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COMPOSITES FROM MALEATED POLYOLEFIN-GRAFTED
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COMPOSITES FROM MALEATED POLYOLEFIN-GRAFTED WOOD PARTICLES
PRODUCED VIA REACTIVE EXTRUSION

By

Karana Carlborn

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ABSTRACT

COMPOSITES FROM MALEATED POLYOLEFIN GRAFTED WOOD PARTICLES PRODUCED VIA REACTIVE EXTRUSION

By

Karana Carlborn

This study examined the concept of using a reactive extrusion process to develop a new, formaldehyde-free binding system for wood composite products. The surfaces of wood particles were modified by grafting maleated polyethylene (MAPE) and maleated polypropylene (MAPP) compounds through a continuous reactive extrusion process. MAPE content was varied to study the effect of material composition on grafting efficiency, while extruder barrel temperatures and rotational screw speeds were varied to evaluate the effects of processing conditions on the modification of wood particles. Polymer molecular weight effects were followed using MAPP with different molecular weights. Efficiency of the modification was assessed using FTIR, ^{13}C NMR and XPS surface analysis techniques, along with a titrimetric analysis to verify the esterification reaction between the wood particles and maleated polyolefins. Composite panels were made from wood particles modified with MAPE and MAPP binding agents under two different manufacturing methods. Specific contrasts of (i) base resin type, PE vs. PP, (ii) molecular weight/maleic anhydride content in MAPP binding agents, and (iii) the manufacturing methods (reactive extrusion vs. hot press) were investigated to determine the effects of these factors on the physico-mechanical properties of the composites. Finally, a response surface method using a Box-Behnken design was constructed to statistically model and optimize the material compositions-processing conditions-mechanical property relationships of formaldehyde-free wood composite panels.

FTIR, ^{13}C NMR, XPS and titration data confirmed the grafting of maleated polyolefins onto the surface of wood particles through an esterification reaction, while the level of grafting of MAPE onto wood particles was determined to be a function of the MAPE concentration. However, there was no significant difference found in grafting efficiency at different extrusion processing conditions; rather all of the conditions resulted in adequate grafting. Similarly, there was no difference in grafting efficiency with the molecular weight of MAPP. Reactive extrusion was found to be a suitable technique for the modification of wood particles with maleated polyolefins for all of the material compositions and processing conditions studied. Mechanical property test results indicated that most composite panels met or even exceeded the standard requirements for particleboard of medium density. While extruding the particles before panel pressing gave better internal bond (IB) strength, superior bending properties were obtained through compression molding alone. MAPP-based panels outperformed MAPE-based panels in stiffness. Conversely, MAPE increased the IB strength of the panels compared to MAPP. Relationships between material compositions, processing conditions and both flexural strength (MOR) and IB strength of the panels were described by linear models. Increasing any of the manufacturing variables resulted in greater MOR and IB strength. Flexural stiffness (MOE) was described by a quadratic regression model. Increased MOE was obtained through higher pressing times, binding agent concentrations and/or pressing temperatures, although binding agent concentration had less effect on MOE at higher pressing temperatures. Numerical optimization showed that panels with desired mechanical properties could be made under a range of manufacturing conditions.

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LIST OF ABBREVIATIONS

AV	--	Acid Value
EPA	--	Environmental Protection Agency (US)
DRIFT	--	Diffuse Reflectance Fourier Transform
FTIR	--	Fourier Transform Infrared Spectroscopy
GI	--	Grafting Index
HI	--	Hydroxyl Index
IB	--	Internal Bond
MAPE	--	Maleated Polyethylene
MAPP	--	Maleated Polypropylene
MDF	--	Medium Density Fiberboard
MF	--	Melamine Formaldehyde
MFI	--	Melt Flow Index
MOE	--	Modulus of Elasticity
MOR	--	Modulus of Rupture
MW	--	Molecular Weight
NMR	--	Nuclear Magnetic Resonance (Spectroscopy)
OSB	--	Oriented Strandboard
PB	--	Particleboard
PE	--	Polyethylene
PP	--	Polypropylene
PF	--	Phenol Formaldehyde
RF	--	Resorcinol Formaldehyde
SV	--	Saponification Value
UF	--	Urea Formaldehyde
WPC	--	Wood-Plastic Composite
XPS	--	X-Ray Photoelectron Spectroscopy

CHAPTER 1

INTRODUCTION

Wood-based composites are a multi-billion dollar industry in North America (1). Manufacturing plants produce vast quantities of reconstituted wood products such as particleboard, oriented strandboard (OSB), medium density fiberboard (MDF) and many others. These composite products are commonly made using formaldehyde-based adhesives, including urea-formaldehyde, melamine-formaldehyde, and phenol-formaldehyde (1-3). In 1998, 1,780 kilotons of adhesive resin solids were used to produce primary glued wood products (excluding the adhesive used to bond furniture and other secondary wood products). Of this amount, nearly 92% were formaldehyde-based adhesives (1). Wood-based composite products find wide use in building construction, where they are utilized as roof sheathing, wall board, floor underlayment, wood I-joists and a number of other applications (1-3). The furniture industry is also a major consumer of wood composites, notably particleboard and medium density fiberboard, which are commonly overlaid with veneer to make cabinets, shelving, tables and more (1-3).

The use of wood composites bound with formaldehyde-based adhesives in indoor applications is a concern because these adhesives are known to release formaldehyde both during panel pressing and service life (1, 4-8). Plants that produce wood composites using formaldehyde-based adhesives emit harmful chemicals to the environment. These include phenol, formaldehyde, ketones, and other volatile organic compounds (1, 4-7), which are classified as hazardous air pollutants (HAPs) by the United States Environmental Protection Agency (EPA) (7). Wood composites bound with

formaldehyde-based adhesives also release formaldehyde over time (1, 7, 9). Although wood composites made today emit far less formaldehyde than those made 20 years ago, the problem has not been eliminated (1). Formaldehyde and other toxic compounds may be present in large amounts in both indoor and outdoor air as a consequence of the use of these adhesives (4-8).

As a result of public concern about the environment, the US EPA enacted new emission standards for facilities that manufacture plywood and composite wood products in September of 2004 (7). These rules affect both new and existing plants that produce at least 10 tons of any one HAP per year, or any combination of 25 tons of HAPs per year. These regulations may spur industry to find new ways to bind composite products without the use of formaldehyde-based adhesives.

In recent years, there have been several studies into environmentally friendly wood composites (1, 9). Some of the areas that have been investigated include urea-formaldehyde adhesives with low formaldehyde-to-urea molar ratios, and the development of natural adhesives such as tannin, lignin, soybean and cornstarch adhesives (1, 9), phenol-formaldehyde resins modified with either lignin (10-12) or tannin (13) and adhesive made from decayed wood (14). Additives that reduce formaldehyde release during composite pressing and during board use have also been developed (1, 9). Different types of fiberboard have been made without synthetic adhesives using steam explosion (15), wood surface activation using Fenton's reagent (16) and wood fiber binding via lignin activation (17). A cellulose-based composite using allyl glycidyl ether grafted polyethylene as a binder was recently reported (18). Esterification of wood particles or other cellulosic material with anhydrides in a solvent

system has also been used as a basis for formaldehyde-free composites (19-25). Although several approaches have been developed to reduce formaldehyde emissions, some of them cannot be implemented in the industrial production of wood composite products because the processes are not cost-effective, not environmentally friendly, or lead to products with undesirable properties such as long press time, dark coloration of the panel, low resistance to moisture, moderate strength, etc.

Control of emissions from wood composite mills and glued wood products is still one of the major challenges facing the wood composites industry since the government is continuously developing and implementing stringent regulations to eliminate formaldehyde emission into the environment. A new approach to reduce and/or eliminate formaldehyde emissions from wood composite products will be addressed in this research project.

The technology proposed in this project is based upon the reaction between the carboxylic acid groups of maleated polyolefins and hydroxyl groups on the surface of wood. This reaction results in the grafting of a pendent polyolefin chain to the wood surface through an ester linkage. Several authors have studied this reaction with maleated compounds and wood particles (or other cellulosic materials), usually in an attempt to evaluate maleated compounds as compatibilizers between hydrophilic wood fibers and the hydrophobic polymer matrix in wood-plastic composites (30-35). However, most of this previous work focused on fibers modified through a solvent-based process where the maleated compounds were dissolved in heated xylene, toluene, N,N-dimethylformamide (DMF) or other organic solvents, followed by the addition of cellulosic particles (30-34). Cellulosic fibers that have been grafted with maleated

polyolefins have to be filtered and dried after modification, which makes this process both cost-ineffective and time consuming (30-34). Solvent disposal is also an issue with this modification process because some solvents may be harmful to workers and the environment.

In order to produce modified wood particles that could be used to make alternative composite panels, it is necessary to change from a solvent-based process to a dry process. A solvent-free process that has been reported in the literature utilized a thermokinetic mixer to modify wood particles with maleated polypropylene (33, 35). In that work, a heated, high-intensity mixer was used to graft maleated polypropylene onto wood fibers. However, the esterification reaction between wood particles and maleated polypropylene could not be confirmed through surface characterization techniques (33, 35).

An effective dry process for grafting maleated polyolefins onto the surface of wood particles is still needed in order to produce the large volume of modified wood particles required to manufacture and commercialize formaldehyde-free wood composite panels. This study will investigate the use of reactive extrusion as a novel dry process for the surface modification of wood particles needed to manufacture formaldehyde-free wood composites.

Reactive extrusion is a technique that can be used for the chemical modification of compounds, usually polymers that can melt during processing. Because no solvent is involved during processing, reactive extrusion is an environmentally friendly technique for surface modification. It also allows for control of reaction times and temperatures through variation of rotational screw speeds and extruder barrel temperatures. Reactive

extrusion offers the advantage of intensive mixing of components in a short time, especially in a twin-screw extruder, which ensures a more thorough reaction of components (36). This process also has the advantage of low retention times in the extruder, so a series of different reaction conditions can be tested in a relatively short period of time. Examples of reactive extrusion for wood fiber surface modification were not found in the open literature, likely because the wood component does not melt and flow in the extruder. However, the ease of processing and control of reaction conditions makes this technique attractive for wood fiber surface modification.

We hypothesized that maleated polyolefins would chemically react with hydroxyl groups on the wood particle surfaces during reactive extrusion (a dry process), resulting in wood particles with surface grafted polyolefin chains. During panel manufacturing, the pendent polyolefin chains attached to the wood particles are expected to melt and flow under heat and pressure in the hot press, forming entanglements. The entangled polymer chains will then lock together after cooling, forming direct particle-particle bonds. This process would result in a formaldehyde-free wood composite panel manufactured without any additional adhesive.

Objectives

The main goal of this work is to study the concept of using a reactive extrusion process as a means of developing a new, formaldehyde-free binding system for wood composite products. The following specific objectives must be accomplished to achieve the main goal of this project:

1. Evaluate the effects of material composition (binding agent types and content) and extrusion processing conditions (temperature profile and rotational screw speed) on the level of grafting (surface properties) of wood particles after the reactive extrusion process;
2. Characterize the surface of unmodified and modified wood particles in terms of chemical compositions (both elemental and functional groups);
3. Manufacture composites and evaluate their physico-mechanical properties;
4. Establish the relationships between material composition, processing conditions, and physico-mechanical properties in order to identify the major factors that govern the performance of formaldehyde-free wood composite products manufactured through a reactive extrusion process.

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CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

Chemical Composition of Wood

Wood is a complex, multi-component material composed of several compounds. Wood is primarily composed of cellulose, hemicellulose and lignin, with minor components extractives and ash. Although amounts of these components vary between species, wood composition is approximately 40-45% cellulose, 15-30% hemicellulose, 20-30% lignin, 1-10% extractives and 0-1% ash (1-4).

Cellulose

Cellulose is the primary component of wood. Carbon, hydrogen and oxygen are arranged into sugar molecules during photosynthesis in the living tree. These β -linked glucose units are further linked together to form long, linear chains. Cellulose chains are generally oriented in one direction, and give strength to the cell wall. The orientation of cellulose is largely due to the presence of a large number of hydroxyl groups. This allows the chains of cellulose to interact and hydrogen bond with adjacent chains, forming crystalline regions within the wood. However, not all of the cellulose is ordered into crystalline domains. Some portion of cellulose is amorphous, and in these regions the hydroxyl groups are free to form hydrogen bonds with water molecules. This accounts for the hygroscopic nature of wood, as water is held in the amorphous portions of cellulose. Water cannot easily enter the crystalline portions of wood as the cellulose chains there are tightly packed and held together by hydrogen bonding across their

hydroxyl groups. There are essentially no free hydroxyl groups available to hold water in the crystalline regions of wood. The amorphous region of cellulose is also the reactive site for wood modification as the hydroxyl groups are accessible for reaction with other compounds (1-4). Cellulose structure is illustrated in Figure 2.1a.

Hemicellulose

Hemicellulose is structurally similar to cellulose, as it is also composed of sugar molecules. However, hemicellulose is formed from various 5 and 6 carbon sugars, connected in short, often branched chains. Hydroxyl groups are also present in the hemicellulose, accounting for some of the hygroscopic nature of wood. Because of the short chain structure, most of the hemicellulose is soluble in water, and can be removed by water extraction (1-4).

Lignin

Like cellulose and hemicellulose, lignin is formed from carbon, hydrogen and oxygen. However, instead of taking the form of a polysaccharide, it is a phenolic compound which exists in a variety of forms. Phenylpropane units form the basic structure, linked together and branched in various ways. The structure of lignin is illustrated in Figure 2.1b. Lignin is primarily concentrated in the outer portions of wood cells and between the wood cells, where it functions as a binding agent to hold cells together. It is a brittle, stiff material that strengthens the cell. There are fewer hydroxyl groups in lignin than cellulose, which makes lignin less reactive (1-4).

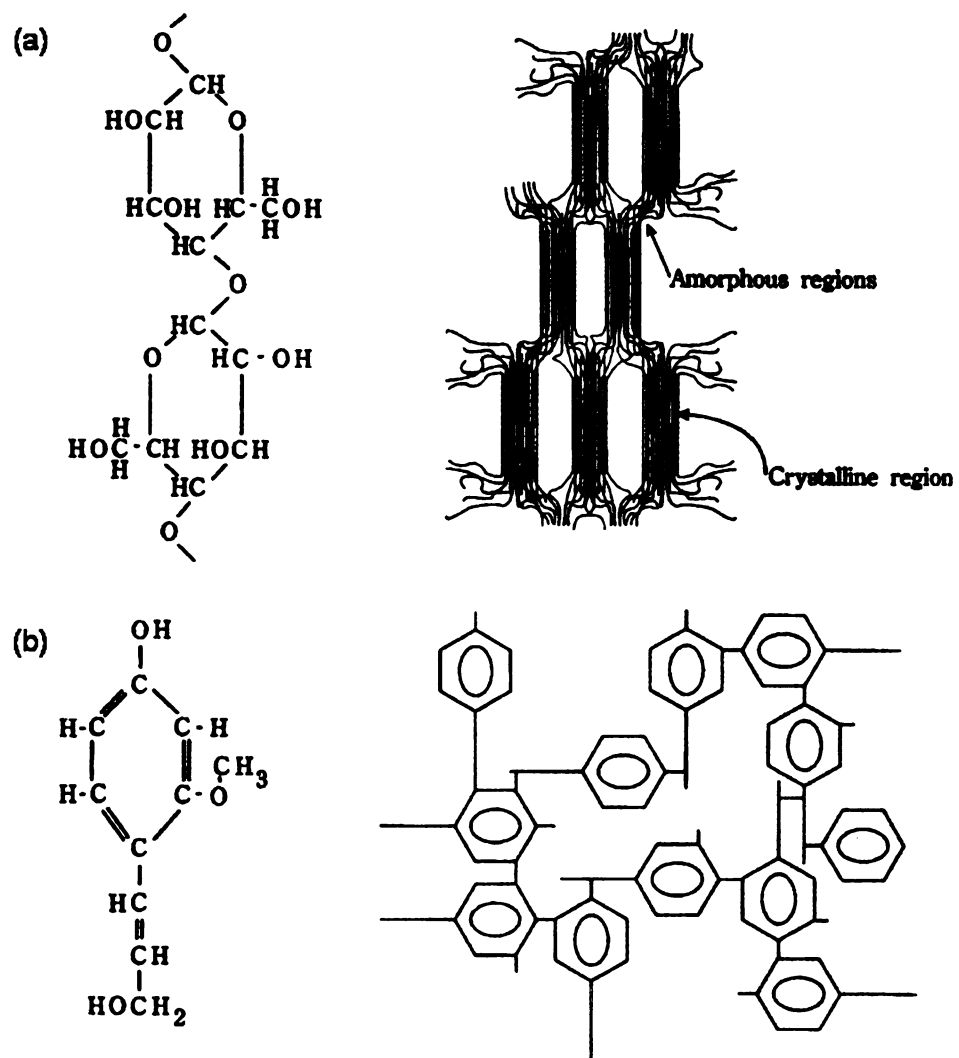


Figure 2.1. Chemical structures of (a) cellulose and (b) lignin (3)

Extractives

Extractives are a class of organic compounds that includes resins, carbohydrates, waxes, tannins, fats, oils, acid, etc. They are called extractives because they are not strongly bound to the wood structure and thus can be easily removed or extracted through processes such as steam distillation and solvent extraction. Extractives are largely responsible for the smell, color, density, flammability and fungal resistance of wood (1-4).

Wood Anatomical Structure

Growth rings are one of the most distinctive features of wood. They are noticeable on a cross section of wood or on the stump remaining when the tree is cut. Figure 2.2 shows an example of a tree cross section with clearly defined growth rings. The age of a tree can be determined by counting the rings, as each ring represents one year of growth. The light-colored portion of the ring is called earlywood and is composed of large, conductive cells that form early in the growing season. In contrast, the dark portion of the ring is latewood, which is composed of cells with thicker walls and more strength. The thickness of the rings and the proportion of earlywood to latewood varies between species, and is also affected by growing conditions (3, 4).

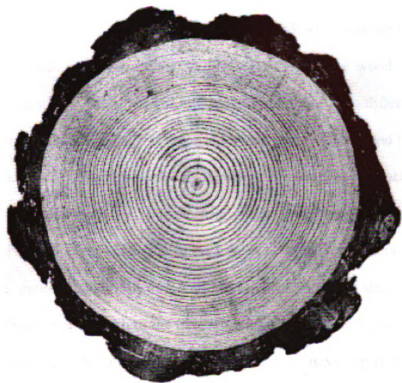


Figure 2.2. Cross section of a ponderosa pine log showing growth rings (4)

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The cells of wood are long and narrow with hollow centers called lumens. Openings called pits connect the cells along their length (3, 4). There are two main types of cells within wood: (i) fibers and (ii) vessels. Fibers give the wood strength, while vessels conduct liquids. Both the size and quantity of these cells differ within a tree. Based on these differences, wood is categorized as softwood or hardwood (3, 4).

Softwoods, or coniferous trees, are characterized by a porous structure formed by a large quantity of fiber tracheids. There are no vessels present, although some softwood has resin canals that transport materials in the tree (3, 4). Softwood fibers are rectangular and very long, approximately 3-8 mm, and are oriented in nearly straight rows (3, 4). The fiber tracheids lend strength to the tree, while also conducting liquids in the vertical direction. Groups of cells called rays are also present to move sap horizontally in the living tree (3, 4). Softwood structure is illustrated in Figure 2.3.

Hardwoods, or deciduous trees, contain both fibers and vessels, randomly oriented within the wood. An example of hardwood structure is illustrated in Figure 2.3. Hardwood fibers are circular and shorter in length than those in softwood (3, 4). A typical hardwood fiber averages only 1 mm in length (3, 4). Vessels form vertical canals for the transport of materials within the tree. Hardwoods also have rays to move materials horizontally through the tree (3, 4).

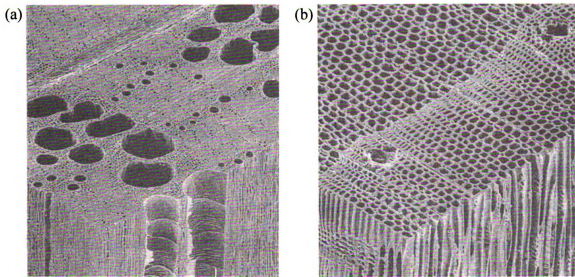


Figure 2.3. SEM micrographs of (a) hardwood red oak at 100X magnification and (b) softwood white pine at 150X (3)

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Moisture Content

Wood is a hygroscopic material (1-4). As a result, wood moisture content varies depending on the moisture content and temperature of its surroundings. The fiber saturation point is defined as the point where the lumens do not contain any free water but the cell wall is fully saturated (3). Below this point, moisture content of wood plays a large role in the dimensional stability, as wood shrinks and swells in response to moisture changes (3). Shrinking and swelling of wood elements can cause problems when wood is used in composites, as these changes weaken glue bonds and reduce interfacial adhesion between fibers and matrix components.

Wood Composites

Glued wood composites can be made from wood of varying geometry, including products based on lumber, sheets of veneer, strips of wood, flakes, particles, fibers and even wood flour (3-7). In the case of this research, wood particles were used to produce formaldehyde-free composites via reactive extrusion. The extrusion process limits the size of the wood material that can be used, as larger fibers or particles would be broken down by the shearing action of the screws in the twin-screw extruder. Glued wood composites made from wood particles or fibers would be most similar to the panels produced via reactive extrusion, thus these will be described in detail.

Medium Density Fiberboard (MDF)

MDF is a panel product composed of wood fibers and a thermoset adhesive. Urea-formaldehyde (UF) is the most common adhesive used in MDF, although some

isocyanate-p-MDI is used for certain applications. Panels are hot pressed to cure the resin and consolidate the fibers to the medium density range, between 500 and 800 kg/m³. MDF panels are often covered with veneer and used in cabinetry and moldings (6, 8).

Particleboard

Particleboard is a panel product made from discrete particles of wood and UF adhesive. The wood and adhesive mixture is formed into a mat and then pressed in a heated press to consolidate the panel. Particleboard is used in some structural applications, such as flooring and wallboard, although it finds a majority of its use in furniture applications such as shelving, in which it is covered with a layer of veneer or laminate (6, 8).

Adhesives for Wood Composites

Two categories of adhesives dominate in the production of glued wood composite products. These are phenolic resins and amino resins, which combined made up over 90% of the adhesives used in wood composites in 1998 (7). Phenolic resins include phenol-formaldehyde (PF) and resorcinol-formaldehyde (RF), whereas amino resins include urea-formaldehyde (UF) and melamine-formaldehyde (MF) (3, 7, 9). Polymeric diphenyl methylene diisocyanate (PMDI) is also used for some specialty applications (3, 7). Phenolic and amino resins are discussed in detail.

Phenolic Resins

Phenol-formaldehyde (PF) resins are made by the reaction of phenol with formaldehyde. There are two basic types of PF resin, resole and novolac (3, 9). The structures of these resins are shown in Figure 2.4.

Resole PF is made through the reaction of phenol with excess formaldehyde in the presence of an alkaline catalyst. This results in a resin with a branched structure. The presence of reactive methylol groups allows this type of PF to self-cure with the application of heat, and thus it does not need an added catalyst (3). Resoles are dark yellow to dark brown in color.

Novolac PF resins are formed from the reaction of excess phenol with formaldehyde under acidic conditions (3). This produces a resin with a linear structure. Novolacs cannot self-cure because there are no residual methylol groups in the structure. As a result, a curing agent must be added to these resins in order to form crosslinks. These resins are lighter in color than the resole PF and also have good moisture resistance.

Resorcinol-formaldehyde (RF) is another type of phenolic resin used in the wood industry. This adhesive is produced by the reaction of resorcinol with formaldehyde. RF resins have two reactive hydroxyl groups in their structure, which allows them to cure rapidly at room temperature with the addition of a catalyst (3). RF is expensive to produce, but is still desirable for high moisture resistance of products made with this adhesive (3).

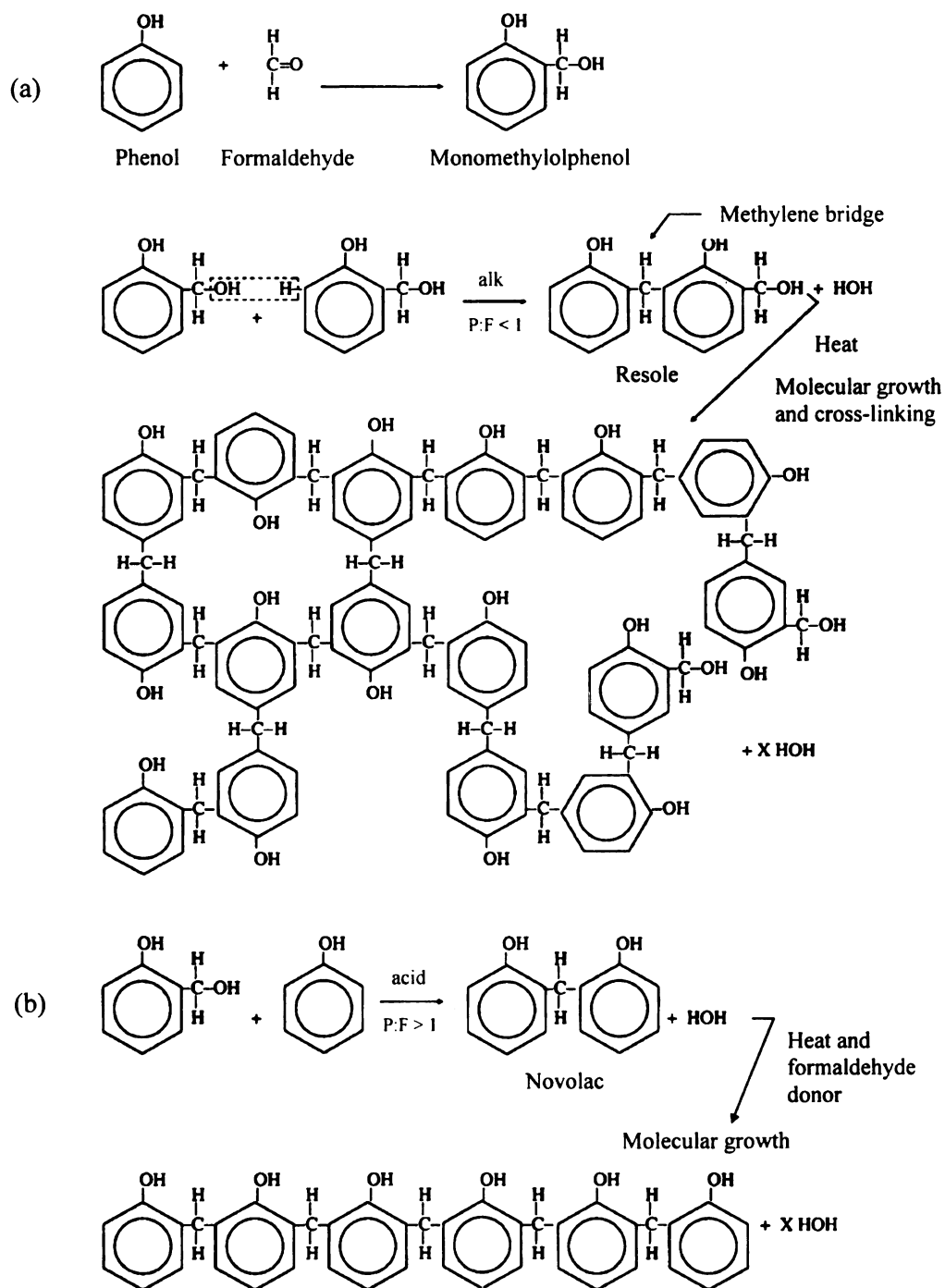


Figure 2.4. The chemistry of PF resin (a) resole and (b) novolac (3)

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Amino Resins

Urea-formaldehyde (UF) resins are the least expensive of the major wood adhesives. They are formed from the polymerization of excess formaldehyde with urea, and react as the four N-H bonds on the urea add across the carbonyl group on the formaldehyde (Figure 2.5). This produces methylol groups, which are suspended in water at about 65% resin solids when sold. The methylol groups crosslink by condensation when an acid catalyst is added, and after final curing the resin is hard, brittle and insoluble. However, cured UF is sensitive to moisture, which causes the resin to break down and release formaldehyde (3, 9). Formaldehyde release from UF bonded wood products is also a concern, especially in light of the new EPA regulations on formaldehyde emissions from wood composite manufacturing facilities (10).

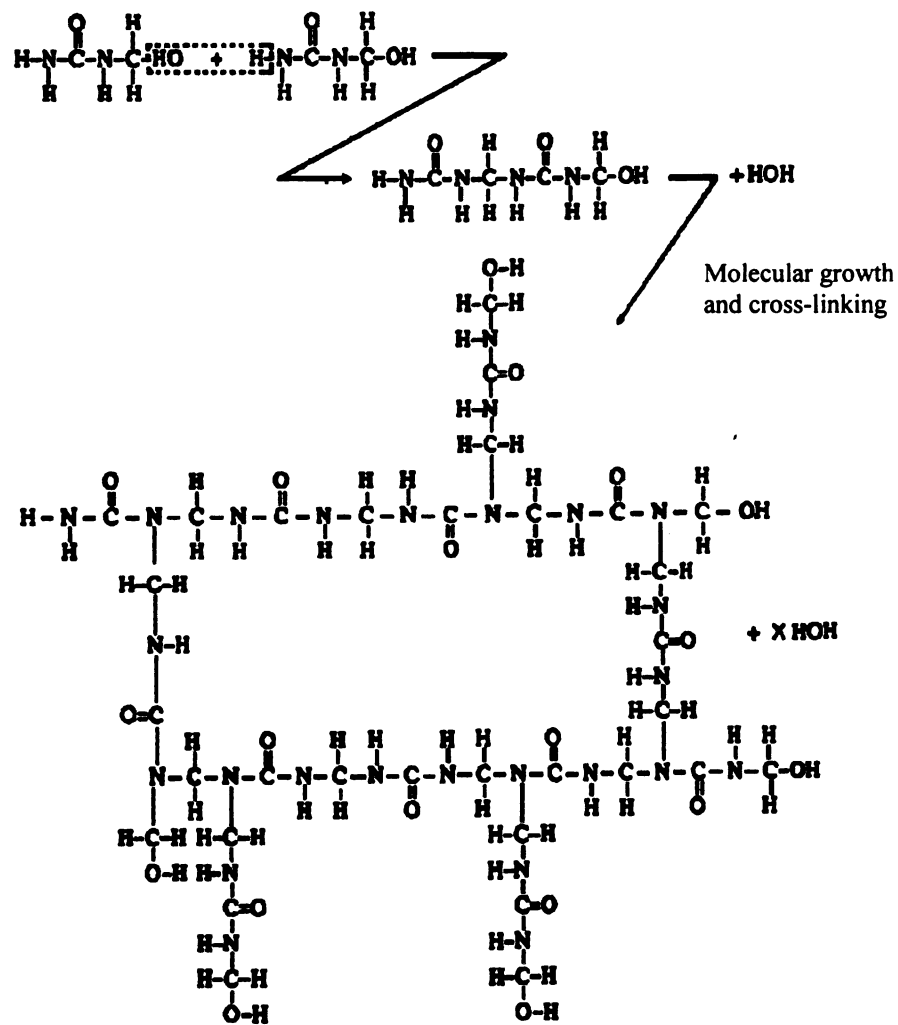
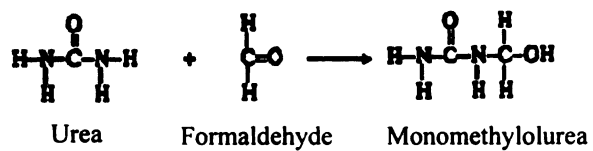


Figure 2.5. Chemistry of urea-formaldehyde resin (3)

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Melamine-formaldehyde (MF) resins are also widely used in wood composites. These resins are produced through the reaction of melamine with formaldehyde as illustrated in Figure 2.6. This produces a resin that is somewhat water resistant because of the low solubility of melamine in cold water. MF glues can be used for interior and exterior applications, but their high cost is a large drawback. MF resins are more expensive than PF, and offer less durability for an increased price. Often, MF and UF resins are blended to produce a resin with lower cost than MF with improved properties compared to UF alone (3, 9).

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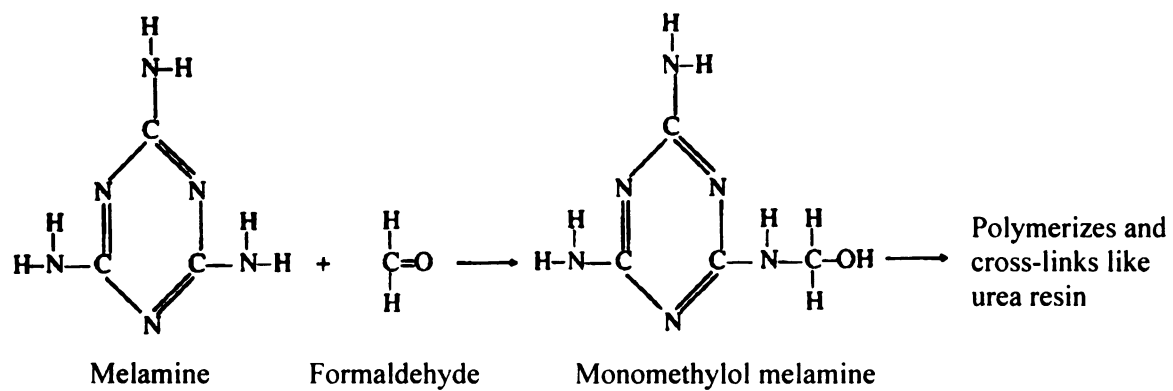


Figure 2.6. Chemistry of melamine-formaldehyde resin (3)

Wood-Plastic Composites

Wood plastic composites (WPCs) are a versatile family of composite materials made from wood fibers, particles, or flour mixed with a thermoplastic polymer and formed into a variety of shapes (11, 12). WPCs are used in a variety of applications such as decking, fencing, docks, automotive applications, playground equipment, etc (12). The decking market has been the largest volume application for WPCs, consuming over 50% of the total WPC produced in 2002 (12). When well-made, WPCs have several advantages over wood or plastic alone such as resistance to fungal decay, high impact strength, low incidence of cracking, etc (11, 12). WPCs are usually manufactured by extrusion, where wood and plastic are melted together and compounded into a composite material (12). The composite can be extruded into lengths of material that resemble lumber, or into profiles with hollow interiors or various layers. More complex shapes can be produced through injection molding, in which the composite is injected into a mold while still melted. The compounded mixture cools in the mold and is removed once solid.

Despite the advantages offered by WPCs, one significant drawback to their use is the lack of compatibility between wood, which is hydrophilic due to the large content of cellulose, and the hydrophobic plastic matrix (13-19). This incompatibility results in reduced strength properties and lower quality products. In order to overcome this drawback, coupling agents have been developed to compatibilize the wood and polymer components (13-19). The most successful examples of WPC coupling agents for polyolefin-based WPCs are maleated polyolefins, which bond with the wood component, while diffusing into the plastic matrix.

Maleated Polyolefins

Maleated polyolefins are usually polypropylene or polyethylene polymer that has been grafted with a small amount of maleic anhydride. These polymers are mainly used as coupling agents to promote interfacial adhesion in wood polymer composites between the non-polar plastic and polar wood components (13-19). The carboxylic acid portion of the maleated compound reacts with hydroxyl groups on the wood surface to form an ester linkage (13, 14, 17). The polymer chain is then free to diffuse into the polymer matrix, forming a physical bond upon cooling. This coupling mechanism is an effective method to promote compatibility between the phases in wood composites (13, 19-21). A small amount of maleated polyolefins (1-5%) is generally used to promote adhesion between the phases (13, 17, 19, 20).

Wood Modification with Anhydrides

Another method of compatibilizing wood and plastic in composite materials is to chemically modify the wood component. Chemical modification of wood with anhydride compounds has been studied extensively for several decades (22-32). Wood reacts with various anhydrides to form ester groups on the wood surface. Esterification has been shown to plasticize the wood, making it more versatile for wood composite applications.

Several investigators have studied wood modification with anhydrides in order to determine thermal properties, moisture resistance, compatibility with polymeric matrices, etc. (22-32). A lower softening temperature, compared to unmodified wood, has been documented in esterified wood after reaction with various anhydrides (22, 27-29). Esterified wood has also been found to resist moisture (22-28, 30-32) and to be more

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compatible than unmodified wood with polyester matrices in the manufacture of composites (22-28, 30-32). A second reaction of the esterified wood with epoxides formed oligoesters, which further thermoplasticized the wood and allowed for better control of structure and resulting properties of the modified wood (22-24, 26-28).

While the thermoplastic nature of esterified and oligoesterified wood modified through these methods has been documented, few authors have exploited this characteristic to make wood composites without added adhesive. Matsuda and co-workers used three dicarboxylic acid anhydrides (maleic, phthalic and succinic anhydride) to esterify wood particles, which were then molded into sheets through compression molding (22, 24). Clemons and co-workers used similar methods to modify wood fibers with anhydrides to prepare fiberboards (25). In both studies, chemically modified wood was able to partially melt when heated and bond without additional adhesive. Formulations containing succinic anhydride were found to have the most thermoplastic character in both studies (22, 24, 25). Further work by Matsuda et al. (22-24) showed enhanced thermoplasticization of wood through the grafting of various types of epoxides onto the already esterified wood surface. The oligoesterified wood produced from these reactions was even more thermoplastic-like in structure than the esterified wood produced through reaction with the anhydrides, and could be easily molded. Using various types of epoxides allowed for different chemical structures in the thermoplasticized wood, and could also be used to form crosslinked wood composites which resembled plastic more than wood (22-24). Recently, Timar and co-workers demonstrated the use of maleic anhydride to esterify wood particles, followed by oligoesterification with glycidyl methacrylate and additional maleic anhydride as a

process to form thermoplastic-like wood particles (26-28). Panels formed through the compression molding of modified wood particles displayed mechanical properties that met or exceeded standard requirements for bending strength and internal bond strength of particleboard or fiberboard (28). These wood composites were also found to be resistant to fungal decay.

Although esterifying and oligoesterifying the wood surface has been shown to be an effective method for manufacturing wood composite materials without additional adhesive, most methods require harmful organic solvents such as xylene, dimethyl sulfoxide, or N,N-dimethylformamide as part of the modification process (22, 24-32). Additionally, the oligoesterification reactions entail a two-step process (or more depending on the precise control of chemical structure desired) to functionalize the wood surface, which is both time consuming and complicated (22-24, 26-28). Removal of solvents and further drying of the wood particles is required before compression molding into panels (22, 24, 25, 28).

Modification of Wood with Maleated Polyolefins

Maleated polyolefins also react with wood particles through an esterification reaction (Figure 2.7). This reaction occurs between the maleated groups of the polyolefins and hydroxyl groups on the wood surface, forming a monoester (Figure 2.7.a) or a diester (Figure 2.7.b). This results in the grafting of a pendent polyolefin chain to the wood surface through the ester linkage.

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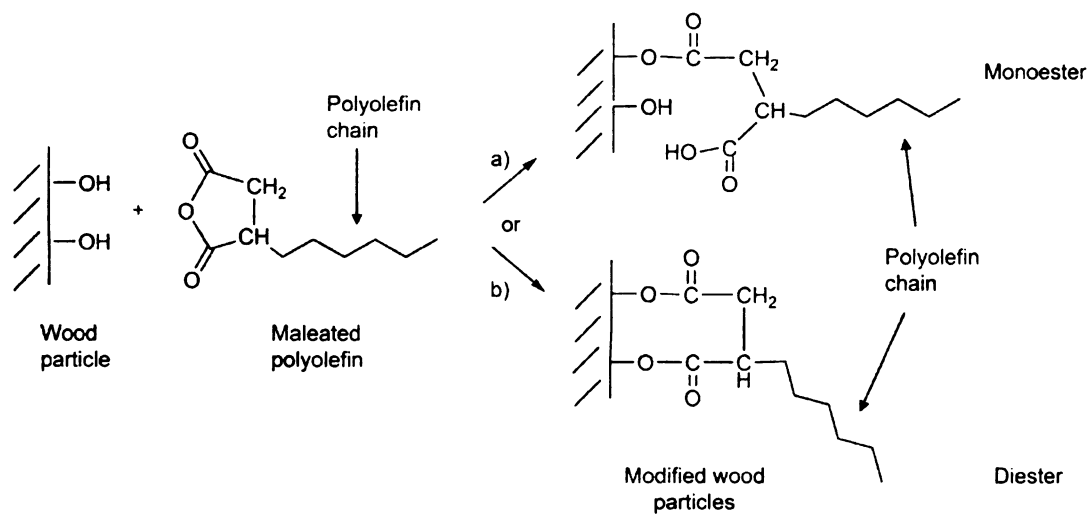


Figure 2.7. Reaction scheme for the modification of wood particles with maleated polyolefins

Several authors have studied this reaction with maleated compounds and wood particles (or other cellulosic materials), usually in an attempt to evaluate maleated compounds as compatibilizers between hydrophilic wood fibers and the hydrophobic polymer matrix in wood-plastic composites (13-18). However, most of this previous work focused on fibers modified through a solvent-based process where the maleated compounds were dissolved in heated xylene, toluene, N,N-dimethylformamide (DMF) or other organic solvents, followed by the addition of cellulosic particles (13-17). As with wood particles esterified or oligoesterified with other anhydride compounds, cellulosic fibers that have been grafted with maleated polyolefins have to be filtered and dried after modification, which makes this process both cost-ineffective and time consuming (13-17). Solvent disposal is also an issue with this modification process because some solvents may be harmful to workers and the environment.

In order to produce modified wood particles that could be used to make alternative composite panels, it is necessary to change from a solvent-based process to a dry process. A solvent-free process that has been reported in the literature utilized a thermokinetic mixer to modify wood particles with maleated polypropylene (16, 18). In that work, a heated, high-intensity mixer was used to graft maleated polypropylene onto wood fibers. However, the esterification reaction between wood particles and maleated polypropylene could not be confirmed through surface characterization techniques (16, 18).

Surface Analysis Techniques

Several techniques are employed in the surface analysis of wood-based materials. These techniques include X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. These techniques are frequently used together to determine chemical composition, structure and information about reactions in materials. An additional chemical characterization technique for wood-based materials is titration analysis, which is used to determine bulk chemical changes through acid-base chemistry. Contact angle measurements are often used to determine wettability and surface tension of wood-based materials. Inverse gas chromatography can be also used to determine thermodynamic properties of modified wood particles. Techniques used to analyze chemical changes resulting from modification of wood particles in reactive extrusion with maleated polyolefins in this work will be discussed in more detail.

X-Ray Photoelectron Spectroscopy (XPS)

XPS is a technique that allows chemical elemental composition of samples to be analyzed in a quantitative manner. A beam of x-ray photons is aimed at the sample, which interacts with the surface and causes electrons to be emitted. The binding energy (E_b) of the emitted electrons is measured by the detector. Since each element has a characteristic E_b , XPS can be used to determine the elemental composition of a sample. This technique is surface sensitive, with a maximum sampling depth of approximately 10 nm, as a result of the limited escape depth of electrons through a solid (33).

Typically, a low resolution scan from 0 to 1100 eV binding energy is performed to determine the identity and concentration of each element present on the surface of a sample, along with atomic ratios of elements. For wood products and polymers, carbon and oxygen are often the primary elements of interest. The oxygen to carbon (O/C) atomic ratio is calculated from the low resolution scan to evaluate oxidative changes resulting from chemical reactions or weathering. To further analyze the chemical bonding of the carbon atoms present in a sample, a high resolution scan of the C_{1s} region from 280 to 300 eV is performed. Four carbon component peaks can be found from the high resolution scan of wood products. Carbon component C1 arises from carbon atoms bonded only to carbon and/or hydrogen atoms (C-C/C-H) and has a characteristic binding energy of 285 eV. Carbon atoms bonded to a single oxygen atom, other than a carbonyl oxygen (C-OH) constitute the C2 component, which has a binding energy of 286.5 eV. Carbon component C3 arises from carbon atoms bonded to two non-carbonyl oxygen atoms or to a single carbonyl oxygen atom (O-C-O, C=O), and C4 from carbon atoms which are linked to a carbonyl and a non-carbonyl group (O-C=O).^{9,11,17} The binding energies of the C3 and C4 components of carbon are 288 and 289 eV, respectively (33).

XPS has been used to determine the chemical changes resulting from grafting lignocellulosic fibers with maleated polyolefins (13-15, 17, 18) and to follow surface changes to wood plastic composites after accelerated weathering (34, 35). It has also been used to document surface chemistry changes in wood pulp after ozonation reactions (36, 37).

Fourier Transform Infrared (FTIR) Spectroscopy

In FTIR spectroscopy, a beam of infrared radiation is used to excite the samples. As a result, infrared radiation is absorbed by organic compounds and converted into vibrational energy (38, 39). The mid IR region ($4000 - 400 \text{ cm}^{-1}$) is most commonly used for analysis of chemical compounds. FTIR can be used to determine the presence of functional groups in liquids or solids, using a variety of sampling methods. For solids, a quantitative method of sample analysis is diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy (39, 40), in which the sample is finely ground and often mixed with a non-absorbing substance such as potassium bromide (40). The method produces a spectrum with bands corresponding to functional groups on the surface of the sample. The spectra are presented in Kubelka-Munk units, which relate sample concentration to the intensity of the bands in the spectra (40). The Kubelka-Munk equation is expressed as:

$$f(R) = \frac{(1 - R)^2}{2R} = \frac{k}{s} \quad (1)$$

Where R is the absolute reflectance of the layer, k is the molar absorption coefficient and s is the scattering coefficient (40).

Within the last two decades, FTIR has been used to study wood structure (41). It has been applied to document the changes in the surface of wood after modification with maleic anhydride (23, 26, 27, 29, 30), and to study the esterification reaction between wood and maleated polyolefins (13, 15-17). FTIR has also been used extensively to

monitor changes in wood composites as a result of accelerated weathering (34, 35, 42-44).

Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectroscopy uses a magnetic field to energize the nuclei of selected atoms. Samples with certain nuclei absorb electromagnetic radiation in the radio frequency region (38). The absorption peaks for these nuclei are plotted versus peak intensity in the NMR spectrum. While several atoms can be used for NMR spectroscopy, the two most common forms, ^1H and ^{13}C , are based on hydrogen and carbon nuclei, respectively (38). Both of these methods provide information about bonding and chemical connectivity in samples, though each has different advantages. For example, the integrated area under each peak in the ^1H spectra correlates well with the number of protons associated with each peak (38). In ^{13}C NMR, the peak areas do not typically correlate with the number of carbon atoms present, so this technique is not quantitative unless run under special conditions. However, each peak in the spectra usually represents a different form of carbon, that is, a different bonding structure (38). For example, a carbon atom with two attached hydrogen atoms will have a different chemical shift than carbon with an attached hydroxyl group. Solid state ^{13}C NMR is a useful technique for analysis of solid materials. Solid state ^{13}C NMR has been used to study cellulose and other lignocellulosic materials and their compounds (45-47). This technique has also been applied to analyzing the carbon structure in wood (45, 46, 48). Solid state ^{13}C NMR was recently used to determine grafting mechanisms in maleic anhydride grafted polypropylene through reactive extrusion (49).

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Titrimetric Analysis

Titrimetric analysis uses acid-base chemistry to determine the quantity of acidic or basic groups in a substance. Techniques have been developed for the detection of acid value (AV), saponification value (SV) and hydroxyl group content (HV) in alkyd resin samples (50). These analyses have been applied to wood and other cellulosic samples for the detection of changes in modified and grafted wood (13, 23, 26, 27, 29).

Acid value determines the amount of free carboxylic acid groups present in a sample, while saponification value measures both acid and ester groups in a sample. Hydroxyl value quantifies the free and accessible hydroxyl groups present in the sample (50). These quantities were calculated using the following formulas:

$$AV = 56.1 \frac{N}{p} \quad (2)$$

$$SV = 56.1 (b - a) \frac{N}{p} \quad (3)$$

$$HV = [(b - a) N (56.1)] + AV \quad (4)$$

where N is the normality of potassium hydroxide (KOH), p is the amount in grams of wood particles, b is the volume of KOH needed to neutralize the blank (solvent only) and a is the volume of KOH required to neutralize the sample. The factor 56.1 accounts for the molecular weight of KOH (50).

AV and SV can provide information about esterification in samples , which is desirable for wood modification studies (13, 23, 26, 27, 29). Hydroxyl group content is also important in analyzing the way samples react (13). If the OH value is reduced after modification, there is evidence that the reaction took place through these groups.

Physical and Mechanical Property Testing

Wood composite panels are classified according to their density as low, medium or high density products (4, 6). To determine whether formaldehyde-free panels made in this study would conform to standard strength requirements for conventional particleboard, density of the panels was assessed and mechanical property data was compared to ANSI standard requirements for particleboard (51).

Density

Density of wood and wood-based samples is one of the most important parameters in assessing sample quality (3, 4, 6). Since mechanical property requirements vary with density, the density of experimental panels must be assessed to determine the appropriate range of standard property values for product comparison (51). A simple mass over volume calculation can be used to determine the average density. However, more information about the density profile can be collected using an X-ray density profiler. This instrument sends an x-ray beam through a sample as the beam travels across the sample thickness. Results of this analysis show the variation in density across the sample and can be used to find areas of high and low density in the sample, which may account for mechanical property variations.

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Flexural Properties

The flexural strength (modulus of rupture or MOR) and flexural stiffness (modulus of elasticity or MOE) of composites are determined via static bending tests. These tests are usually performed on dry samples, conditioned as per ASTM standards before testing. The MOR and MOE can be calculated from the load-deflection curves using the following equations:

$$\text{MOR} = \frac{3 \cdot P_{\max} \cdot L}{2 \cdot b \cdot d^2} \quad (5)$$

$$\text{MOE} = \frac{P \cdot L^3}{4 \cdot b \cdot d^3 \cdot y} \quad (6)$$

where $P_{\max}$ is maximum load (N), P is the load at proportional limit (N), L is length of span (mm), b is specimen width (mm), d is specimen thickness (mm) and y is center deflection at proportional limit load (mm).

Internal Bond (IB) Strength

The internal bond (IB) strength measures the tensile strength perpendicular to the surface of the sample and indicates how well the particles are bonded to each other in the center of the panel. It is measured as the maximum load per unit area. In this test, the stress is applied perpendicular to the plane of the adhesive and the energy required to break the adhesive bond is measured. IB strength is calculated according to Equation 7:

$$IB = \frac{P_{\max}}{b \cdot d} \quad (7)$$

where $P_{\max}$ is maximum load (N), b is the width of the specimen (mm) and d is the depth of the specimen (mm).

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CHAPTER 3

COMPOSITE MATERIALS MANUFACTURED FROM WOOD PARTICLES MODIFIED THROUGH A REACTIVE EXTRUSION PROCESS

This chapter is slightly modified from *Polymer Composites*, published in August 2005. 26 (4): 534-541. It is co-authored by K. Carlborn and L.M. Matuana.

ABSTRACT

Wood-based composites such as particleboard and medium density fiberboard are currently made with formaldehyde-containing adhesives. Since the government is continuously developing and implementing very stringent regulations to eliminate formaldehyde emissions into the environment, alternative approaches must be developed to replace these adhesives. This study examined the concept of using a reactive extrusion process as a means of developing a new, formaldehyde-free binding system for wood composite products. The surfaces of wood particles were modified by grafting maleated polyolefins through a continuous reactive extrusion process. Chemical changes resulting from this treatment were followed by studying the FTIR, ^{13}C NMR and XPS spectra. The modified wood particles were compression-molded into panels, which were tested for mechanical properties. FTIR, ^{13}C NMR and XPS data revealed that chemical reactions had taken place between the hydroxyl groups of wood particles and maleated polyolefins. The mechanical property test results indicated that the composite panels compared favorably with current standard requirements for conventional particleboard.

INTRODUCTION

Wood-based composites are commonly made using formaldehyde-based adhesives, including urea-formaldehyde, melamine-formaldehyde, and phenol-formaldehyde (1-3). In 1998, 1,780 kilotons of adhesive resin solids were used to produce primary glued wood products (excluding the adhesive used to bond furniture and other secondary wood products). Of this amount, nearly 92% were formaldehyde-based adhesives (3).

Plants that produce wood composites using formaldehyde-based adhesives emit harmful chemicals to the environment. These include phenol, formaldehyde, ketones, and other compounds, which are known hazardous air pollutants (HAPs) (4). Common composite products such as plywood, oriented strandboard and particleboard are used in building construction and in furniture, which is a concern as these products also tend to release formaldehyde over time (5). Wood composites made today emit far less formaldehyde than those made 20 years ago, but the problem has not been eliminated. Formaldehyde and other toxic compounds may be present in large amounts in both indoor and outdoor air as a consequence of the use of these adhesives (6, 7).

As a result of public concern about the environment, the Environmental Protection Agency (EPA) proposed new rules for facilities that manufacture plywood and composite wood products in August of 2002 (6). If adopted, these rules would affect both new and existing plants that produce at least 10 tons of any one HAP per year, or any combination of 25 tons of HAPs per year. The California Air Resources Board has gone even further; proposing a regulation that would eliminate urea-formaldehyde based wood composites from being sold in California, regardless of where they were made (7).

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These regulations will force industry to find new ways to bind composite products without the use of formaldehyde-based adhesives.

In recent years, there have been several studies into environmentally friendly wood adhesives (3). Some of the areas that have been investigated include urea-formaldehyde adhesives with low formaldehyde-to-urea molar ratios, and the development of tannin, lignin, soybean and cornstarch adhesives (3, 8), and phenol-formaldehyde resins modified with lignin (9, 10). Additives that reduce formaldehyde release during composite pressing and during board use have also been developed (8). The regulation of formaldehyde emissions has also lead to some development of fiberboard without synthetic adhesives (11, 12). The binderless boards and those made with natural adhesives tend to have poorer properties than those made with synthetic adhesives.

The approach of this work is to graft maleated polyolefins to wood particles in order to bond the wood particles together without the use of additional adhesive. Prior work demonstrated the ability to graft maleated polyolefins to cellulosic materials through a wet process (13). However, the wet process had the drawback of using organic solvents, which had to be removed through drying. Therefore, the wet process is both expensive and time consuming on an industrial scale.

The main objective of this study was to study the concept of using a reactive extrusion process as a means of developing a new, formaldehyde-free binding system for wood composite products. The effectiveness of the modification was followed by Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and X-ray photoelectron spectroscopy (XPS). FTIR is useful in

determining the presence of functional groups. NMR can determine bonding and chemical connectivity, while XPS can reveal the elemental composition on the surface of materials (13-15). Panels were pressed from the modified wood particles and mechanical properties of the resulting panels were tested and compared with current standard requirements for conventional particleboard (16).

EXPERIMENTAL

Materials

Maple wood particles of 425 micron (40-mesh) and 150 micron (100-mesh) size were supplied by American Wood Fibers (Schofield, WI) and were used as particles. The 150 micron particles were used for the analytical work because the diffuse reflectance IR technique required very small particles to minimize the effects of scattering and specular reflectance in the samples. However, these small particles were difficult to feed into the extruder. Since panel manufacturing required a large quantity of modified particles, larger (425 micron) particles, which were easier to process, were used in panel manufacturing and mechanical property testing. Hydrated zinc acetate, the catalyst, and xylene (99.9%, ACS Grade), the solvent used for Soxhlet extraction, were obtained from Baker Analytical Reagents (JT Baker Co., Phillipsburg, NJ). Maleated polyethylene (G-2608 or MAPE) and maleated polypropylene (G-3003 or MAPP) supplied by Eastman Chemical Co. (Kingsport, TN) were used as the binding agents. Table 3.1 lists the characteristics of these binding agents. The wood particles were dried for 48 hours at 105°C to a final moisture content of less than one percent before processing. All other chemicals were used as received.

Table 3.1. Characteristics of Maleated Polyolefins

Properties	Maleated polyethylene (MAPE or G-2608)	Maleated polypropylene (MAPP or G-3003)
Maleic anhydride content by weight	1.5%	1.5%
Melting point	122°C	156°C
Weight average molecular weight (Mw)	51,700 g/mol	52,000 g/mol
Melt flow index ¹	8 g/10 min	12.7 g/10 min

¹Melt flow index measured at 190°C and 2.16 kg according to ASTM D1238.

Reactive Extrusion of Wood Particles

A 10-liter high intensity mixer (Papenmeier TGAHK20) was used for dry blending of the wood particles, binding agent, and catalyst. All components were combined in the mixer and blended for 10 minutes at room temperature. Amounts of all components used in the formulation are summarized in Table 3.2. The mixture was then fed into a 32 mm conical counter rotating twin-screw extruder (C. W. Brabender Instruments, Inc.) with a L/D ratio of 13:1, driven by a 7.5 hp Intelli-Torque Plasti-Corder Torque Rheometer[®]. Based on preliminary work, the barrel temperatures for the three zones inside the extruder were set at 160°C for maleated polyethylene and 165°C for maleated polypropylene, and the rotational speed of the screws was held at 60 rpm. No die was used to extrude these particles.

Table 3.2. Formulation Used for Surface Modification of Wood Particles

Ingredients	% Total in Composite	Weight (g)
Wood particles	79%	790
Maleated polyolefins	20%	200
Hydrated zinc acetate (catalyst)	1%	10

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Extraction of Wood Particles

Modified and unmodified (unextruded) wood particles used for spectroscopic studies were Soxhlet extracted with xylene following the approach described by Li and Matuana (13). Particles were extracted for 24 hours after modification to remove any unreacted binding agent, oven-dried at 105°C until constant weight was achieved, and were then analyzed by FTIR. A second 24-hour Soxhlet extraction was then performed to make sure the removal of unreacted binding agent was complete from the surface of wood particles upon the first extraction. The infrared spectra of wood particles after this second extraction were collected for comparison with those collected after the first 24-hour extraction. All NMR and XPS analyses were performed on the particles after the second extraction.

Surface Characterization of Wood Particles

Unmodified and modified wood particles were dried to a constant weight at 105°C and analyzed by infrared spectrophotometry, using a Nicolet Protégé 460 FTIR (Nicolet Instrument Co., Madison, WI). Spectra were recorded in Kubelka-Munk units in the range of 4000-400 cm^{-1} , with a resolution of 4 cm^{-1} and a coaddition of 128 scans for each spectrum. Pure powdered potassium bromide (KBr) was used as a reference substance while no dilution of powdered-wood particles in KBr was required to obtain a spectrum. Diffuse reflectance was used with the FTIR for transfer of infrared radiation and data analysis was performed using WinFIRST software (Thermo-Nicolet, Madison, WI).

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Solid-state carbon 13 nuclear magnetic resonance (^{13}C NMR) spectra were obtained using a ^1H - ^{13}C Cross-Polarization Magic Angle Spinning (CP-MAS) experiment on a Varian-Chemmagetics (Varian Inc., Palo Alto, CA) 400 MHz NMR Spectrometer operating at 100.529 MHz. The spectrometer was equipped with a double resonance probe. Samples were spun in a 6 mm rotor at 4 kHz, at the magic angle (54.7°) and at ambient temperature. Pulse widths, contact time and pulse amplitudes for the CP were optimized on an adamantane standard. The contact time in all cases was 1 ms. The recycle delay (pulse delay) was 2.0 s. Spectra were processed using exponential weighting (100 Hz).

X-ray photoelectron spectroscopy (XPS) was used to determine the concentration and types of carbon atoms, as well as the oxygen-to-carbon atomic ratios present on the surface of the wood particles before and after modification. XPS analysis was carried out on a Physical Electronics Phi 5400 ESCA System, (Physical Electronics USA, Chanhassen, MN) using a non-monochromatic Mg source and a takeoff angle of 45° . The procedure for XPS data collection and analysis was detailed in other articles (13, 14).

Panel Manufacturing and Mechanical Property Testing

Panels were prepared from modified 425 micron wood particles using a hydraulic press from Erie Mill Co. (Erie, PA). Panel dimensions were 380 by 380 by 6 mm, with a target density of 720 kg/m^3 . Panels were pressed at 193°C for 7 minutes using 8 MPa of pressure. After pressing, panels were removed from the hot press and cooled at room temperature under compression for 15 minutes.

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Three-point flexural tests and internal bond (IB) strength tests were performed on an Instron 4206 testing machine (using Series IX software). For three-point flexural tests, the crosshead speed was 3.05 mm/min, while the crosshead speed for IB strength tests was 8.13 mm/min in accordance with the procedure outlined in ASTM standard D1037-99 (17). At least six samples were tested to obtain an average value for modulus of rupture (MOR), modulus of elasticity (MOE), and IB strength, which were compared with the values listed in the standard ANSI A208.1-1999 Particleboard (16).

Statistical Analysis

A two-sample *t*-test was carried out with an α significance value of 0.05 to determine the effect of binding agent type (MAPE vs. MAPP) on the flexural and internal bond properties of the composites. Statistical analysis was performed using Design Expert software (Version 6) from Stat-Ease, Inc. Minneapolis, MN.

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RESULTS AND DISCUSSION

Surface Characterization of Wood Particles

Modification of the wood particles was expected to take place through the mechanisms proposed in Figure 3.1, where a monoester or a diester could be formed through reaction of the maleated polyolefin with hydroxyl groups on the wood surface (13-15). Various surface characterization techniques were then used to document changes in the chemistry of the unmodified wood particles and wood particles modified with maleated polyolefins through a reactive extrusion process.

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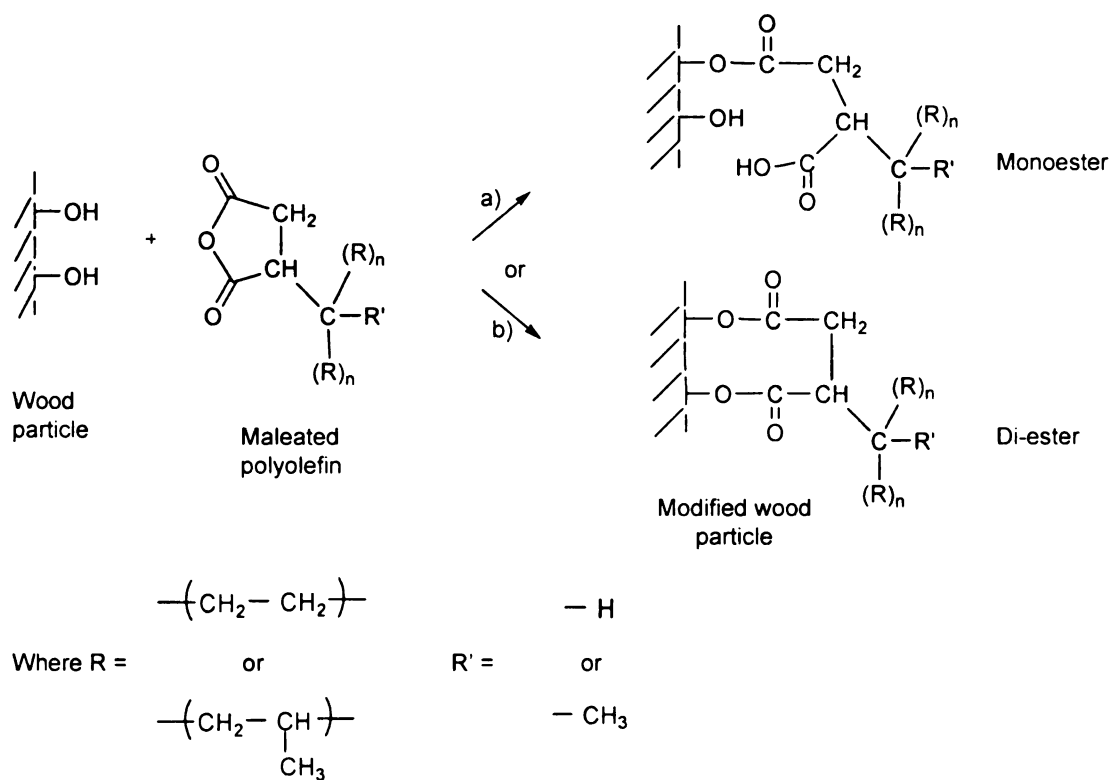


Figure 3.1. Modification scheme for esterification reaction between wood particles and maleated polyolefins: (a) mono-ester and (b) di-ester formation.

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The FTIR spectra of unmodified and modified wood particles, along with the maleated polyethylene are shown in Figure 3.2. Similarly, the FTIR spectra of unmodified and modified wood particles, along with the maleated polypropylene are shown in Figure 3.3. The unmodified wood particles (spectrum A in Figures 3.2 and 3.3) showed an absorbance band at 3400 cm^{-1} , which was attributed to hydroxyl group stretching vibrations, and another at 2900 cm^{-1} , which was associated with C-H stretching vibrations. A band near 1740 cm^{-1} was associated with C=O stretching vibrations, and another at 1122 cm^{-1} was likely due to C-O stretching vibrations and C-C stretching from components of cellulose (13, 15).

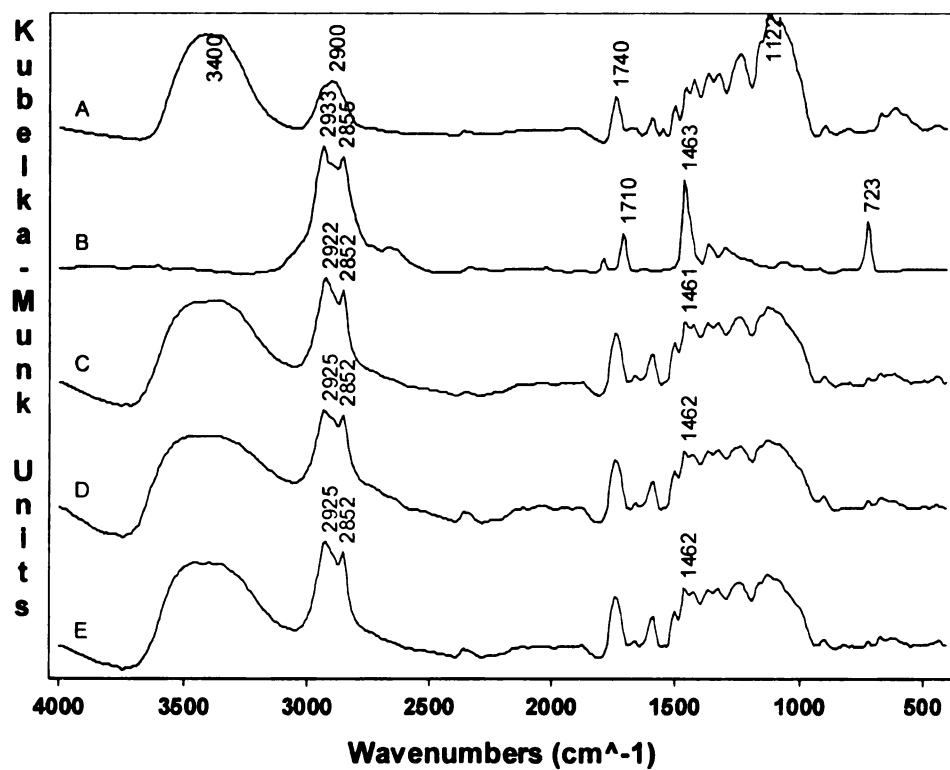


Figure 3.2. FTIR spectra of unmodified wood particles (A), maleated polyethylene-MAPE (B), MAPE-modified wood particles without extraction (C), with 24 hour-Soxhlet extraction (D), and after a second 24 hour-Soxhlet extraction (E) in the region 4000-400 cm⁻¹.

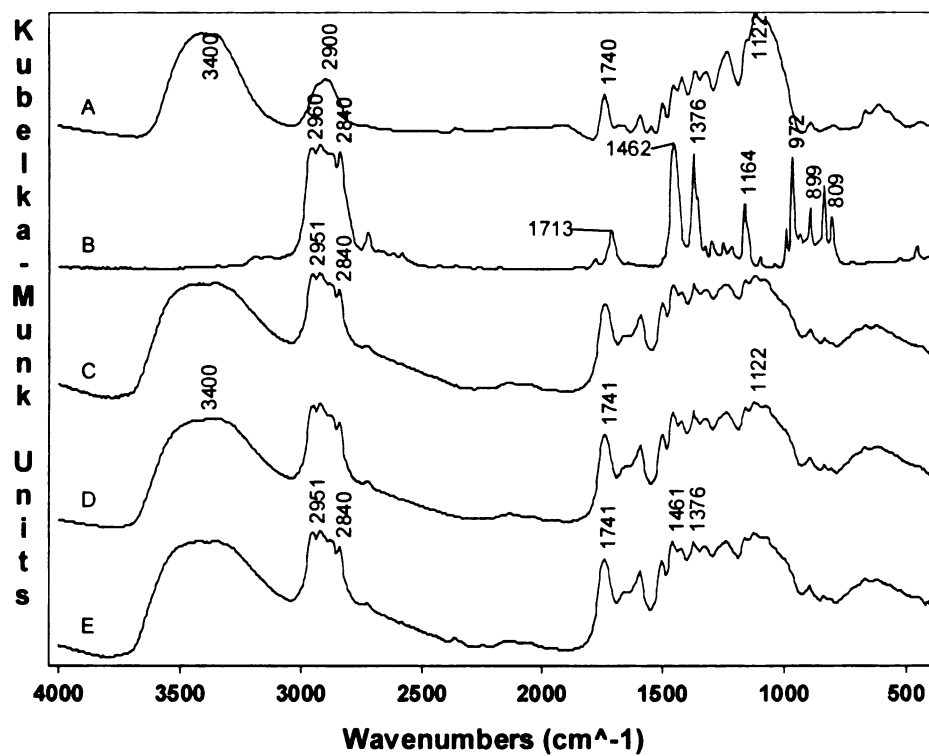


Figure 3.3. FTIR spectra of unmodified wood particles (A), maleated polypropylene-MAPP (B), MAPP-modified wood particles without extraction (C), with 24 hour-Soxhlet extraction (D), and after a second 24 hour-Soxhlet extraction (E) in the region 4000-400 cm⁻¹.

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The spectra of maleated polyethylene and maleated polypropylene (spectrum B in Figures 3.2 and 3.3, respectively) showed four distinct absorption bands. The bands between 2960 cm^{-1} and 2840 cm^{-1} were due to symmetrical and asymmetrical C-H stretching vibrations of CH_2 and CH_3 in the polyolefin chain (13, 15). The small band near 1786 cm^{-1} was attributed to anhydride C=O stretching. Bands found between $1720\text{--}1710\text{ cm}^{-1}$ arose from C=O stretching vibrations in the maleated polyolefins and the absorbance bands from $1463\text{ to }1300\text{ cm}^{-1}$ were from C-H deformation vibrations of CH_2 and CH_3 . The bands below 1250 cm^{-1} were associated with rocking vibrations of CH_2 and CH_3 , or C-C stretching vibrations from the polyolefin chain (13, 15).

The infrared spectra of wood modified with maleated polyolefins are also illustrated in Figures 3.2 and 3.3 (spectra C-E). For the interpretation of infrared spectra, it is important that all the unreacted maleated polyolefins are removed in the 24 hour Soxhlet extraction with solvent. It is seen from these figures that there was very little difference in the spectra of the modified wood particles after the first (spectrum D) and second extractions (spectrum E). This finding provides important evidence that the maleated polyolefins were chemically bonded to the wood particles. If the maleated polyolefins had not grafted to the particles, a decrease in peak intensity or a loss of the band with distinct peaks between $2960\text{ and }2840\text{ cm}^{-1}$ would have been expected after the extraction, which would remove any polyolefins not chemically bonded to the wood particles (13).

The modified wood particles (spectra C-E in Figures 3.2 and 3.3) also showed absorption bands at 3400 cm^{-1} , but the intensity of this peak decreased compared to the unmodified wood particles, indicating that there were less OH groups on the surface of

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modified samples. This was expected based on the reaction scheme shown in Figure 1, where the maleated polyolefin reacted with the OH groups of wood particles forming an ester link (13). The reaction may form either a single ester link or a diester where both reactive groups on the maleated polyolefin bond with hydroxyl groups on the wood surface. A distinct change was found near 2900 cm^{-1} , where a large band between 2960 and 2840 cm^{-1} , having distinct peaks similar in appearance to the maleated polyolefin, replaced the single peak in the unmodified wood particle spectrum. This feature is characteristic of the maleated polyolefins (spectrum B), and is due to C-H stretching vibrations (13, 15). Another indication of grafting of the maleated polyolefin was an increased intensity in the band at around 1740 cm^{-1} , possibly due to esterification reaction. Although not clearly seen in Figures 3.2 and 3.3 due to stacking of five spectra in one figure, the individual spectra of modified wood particles showed an increased intensity in the peaks at 1462 and 1376 cm^{-1} which is also indicative of the grafting reaction, suggesting more C-H character in the modified samples (13, 15). It should also be mentioned that the intensity of the band at 1122 cm^{-1} decreased, likely due to less cellulose being detected on the surface because of the grafting of the long aliphatic hydrocarbon chain of maleated polyolefin (13-15).

The evidence supporting the chemical bonding of maleated polyolefins to the surface of wood particles obtained by infrared was further supplemented by NMR spectra, as illustrated in Figure 3.4. The solid state ^{13}C NMR maleated polyethylene (spectrum A) showed only one distinct peak at 30 ppm , which was due to CH_2 chain carbons of the maleated polyethylene (18). Oxidized carbons from the maleated group did not appear, likely due to their low concentration in the maleated polyethylene

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compounds. By contrast, spectra of both unmodified wood (spectrum B) and modified wood particles (spectrum C) showed several characteristic peaks. The carbon peak at 152 ppm is attributed to lignin compounds in the wood. Bands from different types of carbon atoms in cellulose appeared at 106 and 73 ppm. Wood particles also showed a small peak near 55 ppm attributed to methoxy groups found in wood lignin and hemicelluloses (19). As expected, a large increase in the peak intensity at 30 ppm was observed in the modified wood particles (spectrum C), clearly indicating that the maleated polyethylene was chemically bonded to the wood particles. Any unbound maleated polyethylene would have been removed by the Soxhlet extraction process, and would not appear in the spectrum.

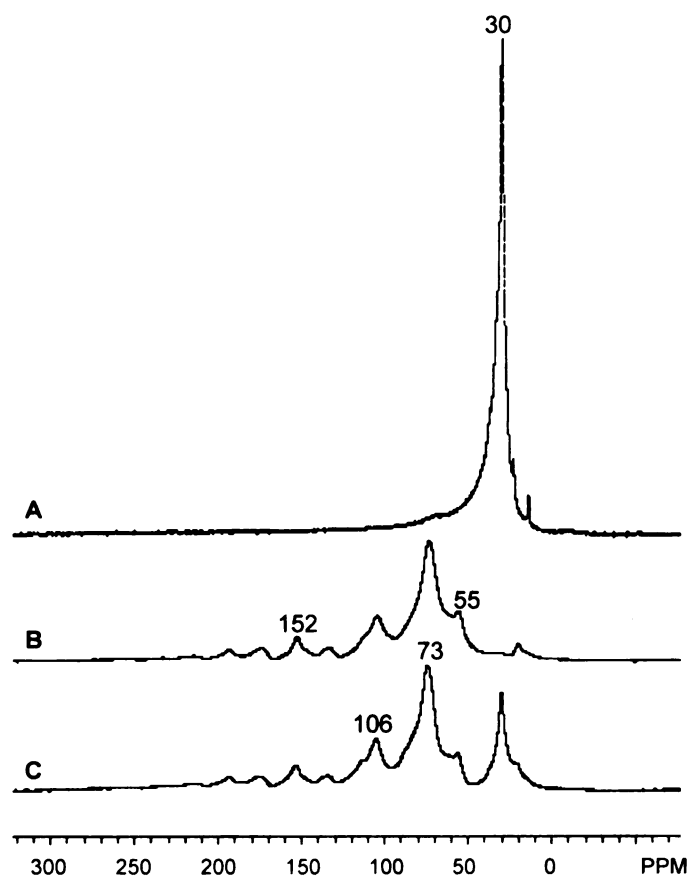


Figure 3.4. Solid-state ^{13}C NMR spectra of (A) MAPE, (B) unmodified wood particles, and (C) wood particles modified with MAPE.

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The XPS data summarized in Table 3.3 also confirmed the findings of the FTIR analysis. As expected from compounds rich in carbon-containing groups, a significant increase in C1 was observed after surface modification of wood particles with maleated polyolefins. In addition, the content of oxidized carbon atoms (C2-C4) significantly decreased in the modified wood particles, along with the O/C atomic ratio, which was also expected due to the large increase in aliphatic carbon atoms on the surface of the modified wood particles (13, 14). The O/C atomic ratios showed that the surface of the wood particles changed dramatically with modification, decreasing from 0.47 to 0.03 with maleated polyethylene and from 0.47 to 0.06 with maleated polypropylene. Changes this large likely indicate that the reactive extrusion procedure was very successful in grafting maleated polyolefins to the wood particles.

Table 3.3. High-Resolution C_{1s} Peaks and Elemental Surface Compositions of Wood Particles Determined by XPS

Materials ¹	Analysis of C _{1s} peaks (%) ²				Elemental compositions (%)		O/C atomic ratios
	C1	C2	C3	C4	O	C	
Unmodified wood particles (unextruded)	39.75	51.20	8.46	0.58	31.85	68.15	0.47
Maleated Polyethylene (MAPE)	87.1	7.7	5.2	0.0	10.1	89.9	0.11
Wood particles modified with MAPE	95.08	4.34	0.58	0.0	2.97	97.03	0.03
Maleated Polypropylene (MAPP)	96.58	2.57	0.84	0.0	3.28	96.72	0.03
Wood particles modified with MAPP	90.99	6.19	2.83	0.0	5.87	94.13	0.06

¹Unmodified and modified wood particles used were those obtained after a second 24 h Soxhlet extraction.

²Carbon component C1 arises from carbon atoms bonded only to carbon and/or hydrogen atoms (C-C/C-H), C2 from carbon atoms bonded to a single oxygen atom, other than a carbonyl oxygen (C-OH), C3 arises from carbon atoms bonded to two non-carbonyl oxygen atoms or to a single carbonyl oxygen atom (O-C-O, C=O), and C4 carbon type comes from carbon atoms which are linked to a carbonyl and a non-carbonyl group (O-C=O) (13).

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Mechanical Properties

Surface analysis techniques provided evidence that the maleated groups of the binding agent had chemically bonded with hydroxyl groups on the wood particle surface, as illustrated in Figure 3.1. This process resulted in the formation of an ester linkage between the wood surface and the maleated group of the binding agent, which produced a wood particle with a pendant polyolefin chain. Bonding between wood particles was expected to occur through diffusion and entanglement of the pendant polyolefin chains, as shown in Figure 3.5. During compression molding, the pendant polyolefin chains would melt and flow under the influence of heat and pressure, causing them to entangle. Upon cooling, the entangled polyolefin chains would be locked together, forming a direct particle-to-particle bond between the modified wood particles, without the addition of any adhesive.

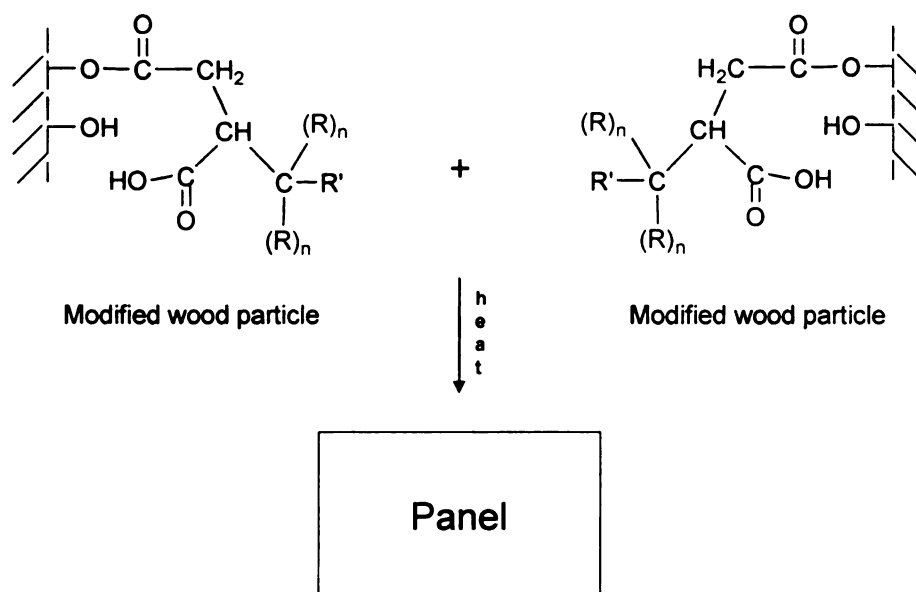


Figure 3.5. Panel manufacture scheme for modified wood particles where R is an ethylene or propylene repeat unit and R' is hydrogen or a methyl group.

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To determine whether panels made by this process would conform to standard strength requirements for conventional particleboard, mechanical property data was compared to ANSI standard requirements for particleboard. Table 3.4 lists the MOR, MOE, and IB strength requirements for particleboard of medium density, ranging from 640-800 kg/m³. There are four grades of particleboard of medium density, all of which can be made with either interior or exterior adhesives. Grades M-1 and M-S are commercial grade boards, while M-2 and M-3 are intended for industrial use. Panels for outdoor use must also be labeled exterior, according to the ANSI standard for particleboard (16). The composite panels manufactured in this study were within this range, with an average density value of 778 ± 12 kg/m³ for panels made with maleated polyethylene and 775 ± 8 kg/m³ for panels made with maleated polypropylene.

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Table 3.4. Requirements for Various Grades of Particleboard of Medium Density (640-800 kg/m³)

Properties	Grades ¹				Experimental Values ²	
	M-1	M-S	M-2	M-3	Wood/MAPE	Wood/MAPP
MOR (N/mm ²)	11.0	12.5	14.5	16.5	20.7 ± 3.4 ^A	22.9 ± 4.3 ^A
MOE (N/mm ²)	1725	1900	2250	2750	1296 ± 195 ^A	2870 ± 320 ^B
IB (N/mm ²)	0.40	0.40	0.45	0.55	2.06 ± 0.7 ^A	1.50 ± 0.3 ^A

¹From Standard ANSI A208.1-1999 Particleboard (16).

²The capitalized letters represent the ANOVA results. The means with the same letter denote that the difference between these two treatments is not statistically significant. Otherwise, the difference is statistically significant at values of $\alpha = 0.05$.

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Regardless of the maleated polyolefin type, the MOR and IB strength results of panels manufactured in this study indicated that the standard requirements have been met and surpassed for all grades of particleboard of medium density. No significant difference in both MOR and IB was observed between maleated polyethylene and maleated polypropylene. However, the MOE data are below the standard requirements for stiffness when maleated polyethylene was used as a binding agent for wood particles. By contrast, the experimental panels exceeded the MOE requirements for all grades of particleboard of medium density when maleated polypropylene was used as binding agent. Panels bonded with maleated polypropylene were statistically superior in MOE compared to the maleated polyethylene counterparts. This difference is due to the higher stiffness of polypropylene when compared to polyethylene. These results are significant because particleboard is currently manufactured with formaldehyde-based adhesives. The formaldehyde-free wood composites manufactured in this study are more environmentally friendly and often outperform the requirements listed in the standard ANSI A208.1.

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CONCLUSIONS

This study examined the possibility of modifying wood particles with maleated polyolefins in a reactive extrusion procedure in order to make formaldehyde-free wood-based composite panels. FTIR, ^{13}C NMR and XPS results verified the reaction between wood particles and maleated polyolefins. This proved that the maleated polyolefins could be successfully grafted to wood particles using a reactive extrusion process, without the use of any solvents. The study also showed that a new type of environmentally friendly wood composite product could be formed from the modified wood particles. This composite contained no formaldehyde-based adhesive, but still performed very well in mechanical tests, in some cases exceeding the standard requirements for particleboard of medium density.

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CHAPTER 4

FUNCTIONALIZATION OF WOOD PARTICLES THROUGH A REACTIVE EXTRUSION PROCESS

This chapter is in press for the *Journal of Applied Polymer Science* (2006). It is co-authored by K. Carlborn and L.M. Matuana.

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ABSTRACT

Wood particles were modified in a reactive extrusion process with maleated polyethylene (MAPE) and maleated polypropylene (MAPP) compounds. Contents of MAPE were varied to study the effect of material composition on grafting efficiency during reactive extrusion, while extruder barrel temperatures and rotational screw speeds were varied to evaluate the effects of processing conditions on the modification of wood particles. Polymer molecular weight effects were investigated using MAPP with different molecular weights. Efficiency of the modification was assessed using FTIR and XPS surface analysis techniques, along with a titrimetric analysis to verify the esterification reaction between the wood particles and maleated polyolefins. The grafting of maleated polyolefins onto the surface of the wood particles through a reaction of hydroxyl groups on the wood surface with the maleated groups of the maleated polyolefins was confirmed, while the level of grafting of MAPE onto wood particles was determined to be a function of the MAPE concentration. However, there was no significant difference found in grafting efficiency at different extrusion processing conditions; rather all of the conditions resulted in adequate grafting. Similarly, there was no difference in grafting efficiency with the molecular weight of MAPP. Reactive extrusion was found to be a suitable technique for the modification of wood particles with maleated polyolefins for all of the material compositions and processing conditions studied.

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INTRODUCTION

In response to the need for new adhesives for wood composite products, a formaldehyde-free binding system for wood particles which used only maleated polyolefins to create direct wood particle to wood particle bonding was developed in our prior work (1, 2). Wood composite panels were manufactured from maleated polyolefin-modified wood particles, without using any additional adhesive. These panels met and in some cases even exceeded standard requirements for particleboard made with formaldehyde-based adhesive. However, the mechanism for the adhesive bonding was not fully developed.

Maleated polyolefins react with wood particles through an esterification reaction (Figure 4.1). This reaction occurs between the maleated groups of the polyolefins and hydroxyl groups on the wood surface, forming a monoester or a diester. This results in the grafting of a pendant polyolefin chain to the wood surface through the ester linkage. Several authors have studied this reaction with maleated compounds and wood particles (or other cellulosic materials) (3-14). However, most of this previous work focused on fibers modified through a solvent-based process where the maleated compounds were dissolved in heated xylene, toluene, N,N-dimethylformamide (DMF) or other organic solvents and cellulosic particles were added (3-10, 12-14). Cellulosic fibers have to be filtered and dried after modification, which makes this process both cost-ineffective and time consuming, and the often harmful organic solvents must be properly disposed of. In order to produce modified wood particles that could be used to make alternative composite panels, it is necessary to change from a solvent-based process to a dry process.

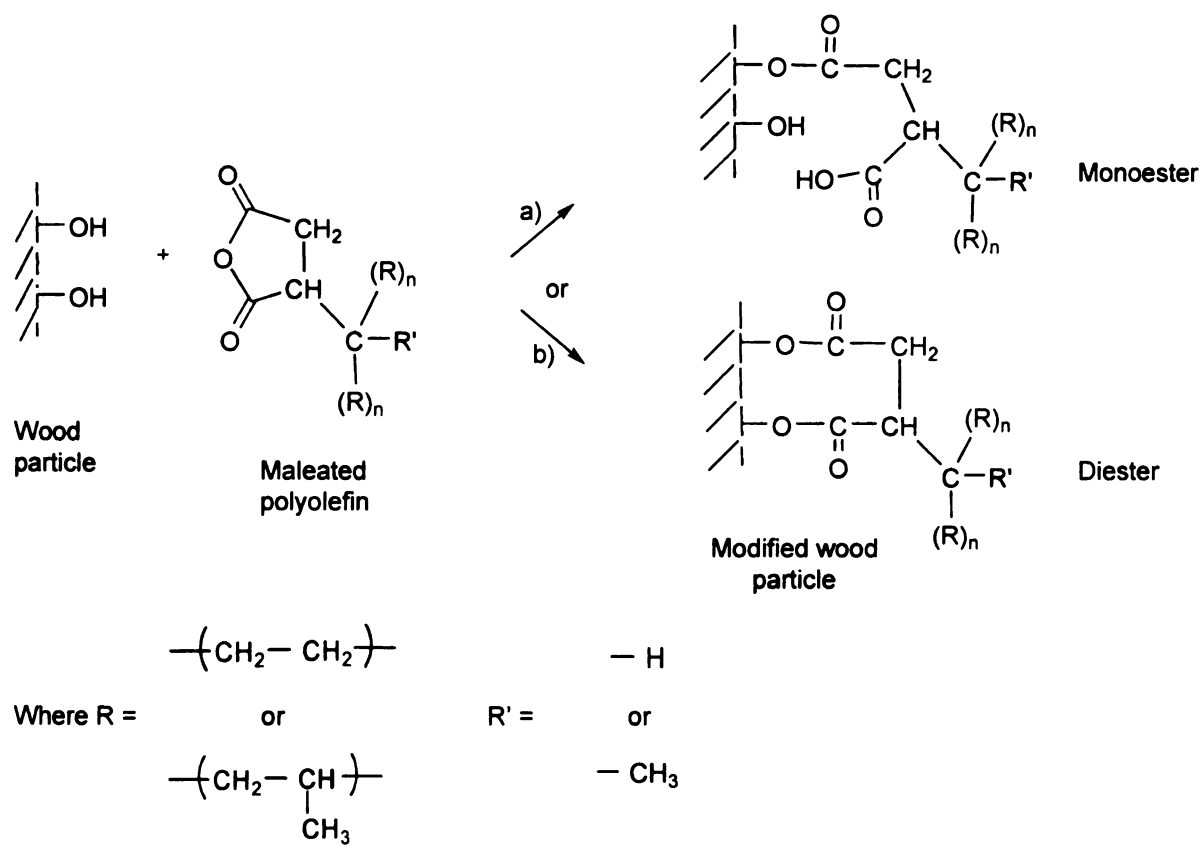


Figure 4.1. Modification scheme for esterification reaction between wood particles and maleated polyolefins: (a) monoester and (b) diester formation.

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A solvent-free process that has been reported in the literature utilized a thermokinetic high-intensity mixer to graft maleated polypropylene (MAPP) onto wood fibers (11, 12). However, the esterification reaction of wood particles and MAPP could not be confirmed through surface characterization techniques. An effective dry process for grafting maleated polyolefins onto the surface of wood particles is still needed to produce a large volume of modified wood particles required to manufacture formaldehyde-free wood composite panels.

Reactive extrusion is a technique that can be used for the chemical modification of compounds, usually polymers that can melt during processing. Because no solvent is involved during processing, reactive extrusion is an environmentally friendly technique for surface modification. It also allows for control of reaction times and temperatures through variation of rotational screw speeds and extruder barrel temperatures. Reactive extrusion offers the advantage of intensive mixing of components in a short time, especially in a twin-screw extruder, which ensures a more thorough reaction of components (15). This process also has the advantage of low retention times in the extruder, so a series of different reaction conditions can be tested in a relatively short period of time. Reactive extrusion has only rarely been used for wood fiber surface modification (1, 2) probably because the wood component does not melt and flow in the extruder. However, the ease of processing and control of reaction conditions makes this technique attractive for wood fiber surface modification.

In this study, reactive extrusion was employed to graft maleated polyethylene (MAPE) and MAPP compounds to wood particles, with an ultimate goal of determining optimum surface modification conditions. Particular emphasis was placed on examining

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the efficiency of grafting of the surface modification as functions of material compositions (MAPE contents and molecular weights of MAPP compounds) and extrusion processing conditions (barrel temperatures and rotational screw speeds). X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy and titrimetric analysis were used to monitor chemical changes on the surface of the wood particles before and after reactive extrusion with maleated polyolefins. XPS has an approximate sampling depth of 0.1-8 nm (16), which makes it even more surface sensitive than FTIR. When used together, these techniques provide detailed information about the surface chemistry and bonding mechanism in modified wood fibers.

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EXPERIMENTAL

Materials

Maple wood particles of 150 micron (100-mesh) size used in this study were supplied by American Wood Fibers (Schofield, WI). Hydrated zinc acetate, the catalyst, and xylene (99.9%, ACS Grade), the solvent used for Soxhlet extraction, were obtained from Baker Analytical Reagents (JT Baker Co., Phillipsburg, NJ). Maleated polyethylene (MAPE or G-2608) and several maleated polypropylenes (MAPP or G-3216, G-3015, G-3003, and E-43) supplied by Eastman Chemical Co. (Kingsport, TN) were used as the binding agents. Characteristics of these maleated polyolefins are listed in Table 4.1. Hydrochloric acid (concentrated) obtained from EM Science (Cherry Hill, NJ), sodium hydroxide, methanol (absolute), pyridine (99.9%), toluene (100%), 1-butanol (99.6%), ethanol (190 proof), and acetic anhydride (100%), all obtained from Baker Analytical Reagents (JT Baker Co., Phillipsburg, NJ), were used as titration reagents. Titration reagents were used as directed in Pure and Applied Chemistry methods (17). The wood particles were dried for 48 hours at 105°C to a final moisture content of less than one percent before processing. All other chemicals were used as received.

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Table 4.1. Characteristics of Maleated Polyolefins

Properties	MAPE	MAPP²			
	G-2608	E-43	G-3216	G-3015	G-3003
Weight % maleic anhydride	1.5	8	2.5	2.5	1.5
Melting point (°C)	122	155	142	155	156
Approximate weight average molecular weight Mw (g/mol)	51,700	11,200	39,000	47,000	52,000
Melt flow index at 190°C ¹	8	----	----	----	12.7
Viscosity at 190°C, cP	----	300	20,000	25,000	60,000

¹Melt flow index measured at 190°C and 2.16 kg according to ASTM standard D1238.

²G-3216 is a maleated PE/PP copolymer.

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Surface Modification of Wood Particles with Maleated Polyolefins in Reactive Extrusion

A 10-liter high intensity TGAHK20 mixer (Papenmeier, Germany) was used for dry-blending of the wood particles, binding agent, and catalyst. All ingredients were combined in the mixer and blended for 10 minutes at room temperature. Amounts of all components used in the formulation are listed in Table 4.2. These mixtures were then fed into a 32 mm conical counter-rotating twin-screw extruder (C. W. Brabender Instruments, Inc., South Hackensack, NJ) with a length to diameter (L/D) ratio of 13:1. The extruder was driven by a 5.6 kW Intelli-Torque Plasti-Corder Torque Rheometer[®]. The extruder had three temperature zones on the barrel (Figure 4.2) and an adjustable rotational screw speed. Various processing temperatures and rotational screw speeds were used to study the effects of processing conditions on the effectiveness of grafting maleated polyolefins to the surface of the wood particles. In all cases, a uniform barrel temperature was set for each test. For example, when the desired processing temperature was 130°C, all three zones were set at that temperature. This was done similarly for the other studied processing temperatures of 140, 160 and 180°C.

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Table 4.2. Formulations Used for Modified Wood Particles

Binder content (%)	Ingredients in the formulations		
	Maple particles (g)	MAPE or MAPP (g)	Hydrated zinc acetate (g)
5	94	5	1
10	89	10	1
15	84	15	1
20	79	20	1

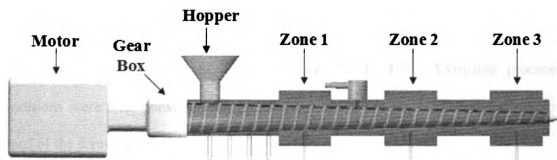


Figure 4.2. Diagram of the extruder showing the three heating zones.

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The effect of material composition on the grafting of MAPE onto wood particles in a reactive extrusion process was investigated by holding the extruder barrel temperature and rotational screw speed constant at 160°C and 60 rpm, respectively. Whereas, the MAPE contents were varied from 5 to 20% of the total batch weight (Table 4.2).

To determine the effects of processing conditions on grafting efficiency of modified wood particles, the MAPE concentration was fixed at 20% and the extruder barrel temperatures and rotational screw speeds were varied. Barrel temperatures were limited to the range above the melting point of MAPE and below the degradation temperature of wood (130, 140, 160 and 180°C). The rotational speed of the screws was varied from 20 to 80 rpm in 20-rpm increments at each barrel temperature profile.

The influence of molecular weight on the efficiency of the grafting reaction was studied using four different MAPP compounds (Table 4.1). Extrusion processing conditions were held constant with the barrel temperature at 160°C and the rotational speed of the screws at 60 rpm.

Extraction of Wood Particles

Unmodified wood particles were Soxhlet extracted with acetone for 24 hours to remove impurities, air dried for 60 hours, and then oven dried at 105°C to a constant weight before using for further analysis. Modified wood particles were also Soxhlet extracted with xylene for 24 hours to remove any unreacted maleated polyolefins which had not been linked to the wood particles, followed by air drying for 60 hours, and oven

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drying to a constant weight at 105°C. These modified wood particles were then analyzed by FTIR. A second 24-hour Soxhlet extraction was performed to ensure the removal of unreacted maleated polyolefin was complete from the surface of wood particles upon the first extraction. Following the second extraction, modified wood particles were again air dried for 60 hours and then dried to a constant weight at 105°C, after which FTIR, XPS and titrimetric analyses were performed.

Surface Characterization of Wood Particles

FTIR spectra of both unmodified and modified wood particles were obtained using a Nicolet Protégé 460 FTIR spectrometer (Nicolet Instrument Co., Madison, WI) to determine the functional groups present at the surface of the samples before and after modification. Spectra were recorded in Kubelka-Munk units in the range of 4000-400 cm^{-1} , with a resolution of 4 cm^{-1} and a coaddition of 128 scans for each spectrum. All spectra were collected using diffuse reflectance with FTIR for transfer of IR radiation. Pure powdered potassium bromide (KBr) was used as a reference substance. No dilution of the wood particles in KBr was required to obtain the spectra. Data analysis was performed using WinFIRST software from Thermo Nicolet (Madison, WI). No baseline modification was done before performing data analysis of the spectra.

Based on prior work (1), the regions of interest in the FTIR spectra of modified wood particles with maleated polyolefins were the absorbance bands near 2900 cm^{-1} and 1740 cm^{-1} , for CH stretching of aliphatic carbon chains and carbonyl group stretching suggesting the formation of ester linkages, respectively. Using the integrated area under these peaks, a grafting index (GI) was calculated using the following equation:

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$$GI_X = \frac{A_X \text{ (Modified)}}{A_X \text{ (Unmodified)}} \quad (1)$$

where x represents the absorbance band at either 2900 cm⁻¹ or 1740 cm⁻¹, $A_X \text{ (Modified)}$ represents the integrated area of the peak after modification and $A_X \text{ (Unmodified)}$ represents the integrated peak area of the unmodified wood particles.

X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Physical Electronics Phi 5400 ESCA System, (Physical Electronics USA, Chanhassen, MN) using a non-monochromatic Mg source and a takeoff angle of 45° relative to the detector. A low resolution scan from 0 to 1100 eV binding energy was used to determine the concentration of each element present on the surface of the samples, along with the oxygen to carbon (O/C) atomic ratio, whereas a high resolution scan of the C_{1s} region from 280 to 300 eV was performed to further analyze the chemical bonding of the carbon atoms. Carbon components C1 arise from carbon atoms bonded only to carbon and/or hydrogen atoms (C-C/C-H), C2 from carbon atoms bonded to a single oxygen atom, other than a carbonyl oxygen (C-OH), C3 from carbon atoms bonded to two non-carbonyl oxygen atoms or to a single carbonyl oxygen atom (O-C-O, C=O), and C4 from carbon atoms which are linked to a carbonyl and a non-carbonyl group (O-C=O) (9, 11, 17). The procedure for XPS data collection and analysis was detailed in other articles (9, 11).

As mentioned, the chemical reaction of maleated polyolefins and wood particles takes place between the maleate groups of the polyolefin and hydroxyl groups on the

surface of wood. Since C2 component arises from atoms bonded to a single oxygen atom, other than a carbonyl oxygen (C=O), the change in the content of C2 component before and after modification can be used to monitor the occurrence of the esterification between the maleated polyolefins and the wood particles. To quantify this change, a hydroxyl index (HI) was calculated from C2 component of C_{1s} data as follows:

$$HI = \frac{C2_{Modified}}{C2_{Unmodified}} \quad (2)$$

where $C2_{Modified}$ and $C2_{Unmodified}$ represent C2 after modification and in the unmodified wood particles, respectively.

A complimentary technique to FTIR and XPS analyses, titrimetric analysis was also performed on unmodified and modified wood particles to provide additional proof of the esterification reaction, and to elucidate the mechanism of the chemical reaction between wood and MAPE. Titrations were carried out following a procedure described elsewhere (17), using an Oakton pH CON 510 pH meter. Accurate endpoints were difficult to determine when a visual indicator was used because wood particles significantly darkened the solution color. To insure greater accuracy, potentiometric titrations were used with a first derivative method for endpoint determination (18). Four samples each of unmodified and modified wood particles were analyzed for acid value (AV), saponification value (SV), and hydroxyl value (HV). Acid value accounts for the amount of free carboxylic acid groups present in the sample, while saponification value

measures both acid and ester groups in the sample. Hydroxyl value quantifies the free and accessible hydroxyl groups present in the sample (17). These quantities were calculated using the following formulas (17):

$$AV = 56.1 \frac{N}{p} \quad (3)$$

$$SV = 56.1 (b - a) \frac{N}{p} \quad (4)$$

$$HV = [(b - a) N (56.1)] + AV \quad (5)$$

where N is the normality of potassium hydroxide (KOH), p is the amount in grams of wood particles, b is the volume of KOH needed to neutralize the blank (solvent only) and a is the volume of KOH required to neutralize the sample. The factor 56.1 accounts for the molecular weight of KOH.

RESULTS AND DISCUSSION

Effect of Maleated Polyethylene (MAPE) Content

FTIR spectroscopy was used to monitor and quantify changes that occurred on the surface of wood particles after reactive extrusion with MAPE. Infrared spectra of unmodified wood particles, pure MAPE, and wood particles modified with various concentrations of MAPE are shown in Figure 4.3. Table 4.3 lists the wavenumbers of peaks found in these spectra, along with assignments of corresponding functional groups. Regardless of the MAPE content, evidence of the grafting of MAPE compound to the surface of wood particles was apparent in the spectra of modified wood particles (spectra C-F). A distinct change was clearly seen near the absorption band at 2900 cm^{-1} , where a large band between 2920 and 2850 cm^{-1} , having two distinct peaks similar in appearance to pure MAPE (spectrum B), replaced the single peak in the unmodified wood particle (spectrum A). This change was most noticeable at MAPE concentrations above 10% where the integrated area under the absorption band near 2900 cm^{-1} increased in the modified wood particles, compared to the unmodified ones, implying the grafting of the pendant polyethylene chain of MAPE to the surface of wood particles. Similarly, the integrated area under the absorption band near 1740 cm^{-1} has significantly increased for wood particles extruded with MAPE compound. Several authors have correlated the increased integrated area or peak height of this band with the esterification reaction between wood particles and maleated compounds, since absorbance in the range of 1725 - 1750 cm^{-1} is characteristic of ester carbonyl stretching (5-10, 12-14, 19).

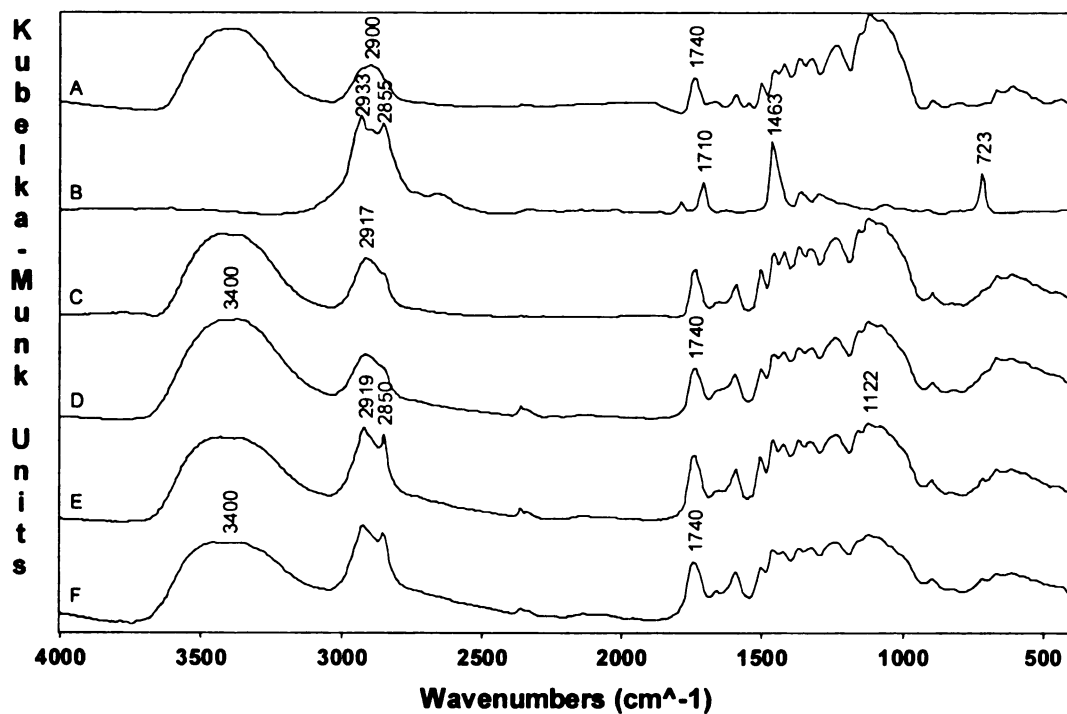


Figure 4.3. FTIR spectra of unmodified wood particles (spectrum A), pure maleated polyethylene-MAPE (spectrum B), wood particles modified with 5% MAPE (spectrum C), 10% MAPE (spectrum D), 15% MAPE (spectrum E), and 20% MAPE (spectrum F) after a second 24-hour Soxhlet extraction in the region $4000\text{--}400\text{ cm}^{-1}$.

Table 4.3. FTIR Absorption Bands and Assignments for Unmodified Wood Particles, Pure MAPE, Pure MAPP and Modified Wood Particles

Unmodified wood (cm ⁻¹)	Pure MAPE (cm ⁻¹)	Pure MAPP (cm ⁻¹)	Wood particles modified with MAPE (cm ⁻¹)	Wood particles modified with MAPP (cm ⁻¹)	Peak assignments	References
3500-3100	-----	-----	3500-3100	3500-3100	OH stretching	10,14,19
2900	2933-2855	2960-2839	2925-2852	2951-2840	CH stretching of CH ₂ , CH ₃	10,14,19
-----	1775	1775	-----	-----	Anhydride C=O stretching	10,19
1740	-----	-----	1740	1740	C=O stretching (ester carbonyl)	6,9,10,13,19
-----	1710	1713	-----	-----	C=O stretching (acid carbonyl)	6,9,10,13,19
1590-1400	-----	-----	1590-1400	1590-1400	Aromatic ring stretching	10,19
1480-1435	1463	1456	1461-1462	1460-1462	CH ₂ deformations	19
1400-1300	-----	1376	-----	1376	CH ₂ deformations	19
1240, 1122	-----	1164-1166	1240, 1122	1240, 1122-1128	C-O and C-O-C stretching, OH deformation	10,13, 19
-----	-----	997-809	-----	-----	CH rocking vibration	19
-----	723	-----	-----	-----	(CH ₂) _n rocking vibration (n > 3)	19

The grafting efficiency of wood particles with various MAPE contents through a reactive extrusion process was quantified by calculating the grafting index (Equation 1) from the integrated area under the peaks near 2900 cm^{-1} and 1740 cm^{-1} for unmodified and modified wood particles. Figure 4.4 clearly illustrates that the grafting index increased with MAPE content up to 15%, independent of the absorption peak used. There appeared to be some leveling off between 15% and 20% MAPE concentration, which may indicate a level of maximum grafting efficiency has been reached. These results suggest that the esterification reaction was a function of the MAPE concentration used.

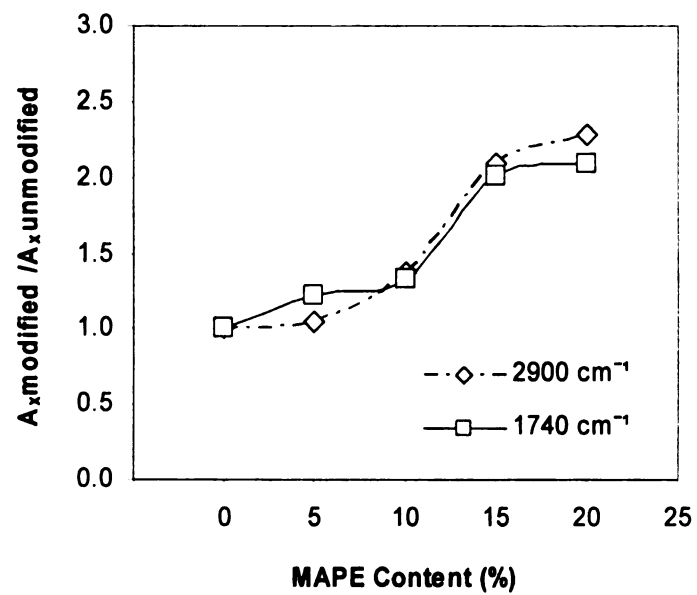


Figure 4.4. Grafting index for FTIR absorbance bands near 2900 cm⁻¹ and 1740 cm⁻¹ for unmodified wood particles and wood particles modified with 5-20% MAPE.

XPS and titrimetric data listed in Tables 4.4 and 4.5, respectively, corroborated the conclusions drawn from FTIR analysis. As expected, reactive extrusion of wood particles with MAPE caused an increase in the concentration of unoxidized carbon atoms (C1 component) and decreased the contents of oxidized carbon atoms (C2-C4 components). Consequently, a significant decrease of the O/C atomic ratios was observed due to the presence of aliphatic carbons of polyethylene chains of MAPE. Furthermore, both the hydroxyl index (HI in Table 4.4) and the free and accessible hydroxyl groups (HV in Table 4.5) significantly decreased after modification with MAPE compounds through a reactive extrusion process. The decrease in both hydroxyl index and free and accessible hydroxyl groups after modification implied that esterification reaction took place through the hydroxyl groups on the surface of the wood particles.

Unlike FTIR, which clearly showed an increase in ester carbonyl as a function of MAPE content, C3 component (carbonyl groups) showed a decreasing trend as MAPE content increased, while C4 component (ester groups) was not detected at all on the surface of the modified wood particles. This apparent difference can be explained by the higher surface sensitivity of XPS, which has a probing depth of only a few nanometers (11, 16). Unoxidized carbon from the pendant polyolefin chain of MAPE was concentrated on the wood particle surface, as evidenced by the high content of C1 component (Table 4.4), and may have obstructed the detection of C3 and C4 components during XPS analysis.

Table 4.4. Elemental Surface Compositions and High-Resolution C_{1s} Peaks of Wood Particles Determined by XPS

Materials ¹	Elemental compositions (%)			O/C atomic ratios	Analysis of C _{1s} peaks (%)				OH index (HI) ³
	O	C	Zn ²		C1	C2	C3	C4	
Unmodified wood particles	31.85	68.15	0.00	0.47	39.75	51.20	8.46	0.58	1.00
Pure MAPE	10.09	89.91	0.00	0.11	87.13	7.71	5.16	0.00	0.15
Wood particles modified with 5% MAPE	15.44	83.69	0.87	0.18	82.22	13.30	4.48	0.00	0.26
Wood particles modified with 10% MAPE	11.97	87.39	0.64	0.14	85.32	10.97	3.71	0.00	0.21
Wood particles modified with 15% MAPE	6.37	93.39	0.24	0.07	92.80	5.29	1.91	0.00	0.10
Wood particles modified with 20% MAPE	2.97	97.03	0.00	0.03	95.08	4.34	0.58	0.00	0.08

¹Unmodified and modified wood particles used were those obtained after a second 24 h Soxhlet extraction.

²Zn from the esterification catalyst was detected in some samples.

³OH index calculated from Equation 2.

Table 4.5. Hydroxyl Value, Acid Value and Saponification Value Determined by Titrimetric Analysis

Wood particles ¹	Titration values ²		
	Hydroxyl value (HV) (eq/kg)	Acid value (AV) (eq/kg)	Saponification value (SV) (eq/kg)
Unmodified	268 ± 4	3.15 ± 0.11	64 ± 6
Modified with 5% MAPE	233 ± 8	3.37 ± 0.23	65 ± 4
Modified with 10% MAPE	233 ± 26	3.53 ± 0.12	79 ± 8
Modified with 15% MAPE	217 ± 11	3.87 ± 0.20	132 ± 10
Modified with 20% MAPE	215 ± 3	4.00 ± 0.24	131 ± 8

¹Unmodified and modified wood particles used were those obtained after a second 24-h Soxhlet extraction.

²Titration values represent an average of four samples.

As shown in Figure 4.1, two possible reactions could occur between MAPE and wood particles in a reactive extrusion process: a single site reaction, which lead to the formation of monoester with carboxylic acid pendent groups (Figure 4.1a) and/or or diester formation without carboxylic acid pendent groups (Figure 4.1b) (9, 13). Acid value (AV) and saponification value (SV) determined by titrimetric analysis (Table 5) were used to elucidate which reaction had occurred. The AV, which accounts for the free carboxylic acid group content in the system, slightly increased in the samples after modification (Table 4.5). However, this increase was not significant compared to the unmodified wood particles. Thus, there were a negligible amount of free carboxylic acid groups in the system. By contrast, SV, which accounts for both ester and acid groups, increased significantly after modification (Table 4.5). Since there was a negligible amount of free carboxylic acid groups on the surface of the modified wood particles, the increased SV originated mainly from the formation of maleate ester with OH groups on the wood particle surface. This result suggests that most of the MAPE was attached to the wood particle surface via two acid groups from the cyclic anhydride of the MAPE, i.e., through diesterification reaction (Figure 4.1b). Moreover, FTIR spectra shown in Figure 4.3 support this mechanism. Two distinct peaks in the range $1700\text{-}1750\text{ cm}^{-1}$ should have been detected if the esterification reaction had occurred through monoester reaction (6, 9, 13). The first peak at around $1705\text{-}1710\text{ cm}^{-1}$ is associated with the non-reacted carboxylic acid (monoester formation) whereas the second one near $1725\text{-}1750\text{ cm}^{-1}$ are caused by the ester carbonyl absorption of the reacted MAPE with the OH groups of wood (diester formation) (6,9,13). As seen in Figure 4.3, all spectra of modified wood particles showed only one peak at 1740 cm^{-1} , which is characteristic of

ester carbonyl, and the absence of bands at 1705-1710 cm^{-1} in these spectra clearly proved that there were no free carboxylic acid groups in the samples, thus confirming diester formation.

The relatively high temperature (160°C) used to modify the wood particles in the reactive extrusion process may also explain why the diester form was predominant in this system. Other authors have reported higher monoester formation in the reaction of maleated compounds with wood particles in solvents at room temperature (3-8). Additional heat was required to cause the second acid group of the maleated compound to react with wood particles, forming the diester (4,6). Hon and Xing determined that diesters began to increase in their system at temperatures above 140°C (4). Similarly, Felix and Gatenholm found more diester content than monoester in cellulosic particles modified with MAPP at 100°C (13). Since the temperature used for reactive extrusion of wood particles in this study was even higher than those reported by other authors, it was likely sufficient to cause the reaction of both acid groups in the MAPE with hydroxyl groups on the wood particle surface, resulting in diester as the primary ester form.

Although AV and SV were calculated, it was not possible to quantify the total ester content in these samples because calculation of monoester, diester and total ester content require sample weight gain after modification (3, 4). During the reactive extrusion process, waste material is produced at the beginning and end of the run, so not all modified sample can be collected. Even without this information, evidence of the grafting reaction suggests that reactive extrusion is an efficient process for modifying wood particles with binding agents such as MAPE compounds.

Effect of Extrusion Processing Conditions

In a prior part of this study, wood particles were modified at a constant extrusion temperature profile (160°C) and rotational screw speed (60 rpm). Since the chemical reaction between wood particles and maleated polyolefins can be affected by both temperature and residence time in the extruder, it is important to understand how these extrusion processing conditions would affect the grafting efficiency of wood particles modified through reactive extrusion.

Figure 4.5 shows the grafting indices for the absorption bands near 2900 cm^{-1} (Figure 4.5a) and 1740 cm^{-1} (Figure 4.5b) plotted for each extruder barrel temperature over the range of rotational screw speeds investigated. There was a clear indication that the grafting indices increased after modification, irrespective of the extrusion temperature profile and rotational screw speed used. The increased grafting index values indicated that more CH_2 and C=O groups had been attached to the wood particle surface, which implied that the esterification reaction had occurred between the wood particles and MAPE. However, surface modification was not a function of processing conditions used since no trend in grafting index was observed with increasing the extruder's temperature profile or increasing rotational screw speed for either absorbance band.

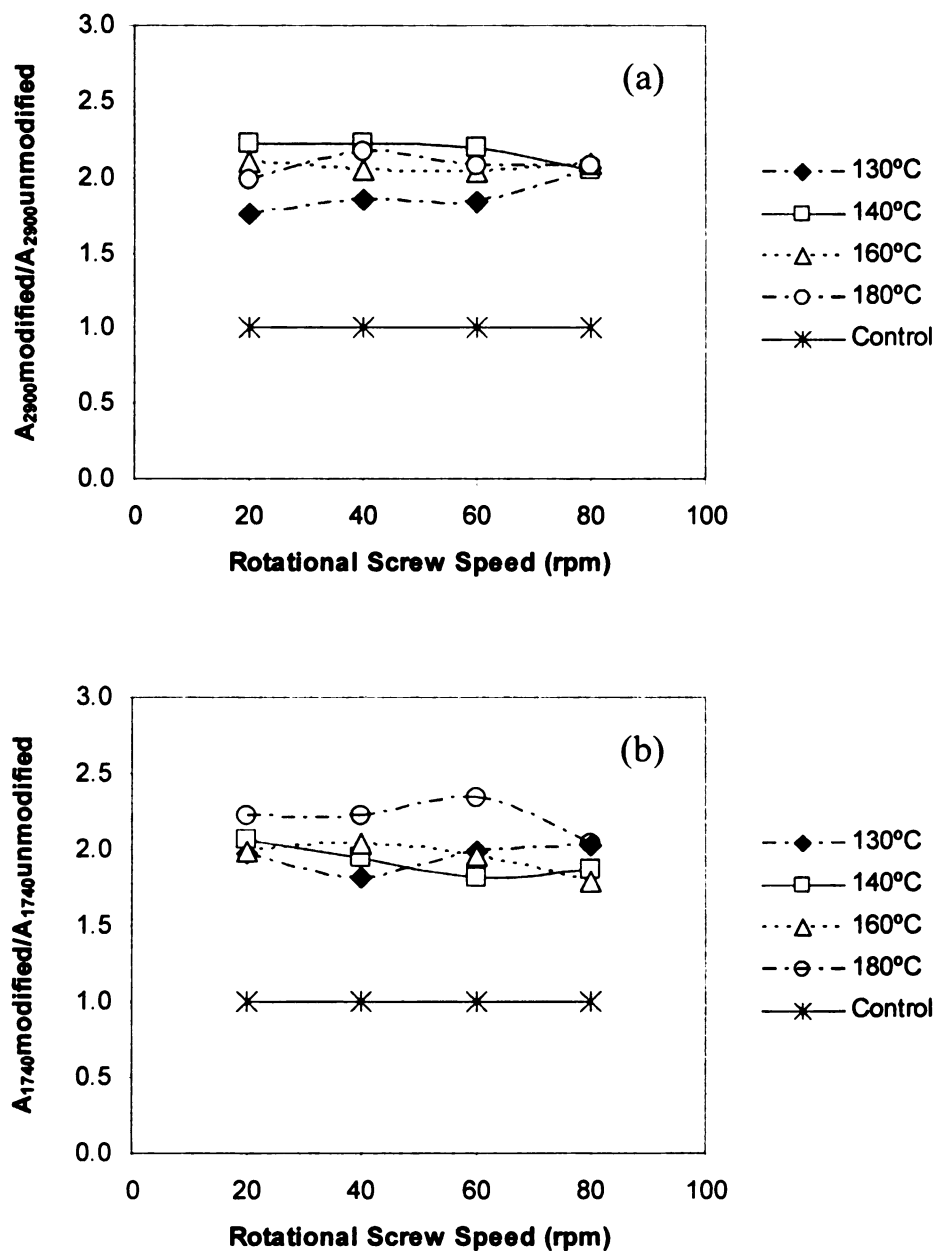


Figure 4.5. Effect of processing conditions on grafting index for unmodified and modified wood particles over the range of extruder barrel temperature and rotational screw speed combinations: (a) band near 2900 cm^{-1} and (b) band near 1740 cm^{-1} .

XPS results agreed with the above conclusions obtained from the infrared spectroscopy (Tables 4.6 and 4.7). Changing the extruder's rotational screw speeds while maintaining a constant temperature profile (Table 4.6) or vice versa (Table 4.7) did not affect the grafting efficiency. In both cases, it was apparent that the surfaces of modified wood particles had been chemically changed from the unmodified wood particles, as evidenced by the large increase in the concentration of unoxidized carbon atoms (C1 component) coupled with a significant reduction in both the O/C atomic ratios and hydroxyl indices (HI) under all processing conditions. However, no trend was observed in C1, HI or the O/C atomic ratio as the extruder's rotational screw speed or barrel temperature was increased.

Table 4.6. Effect of Extruder's Rotational Screw Speed on Surface Chemistry of Wood Particles Modified with 20% MAPE at 160°C

Extruder's rotational screw speed (rpm)	Elemental compositions (%)		O/C atomic ratios	Analysis of C _{1s} peaks (%)				OH index (HI)
	O	C		C1	C2	C3	C4	
Unextruded (control)	31.85	68.15	0.47	39.75	51.20	8.46	0.58	1.00
20	5.61	94.39	0.06	92.62	5.12	2.26	0.00	0.10
40	3.72	96.28	0.04	95.80	3.40	0.80	0.00	0.07
60	2.39	97.61	0.02	96.90	3.10	0.00	0.00	0.06
80	2.97	97.03	0.03	95.08	4.34	0.58	0.00	0.08

Table 4.7. Effect of Extruder's Barrel Temperature on Surface Chemistry of Wood Particles Modified with 20% MAPE at 60 rpm

Extruder's barrel temperature (°C)	Elemental compositions (%)		O/C atomic ratios	Analysis of C _{1s} peaks (%)				OH index (HI)
	O	C		C1	C2	C3	C4	
Unextruded (control)	31.85	68.15	0.47	39.75	51.20	8.46	0.58	1.00
130	3.36	96.64	0.03	95.27	3.04	1.69	0.00	0.06
140	5.47	94.53	0.06	92.61	5.26	2.12	0.00	0.10
160	2.39	97.61	0.02	96.90	3.10	0.00	0.00	0.06
180	5.05	94.95	0.05	95.24	4.76	0.00	0.00	0.09

Effect of Maleated Polypropylene (MAPP) Molecular Weight

Maleated polyolefins with a wide variety of molecular weights are available on the market. Four different MAPP compounds were used (Table 4.1) to determine how different molecular weights (from a low of 11,200 to a high of 52,000 g/mol) affect the surface modification of wood particles in reactive extrusion process. To achieve this objective, the MAPP content was held constant at 20% while the extrusion temperature profile and rotational speed of the screws were set at 160°C and 60 rpm, respectively.

Figures 4.6 and 4.7 illustrate the FTIR spectra of pure MAPP compounds with various molecular weights and wood particles modified with these MAPPs, respectively. The peak assignments for these spectra are also listed in Table 4.3. Evidence of the grafting of MAPP to the wood particles through esterification is apparent in the modified wood spectra (Figure 4.7, spectra B-E) because the single absorption band near 2900 cm^{-1} in the spectrum of unmodified wood particles has been replaced by a large band between 2955 and 2840 cm^{-1} , having distinct peaks similar in appearance to the pure MAPP counterparts. Another indication of grafting of the maleated polyolefin was an increased area of the absorption band at around 1740 cm^{-1} , from C=O groups attached to the wood surface, likely from the esterification reaction (5-10, 12-14). Although not clearly seen in Figure 4.7 due to stacking of five spectra in one figure, the individual spectra of modified wood particles showed an increased intensity in the bands at 1462 and 1376 cm^{-1} which also indicated the grafting reaction had occurred and added more C-H to the surface of the modified samples (10, 12, 14).

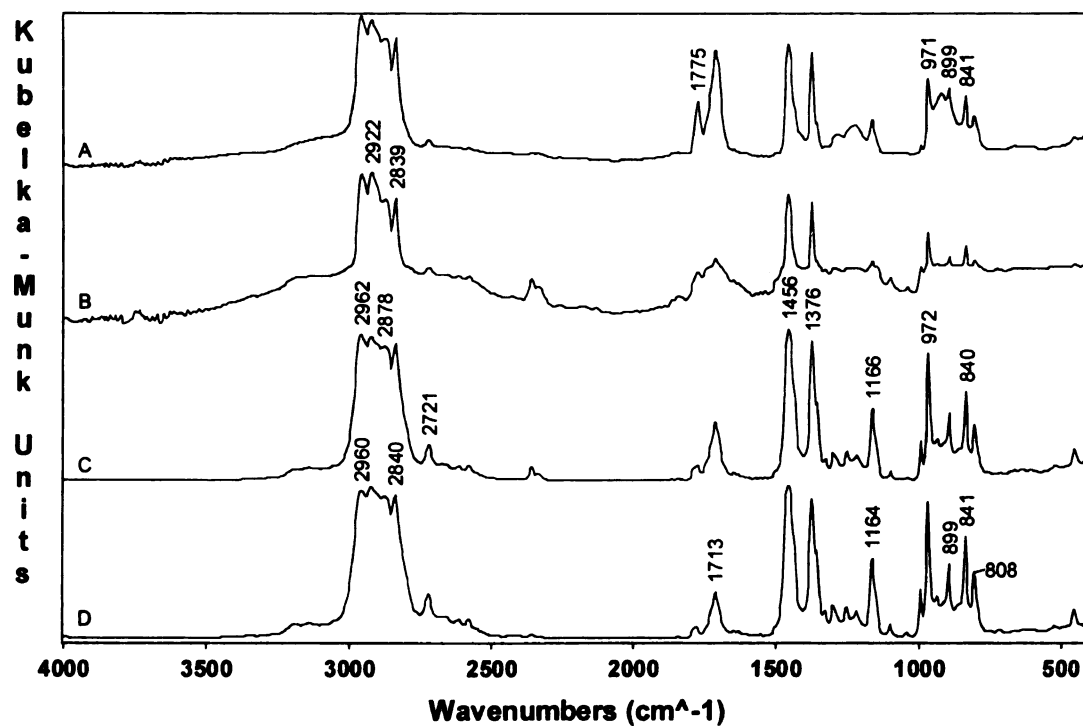


Figure 4.6. FTIR spectra of pure MAPP compounds with various molecular weights: 11,200 g/mol or E-43 (spectrum A), 39,000 g/mol or G-3216 (spectrum B), 47,000 g/mol or G-3015 (spectrum C) and 52,000 g/mol or G-3003 (spectrum D) in the region 4000-400 cm⁻¹.

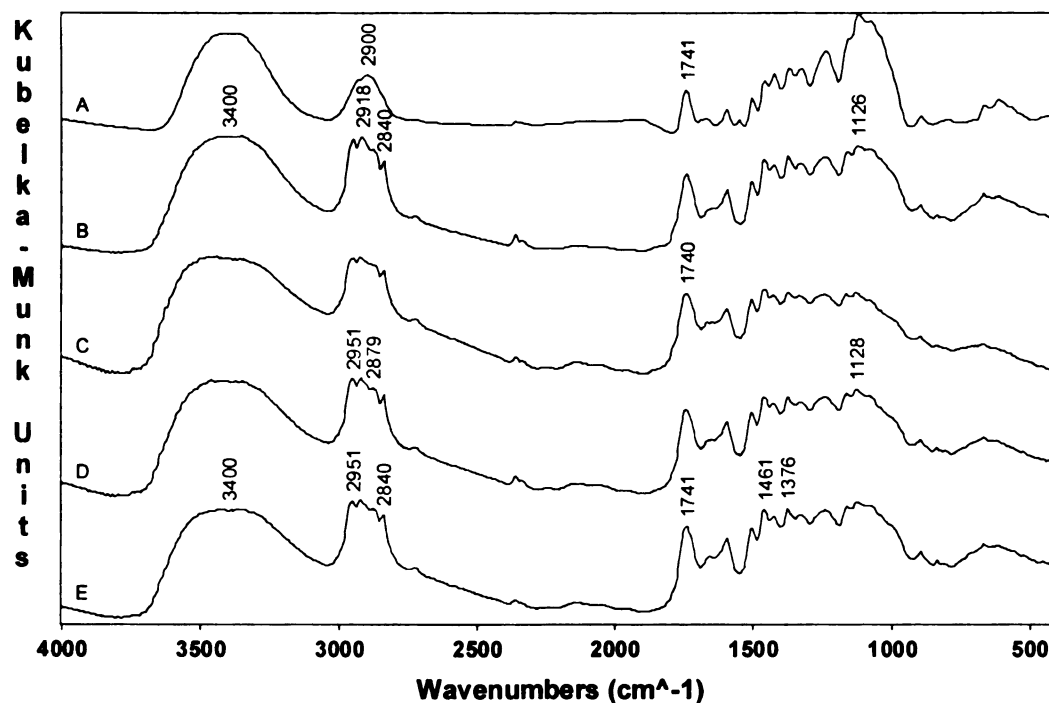


Figure 4.7 FTIR spectra of unmodified wood particles (spectrum A), wood particles modified with MAPP compounds of various molecular weights: 11,200 g/mol or E-43 (spectrum B), 39,000 g/mol or G-3216 (spectrum C), 47,000 g/mol or G-3015 (spectrum D), and 52,000 g/mol or G-3003 (spectrum E) in the region 4000-400 cm⁻¹.

Moreover, all four MAPP compounds had significantly increased grafting indices as compared to unmodified wood particles (Figure 4.8). However, no significant difference in grafting index was observed between the four types of MAPP-modified wood particles. These results were in agreement with those obtained from the XPS analysis (Table 4.8). As expected, the surface of modified wood particles resulted in an increased C1 content and a significant decrease in both O/C atomic ratio and hydroxyl index (HI), all of which provided evidence of the surface modification through esterification reaction.

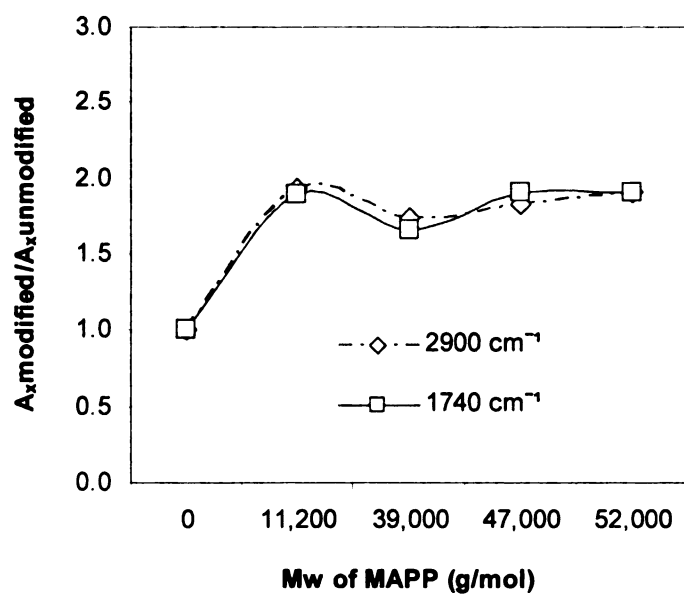


Figure 4.8. Effect of molecular weight on grafting index for unmodified wood particles and wood particles modified with 20% MAPP compounds.

Table 4.8. Elemental Surface Compositions and High-Resolution C_{1s} Peaks of MAPP, Wood Particles, and Wood Particles Modified with MAPP Determined by XPS

Materials	Elemental compositions (%)		O/C atomic ratios	Analysis of C _{1s} peaks (%)				OH index (HI)
	O	C		C1	C2	C3	C4	
E-43 (Mw=11,200)	4.89	95.11	0.05	94.92	4.35	0.74	0	0.08
G-3216 (Mw=39,000)	3.86	96.14	0.04	95.85	3.24	0.91	0	0.06
G-3015 (Mw=47,000)	3.77	96.23	0.04	96.01	2.62	1.37	0	0.05
G-3003 (Mw=52,000)	3.28	96.72	0.03	96.58	2.57	0.84	0	0.05
Unmodified Wood	31.85	68.15	0.47	39.75	51.20	8.46	0.58	1.00
Wood-E-43	7.22	92.78	0.08	93.39	4.75	1.86	0	0.09
Wood-G-3216	3.60	96.40	0.04	94.86	4.17	0.97	0	0.08
Wood-G-3015	3.36	96.64	0.04	95.38	4.20	0.42	0	0.08
Wood-G-3003	5.87	94.13	0.06	90.99	6.19	2.83	0	0.12

However, no distinct trend was observed between molecular weight of MAPP and grafting efficiency through a reactive extrusion process. Since both FTIR and XPS results confirmed that there were no significant differences in grafting of MAPP with various molecular weights, the molecular weight range studied (11,200-52,000 g/mol) may not have been large enough to observe differences in reactivity. Another possibility could be that at 20% MAPP content, the maximum level of grafting had already been achieved with each compound, regardless of its molecular weight. Thus the differences in the grafting efficiency were not detected. Moreover, Figure 4.4 clearly illustrates that the GI leveled off between 15 and 20% maleated polyolefin content, which may indicate a level of maximum grafting efficiency had been reached. Perhaps another study at lower MAPP concentrations would elucidate differences of MAPP molecular weight on the efficiency of the grafting reaction.

CONCLUSIONS

This study examined the chemical reactions between maleated polyolefins and wood particles in a reactive extrusion process. The effects of maleated MAPE content, extrusion processing conditions (barrel temperature and rotational screw speed), and molecular weight of MAPP were studied, with the goal of determining the effects of each set of conditions on the grafting efficiency of modified wood particles in a reactive extrusion process. Efficiency of the modification was evaluated using FTIR, XPS and titrimetric analysis. From the experimental results, the following conclusions can be drawn:

1. The esterification reaction between wood particles and MAPE was a function of the MAPE concentration used to modify the wood particles. The grafting reaction produced mostly the diester form of the modified wood particle during reactive extrusion.
2. No significant difference was found in grafting efficiency of the modified wood particles at different extrusion processing conditions. Changing the extruder's barrel temperature profile (130-180°C) and/or its rotational screw speed (20-80 rpm) resulted in adequate grafting, which indicated that the esterification reaction was not a function of processing conditions over the range studied.
3. Regardless of MAPP molecular weight (from a low of 11,200 to a high of 52,000 g/mol) all investigated MAPP compounds were effective in changing the surface of wood particles after modification, compared to unmodified wood particles. However, no distinct trend was observed between molecular weight of MAPP and grafting efficiency through a reactive extrusion process. It is believed that the

high content of MAPP (20%) used in this study prevented the detection of differences in the grafting efficiency because the maximum level of grafting reaction had already occurred with each component at 20% MAPP content.

4. The reactive extrusion process was found to be a suitable way to modify wood particles with maleated polyolefins as it worked quickly and without the use of solvents. This process would be industrially friendly, and in light of our prior success bonding the modified fibers together in a hot press, would allow large quantities of modified wood particles to be produced for the manufacture of a formaldehyde-free wood composite product.

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CHAPTER 5

INFLUENCE OF PROCESSING CONDITIONS AND MATERIAL COMPOSITIONS ON THE PERFORMANCE OF FORMALDEHYDE-FREE WOOD-BASED COMPOSITES

This chapter is in press for *Polymer Composites* (2006). It is co-authored by K. Carlborn and L.M. Matuana.

ABSTRACT

This study examined the differences between formaldehyde-free wood composite panels made with maleated polyethylene (MAPE) and maleated polypropylene (MAPP) binding agents. Specifically, the study investigated the contrasts of (i) base resin type, PE vs. PP, (ii) molecular weight/maleic anhydride content in MAPP binding agents, and (iii) the manufacturing methods (reactive extrusion vs. hot press) on the physico-mechanical properties of the composites. FTIR and XPS analyses of unmodified and modified wood particles after reactive extrusion with maleated polyolefins provided evidence of chemical bonding between the hydroxyl groups of wood particles and maleated polyolefins. While extruding the particles before panel pressing gave better internal bond strength, superior bending properties were obtained through compression molding alone. MAPP-based panels outperformed MAPE-based panels in stiffness. Conversely, MAPE increased the IB strength of the panels compared to MAPP. Polymer base resin had no effect on modulus of rupture or screw holding capacity. Differences between the two maleated polypropylene compounds were not significant for any of the mechanical properties tested. Formaldehyde-free wood composites manufactured in this study often outperformed standard requirements for conventional particleboard, regardless of material composition or manufacturing method used.

INTRODUCTION

The chemical reaction between wood and anhydride compounds has been shown to plasticize the wood, making it more versatile for wood composite applications. Several investigators have studied wood modification with anhydrides in order to determine thermal properties, moisture resistance, compatibility with polymeric matrices, etc. (1-11). A lower softening temperature, compared to unmodified wood, has been documented in esterified wood after reaction with various anhydrides (2, 8, 10, 11). Esterified wood has also been found to resist moisture (1, 3, 4-11) and to be more compatible than unmodified wood with polyester matrices in the manufacture of composites (4-6). A second reaction of the esterified wood with epoxides formed oligoesters, which further thermoplasticized the wood and allowed for better control of structure and resulting properties of the modified wood (1, 7-11).

While the thermoplastic nature of esterified and oligoesterified wood modified through these methods has been documented, few authors have exploited this characteristic to make wood composites without added adhesive. Matsuda and co-workers used three dicarboxylic acid anhydrides (maleic, phthalic and succinic anhydride) to esterify wood particles, which were then molded into sheets through compression molding (1, 8). Clemons and co-workers used similar methods to modify wood fibers with anhydrides to prepare fiberboards (3). In both studies, chemically modified wood was able to partially melt when heated and bond without additional adhesive. Formulations containing succinic anhydride were found to have the most thermoplastic character in both studies (1, 3, 8). Further work by Matsuda et al. (1, 7, 8) showed enhanced thermoplasticization of wood through the grafting of various types of

epoxides onto the already esterified wood surface. The oligoesterified wood produced from these reactions was even more thermoplastic-like in structure than the esterified wood produced through reaction with the anhydrides, and could be easily molded. Using various types of epoxides allowed for different chemical structures in the thermoplasticized wood, and could also be used to form crosslinked wood composites which resembled plastic more than wood (1, 7, 8). Recently, Timar and co-workers demonstrated the use of maleic anhydride to esterify wood particles, followed by oligoesterification with glycidyl methacrylate and additional maleic anhydride as a process to form thermoplastic-like wood particles (9-11). Panels formed through the compression molding of modified wood particles displayed mechanical properties that met or exceeded standard requirements for bending strength and internal bond strength of particleboard or fiberboard (11). These wood composites were also found to be resistant to fungal decay.

Although esterifying and oligoesterifying the wood surface has been shown to be an effective method for manufacturing wood composite materials without additional adhesive, most methods require harmful solvents such as xylene, dimethyl sulfoxide, or N,N-dimethylformamide as part of the modification process (1-6, 8-11). Additionally, the oligoesterification reactions entail a two-step process (or more depending on the precise control of chemical structure desired) to functionalize the wood surface, which is both time consuming and complicated (1, 7-11). Removal of solvents and further drying of the wood particles is required before compression molding into panels (1, 3, 8, 11).

A simpler approach of functionalizing wood particles to produce wood composite panels without additional adhesive has been developed in our prior work, which

demonstrated the concept of using a reactive extrusion process as a means of developing a new, formaldehyde-free binding system for wood composite products (12). It has been shown that the surface modification of wood particles with maleated polyolefins as the binding agent could be achieved through a continuous reactive extrusion process without the use of solvents (i.e., dry process). Surface analysis of the modified wood particles indicated that the maleate groups of the binding agent were attached to the surface of the wood particles via an esterification reaction, exposing polyolefin chains on the surface of the particles (12, 13). The modified wood particles were then compression molded to produce formaldehyde-free wood composite panels. During panel manufacturing, the pendant polyolefin chains attached to the wood particles melted and flowed under heat and pressure in the hot press, forming entanglements. The entangled polymer chains locked together after cooling, forming direct particle-particle bonds. The physico-mechanical properties of these composite panels, which contain no formaldehyde-based adhesive, compared favorably with or even exceed current standard requirements for particleboard of medium density.

Although formaldehyde-free wood composite panels were successfully manufactured through a reactive extrusion process (12), the process required two different steps: (i) reaction of the wood particles with the maleated polyolefin, and (ii) hot pressing the modified particles into panels. A method that could reduce this process to one step would save time and reduce production costs. Therefore, we hypothesized that both the esterification reaction and binding into panels could occur simultaneously during compression molding, which would greatly simplify the panel manufacturing process.

Furthermore, there currently are many types of maleated polyolefins, differing in molecular weight, base resin type, acid value, percentage of maleic anhydride, etc. Research has not been carried out to examine the effects of these maleated polyolefin variables on the performance of formaldehyde-free wood composites.

Thus, the objective of this work was to investigate the effects of material compositions as (i) base resin type of the maleated polyolefin, either polyethylene or polypropylene, and (ii) maleic anhydride content/molecular weight of maleated polypropylene, as well as manufacturing methods (reactive extrusion vs. hot press) on the physico-mechanical properties of the composites. Emphasis was also placed on determining the effectiveness of the modification after reactive extrusion of wood particles with maleated polyolefins using Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Materials

Maple wood particles of 425 micron (40-mesh) and 150 micron (100-mesh) size were supplied by American Wood Fibers (Schofield, WI) and were used as particles. The smaller particles (150 micron) were used for surface characterization to minimize the effects of scattering and specular reflectance in the diffuse reflectance IR analysis. However, panel manufacturing required a large quantity of modified particles, so larger (425 micron) particles, which were easier to process, were used in panel manufacturing and property testing. Hydrated zinc acetate, the catalyst, and xylene (99.9%, ACS Grade), the solvent used for Soxhlet extraction, were obtained from Baker Analytical Reagents (JT Baker Co., Phillipsburg, NJ). Maleated polyethylene-MAPE (G-2608) and two maleated polypropylenes-MAPP (G-3003 and G-3015) supplied by Eastman Chemical Co. (Kingsport, TN) were used as binding agents. Characteristics of the maleated compounds are listed in Table 5.1. All chemicals were used as received.

Table 5.1. Characteristics of the maleated polyolefins used as binding agents

Properties	MAPE G-2608	MAPP G-3003	MAPP G-3015
Weight % maleic anhydride	1.5	1.5	2.5
Melting point (°C)	122	156	155
Average molecular weight (g/mol)	51,700	52,000	47,000
¹ Melt flow index at 190°C	8	12.7	---
Viscosity at 190°C	---	60,000	25,000

¹Melt flow index measured at 190°C and 2.16 kg according to ASTM D1238.

Surface Characterization of Wood Particles

For batch compounding, 150 micron size wood particles were dried for 48 hours at 105°C to a final moisture content of less than one percent before processing. A 10-liter high intensity mixer (Papenmeier TGAHK20) was used for dry blending of the wood particles, binding agent, and catalyst. The wood:binding agent:catalyst weight ratio was 79:20:1. All components were combined in the mixer and blended for 10 minutes at room temperature.

Reactive extrusion of wood particles was achieved by feeding the compounded wood particles into a 32 mm conical counter rotating twin-screw extruder (C. W. Brabender Instruments, Inc.) with an L/D ratio of 13:1, driven by a 7.5 hp Intelli-Torque Plasti-Corder Torque Rheometer[®]. The barrel temperatures for the three zones inside the extruder were set at 160°C for maleated polyethylene and 165°C for maleated polypropylene, and the rotational speed of the screws was held at 60 rpm during the experiments.

Following the procedures used in prior work, unmodified wood particles and wood particles that had been modified through reactive extrusion were Soxhlet extracted, dried to a constant weight at 105°C and analyzed by FTIR (12, 13). Based on previous studies (12, 13), the regions of interest in the FTIR spectra of wood particles modified with maleated polyolefins were the absorbance bands near 2900 cm⁻¹ and 1740 cm⁻¹, for CH stretching of aliphatic carbon chains and carbonyl group stretching suggesting the formation of ester linkages, respectively. Using the integrated area under these peaks, a grafting index (GI) was calculated using the following equation:

$$GI_X = \frac{A_{X \text{ (Modified)}}}{A_{X \text{ (Unmodified)}}} \quad (1)$$

where x represents the absorbance band at either 2900 cm⁻¹ or 1740 cm⁻¹, $A_{X \text{ (Modified)}}$ represents the integrated area of the peak after modification and $A_{X \text{ (Unmodified)}}$ represents the integrated peak area of the unmodified wood particles (13).

X-ray photoelectron spectroscopy (XPS) was performed on both unmodified wood and wood modified with maleated polyolefin binding agents following the procedure used in prior work (12, 13). A high resolution scan of the C_{1s} region from 280 to 300 eV was run to elucidate the chemical bonding of the carbon atoms. Curve fitting of this high resolution area resolved four different forms of carbon for unmodified wood particles, whereas three different forms were resolved for modified wood particles. Carbon components C1 arise from carbon atoms bonded only to carbon and/or hydrogen atoms (C-C/C-H), C2 from carbon atoms bonded to a single oxygen atom, other than a carbonyl oxygen (C-OH), C3 from carbon atoms bonded to two non-carbonyl oxygen atoms or to a single carbonyl oxygen atom (O-C-O, C=O), and C4 from carbon atoms which are linked to a carbonyl and a non-carbonyl group (O-C=O). Particular attention was given to the C2 component from the high resolution scan because C2 component arises from atoms bonded to a single oxygen atom, other than a carbonyl oxygen (C-OH). Therefore, change in the content of C2 component before and after modification can be used to monitor the occurrence of the esterification between the maleated polyolefins and the wood particles, which occurs at the hydroxyl groups on the wood surface. To

quantify this change, hydroxyl index (HI) was calculated from C2 component of C_{1s} data as follows:

$$HI = \frac{C2_{Modified}}{C2_{Unmodified}} \quad (2)$$

where C2_{Modified} and C2_{Unmodified} represent C2 after modification and in the unmodified wood particles, respectively (13).

Panel Manufacture

Larger wood particles (425 micron size) were compounded at room temperature using the same procedure described above for the surface analysis.

Following the mixing step, two different methods were used to manufacture the composite panels from the compounded wood particles as follows:

The first method was a one-step process where the compounded wood particle mixtures were directly hot pressed without the reactive extrusion step. Compression molding was performed using a hydraulic press from Erie Mill Co. (Erie, PA). Panels were pressed at 193°C for 7 minutes using 8 MPa pressure. After pressing, panels were removed from the press and cooled at room temperature under compression for 15 minutes. Panel dimensions were 380 by 380 by 6 mm, with a target density of 720 kg/m³.

The second method was a two-step process where wood particles were modified with maleated polyolefins in a reactive extrusion process, and then compression molded in a hot press. Reactive extrusion of wood particles followed the same procedure as previously described for the modification of wood particles for surface characterization. Once extruded, the wood particles were compression molded into panels using the above-described pressing conditions.

Panel Property Testing

Density was measured by two different methods for all panels: (i) a simple mass over volume calculation for three panels of each type and (ii) internal density profile (X-ray density analysis) using a Quintek QMS Density Profiler, model QDP-01X, with 5 replicates per panel type.

Three-point flexural, internal bond (IB) strength and screw holding capacity tests were performed on an Instron 4206 testing machine (using Series IX software) in accordance with procedures outlined in ASTM standard D1037-99 (14). The crosshead speeds were 3.05 mm/min, 8.13 mm/min, and 0.6 mm/min for flexural, IB, and screw holding capacity tests, respectively. Screw holding capacity was carried out from the face of the panels. At least six samples were tested to obtain an average value for modulus of rupture (MOR), modulus of elasticity (MOE), IB strength and screw holding capacity, all of which were compared with values listed for particleboard of medium density in the standard ANSI A208.1-1999 (15).

Statistical Analysis

A two-sample *t*-test was carried out with an α significance value of 0.05 to determine the effects of material compositions and manufacturing method on the density, flexural, internal bond and screw holding properties of the composites. Comparisons between binding agents' base resin types and maleic anhydride contents/molecular weights were made under one manufacturing method. Whereas comparisons between manufacturing methods were performed under one base resin type or maleic anhydride content/molecular weight. All statistical analysis was performed using Design Expert software (Version 6) from Stat-Ease, Inc. Minneapolis, MN.

RESULTS AND DISCUSSION

Surface Characterization of Wood Particles

As mentioned, the reaction of wood particles with maleated polyolefins occurs between maleate groups of the maleated polyolefin and hydroxyl groups on the surface of wood, which lead to the formation of a monoester with carboxylic acid pendant groups (Figure 5.1a) and/or diester formation where both carboxylic acid groups react with the wood particle surface (Figure 5.1b). In order to form a wood composite panel, the pendant polyolefin chains grafted to the wood surfaces must melt and flow under heat and pressure during compression molding, forming entanglements. Upon cooling, these entangled polymer chains would be locked together, forming the panel (Figure 5.2).

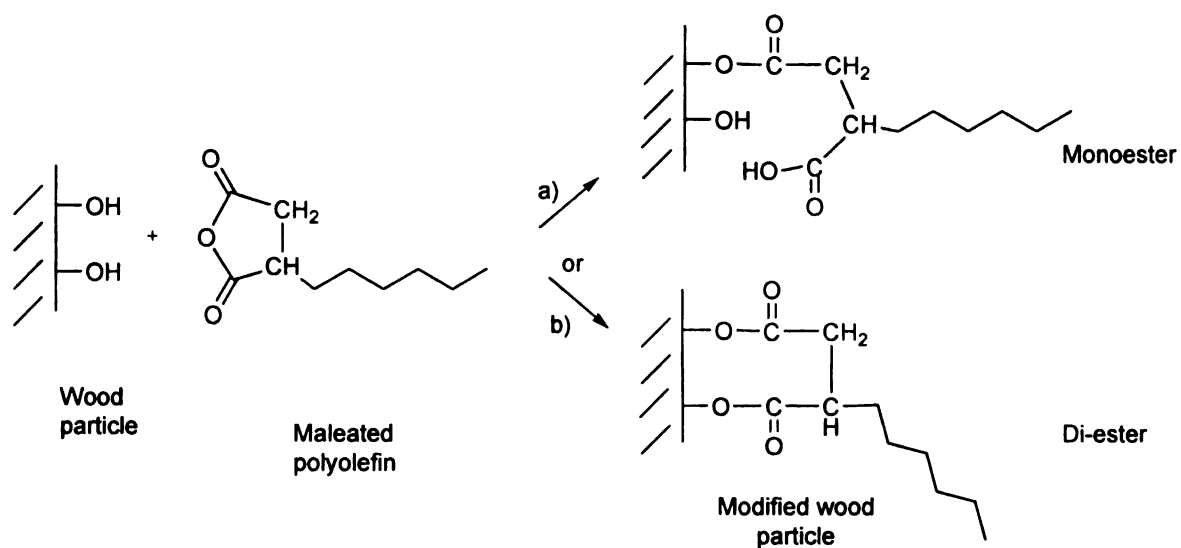


Figure 5.1. Modification scheme for esterification reaction between wood particles and maleated polyolefins: (a) monoester and (b) diester formation.

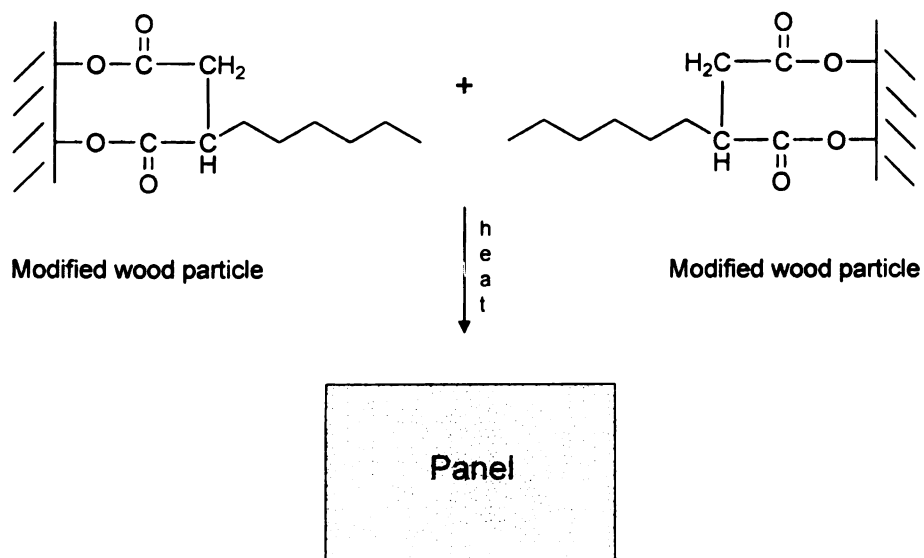


Figure 5.2. Panel manufacturing scheme for the two-step method showing the bonding of pre-reacted wood particles.

FTIR spectroscopy was used to observe and quantify changes that occurred on the surfaces of wood particles after reactive extrusion with maleated polyolefins. FTIR spectra of unmodified wood, maleated polyethylene (MAPE G-2608) and wood particles modified with MAPE after reactive extrusion are shown in Figure 5.3. As stated earlier, the bands of interest in the FTIR spectra occurred near 2900 cm^{-1} and 1740 cm^{-1} . In the spectrum of modified wood particles (spectrum C), two distinct peaks between 2927 cm^{-1} and 2853 cm^{-1} similar in appearance to pure MAPE (spectrum B) replaced the single peak near 2900 cm^{-1} in the unmodified wood (spectrum A). The integrated area under this band increased after modification with MAPE (spectrum C), implying the grafting of the polyolefin chain of MAPE to the surface of the wood particles. Similarly, the integrated area under the absorption band near 1740 cm^{-1} significantly increased for wood particles extruded with MAPE. Several authors have correlated the increased integrated area or peak height of this band with the esterification reaction between wood particles and maleated compounds, since absorbance in the range of $1725\text{-}1750\text{ cm}^{-1}$ is characteristic of ester carbonyl stretching (1-6, 9, 10). Although not shown, similar infrared spectra were obtained for wood particles treated with maleated polypropylene binding agents, i.e., MAPP G-3003 and G-3015.

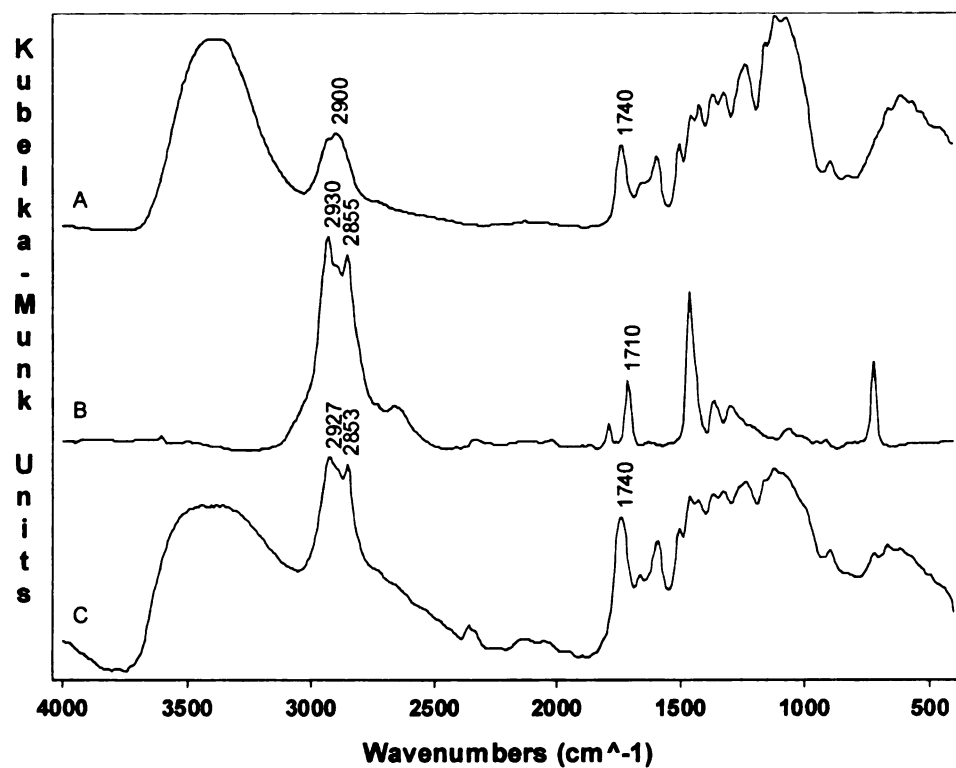


Figure 5.3. Example FTIR spectra of unmodified wood particles (A), pure MAPEG-2608 (B), and wood particles modified with MAPEG-2608 (C) in the region 4000 to 400 cm^{-1} .

The grafting efficiency of wood particles modified with MAPE (G-2608) and two types of MAPP (G-3003 and G-3015) through a reactive extrusion process was quantified by calculating the grafting index (Equation 1) from the integrated area under the peaks near 2900 cm^{-1} and 1740 cm^{-1} for unmodified and modified wood particles. Results listed in Table 5.2 show that grafting index increased after reactive extrusion with each maleated polyolefin, independent of the absorption peak used. These results suggest the esterification reaction had occurred during reactive extrusion.

Table 5.2. Grafting index for peaks near 2900 cm^{-1} and 1740 cm^{-1} for unmodified and modified wood particles with various maleated polyolefin compounds

Samples	Grafting Index (GI) ¹	
	2900 cm^{-1}	1740 cm^{-1}
Unmodified wood particles	1.0	1.0
Wood modified with MAPE G-2608	2.3	2.1
Wood modified with MAPP G-3003	1.9	1.9
Wood modified with MAPP G-3015	1.8	1.9

¹GI is calculated using Equation 1.

XPS data listed in Table 5.3 supported the results of FTIR analysis. As expected, reactive extrusion of wood particles with each of the maleated polyolefins caused a significant increase in the concentration of unoxidized carbon atoms (C1 component) and corresponding decrease in the contents of oxidized carbon atoms (C2-C4 components) in the modified wood particles. Additionally, the hydroxyl index (HI) has significantly decreased after modification with MAPE or MAPP compounds through a reactive extrusion process. The reduction in hydroxyl index suggested that for all three maleated polyolefins, the esterification reaction took place through the hydroxyl groups on the surface of the wood particles.

While the grafting index calculated from the FTIR analysis for the band near 1740 cm^{-1} indicated an increase in ester groups after modification, regardless of the type of maleated polyolefin used, C3 component (carbonyl groups) was reduced in all samples after reactive extrusion with maleated polyolefins, while C4 component (ester groups) was not detected at all on the surface of the modified wood particles (Table 5.3). This apparent difference can be explained by the higher surface sensitivity of XPS, which has a probing depth of only a few nanometers (16). Unoxidized carbon from the pendant polyolefin chain of MAPE or MAPP was concentrated on the wood particle surface, as evidenced by the high content of C1 component (Table 5.3), and may have obstructed the detection of C3 and C4 components during XPS analysis (13).

Table 5.3. High-Resolution C_{1s} Peaks of Wood Particles Determined by XPS

Materials	Analysis of C _{1s} peaks (%)				OH index (HI) ¹
	C1	C2	C3	C4	
Unmodified wood particles	39.75	51.20	8.46	0.58	1.00
Pure MAPE G-2608 (Mw=51,700 g/mol)	87.13	7.71	5.16	0.00	0.15
Wood modified with MAPE G-2608	95.08	4.34	0.58	0.00	0.08
Pure MAPP G-3003 (Mw=52,000 g/mol)	96.58	2.57	0.84	0.00	0.05
Wood modified with MAPP G-3003	90.99	6.19	2.83	0.00	0.12
Pure MAPP G-3015 (Mw=47,000 g/mol)	96.01	2.62	1.37	0.00	0.05
Wood modified with MAPP G-3015	95.38	4.20	0.42	0.00	0.08

¹OH index calculated from Equation 2.

Physico-Mechanical Properties

Density

Table 5.4 summarizes the density (calculated and profile) for the panels manufactured in this study. An example of the x-ray density profile, illustrating the density of the sample at the face and core regions, is shown in Figure 5.4.

Experimental panels were within the medium density range as specified in the ANSI standard A208.1, with average calculated density values ranging from 775-780 kg/m³ (Table 5.4). The calculated and overall (x-ray profile) density of the panels was nearly the same, regardless of the panel manufacturing method. However, the manufacturing method showed two distinct trends in the density profiles of the composite panels. Panels made from unextruded wood particles (one step process, i.e. hot press only) had a higher density in the face region than those containing extruded wood particles (two step process, e.g., reactive extrusion followed by hot press). This feature is typical of conventional glued particleboard, due to greater compaction and solidification of the faces of the panels which experience direct heat during the pressing cycle (17, 18). Conversely, panels manufactured from extruded wood particles had a higher density in the core region.

Table 5.4. Density data for experimental panels bound with maleated polyolefins

Panel Types	Calculated Density (kg/m ³)	X-ray Density Profile		
		Overall (kg/m ³)	Face (kg/m ³)	Core (kg/m ³)
MAPE G-2608 – unextruded	780	780	905	748
MAPE G-2608 – extruded	778	779	881	759
MAPP G-3015 – unextruded	780	781	906	745
MAPP G-3015 – extruded	782	783	833	783
MAPP G-3003 – unextruded	775	778	866	760
MAPP G-3003 – extruded	775	776	821	760

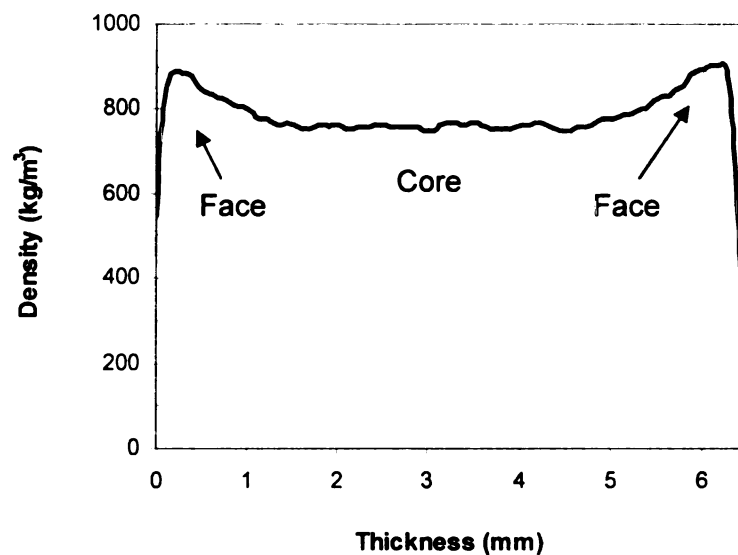


Figure 5.4. X-ray density profile of a sample made from unextruded MAPP G-3003, illustrating the face and core regions of a typical sample.

Mechanical properties of a material are strongly influenced by its density. Therefore, the above results suggest that the mechanical properties of the composites may be dependent on the processing conditions since density differences exist in the face and core region of the panels due to the manufacturing process. Since the overall density was relatively the same between the panels with extruded and unextruded wood particles, differences in mechanical properties associated with the processing conditions might be attributed to the density profile in the panels.

Effects of Processing Conditions

The modulus of rupture (MOR), modulus of elasticity (MOE), internal bond (IB) strength and screw holding capacity data for panels manufactured in this study, along with standard requirements for particleboard of medium density grades, ranging from 640-800 kg/m³, are presented in Table 5.5. To determine significant differences between processing conditions, comparisons were made by varying the processing conditions (rows 1 vs. 2 and 3 vs. 4 under experimental panels) while holding the maleated polyolefin type constant.

Table 5.5. Effects of processing methods and material compositions on the mechanical properties of particleboard panels bound with maleated polyolefins.

Panel Types	Mechanical Properties ¹			
	MOR (MPa)	MOE (MPa)	IB Strength (MPa)	Screw Holding (N)
Medium Density Grades ¹	11.0 – 16.5	1725 – 2750	0.40 - 0.55	900 – 1100
Experimental Panels ²				
MAPE – unextruded	25.41 ± 3.0 ^A	2068 ± 233 ^A	1.22 ± 0.32 ^A	1353 ± 184 ^A
MAPE – extruded	20.70 ± 3.4 ^B	1296 ± 195 ^B	2.07 ± 0.69 ^B	1563 ± 180 ^A
MAPP – unextruded	30.04 ± 6.6 ^A	3582 ± 567 ^C	0.43 ± 0.19 ^C	1469 ± 330 ^A
MAPP – extruded	23.00 ± 4.7 ^B	2875 ± 347 ^D	1.50 ± 0.29 ^D	1580 ± 299 ^A

¹Property requirement data is from standard ANSI A208.1- 1999-Particleboard.

²The means with different letters indicate significance between treatments at the $\alpha = 0.05$ level, while the means with the same letter indicates no difference between treatments.

Mechanical properties of the composite panels differed depending on manufacturing processes. Panels had significantly higher MOR and MOE values when the wood particles were not extruded prior to pressing. This was likely due to localized melting of the unreacted maleated compounds and greater flow at the faces of the panels, causing compaction in the face region, due to the direct heat from the platens. The faces would see more heat throughout the pressing cycle, likely causing the reaction between the wood and binding agent as well. Greater compaction of the face region of the panels was supported by the higher density of that region, as determined through X-ray density profile analysis (Table 5.4). High face region density has been correlated to increased MOR and MOE in conventional particleboard made with formaldehyde-based adhesives (17, 18). In addition, increasing density is related to increased strength properties through a power law relationship (19). Since overall density was relatively the same between the panels with extruded and unextruded wood particles, the increased face density of panels with unextruded wood particles must be responsible for the enhanced bending properties of these panels. Although panels made with extruded wood particles had lower bending properties than their unextruded counterparts, these panels still exceeded the requirements for conventional particleboard in most cases.

Table 5.5 also summarizes the IB strength of composite panels under different manufacturing methods. Internal bond strength is an indication of how well the particles are bonded in the panel, particularly at the core region. The experimental results indicated that the unextruded wood particles underwent both the grafting reaction and entanglement during compression molding since panels were successfully produced without pre-reacting wood particles in the extruder. Unlike the bending properties,

panels prepared from unextruded wood particles had lower IB strength, compared to those made from extruded wood particles. Therefore, the lesser IB strength of composite panels with untreated wood particles was attributed to the reduced density in the core region of these boards, due to the heat not flowing to the center of the panel fast enough to cause adequate polymer flow and panel compaction during the limited pressing time. Similar trends have been reported for conventional glued particleboard (17, 18). In addition, heat is required to drive the reaction between the wood particles and the maleated polyolefins. Since the unextruded wood particles experience heat only during the hot pressing step, they may not receive sufficient heat to complete the esterification reaction and form chemical bonds between the wood and maleated polyolefins, especially in the core region of the panels. By contrast, wood particles that were pre-reacted in the extruder likely had more extensive bonding due to the extra heat and mixing during the extrusion step. This accounts for the significantly higher IB strength in panels made with extruded wood particles.

Processing methods had no effect on the screw holding capacity, which was higher than the requirements for particleboard of medium density (Table 5.5).

Effects of Binding Agent Compositions

Two comparisons were made to determine significant effects of maleated polyolefin base resin types (PE vs. PP) (Table 5.5), and maleic anhydride content in maleated polypropylene (1.5% vs. 2.5% by weight)/molecular weight (52,000 vs. 47,000 g/mol) on the mechanical properties of the composites (Table 5.6).

Table 5.6. Effect of molecular weight/maleic anhydride content of MAPP on the mechanical properties of particleboard panels bound with maleated polypropylenes

Panel Types	Mechanical Properties ¹			
	MOR (MPa)	MOE (MPa)	IB Strength (MPa)	Screw Holding (N)
Medium Density Grades ¹	11.0 – 16.5	1725 - 2750	0.40 - 0.55	900 – 1100
Experimental Panels ²				
MAPP G-3003 unextruded	30.04 ± 6.6 ^A	3582 ± 567 ^A	0.43 ± 0.19 ^A	1469 ± 330 ^A
MAPP G-3015 unextruded	30.24 ± 8.6 ^A	3586 ± 698 ^A	0.36 ± 0.16 ^A	1445 ± 157 ^A
MAPP G-3015 extruded	19.86 ± 4.9 ^B	2663 ± 270 ^B	1.60 ± 0.64 ^B	1552 ± 193 ^A
MAPP G-3003 extruded	23.00 ± 4.7 ^B	2875 ± 347 ^B	1.50 ± 0.29 ^B	1580 ± 299 ^A

¹Property requirement data is from standard ANSI A208.1- 1999-Particleboard.

²The means with different letters indicate significance between treatments at the $\alpha = 0.05$ level, while the means with the same letter indicates no difference between treatments.

For the comparison of PE vs. PP-based binding agents, the specific comparisons made in Table 5.5 were rows 1 vs. 3 and rows 2 vs. 4. In this way, processing condition was held constant, while the polymer base resin was varied. Composite panels with polypropylene-based binding agents outperformed their polyethylene counterparts in stiffness (MOE), regardless of manufacturing method used, mainly due to the higher stiffness of polypropylene in the binding agent (Table 5.5). However, the strength of the composites (MOR) was not affected by the type of base resin of the maleated polyolefin since both PE and PP behave similarly, regardless of the processing method. Conversely, panels made with maleated polyethylene outperformed those made with maleated polypropylene in IB strength, likely due to the lower melting temperature of polyethylene. Lower melting temperature would allow the polyethylene-based compound to flow to a greater extent even into the center region of the panels, causing stronger internal bonding. The screw holding capacity of the panels was not affected by the base resin type in maleated polyolefin.

Differences between the two maleated polypropylene compounds were not significant for any of the mechanical properties tested (Table 5.6). Specific comparisons made were row 1 vs. 2 and row 3 vs. 4, where processing condition was held constant while the molecular weight/maleic anhydride content of MAPP was varied. The weight average molecular weights of the two MAPPs differed only by 5,000 g/mol and the difference in maleic anhydride content was 1% between the two. These polymers may have been similar enough that they did not create significant differences in the composite panel properties.

Comparison with Standard ANSI A208.1

The MOR, IB strength and screw holding capacity results for experimental panels manufactured in this study indicated that the standard requirements were met or surpassed for all grades of particleboard of medium density when the particles were extruded before pressing (Tables 5.5-5.6). Without the extrusion step, the IB strength was within the required range with maleated polypropylene, and surpassed when PE-based binding agent was used. MOE data were below the standard requirements for stiffness when MAPE was used with extrusion, but the panels with unextruded wood particles bonded with MAPE surpassed the stiffness requirements. Additionally, when MAPP was used, the panels exceeded the requirements for all grades of particleboard of medium density, regardless of processing conditions.

CONCLUSIONS

This study examined the differences between panels made with MAPE and MAPP binding agents, specifically the contrasts of: (i) base resin type, PE or PP, and (ii) molecular weight/maleic anhydride content in MAPP binding agents, along with the effects of the manufacturing process. Particles were either pre-reacted with maleated binding agents in the extruder and then compression molded in a two-step process, or directly compression molded without the extrusion step.

Surface characterization of unmodified and modified wood particles after reactive extrusion with maleated polyolefins showed similar changes in the wood particle surfaces after reaction, regardless of maleated polyolefin used. This evidence suggested that the wood particles can undergo the same reaction in a one-step process, without any obvious differences in reactivity.

Differences in mechanical properties of the panels were correlated to the type of base resin used in the binding agent and to panel density profile. Results showed that while extruding the particles before panel pressing gave better overall internal bond strength, superior bending properties were obtained through compression molding alone. MAPP based panels outperformed MAPE based panels in stiffness, likely due to the higher stiffness of the PP base resin. MAPE enhanced the IB strength compared to MAPP, attributed to better melting and flow of the polyethylene. Polymer base resin had no effect on MOR or screw holding capacity. Differences between the two maleated polypropylene compounds were not significant for any of the mechanical properties tested.

The study also showed that a new type of environmentally friendly wood composite product could be formed from modified wood particles, regardless of processing conditions. This composite contained no formaldehyde-based adhesive, but still performed very well in mechanical tests, in many cases exceeding the standard requirements for particleboard of medium density.

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CHAPTER 6

MODELING AND OPTIMIZATION OF FORMALDEHYDE-FREE WOOD COMPOSITES USING A BOX-BEHNKEN DESIGN

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It is co-authored by K. Carlborn and L. M. Matuana

ABSTRACT

A response surface model using a Box-Behnken design was constructed to statistically model and optimize the material compositions-processing conditions-mechanical property relationships of formaldehyde-free wood composite panels. Three levels of binding agent content, pressing time and press temperature were studied and regression models were developed to describe and optimize the statistical effects of the formulation and processing conditions on the mechanical properties of the panels. Linear models best fit both the flexural strength (MOR) and internal bond (IB) strength of the panels. Increasing any of the manufacturing variables resulted in greater MOR and IB strength. Flexural stiffness (MOE) was best described by a quadratic regression model. Increased MOE could be obtained through higher pressing times, binding agent concentrations and/or pressing temperatures. However, binding agent concentration had less effect on increasing the MOE at higher pressing temperatures. Numerical optimization showed that formaldehyde-free panels with desired mechanical properties could be manufactured at pressing temperatures ranging from 187.18–199.97°C, pressing time from 3.31–8.83 minutes, and binding agent concentration from 7.66–11.86%.

INTRODUCTION

The recent implementation of more stringent emissions regulations for manufacturing facilities that produce particleboard and other wood composite panels (1) has spurred research into alternative binding technologies that do not involve formaldehyde. Our prior work demonstrated the efficiency of the reactive extrusion process as a way to graft maleated polyolefins onto the surface of wood particles, which could then be bound together without any additional adhesive (2-4). A new type of environmentally-friendly wood composite product was manufactured from the modified wood particles. This composite contained no formaldehyde-based adhesive, but still performed very well in mechanical tests, in some cases exceeding the standard requirements for particleboard of medium density.

In previous work, the effects of extrusion processing conditions on the grafting of maleated polyolefins to wood particles were investigated, but work is still needed to determine the relationships between the mechanical properties of the formaldehyde-free composite panels and the material composition and panel manufacturing variables (2-4).

The quality of wood composite materials such as particleboard depends heavily on material composition and manufacturing condition variables such as resin content, pressing temperature and pressing time (5). When multiple variables are involved, it becomes difficult to study the system using the common approach of varying only one factor at a time, while holding the others constant. This approach is not only time-consuming, but can also be costly and does not easily identify all of the interactions between factors (6, 7). A more efficient way to investigate these systems is to develop a mathematical model describing the relationship between the response and independent

variables, in which the significance of individual factors and multi-factor interactions can be determined (6-9).

A Box-Behnken design (BBD) is a versatile method to statistically model and optimize response variables that are affected by multiple independent factors. Compared to full factorial or central composite designs, the BBD requires fewer trials and can efficiently model quadratic or higher-order relationships. Because of these features, the BBD has been used to study a variety of wood composite products (10-13).

In this study, the effects of binding agent content, pressing time and pressing temperature on the mechanical properties of the resulting panels were evaluated using a Box-Behnken design to statistically model the system. Mechanical properties studied included modulus of rupture (MOR), modulus of elasticity (MOE) and internal bond (IB) strength, all of which are key parameters for assessing panel quality. Numerical optimization was performed in order to determine the best conditions for the manufacture of formaldehyde-free wood composite panels.

EXPERIMENTAL

Materials

Maple wood particles of 425 micron (40-mesh) size used in this study were supplied by American Wood Fibers (Schofield, WI). Hydrated zinc acetate, the catalyst, was obtained from Baker Analytical Reagents (JT Baker Co., Phillipsburg, NJ). Maleated polypropylene (MAPP or G-3003) supplied by Eastman Chemical Co. (Kingsport, TN) was used as the binding agent. The MAPP had a weight average molecular weight (M_w) of 52,000 g/mole, approximate viscosity of 60,000 cP at 190°C and maleic anhydride content of 1.5% by weight.

Experimental Design

The Box-Behnken design (BBD) is a three-level design based upon the combination of two-level factorial designs and incomplete block designs (6, 7). BBDs are spherical designs, with the design points for high and low levels located at an equal distance from the center of the design. These designs have excellent predictability within the spherical design space and require fewer experiments than full factorial designs or central composite designs (CCDs) with the same number of factors. For example, an investigation with three factors would require at least 27 experiments in a full factorial design, 15 experiments in a CCD, or 13 experiments in a BBD, with additional replicates of the center point as necessary in each design to estimate experimental error. Additionally, BBDs are rotatable or nearly rotatable regardless of the number of factors studied (6, 7).

All statistical analysis, modeling and numerical optimization was performed using Design Expert software, v.6 (Stat-Ease, Inc. Minneapolis, MN). The BBD matrix generated by Design Expert software displays factor levels in the experimental design in two ways (i) the actual factor levels, which are the values from the experiment, and (ii) the coded factor levels, +1, -1, and 0, for high levels, low levels, and center point, respectively. Coded factor levels are defined as:

$$\text{Coded factor levels} = \frac{\text{Actual value} - \text{Factor mean}}{(\text{Range of factorial values}/2)} \quad (1)$$

The BBD experimental design matrix is shown in terms of both actual and coded factor levels in Table 6.1. Twelve replicates were run for each experiment.

Table 6.1. Box-Behnken Design Matrix in terms of Both Actual and Coded Factor Levels Generated by Design Expert Software.

Experiment Number	Point Type	Factors		
		A: Press Temperature (°C)	B: Press Time (min)	C: Binding Agent Concentration (%)
1	IBFact	160 (-1)	6 (0)	18 (+1)
2	Center	180 (0)	6 (0)	10.5 (0)
3	IBFact	180 (0)	3 (-1)	18 (+1)
4	IBFact	160 (-1)	9 (+1)	10.5 (0)
5	IBFact	160 (-1)	6 (0)	3 (-1)
6	IBFact	180 (0)	9 (+1)	18 (+1)
7	IBFact	180 (0)	3 (-1)	3 (-1)
8	IBFact	200 (+1)	9 (+1)	10.5 (0)
9	IBFact	200 (+1)	6 (0)	3 (-1)
10	IBFact	200 (+1)	6 (0)	18 (+1)
11	IBFact	160 (-1)	3 (-1)	10.5 (0)
12	IBFact	180 (0)	9 (+1)	3 (-1)
13	IBFact	200 (+1)	3 (-1)	10.5 (0)

Compounding and Panel Manufacture

The wood particles were dried for 48 hours at 105°C to a final moisture content of less than one percent before processing. A 10-liter high intensity mixer (Papenmeier TGAHK20) was used for dry blending of the wood particles, binding agent, and catalyst. Levels of binding agent were varied as indicated in Table 6.1, based on the oven dry weight of wood flour. Zinc acetate esterification catalyst was added at 1% of the binding agent weight in all cases. All components were combined in the mixer and blended for 10 minutes at room temperature. Following blending, reactive extrusion was used to induce the esterification reaction between maleated polypropylene and wood particles.

This was achieved as follows: the compounded wood particles were fed into a 32 mm conical counter rotating twin-screw extruder (C. W. Brabender Instruments, Inc.) with an L/D ratio of 13:1, driven by a 7.5 hp Intelli-Torque Plasti-Corder Torque Rheometer®. The barrel temperatures for all three zones inside the extruder were set at 165°C, and the rotational speed of the screws was held at 60 rpm.

Once extruded, the wood particles were compression molded into panels using 3.4 MPa of pressure at various pressing times and temperatures set at levels indicated in Table 6.1. After pressing, panels were removed from the press and cooled at room temperature under compression for 15 minutes. Panel dimensions were 380 by 380 by 6 mm, with a target density of 750 kg/m³.

Property Testing

Three-point flexural and internal bond (IB) strength tests were performed on an Instron 4206 testing machine (using Series IX software) in accordance with procedures outlined in ASTM standard D1037-99 (14). The crosshead speeds were 3.05 mm/min and 8.13 mm/min for flexural and IB tests, respectively. Values for modulus of rupture (MOR), modulus of elasticity (MOE) and IB strength were compared with values listed for particleboard of medium density in the standard ANSI A208.1-1999 (15).

RESULTS AND DISCUSSION

Mechanical Properties

To determine whether experimental panels would conform to standard strength requirements for conventional particleboard, mechanical property data was compared to ANSI standard requirements for particleboard. Table 6.2 lists the MOR, MOE, and IB strength requirements for particleboard of medium density, ranging from 640-800 kg/m³. In previous studies, composite panels manufactured through this process were within this range, with average densities ranging from 775-782 kg/m³ (2, 4). There are four grades of particleboard of medium density, all of which can be made with either interior or exterior adhesives. Grades M-1 and M-S are commercial grade boards, while M-2 and M-3 are intended for industrial use.

Results of MOR, MOE and IB strength tests revealed a large range of property values for the experimental panels (Table 6.2). At the lowest levels of pressing time, temperature and binding agent concentration, panels were below the standard property requirements. However, at the highest levels of these factors, most panels met the standard requirements for particleboard of medium density. Several panels even exceeded the standard requirements for various grades of particleboard. These results are significant because particleboard is currently manufactured with formaldehyde-based adhesives. The formaldehyde-free wood composites manufactured in this study are more environmentally friendly and often outperform the requirements listed in the standard ANSI A208.1.

Table 6.2. Standard Property Requirements for Various Grades of Particleboard of Medium Density (640-800 kg/m³)

Properties	Grades ¹				Experimental Values ²
	M-1	M-S	M-2	M-3	Property Range
MOR (MPa)	11.0	12.5	14.5	16.5	0.48 – 17.91
MOE (MPa)	1725	1900	2250	2750	101.2 – 2556
IB (MPa)	0.40	0.40	0.45	0.55	0.04 – 2.69

¹From Standard ANSI A208.1-1999 Particleboard.

²Experimental values are from panels manufactured under the various factor combinations specified in Table 1. Minimum values are from panels pressed at 160°C for 6 minutes with 3% MAPP, while maximum values are from panels pressed at 200°C for 6 or 9 minutes with 10.5 or 18% MAPP.

Statistical Analysis of the Model

Regression analysis was performed on the mechanical property results in order to develop best-fit models for the experimental data. A separate regression analysis was run for each of the three mechanical properties studied to determine the relationships between mechanical properties and binding agent content, pressing time and pressing temperature.

Modulus of Rupture (MOR) and Internal Bond (IB) Strength

For both MOR and IB strength, regression analysis of the experimental data showed that a linear model best fit the relationship between the response (MOR or IB) and the binding agent content, pressing time and pressing temperature. In both cases, a square root transformation was applied to the data in order to normalize the variance of the residuals. These models, described in terms of coded factors, were described as:

$$\sqrt{\text{MOR}} = +2.75 + 0.78A + 0.23B + 0.91C \quad (2)$$

and

$$\sqrt{\text{IB strength}} = +1 + 0.30A + 0.084B + 0.54C \quad (3)$$

where A is press temperature, B is press time, and C is binding agent concentration.

For both MOR and IB strength, only the three main factors were significant, with no interactions found between them. Since the equations are displayed in terms of coded factors, the relative effect of each variable on the response can be evaluated by comparing the absolute value of its coefficient and its algebraic sign. As shown in

Equations 2 and 3, the effects of all of the factors had positive algebraic signs, which indicated that increasing any one would increase the MOR or IB strength. In both cases, concentration of binding agent (factor C) had the largest effect on the mechanical properties, followed by pressing temperature (factor A) and pressing time (factor B). This is illustrated by a cube graph in Figure 6.1(a) for MOR and 6.1(b) for IB. Increasing the amount of binding agent resulted in better adhesion between the wood particles as a result of having more polymer chains attached to the wood particles which would entangle to hold the panel together. Similarly, an increase in temperature would allow more thorough melting and flow of the polymer chains attached to the wood particles, thus increasing the efficiency of binding. Although longer pressing time did increase both MOR and IB, the effect was much smaller which indicated that pressing time was much less important in improving the MOR and IB than binding agent concentration or press temperature.

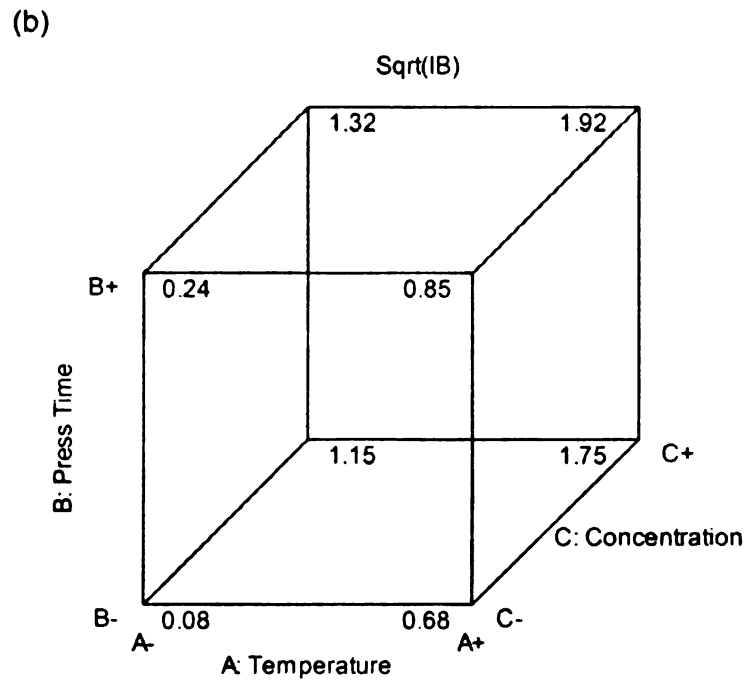
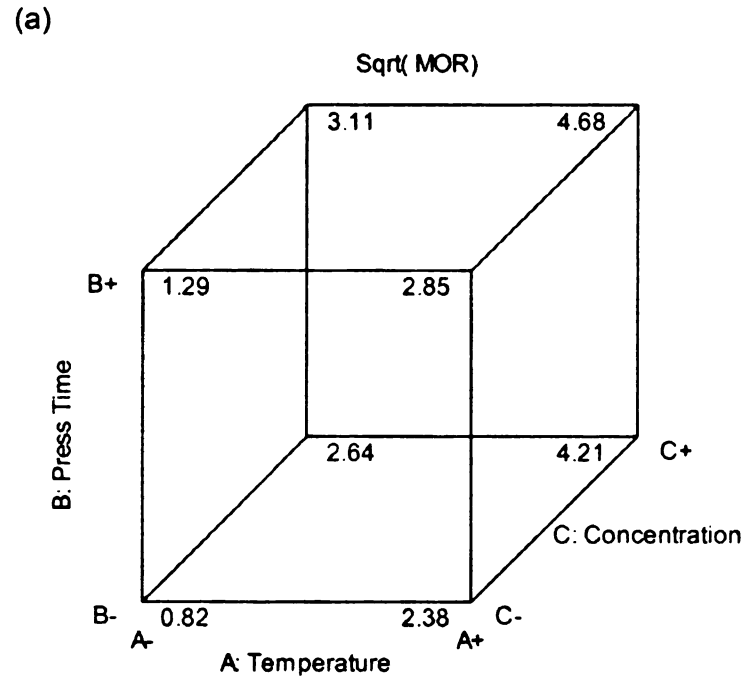


Figure 6.1. Cube graphs of the linear relationship between mechanical property results and press temperature, pressing time, and binding agent concentration for (a) MOR and (b) IB strength.

Modulus of Elasticity (MOE)

Results of the regression analysis for MOE suggested that the data was best fit by a quadratic model. A square root transformation was also applied to the data for MOE in order to normalize the variance of the residuals in the system. Table 6.3 shows the analysis of variance (ANOVA) results for the response surface quadratic model. As listed in the table, some of the factors were not significant (Probability > F greater than 0.0500), so the model was reduced by removing the insignificant factors. The reduced model, containing only significant terms and described in terms of coded factors is:

$$\sqrt{\text{MOE}} = +33.49 + 9.47A + 3.15B + 9.99C + 1.14A^2 + 2.70B^2 - 2.44C^2 - 2.02AC \quad (4)$$

For MOE, all main effects (A, B and C) were significant, along with the second-order main effects (A^2 , B^2 and C^2), and the AC interaction. Because A, B and C had positive algebraic signs, an increase in temperature, pressing time or binding agent concentration would improve the MOE. By contrast, the two-factor AC interaction had a negative algebraic sign, which indicated a negative effect on MOE.

Table 6.3. Analysis of Variance (ANOVA) for Response Surface Quadratic Model

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-Value	Prob. > F ¹
Quadratic Model	1671.35	9	185.71	379.34	< 0.0001
A	716.70	1	716.70	1463.99	< 0.0001
B	79.35	1	79.35	162.08	< 0.0001
C	799.04	1	799.04	1632.19	< 0.0001
A ²	5.49	1	5.49	11.21	0.0123
B ²	30.59	1	30.59	62.49	< 0.0001
C ²	25.00	1	25.00	51.07	0.0002
AB	0.58	1	0.58	1.18	0.3137
AC	16.30	1	16.30	33.30	0.0007
BC	0.89	1	0.89	1.83	0.2187

¹Values of “Prob. > F” less than 0.0500 indicate model terms are significant. In this case A, B, C, A², B², C² and AC are the significant model terms.

The perturbation plot of the square root of MOE against temperature, pressing time and binding agent concentration shows the contribution of each factor to the MOE (Figure 6.2). The perturbation plot illustrates the changes in MOE as each factor moves from the chosen reference with all other factors held constant at the middle level of the design space (6, 7). Pressing temperature and binding agent content (factors A and C) are shown to have the largest effect on the MOE, while pressing time (factor B) shows only a small effect on MOE.

Because two of the main factors (A and C) that increase the MOE are part of a significant interaction, it would not be appropriate to investigate these factors separately. The effect of one factor will depend upon the level of the other, since the interaction is significant.

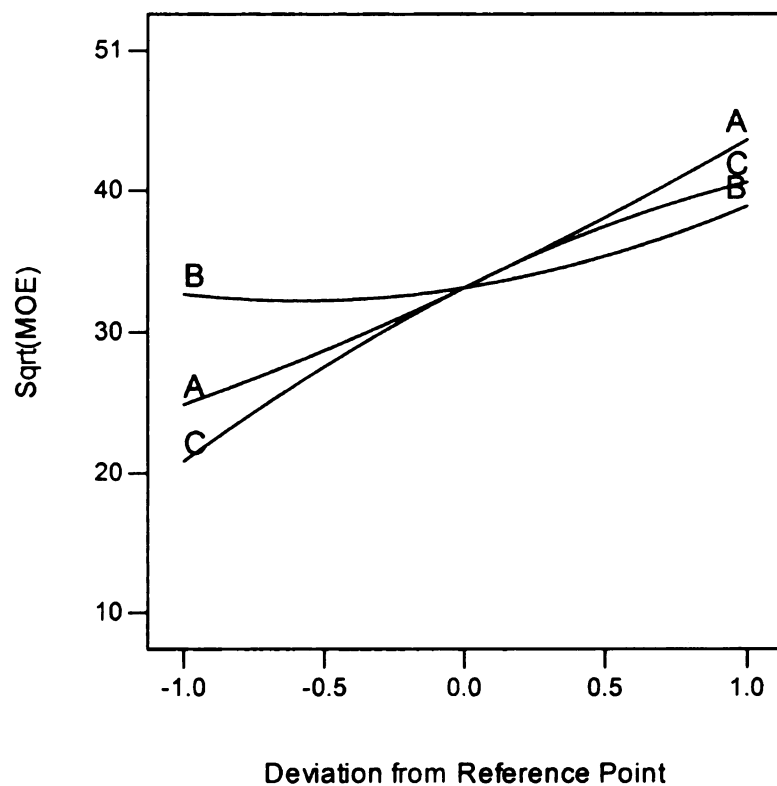


Figure 6.2. Perturbation plot of square root of MOE against pressing temperature (A), pressing time (B) and binding agent concentration (C).

Figure 6.3 shows the interaction graphs of the change in MOE as a function of the temperature-concentration interaction. The effect of the temperature-concentration interaction is illustrated at the lowest pressing time, 3 minutes, in Figure 6.3(a) and at the highest pressing time, 9 minutes, in 6.3(b). A small increase in MOE resulted from increased pressing time, regardless of the temperature or binding agent concentration. However, this effect was quite small, resulting in gains of only 3-8 MPa to the MOE over the range studied.

The binding agent concentration had greater effect on MOE when the pressing temperature was the lowest. At higher temperatures, the differences between low and high binding agent concentration were reduced. This can be verified by comparing the magnitude of the difference between the lines for high and low binding agent concentration. At the lowest temperature, the difference in MOE was large, but was reduced as the temperature increased. This reduced efficiency of binding agent concentration to increase the MOE at higher temperatures accounts for the negative effect of the temperature-binding agent interaction, which was shown by the negative algebraic sign on AC in Equation 4. The effect of this interaction is that less binding agent is required at higher temperatures to produce panels with sufficient MOE values. At lower temperatures, more binding agent would be required to manufacture composites with the same range of MOE values. A greater degree of melting and flow of the polymer attached to the wood particles likely occurs at higher temperatures, which would allow a smaller amount of binding agent to be as more efficient in creating particle-particle bonds.

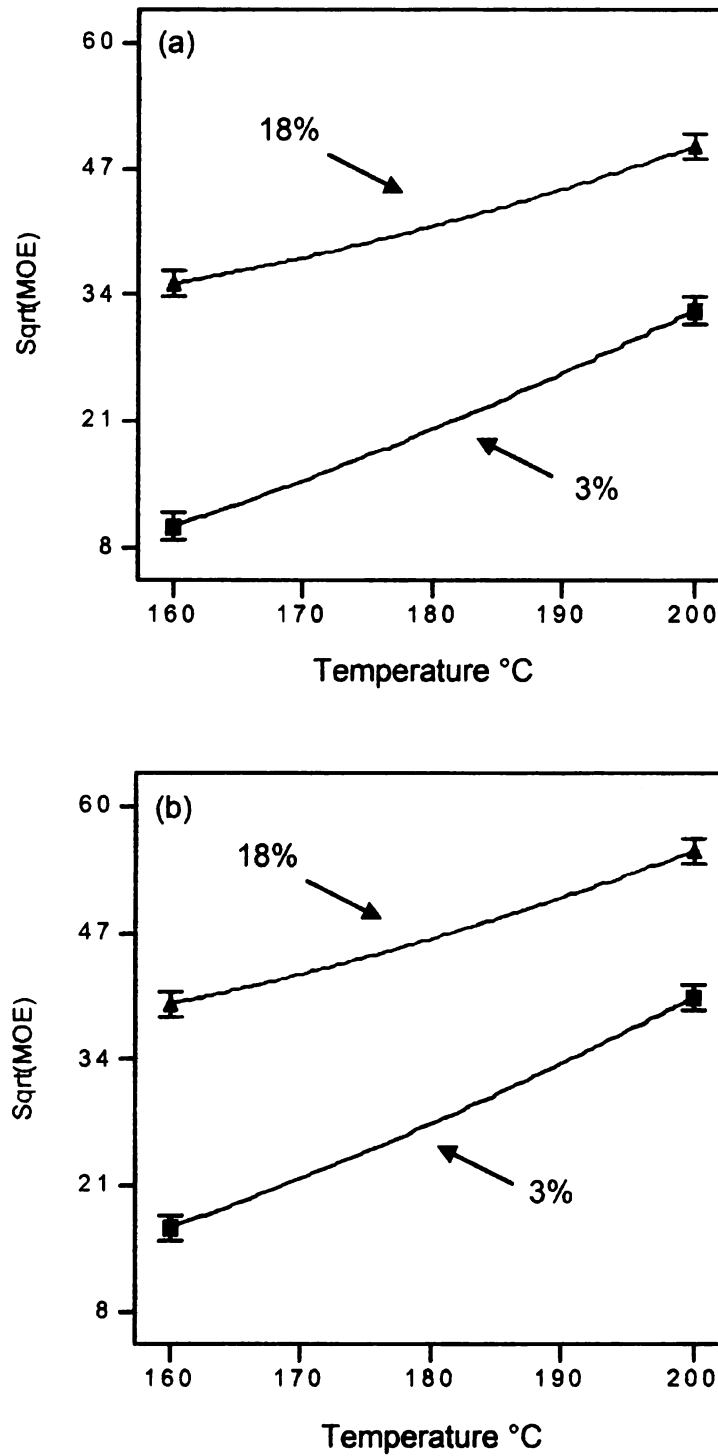


Figure 6.3. Interaction plots of the variation in square root of MOE as a function of the interaction between pressing temperature and binding agent concentration at (a) low press time (3 minutes) and (b) high press time (9 minutes).

Numerical Optimization of Mechanical Properties

The numerical optimization function in Design Expert software was used to determine combinations of binding agent concentration, panel pressing time and temperature that would result in the most favorable mechanical properties of the resulting composites. The numerical optimization function of Design Expert is based on the desirability function developed by Derringer and Suich (16), which transforms each response value to a desirability index (d_i). Each desirability index is defined by three parameters: goal, lower and upper, and the program allows the d_i goal parameter to be to one of five options: minimum, maximum, target, in range, or equal to. Once these settings have been defined, d_i varies between zero (worst case) and one (ideal case). Design Expert searches for the largest overall d_i and presents a series of solutions which best maximize the d_i .

Table 6.4 lists the optimization criteria settings used to optimize the mechanical properties of the composite panels. In order to produce a composite panel that had adequate strength (MOR), stiffness (MOE), and IB strength, the goal for each property was initially set in range based upon the property requirements of the particleboard standard ANSI A208.1 (Table 6.2). For example, square root of MOR was set in range 3.32–4.06 MPa, MOE was set in range 41.53–52.44 MPa and IB strength was set in range 0.63–0.74 MPa (15). However, the data for IB strength showed that the standard property requirements were met and even exceeded at very low concentrations of binding agent. Since the IB would be higher than required at nearly all combinations of pressing temperature, panel pressing time and binding agent concentration, the IB criteria was set in range over all experimental values instead of in range of the property requirement

values. In this way, the MOR and MOE could be targeted to the necessary values, with the understanding that IB strength would likely be much higher than required. Additionally, because we wanted to determine which combination of material composition and processing conditions would produce panels with the desired properties, the optimization criteria for all of these factors were set in range over the entire set of studied values. For this analysis, the desirability functions of the mechanical properties were set as follows:

- (i) if $\sqrt{\text{MOR}} < 3.32$ or $\sqrt{\text{MOR}} > 4.06$ MPa, and $\sqrt{\text{MOE}} < 41.53$ or $\sqrt{\text{MOE}} > 52.44$ MPa then $d_i = 0$ (worst case)
- (ii) if $3.32 \leq \sqrt{\text{MOR}} \leq 4.06$ and $41.53 \leq \sqrt{\text{MOE}} \leq 52.44$, then $d_i = 1$ (ideal case)

All other optimization parameters were set to the default settings of one for the weights of upper and lower limits for the input factors, and three for the importance (a relative scale that weights each of the resulting d_i s in the overall desirability product). Ten cycles were run per optimization, with the epsilon value for the minimum difference in eliminating duplicate results set at its default value.

Table 6.4. Numerical Optimization Settings and Results

Response Constraints							
Factor	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance	
Pressing Temperature (°C)	In range	160	200	1	1	3	
Pressing Time (min)	In range	3	9	1	1	3	
Binding Agent Concentration (%)	In range	3	18	1	1	3	
Sqrt(MOR) (MPa)	In range	3.32	4.06	1	1	3	
Sqrt(MOE) (MPa)	In range	41.53	52.44	1	1	3	
Sqrt(IB) (MPa)	In range	0.20	1.64	1	1	3	
Optimum Solutions							
Solution	Temperature (°C)	Press Time (min)	Binding Agent Concentration (%)	Sqrt(MOR) (MPa)	Sqrt(MOE) (MPa)	Sqrt(IB) (MPa)	Desirability
1	199.96	8.15	7.66	3.35	44.73	1.16	1.00
2	199.05	8.83	7.70	3.37	46.08	1.17	1.00
3	199.97	3.31	11.13	3.39	43.76	1.27	1.00
4	199.49	3.42	11.58	3.44	43.93	1.30	1.00
5	199.25	6.07	9.03	3.33	42.06	1.18	1.00
6	187.18	8.57	11.86	3.40	43.36	1.28	1.00
7	194.21	8.02	11.54	3.59	45.40	1.34	1.00
8	190.42	7.35	11.38	3.37	41.78	1.26	1.00
9	198.74	8.76	8.12	3.41	46.18	1.19	1.00

Numerical optimization results produced 9 optimum solutions, all with desirability of 1.00. These results are displayed in Table 6.4. As listed in the table, pressing temperatures ranged from 187.18–199.97°C, pressing time ranged from 3.31–8.83 minutes, and binding agent concentration from 7.66–11.86%. These results showed that formaldehyde-free wood composite products could be made under a variety of conditions, many of which are not all that different than those used to manufacture conventional particleboard. In addition, a desired solution could be employed if the goal was to minimize a particular factor, such as pressing time, in order to reduce manufacturing costs.

CONCLUSIONS

Three panel manufacturing variables (pressing temperature, pressing time and binding agent content) were analyzed by developing statistical models for their relationships with mechanical properties MOR, MOE and IB strength. Additionally, numerical optimization was used to determine the best conditions for manufacturing the panels in terms of the mechanical properties. The following conclusions were obtained:

1. Both MOR and IB were best fit with linear models. Increasing any of the manufacturing variables (pressing temperature, pressing time and binding agent content) resulted in greater MOR and IB strength.
2. A quadratic model best fit the MOE. Increased MOE could be obtained through longer pressing times, but the effect of this variable was small. Larger effects on MOE were obtained by increasing the binding agent concentrations and pressing temperatures. However, the negative interaction between temperature and binding agent concentration indicated that binding agent concentration had less effect on increasing the MOE as the pressing temperature increased.
3. Panels with mechanical property values in the range of the mechanical property requirements for particleboard of medium density could be produced using several pressing temperature-pressing time-binding agent concentration combinations with maximum desirability. This showed that formaldehyde-free panels could be produced at similar adhesive contents and processing conditions used for conventional glued particleboard made with formaldehyde-based adhesive.

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CHAPTER 7

SUMMARY OF FINDINGS

Public awareness about formaldehyde and other toxic chemicals being released to the environment has helped to drive new government standards for wood composite products. As environmental regulations become more stringent, the need for formaldehyde-free adhesive systems for wood composite products will likely increase. The main goal of this work was to study the concept of using a reactive extrusion process as a means of developing a new, formaldehyde-free binding system for wood composite products. The following specific objectives were accomplished to achieve the main goal of this project:

1. Evaluate the effects of material composition (binding agent types and content) and extrusion processing conditions (temperature profile and rotational screw speed) on the level of grafting (surface properties) of wood particles after the reactive extrusion process;
2. Characterize the surface of unmodified and modified wood particles in terms of chemical compositions (both elemental and functional groups);
3. Manufacture composites and evaluate their physico-mechanical properties;

4. Establish the relationships between material composition, processing conditions, and physico-mechanical properties in order to identify the major factors that govern the performance of formaldehyde-free wood composite products manufactured through a reactive extrusion process.

The following sections relate the findings of this work to these objectives.

Objectives 1 and 2:

Results of FTIR, ^{13}C NMR, XPS and titration analysis verified the reaction between wood particles and maleated polyolefins. This proved that the maleated polyolefins could be successfully grafted to wood particles using a reactive extrusion process, without the use of any solvents. The esterification reaction between wood particles and MAPE was found to be a function of the MAPE concentration used to modify the wood particles. The grafting reaction produced mostly the diester form of the modified wood particle during reactive extrusion. However, no significant difference was found in grafting efficiency of the modified wood particles at different extrusion processing conditions. Changing the extruder's barrel temperature profile (130-180°C) and/or its rotational screw speed (20-80 rpm) resulted in adequate grafting, which indicated that the esterification reaction was not a function of processing conditions.

Regardless of MAPP molecular weight (from a low of 11,200 to a high of 52,000 g/mol) all investigated MAPP compounds were effective in changing the surface of wood particles after modification, compared to unmodified wood particles. However, no distinct trend was observed between molecular weight of MAPP and grafting efficiency through a reactive extrusion process. Regardless of molecular weight, it is believed that

the high content of MAPP (20%) used in this study prevented the detection of differences in the grafting efficiency because the maximum level of grafting reaction had already occurred with each component at 20% MAPP content.

The reactive extrusion process was found to be a suitable way to modify wood particles with maleated polyolefins as it worked quickly and without the use of solvents. This process would be industrially friendly and would allow large quantities of modified wood particles to be produced for the manufacture of a formaldehyde-free wood composite product.

Objective 3:

Modified wood particles made with MAPE were successfully formed into formaldehyde-free composite panels without the use of any additional adhesive. The composite contained no formaldehyde-based adhesive, but still performed very well in mechanical tests, in many cases exceeding the standard requirements for particleboard of medium density.

Additional work focused on the differences between panels made with MAPE and MAPP binding agents, specifically the contrasts of: (i) base resin type, PE or PP, and (ii) molecular weight/maleic anhydride content in MAPP binding agents, along with the effects of the manufacturing process. Particles were either pre-reacted with maleated binding agents in the extruder and then compression molded in a two-step process, or directly compression molded without the extrusion step.

Differences in mechanical properties of the panels were correlated to the type of base resin used in the binding agent and to panel density profile. Results showed that while extruding the particles before panel pressing gave better overall internal bond strength, superior bending properties were obtained through compression molding alone. MAPP based panels outperformed MAPE based panels in stiffness, likely due to the higher stiffness of the PP base resin. MAPE enhanced the IB strength compared to MAPP, attributed to better melting and flow of the polyethylene. Polymer base resin had no effect on MOR or screw holding capacity. Differences between the two maleated polypropylene compounds were not significant for any of the mechanical properties tested.

Objective 4:

In a final phase of the study, three panel manufacturing variables (pressing temperature, pressing time and binding agent content) were analyzed by developing statistical models for their relationships with mechanical properties MOR, MOE and IB strength. Additionally, numerical optimization was used to determine the best conditions for manufacturing the panels in terms of the mechanical properties.

Statistical modeling revealed that both MOR and IB were best fit with linear models. Increasing any of the manufacturing variables (pressing temperature, pressing time and binding agent content) resulted in greater MOR and IB strength. However, the MOE was best fit by a quadratic model. Increased MOE could be obtained through longer pressing times, but the effect of this variable was small. Larger effects on MOE were obtained by increasing the binding agent concentrations and pressing temperatures.

However, the negative interaction between temperature and binding agent concentration indicated that binding agent concentration had less effect on increasing the MOE as the pressing temperature increased.

Panels with mechanical property values in the range of the mechanical property requirements for particleboard of medium density could be produced using several pressing temperature-pressing time-binding agent concentration combinations with maximum desirability. This showed that formaldehyde-free panels could be produced at similar adhesive contents and processing conditions used for conventional glued particleboard made with formaldehyde-based adhesive.

Future Work

This work resulted in the development of a new type of formaldehyde-free wood composite material that could be produced through a dry process. The surface composition of unmodified and modified wood particles and maleated polyolefins were studied in detail in order to verify that the reaction had occurred, and to determine the efficiency of the modification under several different material compositions and processing conditions. However, hardwood maple was used as the wood component in nearly all of the work. Only one set of pine panels was manufactured in order to determine a baseline comparison between wood species (see appendix). The effect of wood species, specifically hardwood vs. softwood, should be studied in greater detail to determine whether the wood type has an effect on the grafting efficiency during reactive extrusion. The presence of naturally occurring resins in some softwood species might have an effect on the grafting reaction, which may cause differences in the quality of panels produced with this method. A large portion of particleboard is currently made with softwood species such as pine, so this study would be relevant for industrial application of the technology.

No differences were found in between modified wood particles produced under various extrusion processing conditions when the concentration of MAPE was held constant at 20%. The results of that portion of the study suggested that 20% by weight might be too much binding agent to see any differences that may exist under these conditions. In order to determine whether differences could be observed at lower binding agent concentrations, a similar investigation should be run at a lower concentration, perhaps between 5-10% by weight. This would be below the level that was determined to

cause maximum grafting, around 15%. If differences in grafting efficiency were found with this lower concentration, the extrusion conditions could be modified for future work in order to produce the greatest amount of grafting in the modified particles. Since this work indicated that panels with properties within the standard requirement range could be made at much lower concentrations than the 20% used in early studies, this would ensure that the panel quality would be high when made with low binding agent concentrations.

In addition, the moisture resistance of wood composite panels such as particleboard or MDF made with UF adhesive is generally very poor. Results of thickness swelling tests after a 24 hour cold soak (see appendix) indicated that formaldehyde-free composites had low swelling. Standard property requirement values for particleboard and medium density fiberboard vary depending upon grade and density, and not all grades specify thickness swelling requirements. Therefore, laboratory tests should be performed using commercial particleboard or MDF as a control to determine whether these formaldehyde-free panels have an advantage in moisture resistance. These panels may prove to be better at resisting moisture than the conventional glued particleboard and MDF, which would be another industrial selling point.

Finally, the studies done to determine whether panels with suitable mechanical properties could be made through a one-step process (extrusion only) suggested that the IB strength of these panels was lower than those made through the two-step process. This was viewed as a drawback of this manufacturing method, even though the IB strength was close to or within the standard property requirement range from ANSI. These panels were made at only one pressing condition, which had previously been determined to produce panels with good mechanical properties in the two-step method.

However, this pressing setup did not necessarily account for the extra time needed to properly melt the maleated polyolefin throughout the entire mat thickness and allow completion of the chemical reaction between the wood and maleated polyolefin during pressing. A study should be undertaken to optimize the pressing conditions for the one-step panels, as these are the most likely to be industrially viable considering start-up costs for producers that are currently making other wood-based products that are not extruded. If the IB strength could be improved through longer pressing, perhaps at lower temperatures or with a pre-pressing step under low pressure, these panels would be even more advantageous from an industrial perspective.

APPENDIX

Table A.1. Standard Property Requirements for Particleboard and Medium Density Fiberboard

Panel Type	Thickness (mm)	Density (kg/m ³)	Water Absorption (%)	Thickness Swelling (%)	MOR (MPa)	MOE (MPa)	IB (MPa)
Particleboard^{1,3}							
M-1	ns	640-800	ns	ns	11.0	1725	0.40
M-S	ns	640-800	ns	ns	12.5	1900	0.40
M-2	ns	640-800	ns	ns	14.5	2225	0.45
M-3	ns	640-800	ns	ns	16.5	2750	0.55
LD-1	ns	<640	ns	ns	3.0	550	0.10
LD-2	ns	<640	ns	ns	5.0	1025	0.15
PB Underlayment	ns	ns	ns	ns	11.0	1725	0.40
MDF^{2,3}							
HD-interior	ns	>800	ns	ns	34.5	3450	0.75
MD-interior	<21	640-800	ns	ns	24.0	2400	0.60
LD-interior	<21	<640	ns	ns	14.0	1400	0.30
MD-exterior	<21	640-800	ns	ns	34.5	3450	0.90

¹From standard ANSI A 208.1-1999-Particleboard

²From standard ANSI A 208.2-1999 Medium Density Fiberboard (MDF)

³ns = not specified

Table A.2. Mechanical Property Data for Experimental Maple Panels Bound with MAPE

Panel Type	Thickness (mm)	Density (kg/m ³)	Water Absorption (%)	Thickness Swelling (%)	MOR (MPa)	MOE (MPa)	IB (MPa)
Extruded MAPE							
5%, 7 min	6	770	99	43	2.6	802	0.20
7.5%, 7 min	6	772	79	34	7.9	1401	0.18
10%, 7 min	6	772	66	24	10.8	1482	0.69
15%, 7 min	6	772	46	16	12.5	1197	0.83
20%, 7 min	6	770	32	8.7	17.7	1229	1.70
20%, 3 min	6	770	32	8.7	17.7	1229	1.70
20%, 7 min	6	778	9	5.3	20.7	1296	2.06
20%, 9 min	6	775	12	9.5	18.0	1245	2.34
20%, 12 min	6	772	12	7.6	18.5	1199	1.63
Unextruded MAPE							
20%, 7 min	6	780	28	8.5	26.3	2083	1.16
20%, 9 min	6	784	19	6.6	24.7	1905	1.34

Table A.3. Mechanical Property Data for Experimental Maple Panels Bound with MAPP

Panel Type	Thickness (mm)	Density (kg/m ³)	Water Absorption (%)	Thickness Swelling (%)	MOR (MPa)	MOE (MPa)	IB (MPa)
Extruded MAPP							
E-43	6	780	16	11	10	2558	0.43
G-3216	6	776	18	11	26	3020	1.21
G-3003	6	775	12	7	22.9	2870	1.50
G-3015	6	782	16	6	19.6	2635	1.59
Unextruded MAPP							
E-43	6	774	18	10	12.16	3431	0.62
G-3216	6	778	35	11	18.62	2967	0.49
G-3003	6	775	21	6	29.37	3487	0.43
G-3015	6	780	32	8	29.16	3456	0.31

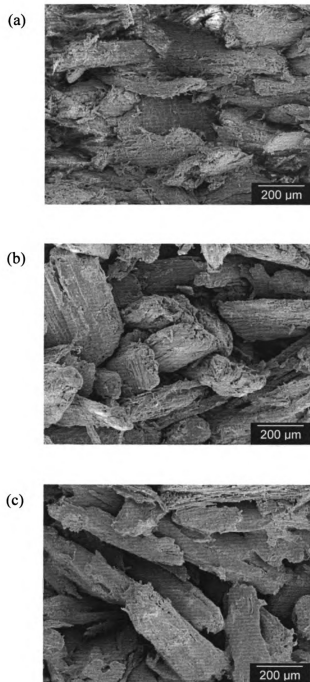


Figure A.1. SEM images of fracture surfaces of panels manufactured from maple with maleated polypropylene, G-3003 at 250X magnification. (a) 3%, (b) 10.5% and (c) 18% MAPP.

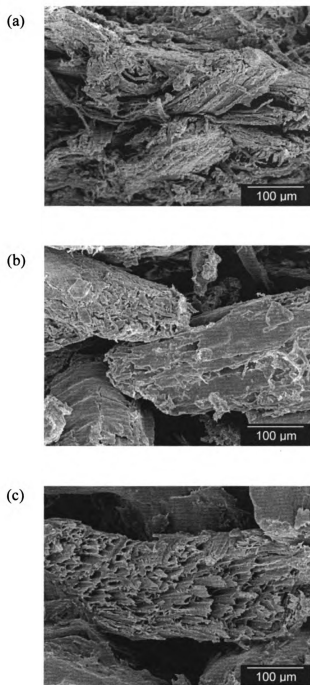


Figure A.2. SEM images of fracture surfaces of panels manufactured from maple with maleated polypropylene, G-3003 at 500X magnification. (a) 3%, (b) 10.5% and (c) 18% MAPP.

Table A.4. Mechanical Property Data for Experimental Panels Bound with 10.5% MAPP, Pressed for 6 Minutes at 180°C and 3.4 MPa Pressure

Wood Species	Thickness (mm)	Density (kg/m³)	MOR (MPa)	MOE (MPa)
Maple	6	774 ± 6	7.6 ± 2	1121 ± 299
Pine	6	769 ± 10	7.7 ± 3	1445 ± 264

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