interactions depending upon the chemistry of the components (acid-base, London dispersion, hydrogen bonding, etc.). This method of adhesion is widely believed to be the mechanism of adhesion in all wood-based composite systems.

The third mechanism considered to be applicable is covalent bonding. This mechanism would be the direct reaction of components at the interface. Covalent bonding is possible by either free radical or ionic reactions. Free radicals are generated when certain chemicals or energy (light, heat, or mechanical disruption) are inputted into the material, which cause homolytic cleavage of primary bonds leaving unpaired electrons. Attachment of modifying agents through covalent bonding is a widely used method to derivatize cellulose fiber surfaces for use in thermoplastic composites.

Research in the wood fiber reinforced composites area has concentrated on the improvement of material properties by the addition of coupling agents through chemical reaction. Studies have investigated a variety of coupling agents that modify wood surfaces to improve performance. There are over forty coupling agents used in wood fiber reinforced thermoplastic composites [20], which include alkoxysilanes, isocyanates, and anhydrides.

Although the source of the improvement of mechanical properties is debatable, if it is increased interaction, change in distribution and orientation of the fibers, or reduced water sorption, the result of the coupling agent is that the fiber surface becomes more hydrophobic. The mechanism of three common compatibilizers: anhydrides, isocyanates and alkoxysilanes, involve interactions and reactions with the hydroxyls on the cellulose surface. The coupling agents also have portions that consist of some aliphatic or benzylic groups [21]. These groups, covalently attached to the reacting ends, must be able to bridge the interface between the wood fiber surface and the thermoplastic matrix. If this does not happen, the matrix will not be intimately entangled with the modified fibers.

Coupling agents are not always effective outside of laboratory operations. A recent study revealed that certain coupling agents lose their effectiveness when applied to large scale extrusion processes [22]. It was suggested that this was due to the addition of lubricants and other additives that negate the efficacy of the coupling agent. On the other hand, if processing conditions promote interaction and reaction between components, as in reactive extrusion, then coupling agents would not be needed.

The ability of water to interact with natural fibers also has a role in the properties of cellulose fiber-PO composites. When surfaces are modified, lowering the surface energy, the accessibility of water to the fiber diminishes, which forms a dimensionally stable fiber. Moisture content of fibers can directly influence material properties because bound water must be driven from the fiber by the PO before it can adhere to the surface. Water vapor was shown to off-gas during processing of wood fiber-PO creating micropores and density gradients within the composite [23].

In addition to the factors already mentioned, low MW species migrating to the fiber-PO interface have an important effect in creating poor adhesion by the formation of a boundary layer. Lipatov, who extensively studied filled polymer systems, explained that an interface causes restrained mobility of polymer chains (reducing entropic contributions) which impacts relaxation [24]. The result is a boundary layer that has different properties from the matrix polymer. Moreover, the lowest surface energy species are driven out of the bulk of the polymer and into the interfacial region [25]. Perapelitayna and co-workers report that the mechanical properties in filled systems are a function of filler concentration and boundary layer thickness [26].

In contrast, it was demonstrated that polypropylene chains interact with model cellulose fibers by nucleating from a cellulose fiber surface during isothermal crystallization [27]. The authors proposed that the alpha member of the polypropylene repeat unit adhered to the cellulose surface and then proceeded to crystallize forming the transcrystalline region. For this system, the results indicated the absence of a boundary layer at the interface because the PO was closely associated with the cellulose surface.

Initial work, using fiber provided by Brooks and Associates, showed that the resulting fibers from co-steam explosion processing were covered with thermoplastic. The fiber surface and thermoplastic have to undergo significant change to achieve long term close association. Any of the three mechanisms of adhesion described above would improve performance of wood-thermoplastic composites, with the latter two (primary and secondary interactions) improving the dimensional stability, durability and toughness of composites made from the co-steam-exploded material.

The research described is focused on the modification of wood fibers by steam explosion processing in the presence of thermoplastics. Three levels of material characterization are performed using microscopy, spectroscopy, and measurement of physical properties. The purpose of this research is to understand the fundamental changes in the steam-exploded materials and find how these changes impact the end properties. Understanding the changes involved would enable the modification of wood and cellulose surfaces with steam-explosion to tailor specific properties like sorption, durability, compatibility and adhesion. Material parameters, as well as, reactivity of the gaseous atmosphere within the reactor of the steam explosion process are investigated to maximize the modification of wood fibers with thermoplastic. Critical issues related to performance are examined: 1) the fibers are quantitatively assessed for degree of modification; 2) the association and location of the thermoplastic on the wood fibers is elucidated; 3) fiber sorption properties are determined; 4) chemical changes within fractionated components are assessed; and 5) morphological characterization of the material is performed.

CHAPTER 2

LITERATURE REVIEW

Fiber Modification

Wood fiber and other plant fibers like flax, ramie and hemp are composed of a large percentage of cellulose, making cellulose the most abundant natural polymer with an estimated gigaton (10^9) being generated in phytobiomass each year. The repeating unit of cellulose is the cellobiose unit consisting of two β -D 1,4 glucopyranose units. This β -linkage, along with the glucopyranose rings in chair conformations creates the opportunity for the cellulose to have a long ribbon shape. As a result, the cellulose aggregates and the crystalline structure is reinforced with intra and inter hydrogen bonding among the chains (Figure 2.1). The aggregates form microfibrils that create the structure for the fiber wall. The described morphology of cellulose gives the plant material high tensile modulus.

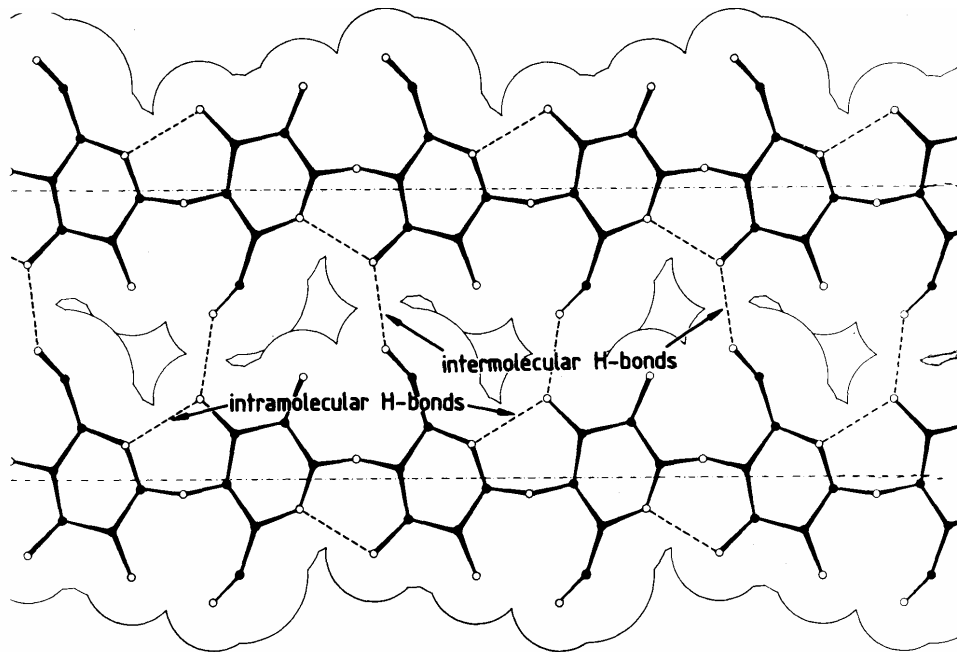


Figure 2.1. Intramolecular and intermolecular hydrogen bonds of cellulose contributing to the aggregate superstructure. From Fengel and Wegener 1989.[6]

A high tensile modulus along with high availability, low cost, and a source from renewable resources make wood an attractive material to be used either alone or in synthetic composite systems. Although, nature has perfected plant fibers for the biological cycle, material scientists are finding ways to increase the incorporation of these natural materials into construction materials and other applications. Herrmann et al. reported that natural bio-composites, combining natural fibers with bio-polymeric matrix (cellulose derivatives, starch derivatives, or polyhydroxybutyrate), have comparable specific mechanical properties to glass fiber reinforced polymers [28]. These materials offer additional options of recovery at the end of their service life that are aligned with natural biological cycles [28]. Along these lines, a process using lyocell fibers to reinforce a cellulose ester matrix has been developed [29-31] and the incorporation of wood and flax fibers into a protein-based matrix (caseinate plastic) was studied [32].

The modification of wood and other plant fiber surfaces has been the subject of a number of reviews and texts [33-36]. The following reviews the scope and current methods for modifying wood and plant fibers.

Chemical Modification ***(Esterification, Etherification, Silanes, and Isocyanates)***

Modification of wood and cellulose is a commercially available practice that has a long history demonstrated by the plethora of uses for cellulose derivatives within our society and the influence of the paper industry on our economy. Moreover, Edgar et al. recently reviewed the many applications of cellulose esters [37]. Two primary categories for wood modification are esterification or etherification [36]. In addition to these categories, modification by alkali is important in the formation of derivatives because aqueous alkali swells the crystal lattice of cellulose and also creates an intermediate to allow for the etherification of cellulose.

Esterification

Esterification is the process of converting the hydroxyl group into an ester group; with wood this is usually done through the nucleophilic addition of an organic acid anhydride or acid

chloride (Figure 2.2). Fengel and Wegener describe the use of an acid catalyst to improve this reaction by making the carbon of the carboxylic group more positive to increase the nucleophile attraction [6].

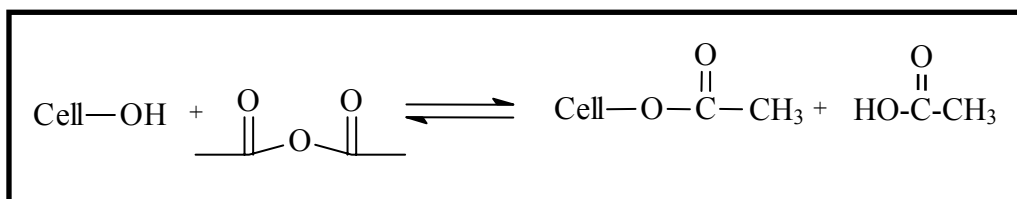


Figure 2.2. Scheme for the esterification of cellulose with an organic acid.

Esterification of wood and agrofiber has primarily focused on the use of anhydrides, with the exception of fatty acids and acid chlorides, to improve dimensional stability, preservation, and wood thermoplastic-matrix compatibility (adhesion and dispersion). A variety of anhydrides with different catalysts and solvents have been used for these applications including acetic anhydride, maleic anhydride, phthalic anhydride, succinic anhydride, and other functionalized anhydrides which are shown in Figure 2.3. The esterification of wood has been studied for a number of years and current research is turning toward methods of simplifying and reducing the cost of modification to make it commercially feasible [38-40]. However, fundamental research is still being conducted on the esterification of wood, exploring previously overlooked parameters and applying recent technology.

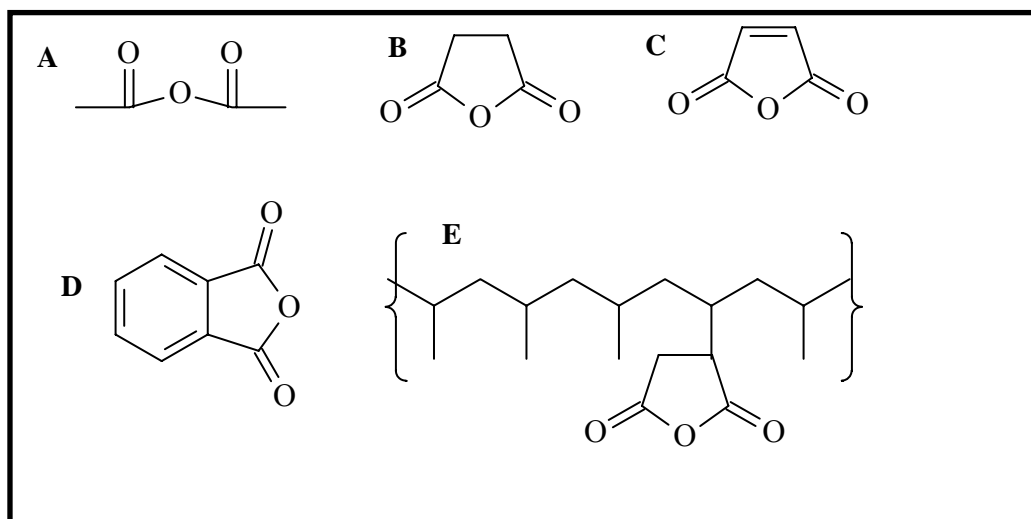


Figure 2.3. Chemical Structures of common anhydrides used to modify cellulose A) Acetic anhydride, B) Succinic Anhydride, C) Maleic anhydride, D) Phthalic anhydride, E) Polypropylene-g-maleic anhydride.

Hill and Jones measured dimensional stability of wood blocks that were subjected to esterification with carboxylic anhydrides of varying chain lengths [41]. They determined that the chain length did not influence dimensional stability. A good predictor was weight percentage gain for the prediction of volumetric swelling percentage. However, after one water soak, octenyl succinic anhydride out performed succinic anhydride in providing dimensional stabilization for wood blocks [42]. The study did not use spectroscopic methods to measure modification. On the other hand, infrared spectroscopy is a technique used to measure the chemical modification of wood by esterification by taking the ratio of absorbance of the stretching carbonyl band to that of the hydroxyl stretching band. Rensch and Riedl used this method in a study where the chain length of aliphatic anhydrides were varied by using acetic, propionic, butyric anhydrides to measure the efficiency for chemical modification of chemithermomechanical pulp [43]. A solvent effect was demonstrated in the study with a more polar solvent increasing the degree of chemical modification. When the non-polar solvent was used, the larger aliphatic anhydrides had low modification of the fiber surface.

The acetylation of wood was first reported and patented by Stamm and Tarkow [44-46]. In order to explore the feasibility of treating methods for larger scale applications, Rowell et al. suggested a treating procedure to acetylate wood with acetic anhydride that contains up to 30% acetic acid [40]. Another system developed that did not require the use of a solvent was reported by Thiebaud and Borredon who used fatty acid chlorides to esterify sawdust [47] and found this method worked well in the esterification of hemicelluloses [48]. Bagasse fiber was successfully esterified by succinic anhydride without solvent [49]. The procedure involved dissolving the succinic anhydride in a minimum amount of acetone and then the solution was mixed with the fibers and placed in a fume hood to evaporate the acetone. After that procedure the mixture was then oven dried.

Durability of wood is important and can be addressed by esterification. To enhance the photostability of wood, anhydrides (acetic, succinic, maleic, phthalic) were reacted with wood to increase the number of chromophores [50]. In the study, Chang and Chang used solid state CP/MAS ^{13}C NMR and determined that the hydroxyl group at the C-6 carbon was the group that was mainly esterified by the anhydride. That is in agreement with Felix and Gatenholm who suggested that the primary alcohol on the glucopyranose ring was the most reactive due to steric hindrance of the secondary alcohols [51]. Esterification of wood by maleic anhydride and further reactions with maleic anhydride and epoxide increased the durability of wood material against attack to white rot fungi [52]. In addition, the modification by anhydride and epoxide created wood with thermoplastic properties, which has been extensively studied and reviewed by Matsuda [53, 54].

Wood material with thermoplastic properties is desirable because it allows for wood to be compression molded, which increases the number of applications for wood use. Timar et al. continued the study of preparing wood with thermoplastic properties by comparing a classical synthesis method to a simplified technology using microwave energy for the [38, 55]. Dissolving grade pulp fibers were esterified by a heterogeneous hexanoylation reaction that made the fibers thermally deformable [56]. In the study an important issue was highlighted, esterification of cellulose with a non-solvent creates a two component composite that contain esterified amorphous cellulose components that act as a matrix while unmodified cellulose I crystallites reinforce this matrix. A scale effect was found with esterified lyocell fibers that contained a skin region of one micron that was hexanoylated, with a core that was not modified [57].

In addition to forming compression moldable materials, esterification of wood with anhydrides increased the reinforcing capability of wood for thermoplastic composites [58-60]. Specific anhydrides allow the esterification of wood surfaces for different matrices; acetic anhydride for cellulose acetate butyrate [61] phthalic anhydride for polystyrene [62], maleic anhydride grafted polypropylene (MAPP) for polypropylene [51, 63-65], maleic anhydride grafted styrene-ethylene-butylene-styrene [66, 67] or maleic anhydride grafted polyethylene [68]) for polyethylene and maleic anhydride grafted trans-1,4-isoprene rubber for trans-1,4-isoprene rubber [69]. Although maleic anhydride modified the surface of sawdust, as evident by carbonyl band in FT-IR spectra [70], Kazayawoko et al. did not find an increase in the carbonyl band of XPS spectra for wood pulp when modified with MAPP [71]. This was in contrast to a study by Felix and Gatenholm that reported after pretreating MAPP (by exposure to temperatures of 170°C), FTIR spectroscopy revealed that MAPP was covalently bonded to the fiber surface [51]. Additionally, a study by Matuana et al. explored the linkage of phthalic anhydride and MAPP to wood fibers and found that the bonding was in the form of a monoester [72]. The ring opening reaction involved the hydroxyl group of cellulose or hemicellulose and one of two carbonyl carbons of the phthalic anhydride or MAPP. Proposed were two possibilities, either the formation of a monoester or a diester. The band of the carboxyl carbonyl group was detected for the treated fibers indicating that the carboxyl group did not further react with the wood surface indicating the formation of a monoester.

Etherification

Another method of chemically modifying wood material is through etherification. As mentioned above sodium hydroxide is important in this process because a charged intermediate species is formed, which allows for the faster nucleophilic addition of epoxides, alkyl halides, benzyl chloride, acrylonitrile, and formaldehyde [36].

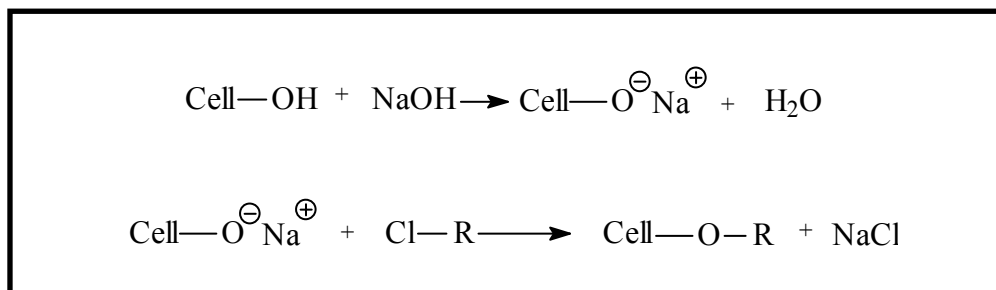


Figure 2.4. Reaction scheme showing alkali catalyzed reaction of cellulose with alkyl halide.

Epoxides, like epichlorohydrin, have a strained ring (3,4-member) containing oxygen that creates electron withdrawal from adjacent carbons. This arrangement makes epoxides relatively reactive with alcohol containing molecules like cellulose. Rowell and Chen report a method of reacting epichlorohydrin with wood preservatives like pentachlorophenol and forming new epoxides to modify wood [73].

In addition to preservation, etherification can also give wood thermoplastic properties. By etherification of wood surfaces with allyl bromide, Ohkoshi bonded two wood surfaces together by hot pressing the modified wood [74]. Results indicated that the shear strength was similar to unmodified wood. Furthermore, this technique was combined by grafting styrene onto the allylated wood surface [75]. The effect of allylation on individual wood components was also explored [76].

The thermoplasticization of wood by benzyl chloride created a wood derivative that could be pressed or extruded into films or molded products [77]. The key to this reaction was the pretreatment of wood with a NaOH concentration greater than 25% at temperatures greater than 90°C to minimize hydrolysis of wood components. Benzylation of wood particles was subsequently explored by comparing benzylated boards to particle boards containing phenol formaldehyde [78]. Although the benzylated boards had much greater internal bond strengths, the particle boards with phenol formaldehyde adhesive had greater modulus of elasticity (MOE) and modulus of rupture (MOR) values. Thermoplasticization of wood [79] and bagasse [80] was achieved at lower reaction temperatures using lower alkali pretreatment concentration by

employing acrylonitrile. Another study comparing the cyanoethylation of wood pulp to cotton found that wood pulp was more reactive because of a lower degree of polymerization for the cellulose [81].

Specific chemical agents (silanes and isocyanates)

Alkoxysilanes have been used regularly in the modification of glass-fibers and wood fiber surfaces. It is reported that the bonding strength for tensile loaded butt-joints of high density polyethylene (HDPE) bonded to wood increased significantly when vinyltrimethoxysilane was used as a coupling agent [3]. Additional evidence for a strong interface was that SEM micrographs revealed HDPE fractured within the bulk and was retained on the wood surface.

The mechanism for modification of cellulose with alkoxysilane is that the alkoxy groups on the silane are hydrolyzed to form a silanetriol as seen in Figure-9. This silanetriol can undergo a condensation reaction with other silanetriols forming polysiloxane. The hydroxyl groups located on the cellulose surface interact with the polysiloxane by the formation of hydrogen bonds with the remaining hydroxyl groups of the polysiloxane [82]. Additionally, Brebner and Schneider suggest that there is a varying degree of interactions between polysiloxane and the wood fiber surface depending upon interhydroxyl spacing [83]. Close hydroxyl spacing results with polysiloxane strongly adsorbed. Spacing is influenced by the crystallinity of the exposed surface. Amorphous cellulose is able to interact with polysiloxane forming hydrogen bonds. After adsorption of polysiloxanes on the fiber surface the alkyl group connected to the silicone of the polymer backbone has the ability to interact with the thermoplastic matrix. Hence the fiber surface is modified in a way that makes the surface compatible with the thermoplastic matrix.

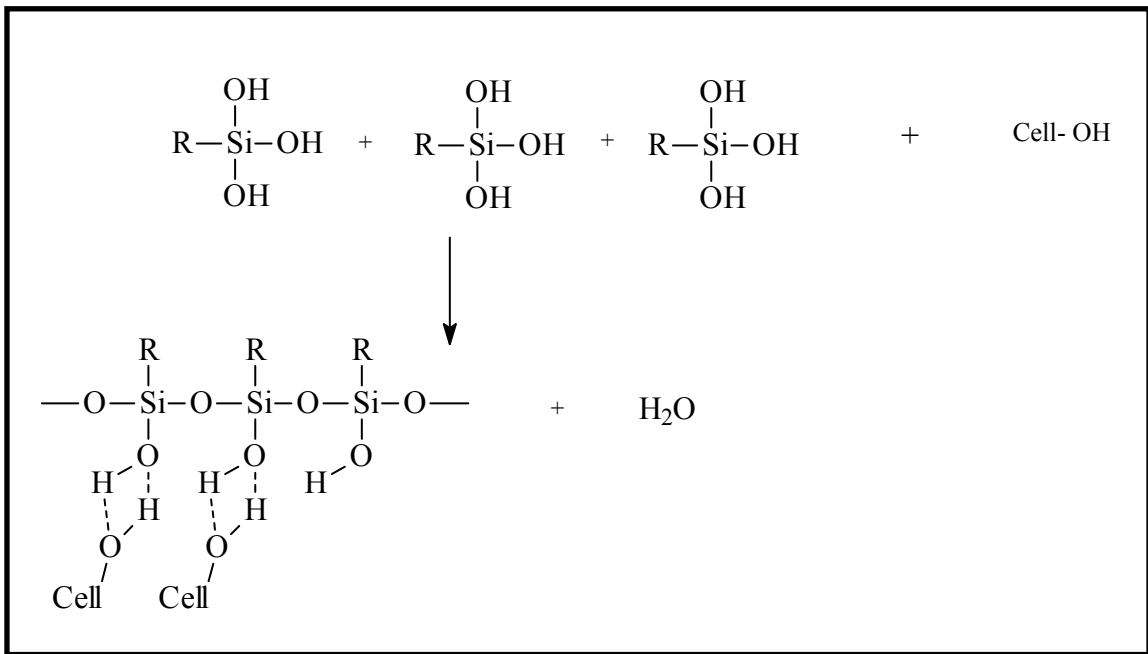


Figure 2.5. Scheme for the reaction of cellulose with alkoxy silane.

In addition to alkoxy silanes, silylation of wood had been achieved with silyl chloride [84] and amino silanes [85, 86]. Zollfrank reported that trimethylsilyl chloride was effective at evenly coating the interior and exterior of wood fibers [84]. Matuana et al. found through the use of XPS that the amino silanes were adsorbed and covalently bonded to mechanical pulp fibers [72].

An application for isocyanates, beside adhesives for wood composites, includes wood surface modifiers. Figure-10 shows the modification of the wood-fiber surface with poly[methylene(poly(phenyl isocyanate))] (PMPPI) and other isocyanates is due to the formation of covalent bonds between the hydroxyls located on the wood surface and the -N=C=O isocyanate group of the PMPPI. Infrared spectroscopy of the fiber surface reveals carbonyl linkages, providing evidence for covalent bonds [87].

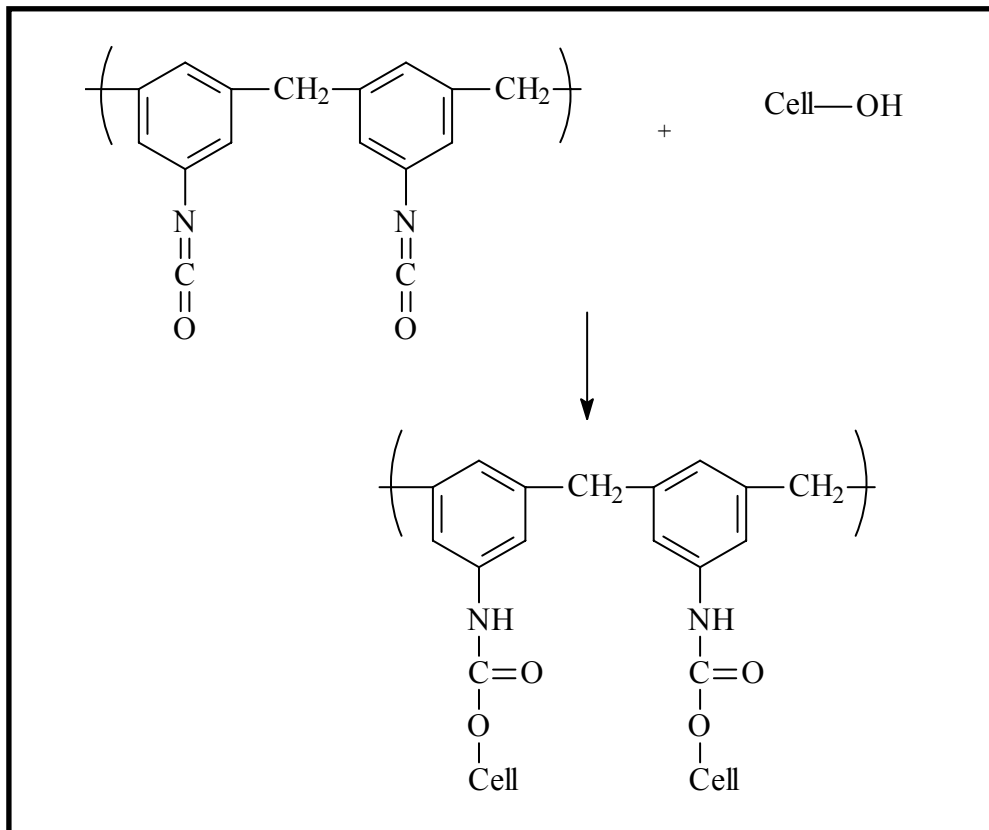


Figure 2.6. Scheme for the reaction of cellulose with PMPPI.

It was suggested that PMPPI is a good compatibilizer for wood-fiber filled polystyrene composites because the π -electrons of the phenyl groups of the PMPPI (which are covalently linked to the wood fiber) interact with the π -electrons of the phenyl groups on the polystyrene [88]. The method of introducing the PMPPI also plays a role in the performance of wood fibers. If the PMPPI was mixed with the wood fiber prior to and during mixing with the polystyrene, the result was an improvement in composite properties compared to that of introducing the PMPPI during mixing of the wood fiber and polystyrene [88]. 4-4'-diphenylmethane diisocyanate was combined with perfluoroalkyl ethanol and reacted with wood to increase the dimensional stability of wood blocks [89]. The increased stability was due to the hydrophobic fluoroalkyl group covalently bonding to the wood surface via the 4-4'-diphenylmethane diisocyanate.

Chemical treatments
(Corona Discharge, Cold Plasma, Ozone gas)

Another avenue to activate a wood surface to achieve better adhesion with polyolefins is by the modification of the surface layer by exposure to plasmas. The plasma discharge can be generated by either corona treatment or cold plasma treatment. Both methods are considered a plasma treatment when ionized gas has an equivalent number of positive and negative charged molecules that react with the surface of the present material [90]. The distinguishing feature between the two categories of plasmas is the frequency of the electric discharge. A high frequency cold plasma can be produced by microwave energy, while a lower frequency alternating current discharge at atmospheric pressure produces a corona plasma [90]. The type of ionized gas and the length of exposure influence the modification of the wood and synthetic polymer surfaces. This has been reviewed [90, 91]. Moreover, Podgorski and Roux have recently compared the polar component of surface energy of pine wood to a number of parameters for plasma modification that include power, treatment time, distance of samples to plasma source, type of gas, and the stability of plasma treatment [92, 93].

Pulp sheets with moisture contents of up to 85% were treated with corona discharge in air and nitrogen atmospheres and the chemical modification of the sheets were studied by dye [94]. No evidence of an increase in carboxylic groups was found on the treated paper surface. However, the quantity of aldehyde groups increased with increasing corona treatment. The authors did not know if the increase in bonding strength was due to a reaction of hydroxyl groups with aldehyde groups or the degradation of hemicelluloses that adsorb between the surfaces of the paper sheets. Previously, by measuring the intrinsic viscosity of cellulose solutions, Uehara and Sakata showed that air corona treatment caused a reduction in the molecular weight of cellulose [95]. With a change in gas to nitrogen, the corona treatment did not lower the intrinsic viscosity value of cellulose, thus demonstrating that the type of gas influences the degree of modification. Also, Uehara and co-workers investigated the effect of corona treatment in air on isolated individual components of wood [96]. Water and methanol extractives increased, indicating that the cellulose and hemicelluloses were changed. However, the ratio of syringyl aldehyde to vanillin (found by alkaline nitrobenzene oxidation) remained unchanged for the

corona treatments, which indicated that the non-condensed type of lignin showed no effects for the corona treatment.

After cold plasma treatment, the surface structures of polypropylene and wood were investigated by atomic force microscopy [97]. The study showed that with oxygen-plasma treatment, formation of nodular texture on polypropylene surface occurred. Upon extended exposure there was indirect evidence that the nodular bumps became stiffer. Also in this study, wood was exposed to a hexamethyldisiloxane plasma. On the nanometer scale it was revealed that Kraft pulp and filter paper both had a “lumpy structure” that was due to the plasma treatment. Additionally, a nodular structure was also noted in oxygen-plasma treated pulps [98]. Furthermore, the hexamethyldisiloxane-plasma was studied on pine wood surfaces [99]. Evidence from X-ray photoelectron spectroscopy, infrared spectroscopy, and atomic force microscopy indicated that a siloxane plasma polymer was deposited upon the surface.

Another method of modifying wood surfaces is by exposure to ozone or oxygen-fluorine gas. Hedenberg and Gatenholm exposed polyethylene and cellulose fibers, films and membranes to ozone gas [100]. The adhesion properties of the composites were improved when only LDPE underwent ozone treatment. Two mechanisms were proposed for the increase in bonding strength, which involved hydrogen bonding of LDPE that contained carbonyl groups (revealed by spectroscopy) and covalent bonding initiated by the decomposition of hydroperoxides. Chtourou and co-workers increased the strength properties of pulp and polyethylene composites by exposing the polyethylene to oxygen-fluorine gas [101]. The authors found that upon exposure, the specific (acid-base) interaction parameter increased, and the improvement of properties was attributed to hydrogen bonding between both carbonyl and hydroxyl groups and fluorine and hydroxyl groups.

Grafting

Graft copolymerization of vinyl monomers onto wood and cellulose based materials was first reported in 1953 [102]. Since that time, modification of cellulose by graft copolymerization has received much attention: see the review of Hebeish for techniques [103] and Meyer who reviewed applications for wood graft copolymers [104]. Stannett highlighted four challenges of modification of cellulose by graft copolymerization; homopolymerization of monomer, limited

cellulose involvement, limited control of molecular weight, and poor replication of grafting yields [102]. Although these challenges were proposed over twenty years ago there has not been a solution that has allowed the commercial production of these products.

An increase in the efficiency of graft copolymerization of monomers onto natural surfaces was reported when the fiber surfaces of wood and plant-based materials have been activated. Hill and Cetin report that methylacrylic anhydride modified wood allowed for the grafting of styrene and methyl methacrylate [105]. A subsequent study by Hill and co-workers used the method to protect wood against UV irradiation [106]. Grelier et al. grafted isocyanate, which contained an UV absorbing chromophore to medium density fiber boards by microwave activation [107]. Maleic anhydride along with allyl glycidyl ether was used to activate pine wood blocks by oligoesterification, in order to graft bis(trimethylsiloxy)methylsilane and hydride-terminated polydimethylsiloxane [108]. Absorbency of cellulose fibers was improved by first activating the surface with an ethoxy silane and then by the copolymerization of acrylic acid onto the surface, initiated by potassium persulfate [109].

Compared with the number of studies for graft copolymerization onto cellulose, research on the copolymerization onto more complex substances like wood and plant fiber is scarce. One reason of this complication is the presence of lignin. Lignin and other extractives found in wood act as antioxidants through resonance stabilization of free radicals, as seen in Figure 2.11, thus inhibiting grafting and polymerization. Lignin causes an inhibition period in the copolymerization process [110]. The nature of lignin (added vs. in-situ) and the type of catalyst influence its inhibiting ability of graft copolymerization [111-112]. However, depending upon the reaction conditions, lignin may become more modified than the holocellulose [113-116] or reduce homopolymerization of monomer due to a chain transfer mechanism [110], as seen in Figure-12.

Zheng and co-workers have described the participation of lignin in the graft copolymerization of polymethylmethacrylate onto bagasse pith initiated by Fe^{2+} and hydrogen peroxide [117] and potassium permanganate [118]. Both papers reported that lignin was more susceptible to grafting and specifically, hydroxycyclohexadienyl radicals formed from lignin participated in the copolymerization. Parallel with the studies on bagasse, the same initiators were used in the graft copolymerization of stone ground wood pulp [116, 119]. It was proposed that phenolic hydroxy radicals produced by reaction with ferric ions initiated copolymerization

[116]. The initial stage of delignification (loss of lignin by 0.6%) by the sodium chlorite method of pulping substantially increased the grafting efficiency, but subsequent delignification did not have the same effect [119]. The authors also proposed, depending upon reaction conditions, that the phenyl ring formed phenoxy radicals that either initiated copolymerization or decomposed the phenyl rings of lignin. Marchetti and co-workers reported the deposition of MnO₂ on the wood cell wall (when KMnO₄ was used as an initiator), which contributed to the radical chain transfer onto wood [120].

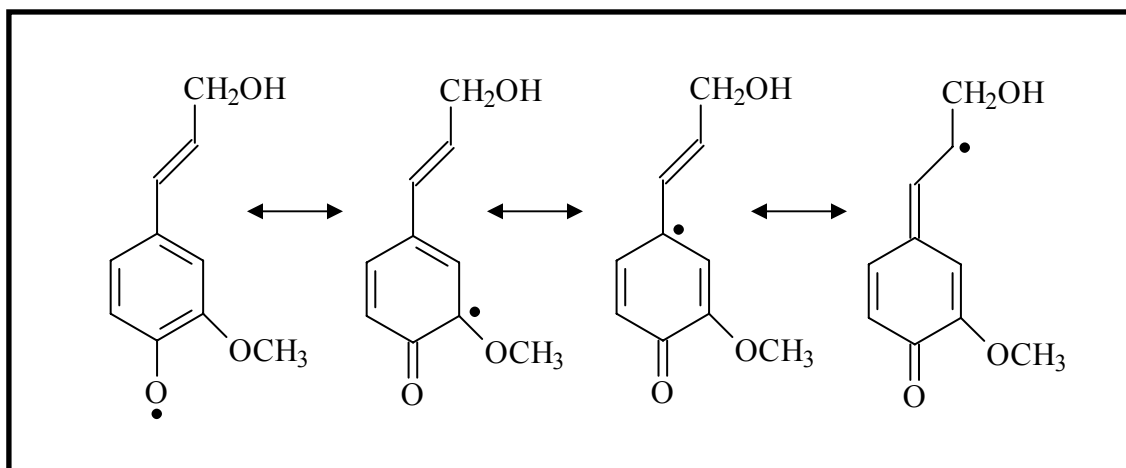


Figure 2.7. Lignin serving as an antioxidant/inhibitor due to resonance stabilization of free radical.

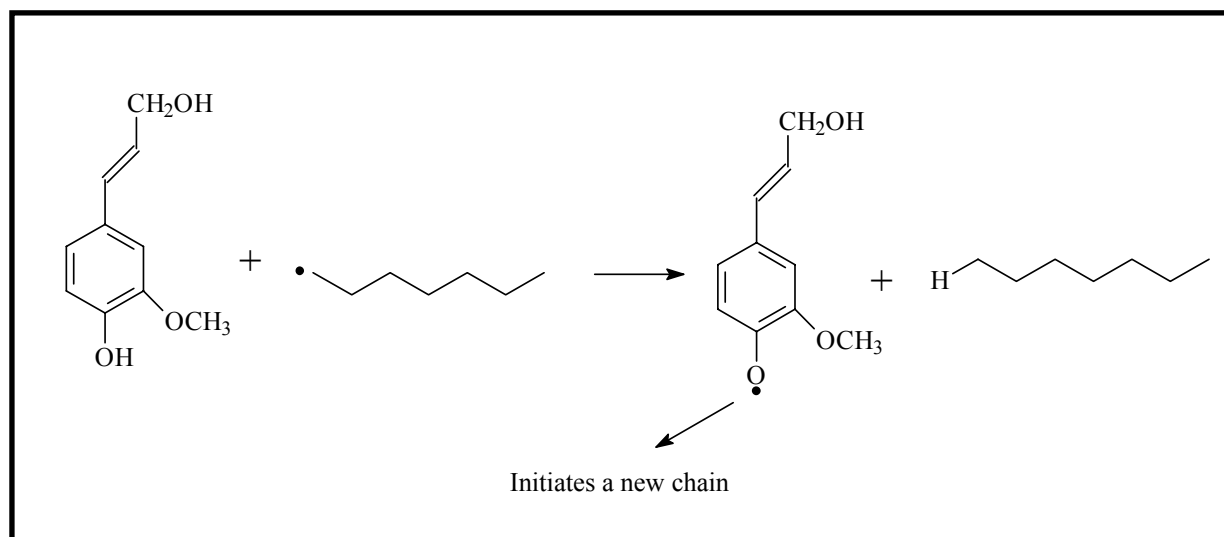


Figure 2.8. Lignin serving as a chain transfer agent limiting homopolymerization.

Ghosh and co-workers explored the effect of lignin on the copolymerization in partially delignified jute fibers. The initial delignification by sodium chlorite only slightly improved percent grafting, but upon the presence of only 0.8% lignin, the grafting efficiency was almost doubled [121]. The initiator used in the study was NaIO_4 and CuSO_4 . The authors suggested that IO_4^- causes oxidation of lignin constituents to quinonoid structures that inhibit grafting [121, 122]. Sikdar et al. reported that in order to graft copolymerize acrylonitrile onto jute, for a 15% weight gain, half of the lignin needed to be removed [123]. Ghosh et al. later used an initiator system comprised of $\text{K}_2\text{S}_2\text{O}_8$ and MgCl_2 and copolymerized acrylamide-formaldehyde resin onto jute fiber [124]. Moreover, in a study by Sahoo et al., a complex initiating system was used and the physical properties of modified fibers were evaluated as a function of the percent grafting for the graft copolymerization of unpulped, pulped, and pulped and bleached jute fiber [125]. Another dual catalyst system, potassium persulfate and copper sulfate was used in the copolymerization mixture of acrylamide and methyl methacrylate onto jute fiber [126]. The mechanical properties of the jute fibers were investigated and there was a balance for optimum values between delignification and percent grafting. High levels of delignification allowed for higher levels of grafting. However, for delignification approximately greater than 50%, the modulus of the grafted fiber was reduced [126].

An important limitation of studying jute and other grasses is that lignin constituents are different for grasses, softwoods, and hardwoods. Meister and co-workers found that hardwood lignin produces the most graft copolymer followed by softwood lignin, and then lignin from grasses [127].

Copolymers of lignin have been derived by using peroxide initiators with redox systems [128-130], derivatized lignin [111, 131, 132] or chemi-enzymatic initiators [111, 133-136]. The chemi-enzymatic approach used laccase to initiate phenoxy radicals or phenoxy quinones that either oxidize or reduce the peroxide [130]. Increased grafting efficiency with the chemi-enzymatic approach compared with a ferrous ion peroxide initiating systems was reported [133]. It was suggested that the increase was due to a greater percentage of lignin radicals compared with initiated monomer chains. This was confirmed in a subsequent study that found the decomposition of peroxide to be improved by the addition of laccase in the presence of 3,4-dihydroxybenzoic acid and guaiacol (model lignins) [134]. In a recent study, Mai and co-

workers demonstrated that alkoxy radical formation was due to the reduction of peroxide and the oxidation of the phenoxy radicals led to quinones [135]. They suggest “a high rate of phenoxy radical generation is more crucial for the initiation of polymerization than is a higher steady state concentration of these radicals”.

Young and Achmadis studied “graft pulping”, as a technique for graft copolymerization between aspen wood and acrylonitrile and styrene during alcohol-based solvent pulping [114]. Free radicals that are produced during delignification are used to initiate the copolymerization of monomers present. The authors found that lignin was the primary site for grafting of the monomer. However, polymer loading (weight gain of fiber by copolymerization) was low with minimal polymerization of monomer. The method was improved by the addition of a two stage pulping process that included a peroxide-ferrous ion initiating system.

Adsorption of Block Copolymers and Amphiphilic Molecules

Intermolecular forces are considered to be one mechanism for adhesion. Another avenue for the modification of wood and wood fiber surfaces is irreversible adsorption of polymers. This is especially relevant for amphiphilic sequential block copolymers that are able to interact with wood and cellulose surfaces while changing the surface energy. Surface modification by adsorption can change the sorption characteristics of fibers, add dimensional stability to wood and compatibilize wood fibers for use in thermoplastic composites.

Mizumachi described how the conformation of adsorbed block copolymers in solution influenced the concentration of polymer adsorbed on the surface-solution interface [137]. Poor solvent polymer interactions produced an adsorbed polymer with a compacted structure, allowing for a higher concentration of adsorbed polymer as seen in Figure-2.13. The extent that the solvent swells the solid (wood fiber) is also important in the saturation value of adsorption [137]. Additionally, Fujimura et al. measured the radius of gyration for hydrophilic acrylic polymers that were adsorbed to wood [138]. They found that the number of hydrophilic portions of the polymer had a greater effect on the saturated amount of adsorption than the increase in the radii of gyration of the polymer.

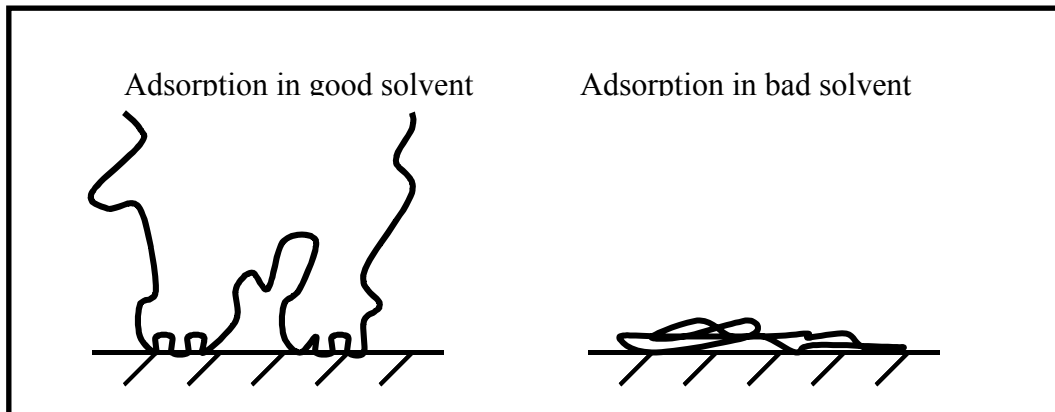


Figure 2.9. Conformation and concentration of adsorbed polymer at a solid-liquid interface is affected by solvent-polymer interactions.

Other areas of polymer science have made use of surface modification through adsorption of block copolymers. Boury and Proust used poly(oxyethylene)-poly(oxypropylene) A-B-A block copolymers to change the surface energy of glass and calcium alginate films and fibers [139]. The authors described how the block copolymers that adsorbed onto the surface of glass rearranged depending upon the polarity of the environment and the rigidity of the block copolymer.

The modification of cellulose surfaces was accomplished with ionic interactions between oppositely charged adsorbed species and wood or cellulose surfaces. Alinec described the use of cationic latex to improve many properties of paper [140]. The benefit of cationic latex was that there was an electrostatic attraction to naturally negative charged pulp fibers. Upon drying of the pulp, the latex formed a film, which imparted a hydrophobic characteristic to the paper. Biswas and Chatteraj studied the adsorption of a variety of cationic surfactants onto cellulose in water [141]. There was a maximum adsorption for a concentration of surfactants in the bulk solution that was below the critical micelle concentration. Also, the authors found that there was a contribution to the intermolecular forces from the hydrophobic interaction between the surfactant and hydrophobic sites on cellulose. Research in the Wood Science and Chemistry Departments of Virginia Tech has demonstrated the importance of the ionic and hydrophobic moiety of

modified hemicelluloses in the adsorption to regenerated cellulose films [142]. Moreover, a model compound, pullulan abetate, with a specific degree of substitution was used to further study the modification of cellulose for the design of wood-based composites [143]. Both of these studies can be found in the appendix.

Block-copolymers have been designed that adhered to wood in order to change the surface free energy of wood. Kosonen et al. made a polystyrene-*block*-poly(styrene-coacrylic acid) polymer that coated wood in a water-based solution [144]. An increase in hydrophobicity of coated veneers was found with a low concentration of the block co-polymer (0.02 wt%). In addition, the ultimate yield stress and strain increased for modified wood flour polystyrene composites. Chen and co-workers reported a similar finding when they adsorbed a modified lignin-styrene graft copolymer from a N,N-dimethylformamide solution onto wood surfaces [128, 129, 145]. The wood samples became more hydrophobic with an increase in contact angle by 60%. Also, the lap shear strengths of styrene coated wood composites increased in these studies.

Other studies have demonstrated modification of wood and paper surfaces through the adsorption of stearic acid vapor [146] and naturally occurring volatile organic compounds [147]. Electron spectroscopy for chemical analysis (ESCA) studies and observations of water droplet spreading were used as evidence of modification. A later study by Raj and Kokta used stearic acid to modify kraft pulp in order to improve dispersion of the pulp within polypropylene composites [148]. Adsorption of stearic acid in vapor and solution phase was investigated in that study. Although adsorption played a role in the modification by fatty acids, it is debatable that the mechanism of modification is always due to adsorption; stearic acid might have become chemically bound through esterification.

Natural amphiphiles like xylans were also used to modify pulp fibers. Henriksson and Gatenholm found that by controlling parameters such as pH, temperature and time the surface of cotton linters had varying morphology due to the adsorbed hemicellulose from water solutions [149]. A subsequent study demonstrated that the adsorbed xylan improved the bonding ability of the fibers [150]. A key factor in sorption modification of fibers was the charge of the xylan. Anionic xylans were able to increase the water retention values of the fibers, which in turned affected the drying of the fiber network. Yllner and Enstrom studied the adsorption of xylans from the sulfate cook onto cellulose fibers [151, 152]. The adsorption was correlated with the

concentration of xylan in the sulfate cook. A portion of the xylan remained adsorbed to the cellulose fibers after cold alkali extraction. The authors attributed this to xylan crystallization on the fiber [152].

The adsorption of lignin, another natural polymer found in wood, was also studied in relation to cellulose fiber surfaces [153-155]. Increasing lignin concentration and calcium ions (that “coagulate the lignin”) both increased the amount of lignin adsorbed to the fiber surface. A cationic polyelectrolyte improved the attachment of the lignin. This attachment of lignin became irreversible at high ratios of lignin and cationic polyelectrolyte, which created a positively charged complex. Additionally, the assembly of the adsorbed lignin was influenced by the procedure of adding cationic polyelectrolyte. With a step procedure of first adding the polyelectrolyte the lignin adsorbed as granular structure. In contrast, adsorption of lignin-polyelectrolyte complexes occurred either in a thin layer or large aggregates.

The above studies demonstrate that the surface of wood can be modified by irreversible adsorption of block copolymers and amphiphilic molecules. Some important factors in adsorption are the charge of molecules, concentration of the molecules, pH of the solution, the solubility of the molecule and the rigidity of the molecule.

Steam-Explosion

Steam-exploded wood was characterized by a number of different authors. Tanahashi reported a complete review of his work that focused on the changes in structural, chemical, and physical properties of steam exploded wood [156]. The steam explosion affected all constitutive polymers of wood. The hemicelluloses were hydrolyzed to oligosaccharides and monosaccharides, which became water extractable. The molecular weight of lignin was reduced and the degradation mechanism was attributed to free radical homolytic cleavage of aryl ether linkages. Amorphous cellulose was either hydrolyzed or transformed to crystalline cellulose. The portion of crystalline Cellulose I α increased. These findings are in agreement with work by other authors [157, 158]. Hemmingson investigated the structure of lignin from steam exploded wood and found that two-thirds of the aryl ether linkages are cleaved in the steam explosion process [159]. Both acid hydrolysis and radical reactions were attributed to the decomposition of lignin.

Additionally, Tanahashi explored the softening temperature of steam-exploded wood [156]. The major difference between the steam-exploded wood and the non-treated wood was the disappearance of a shoulder peak at approximately 260°C and a new peak forming at approximately 150°C. The author attributed the disappearance of the shoulder to the decomposition of the lignin carbohydrate complex and the appearance of the new peak to liberated lignin. The softening of extracted constitutive components from steam-exploded wood was investigated further. The respective softening temperatures for steam-exploded hemicellulose and lignin were 77°C and 138°C.

Furthermore, a number of studies investigated the ultrastructural changes of steam-exploded wood [160-162]. Donaldson et al. reported that steam-explosion of softwood caused lignin to flow and aggregate, and surface tension effects were attributed to the aggregation [160]. The authors described the distribution of lignin as “dense particles of lignin suspended in a web of cellulose microfibrils.” The aggregation of lignin, along with removal of hemicelluloses and fragmentation of the fiber wall increased the porosity of steam-exploded wood. Similar findings were reported by Michalowicz et al. who revealed the formation of lignin droplets inside the lumen up to the size of 1 micrometer [162]. In addition to the lignin clusters found in the lumen, Kallavus and Gravitus reported the appearance of lignin spherical particles within the cell wall between separated wall lamellae [161]. Additionally, the authors revealed the surface morphology of steam-exploded fibers with the use of a scanning electron microscope. The preparation techniques influenced the surface of the fiber. When the fibers were allowed to air-dry, lignin, polyoses and sugars adsorbed to the surface, covering the fibrillated morphology.

The conditions for steam explosion and the wood species influence the resulting morphology. Without flash hydrolysis, lignin still forms spherical droplets when exposed to high-pressure steam [162]. A severity factor (reaction ordinate (R_0)) for steam-explosion characterizes the conditions for explosion and involves temperature and time. Glasser and co-workers have explored how the severity of steam explosion influences the recovery of fractionated polymers from wood [158, 163, 164]. Only the mildest steam-explosion conditions would allow for the recovery of heteropolysaccharides in polymer form [163]. In the same study the authors used a variety of biomass sources, and found diversity in responses for the differing biomass. Kalluvus and Gravitus reported similar findings when they investigated the effect of anatomical features on the explosion of wood. In their conclusions they stated that wood ray

cells retard the steam-explosion process while vessel elements promote it [161]. It should be noted that with severity conditions of $\log R_0$ 4.0, after water extraction, there was no remaining hemicelluloses in red-oak steam exploded fiber [164]. Upon increased severity the recovery of alkali-soluble lignin increased to greater than 80%. The increased severity increased the contamination of lignin with furfural. Hence, steam-explosion has demonstrated the ability to fractionate biomass fiber.

Composites containing Steam-exploded Wood

Steam-explosion for wood and biomass has been utilized for pulping [165], pretreatments for enzymatic hydrolysis of cellulose [166], deinking of recycled paper [167], and pretreating wood for fillers in thermoplastic composites [168]. Takatani and co-workers compared steam-exploded fiber with wood flour for use as a filler in thermoplastic composites [168]. The authors reported that steam-exploded wood-filled thermoplastic composites had higher dimensional stability and greater fracture strength compared with the wood flour. The steam-exploded wood flour also improved the properties of wood flour filled composites when it was used as an extender [168]. Steam-exploded hemp bast fibers were also explored as a filler for polypropylene composites [169]. While the fibers increased the tensile modulus of the composites, percent elongation declined, and strength at yield declined (except for composites with MAPP compatibilizers). Angles et al. used steam-exploded softwood fibers that were untreated and treated with MAPP in propylene composites [170]. Treated fibers were found effective for the improvement of mechanical properties of the wood filled polypropylene composites, while untreated steam-exploded fibers decreased the strength of the composite. The surface of steam-exploded flax fibers was modified with allyl chlorides for the potential use in thermoplastic composites [171]. The above studies demonstrated that steam-explosion was practical in the pretreatment of fibers for thermoplastic composites, but modification with coupling agents improved composite performance.

In addition to composites that contain thermoplastics, steam-exploded wood and other biomass has been used to form “binderless” panels. Angles and co-workers investigated the effect of pressing temperature and time on panel strength and dimensional stability [172]. Elevated temperatures above the softening temperature of lignin were required for composites to

achieve desired physical and mechanical properties. A subsequent study by Angles et al. investigated the pretreatment of softwood with sulphuric acid before steam-explosion and the severity as measured by the reaction ordinate on the properties of compressed panels. Additional lignin was added to the steam-exploded fiber as a natural binder for the compression molded panels, which improved internal bond and mechanical properties of the panel. Startsev and co-workers used the steam-explosion process to make binderless panels, which they named “thermobalite” [173]. They performed extensive dynamic mechanical analysis tests on thermobalite using birch wood as a comparison and found that the thermobalite had a reduced glass transition temperature and was subsequently lowered by pre-humidifying the birch chips prior to steam-explosion. Steam-exploded oil palm frond was also investigated for the manufacture of binderless boards [174]. The authors attributed the strength of the boards to lignin-furfural linkages that were synthesized during compression molding.

Oxidation of Polyolefins

Degradation of polyethylene and polypropylene in the presence of oxygen has a number of schemes involving various side reactions that go beyond the scope of this paper. However, the basic autoxidation of PO involves the formation of peroxide groups on the PO backbone [175]. This leads to scission of the polymer chain along with the formation of a number of functional groups on the degraded PO such as alcohols and ketones.

The activation energies for autoxidation and thermal degradation were determined by a number of authors. Kotoyori determined the activation energy of degradation for commercial polyethylene and polypropylene in air, oxygen and nitrogen [176]. Additionally, the activation energy was determined as a function of relative humidity. As seen in Table-1 the polypropylene had lower activation energies than polyethylene in all three atmospheres. Moreover, the activation energy decreased as the relative humidity increased. Kotoyori indicated that with the presence of oxygen, degradation begins to occur at temperatures around 200°C.

Table-2.1 Activation Energies and Log Frequency Factors for Thermal Degradation of Polyolefins								
	in air		In oxygen		in nitrogen		100% rH	
	activation energy	ln A	activation energy	ln A	activation energy	ln A	activation energy	ln A
Polyolefin	(kcal/mole)		(kcal/mole)		(kcal/mole)		(kcal/mole)	
Polyethylene	14.7	12.6	17.1	15.9	53.6	34.8	10.9	8.8
Polypropylene	13.6	12.1	14	13.7	35.8	22.8	x	x

Data determined by differential thermogravimetric analysis by Kotoyori 1972[176]

A number of studies have approached oxidation of PO that is submerged in an aqueous media while controlling the partial pressure of oxygen of the atmosphere. These wet air oxidation studies have indicated the type of by-products that were formed as a result of degradation. Acetic, formic and glycolic acids were present in the aqueous solution after exposure to temperatures greater than 260° Celsius for at least ten minutes. Partial pressure of the oxygen was a key variable in the wet air oxidation of the PO. Krizner et al. indicated that “no valorizable compounds were detected...”, implicating wet air oxidation as a method for degradation of PO waste [177].

It is important to reiterate key features of the oxidation of PO as it relates to this current research. Oxidation can easily occur at temperatures below the conditions used in steam-explosion. Additionally, the presence of moisture decreases the activation energy of the PO. Both of these factors suggest the feasibility of using steam-explosion to oxidize the thermoplastic.

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