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Title: Improved Interfacial Adhesion in Wood-Plastic Composites: Development of New Compatibilizers

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Redacted for Privacy   Redacted for Privacy

Kaichang Li   John Simonsen

In wood-plastic composites (WPCs) a compatibilizer is often used to improve the interfacial adhesion between the hydrophilic wood filler and the hydrophobic plastic matrix. At present, while the basic concepts of compatibilization are understood, the optimized chemical structures of an effective compatibilizer, including the ideal structures of the wood-binding domain and the plastic-binding domain, are poorly understood. Poly(N-acryloyl dopamine) (PAD), a mimicking polymer of marine adhesive protein, was synthesized. The bonding between PAD and maple veneers was strong and highly water-resistant. The addition of polyethylenimine further increased the adhesive strengths. PAD should be able to serve as an effective

wood-binding domain for a wood-plastic compatibilizer. Terminally functionalized polyethylenes (PE), PE-MDI (methylene diphenyl diisocyanate) and PE-PMDI (polymeric methylene diphenyl diisocyanate), were prepared through the reactions between polyethylene monoalcohol (PEA) and MDI and between PEA and PMDI, respectively. The performance of PEA, PE-MDI and PE-PMDI as compatibilizers for wood-PE composites was investigated. These compatibilizers had well-defined structures with a linear PE chain as a PE-binding domain and a hydroxyl group or an isocyanate group as a wood-binding domain. All these compatibilizers increased the strength of the wood-PE composites. Composites with PE-MDI or PE-PMDI had a higher modulus of rupture (MOR) than those with PEA. The addition of PE-MDI and PE-PMDI decreased the water uptake rate of the composites while PEA increased this rate. The superior compatibilization effects of PE-MDI and PE-PMDI were attributed to the formation of covalent bonding between isocyanate and wood. This covalent bonding was demonstrated by the FTIR spectra of the wood residues after a *p*-xylene extraction. Both PMDI and N-vinylformamide grafted polypropylene (VFPP) were effective compatibilizers for increasing both the strength and stiffness of the resulting wood-PP (polypropylene) composites. The combination of PMDI and VFPP further increased the MOR and the modulus of elasticity (MOE) of the resulting wood-PP composites. This new PMDI-VFPP compatibilizer system was comparable to maleic anhydride-grafted polypropylene (MAPP) in terms of enhancing the strength and stiffness of the wood-PP composites. This PMDI-VFPP compatibilizer system also greatly reduced the water sorption of the resulting wood-PP composites.

Improved Interfacial Adhesion in Wood-Plastic Composites: Development of New Compatibilizers

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APPROVED:

Redacted for Privacy

Co-Major Professor, representing Wood Science

Redacted for Privacy

Co-Major Professor, representing Wood Science

Redacted for Privacy

Head of the Department of Wood Science and Engineering

Redacted for Privacy

Dean of the Graduate School

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Cheng Zhang, Author

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF TABLES

Improved Interfacial Adhesion in Wood-Plastic Composites: Development of New Compatibilizers

1 GENERAL INTRODUCTION AND LITERATURE REVIEW

1.1 GENERAL INTRODUCTION

Wood as a reinforcing filler in thermoplastics has attracted extensive research interests in recent years. Compared with other fillers such as glass fibers and clay, wood has several distinct advantages: low cost, renewability, biodegradability, low specific gravity, abundance and minimal abrasion of processing equipment. However, the strength of wood-reinforced thermoplastics, or normally called wood-plastic composites (WPCs), is typically low because of the poor interfacial adhesion between the hydrophilic wood filler and the hydrophobic plastic matrix. To solve this problem, a coupling agent (commonly called a compatibilizer) is usually added to WPCs. The compatibilizer bridges the interface and improves the stress transfer between wood and plastic.

Although many researchers have studied WPC compatibilizers, the ideal structures of a compatibilizer are still poorly understood. Development of new compatibilizers with optimized chemical structures for further enhancing the performance of WPCs would be possible if a better understanding of the interfacial chemistry in WPCs can be gained.

In WPCs, the bonding between the compatibilizer and the wood is expected to have a significant impact on the properties of the composites. Up to now, the most effective compatibilizers are maleic anhydride-grafted polymers, including maleic anhydride-grafted polyethylene (MAPE) and maleic anhydride-grafted polypropylene (MAPP). It is believed that the anhydride groups of MAPE or MAPP form ester linkages with hydroxyl groups of wood and the PE backbone of MAPE or the PP backbone of MAPP forms entanglements or co-crystallization with polyethylene (PE) or polypropylene (PP) matrix. In this study, a novel wood-binding domain, poly (*N*-acryloyl dopamine) was developed through mimicking the strong adhesion of mussels to rock and other substances in seawater. Poly (*N*-acryloyl dopamine) was investigated as a candidate for the wood-binding domain of a di-block copolymer compatibilizer. Terminally functionalized polyethylenes were synthesized and investigated as compatibilizers for wood-PE composites. These compatibilizers had well-defined structures with a linear PE chain as a PE-binding domain and a hydroxyl group or an isocyanate group as a wood-binding domain. Contributions of the PE-binding domain and different wood-binding domains to the strength and water-resistance of the resulting wood-PE composites were investigated in detail. A novel compatibilizer system that contained polymeric methylene diphenyl diisocyanate (PMDI) as a wood-binding domain and N-vinylformamide grafted PP (VFPP) as a PP-binding domain was developed and characterized for wood-PP composites.

1.2 LITERATURE REVIEW

1.2.1 Introduction

Reinforcing fillers are widely used in thermoplastic polymers to improve certain mechanical properties and to reduce material costs. Currently, commonly used fillers include inorganic materials such as talc, mica, clay, glass fiber and calcium carbonate. In recent years, much interest has been directed to the development of wood fiber-reinforced thermoplastic polymers, or commonly called wood-plastic composites (WPCs), because WPCs have the benefits of both wood and plastic (Klason, Kubat et al. 1984; Schneider 1994; Youngquist 1995; Bledzki, Reihmane et al. 1998; Bledzki and Gassan 1999; Wolcott and Englund 1999; Clemons 2002). Compared with inorganic fillers, wood has several distinct advantages such as low cost, renewability, low specific gravity, abundance and minimal abrasion of processing equipment. Compared with traditional wood composites, WPCs have reduced water sorption, reduced thickness swelling and enhanced durability against biodeterioration. WPCs are normally produced through an extrusion process that gives the flexibility of producing products with different shapes and structures, and alleviates the post-manufacturing steps such as machining and assembly steps that will add cost to the final products. Once produced, WPCs can be finished and fastened just like wood.

1.2.2 Applications of WPCs

1.2.2.1 Building products

The building products market is the largest for WPCs (Optimat Ltd and MERL Ltd 2003). Products in this market include decking, fencing, siding, decorative trim, garden furniture and architectural trim, exterior windows and doors. When compared to solid wood, WPCs as building products require lower maintenance, have higher durability, are more resistant to warping and splintering. However, WPCs have lower mechanical properties such as strength, stiffness and creep resistance than solid wood, especially at elevated temperature. Therefore, WPCs are not suitable for applications that require considerable structural performance (English and Falk 1995; Clemons 2002).

1.2.2.2 Infrastructure

The major applications of WPCs in infrastructure include marine applications and railroad crossties. Currently, preservative-treated lumber is predominately used in marine structures. When compared with preservative-treated lumber, WPCs do not contain toxic preservatives such as CCA (chromated copper arsenate) that may leak into seawater and causes environmental pollution. Because of the restrictions on the logging of old growth timber and tropical hardwood, good-quality wood is becoming less and less available, which makes WPCs more attractive materials for marine applications (March and Jarvis 1997). WPCs as railroad crossties appear to be more

durable than solid wood crossties under high loads and arduous conditions (Optimat Ltd and MERL Ltd 2003).

1.2.2.3 Transportation

Applications of WPCs in transportation include automobile applications and highway applications. In the automotive sector, WPCs are used as substrates for package trays, interior door panels, roof headliners, seat backs, spare-tire covers and trunkliners. Vinyl, carpeting and other coverings are applied later to cover the substrate (Youngquist 1995; Kerrigan and Pfaehler 1997; Vesey and Datta 1997; Sherman 1999). Applications of WPCs in highway uses include highway signs, noise barriers, guardrail posts, and fence posts. Recycled plastics are extensively used for these applications because of their economical and environmental advantages (Coomarasamy and Boyd 1995; Coomarasamy and Boyd 1997; Strybos 1997).

1.2.3 Wood in WPCs

Wood from different species can be used for making WPCs. Commonly used wood species in WPCs are pine, maple and oak (Wolcott and Englund 1999). Other natural fibers such as kenaf, hemp, jute, sisal, flax and rice hulls can also be used (Bledzki and Gassan 1999). Different wood species perform differently in WPCs. Effects of four wood species, ponderosa pine, loblolly pine, maple, and oak, on the mechanical properties of wood-PP composites were investigated by Berger and Stark (Berger and Stark 1997). Hardwood flours provided higher flexural strength and

better tensile properties than softwood flours. However, composites with ponderosa pine exhibited the highest impact strength among all flours used (Berger and Stark 1997).

Wood used in WPCs can be wood particles, wood flour, various types of pulp, and recycled paper products (Bledzki, Reihmane et al. 1998). Effect of the wood flour size on the mechanical properties of wood-PE composites without compatibilizers was investigated by Maiti and Singh (Maiti and Singh 1986). Two ranges of particle sizes (less than 180 μm and 355-425 μm) of the wood flour were used. The wood content varied from 0 to 14 % by volume. Their results showed that the fine wood flour gave a higher modulus of elasticity and a higher relative yield stress than the coarse wood flour. The authors suggested that fine flour resulted in better interfacial adhesion between wood and PE than coarse flour. Effect of wood flour size on the mechanical properties of wood-PP composites was also investigated by Stark and Berger (Stark and Berger 1997). The particle sizes of the wood flour had four ranges: 53-75 μm, 106-150 μm, 180-250 μm and 425-600 μm. The wood content was fixed at 40 wt%. Their results showed that the strength and the modulus of elasticity for both tensile tests and flexural tests were maximized at the particle size of about 250 μm.

The influence of fiber length on the mechanical properties of wood-PP and sisal-PP composites sheets was investigated by Lee et al (Lee, McDonald et al. 2001). The composites were readily compression-molded to form sheets. The wood fibers used in these composites were thermomechanical pulps from radiata pine and eucalyptus. It appeared that the long sisal fibers were not superior to short wood

fibers in terms of enhancing the tensile and flexural strengths and the tensile and flexural modulus of the resulting composites. However, an increase in wood fiber length increased the tensile and flexural strengths and the tensile and flexural modulus for a given fiber content.

1.2.4 Plastics in WPCs

The thermoplastics used for WPCs should have a melting or softening temperature less than the thermal degradation temperature of wood (around 210 °C) (Wolcott and Englund 1999). Commonly used thermoplastics for WPCs include PE, PP, polyvinyl chloride (PVC) and polystyrene (PS). Both virgin and recycled plastics can be used (Bledzki, Reihmane et al. 1998; Wolcott and Englund 1999).

PE is the most commonly used plastic for WPCs with PP coming second (Killough 1995; Optimat Ltd and MERL Ltd 2003). WPCs made from PE and PP are widely used for decking, fencing, infrastructure and transportation applications.

PVC was one of the first plastics used in commercial WPCs (Schut 1999; Optimat Ltd and MERL Ltd 2003). Wood-PVC composites are typically used in window manufacturing. Their applications have recently been extended to decking (Clemons 2002; Leaversuch 2000).

1.2.5 Manufacturing of WPCs

Extrusion is by far the most commonly used manufacturing method for WPCs (Clemons 2002). In an extrusion process, wood, plastic and additives are thoroughly mixed and profile-extruded into different products. The profile can be in a simple solid shape or a highly engineered and hollow shape. Extruders used in WPC manufacturing can be co-rotating, counter-rotating, parallel, or conical twin-screw extruders as well as single-screw extruders (Mapleston 2001b).

Extrusion of WPCs is more challenging than that of regular plastics due to the presence of wood. A mixture of wood and molten plastic normally does not flow as well as pure plastics. The high shear stress during the extrusion could cause degradation of wood fibers. The evaporation of moisture in wood can create devastating bubbles, blisters and weak spots during the extrusion. Wood is a hydrophilic material and most plastics are hydrophobic. Efficient mixing of these two incompatible materials is difficult (Leaversuch 2000; Mapleston 2001b; Mapleston 2001a).

Extensive work has been done to modify the traditional plastic extrusion processes for improving the mixing of wood and plastic (Machado and Martin 1997; Schut 1999; Colvin 2000; Leaversuch 2000; Mapleston 2001b; Mapleston 2001a). One of major modifications was the addition of a compounding step before the extrusion (Park and Balatinecz 1997; Stropoli 1997; Leaversuch 2000; Mapleston 2001b). In compounding, the wood fillers and additives are dispersed in the molten polymer to produce a homogeneous blend. The compounded material can be

immediately extruded into an end product or formed into pellets for future processing. In addition to a better mixing, the introduction of a compounding step reduces the time for extrusion, thus reducing the possibility of wood degradation. The moisture is also removed from wood during compounding, which improves the quality of the final products. Compounding can be carried out in a specifically designed stand alone equipment, such as Buss kneaders, Gelimat mixers and Szego mills, or in a twin-screw extruder (Park and Balatinecz 1997; Stropoli 1997; Leaversuch 2000; Mapleston 2001b).

1.2.6 Improvement of interfacial adhesion in WPCs

The properties of WPCs depend on many factors, including the properties of the polymer and filler, the size and shape of the filler (particulate, fibrous, etc.), the phase state of the polymer matrix (crystalline, rubbery, etc.), the process by which the composite is manufactured, and the nature of the interface between the filler and polymer matrix (Lipatov 1977). While all these factors affect the final performance of the composites, it is the interfacial adhesion between the filler and the matrix that largely determines the mechanical properties of the composites (Raj and Kokta 1991b). The interfacial adhesion has to be strong enough to effectively transfer stress from the polymer matrix to the filler, thus giving WPCs superior strength properties. Unfortunately, the interface between wood filler and thermoplastic matrix is usually weak and fails to transfer stress due to the incompatibility between the hydrophilic

wood and the hydrophobic plastic. This incompatibility has been one of the main obstacles for the broad use of WPCs.

Extensive efforts have been devoted to improve strength and stiffness of WPCs.

1.2.6.1 Physical methods for improving the interfacial adhesion

It was found that stretching and calendaring of wood enhanced the bonding of the wood filler to the polymer matrix, thus improving the mechanical properties of the composites (Semsarzadeh, Lotfali et al. 1984; Semsarzadeh 1986; Zeronian, Kawabata et al. 1990).

Electric discharge treatments of plastics, including plasma treatments and corona treatments, have been successfully used to improve the mechanical and rheological properties of WPCs (Dong, Sapieha et al. 1992; Belgacem, Bataille et al. 1994; Felix, Gatenholm et al. 1994). These physical treatments are able to modify the surface composition and the surface properties of both wood and plastics (Belgacem, Bataille et al. 1994). However, these treatments are more often applied to the wood because the specific surface area of the wood filler is usually larger than that of the plastic particles and the surface of the treated plastic particles may not be in full contact with the wood filler after melting (Belgacem, Bataille et al. 1994).

1.2.6.2 Compatibilizers for WPCs

Compared with previously discussed physical methods, coupling agents (commonly called compatibilizers) are much more frequently used to improve the

compatibility of wood and plastics (Maldas and Kokta 1993; Lu, Wu et al. 2000). A coupling agent is a "chemical substance designed to be added to a matrix resin system, added to and react with both the reinforcement and matrix, to promote a stronger bond at the interface" (Morena 1997). Effective compatibilizers should be able to interact with both the reinforcing filler and the thermoplastic matrix and to promote or establish strong linkages at the wood filler/thermoplastic interface. Compatibilizers can be directly added during the compounding process of the composites. They can also be used to modify the surface of wood filler and then mixed with plastic to form WPCs. There are a wide variety of coupling agents for wood-plastic composites (Maldas and Kokta 1993; Lu, Wu et al. 2000; Djiporovic, Dingova et al. 2003; Geng, Li et al. 2004; Zhang, Li et al. 2004). The efficiency of these coupling agents in improving the interfacial adhesion depends on their chemical structures and their dosage in the composites and their addition methods in the preparation step.

Trialkoxysilanes $(R-(CH_2)_n-Si-(OR')_3)$, coupling agents for glass fiber- or mineral-reinforced polymers, have been investigated as compatibilizers for WPCs (Kokta, Maldas et al. 1990a; Coutinho, Costa et al. 1997; Bledzki and Gassan 1999). The reaction mechanism between silane and the wood fibers is suggested as follow. At the presence of water, silane is hydrolyzed by either an acid or a base to some extent to form a reactive silanol that further reacts with hydroxyl groups of wood. Silanol could also form a layer of siloxane polymer on the wood surface through a condensation reaction (Kokta, Maldas et al. 1990a; Bledzki and Gassan 1999; Mittal

2004) (Figure 1.1). The R group bonds with the polymer through co-polymerization and/or the formation of an interpenetrating network.

$$RSi(OR')_3 \xrightarrow{\ 3H_2O\ } RSi(OH)_3 + 3R'OH$$
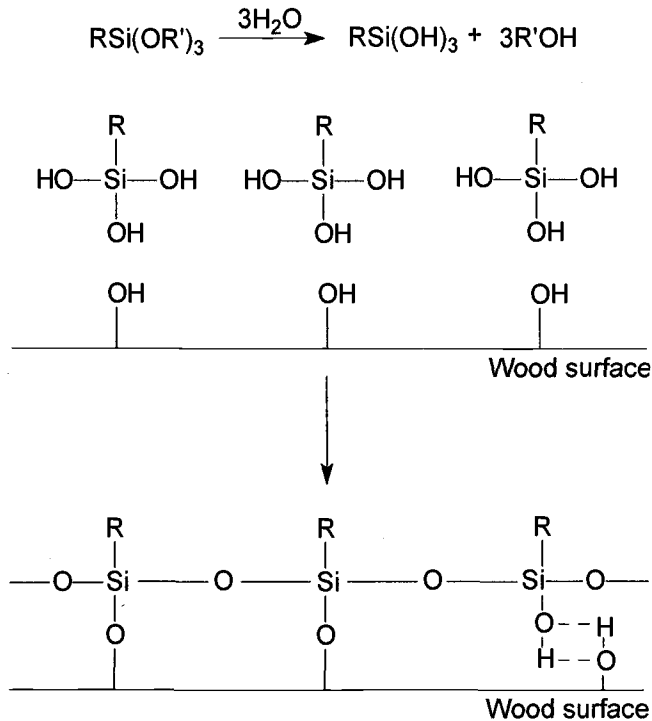
Figure 1.1 A general bonding mechanism between silanes and wood.

Five silanes (A-172, A-174, A-186, A-187 and A-1100) were investigated as coupling agents for hardwood aspen fibers-PVC composites (Kokta, Maldas et al. 1990a). Mechanical properties, including tensile modulus, tensile strength at maximum point, the corresponding elongation and energy, of the composites were evaluated. The R functional group in A-172 or A-174 is a vinyl group. The R group in A-186 or A-187 is an epoxy group, and the R group in A-1100 is an amino group. It was observed that A-1100 treated wood fiber-filled composites had improved

mechanical properties compared to that of untreated ones. However, except for the tensile modulus, the mechanical properties of the composites were significantly lower than those of the original polymer. In the presence of di-*t*-butyl peroxide as a free radial initiator, composites with A-172 and A-174 had slightly enhanced mechanical properties than those with A-1100. Without the peroxide, A-172 and A-174 actually lowered mechanical properties of the composites without a coupling agent. Both tensile strength and tensile modulus of the composites with A-186 or A-187 as a coupling agent were lower than those of composites without a coupling agent when the wood fiber loading was lower than 20 wt%. When the fiber loading was increased to 30 wt%, silane A-186 and A-187 slightly improved the tensile strength and the tensile modulus of the composites.

Effects of A-172, A-174 and A-1100 on the tensile properties of wood-PS composites were investigated by Maldas et al. (Maldas, Kokta et al. 1988). The wood-PS composites with silane-treated wood fibers showed some improvements in mechanical properties when compared to those with untreated fibers. However, except for the tensile modulus, no significant improvement in other properties was observed, when compared to original PS. The authors concluded that the Van der Waals' forces between the silane coupling agents and PS were not sufficient to make a stress transfer between the wood filler and the PS matrix.

The treatment of wood flour with A-172, A-174 or A-1100 moderately increased the tensile strengths of the wood-PE composites (Raj and Kokta 1991a).

The largest increase in tensile modulus was observed from 1.80 GPa for the composite without any silane to 2.07 GPa for the composite with 6 wt% A-174.

The above-mentioned researches suggested that silane had some effectiveness in improving the mechanical properties of the WPCs. Silane adheres to the wood surface through hydrogen bonding or covalent linkages, decreasing the surface energy of the wood and improving the dispersion of wood fillers in the plastic matrix. However, the interaction between silane and the plastic matrix is weak. Therefore, silane was not able to form effective bridges between the wood fillers and the plastic matrix.

In the presence of a peroxide, maleic anhydride was found to be able to improve the mechanical properties of wood-plastic composites to some extent (Maldas and Kokta 1991a; Maldas and Kokta 1991b). It was believed that maleic anhydride is able to form ester linkages with the hydroxyl groups of wood fibers. A radical initiator such as a peroxide catalyst generated free radicals on the polymer matrix. The free radicals then reacted with the carbon-carbon double bond of maleic anhydride. In this way, maleic anhydride formed linkages between wood and polymer matrix (Maldas and Kokta 1991a; Maldas and Kokta 1991b). Phthalic anhydride was found to be ineffective for improving the strengths and stiffness of wood-PS composites (Maldas and Kokta 1990b).

The *in situ* free radical reactions between maleic anhydride and the polymer matrix may be very inefficient, which may account for the low efficacy of maleic anhydride as a compatibilizer (Maldas and Kokta 1990c; Djiporovic, Dingova et al.

2003). Therefore, maleic anhydride is grafted onto polymers first, and the grafted polymers are then used as compatibilizers. Commonly used maleic anhydride-grafted polymers include maleic anhydride grafted PP (MAPP), maleic anhydride grafted PE (MAPE) and maleic anhydride grafted styrene-ethylene-butylene-styrene (MA-SEBS).

MAPP has been extensively studied as a compatibilizer for wood-PP composites (Takase and Shiraishi 1989; Gatenholm, Felix et al. 1992; Gatenholm and Felix 1992; Sanadi, Caulfield et al. 1995; Karnani, Krishnan et al. 1997; Marcovich, Reboredo et al. 1998; Coutinho and Costa 1999; Nitz, Reichert et al. 2000; Bledzki, Faruk et al. 2002; Nunez, Kenny et al. 2002; Bledzki and Faruk 2003). MAPP enhanced tensile and flexural properties and impact resistances of the resulting wood-PP composites (Karnani, Krishnan et al. 1997; Bledzki and Faruk 2003; Pickering and Ji 2004). MAPP also reduced the water sorption of the composites (Bledzki, Faruk et al. 2002; Bledzki and Faruk 2003). It is believed that the succinic anhydride moieties of MAPP form ester linkages and hydrogen bonding with wood hydroxyl groups (Figure 1.2). The PP backbone of MAPP mixes with PP matrix and forms entanglement with bulk PP molecules (Felix and Gatenholm 1991; Gatenholm and Felix 1992; Gatenholm and Felix 1993). MAPP is prepared from grafting of maleic anhydride to PP through a free radical process. The grafting mechanism has been extensively studied (Minoura, Ueda et al. 1969; Ruggeri, Aglietto et al. 1983; Rengarajan, Parameswaran et al. 1990; De Roover, Sclavons et al. 1995). Because the grafting reaction is a random process, the succinic anhydride moiety is proposed to be randomly distributed along the PP chain, forming a comb-like structure (Figure 1.3-a).

A β-scission may be involved in the grafting, which may decrease the molecular weight of PP and result in the succinic anhydride-terminated PP chains (Figure 1.3-b). Little information is published on the distribution of the succinic anhydride on the PP chains and the content of β-scission products. The relationship between the MAPP structure and its compatibilizer effect is still poorly understood.
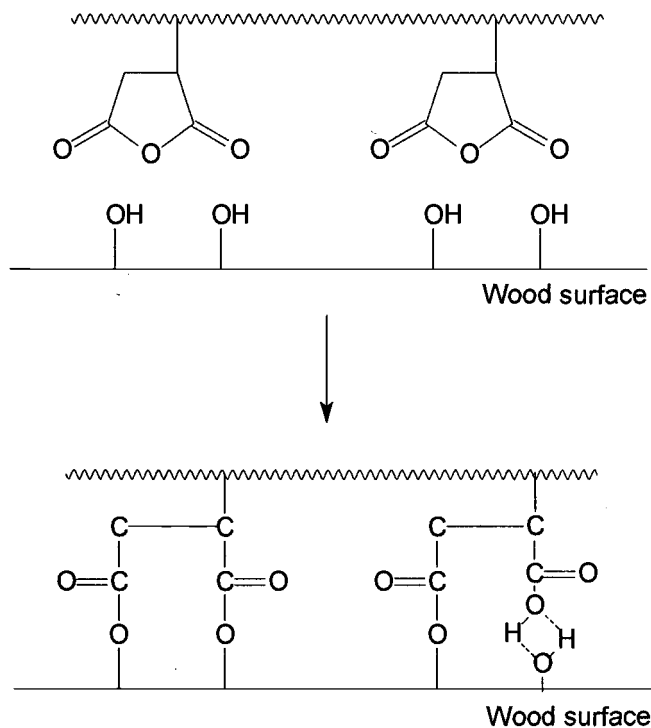
Figure 1.2 A general bonding mechanism between maleic anhydride grafted polymers and wood.

Although MAPE was extensively studied as a compatibilizer in starch-PE composites (Bikiaris and Panayiotou 1998; Sailaja and Chanda 2001; Wang, Liu et al. 2004), only a few references are available on using MAPE as a compatibilizer in wood-PE composites (Raj and Kokta 1991b; Lu, Wu et al. 2005). MAPE was able to

improve the tensile strength, tensile modulus and flexural modulus of the wood-PE composites (Raj and Kokta 1991b; Lu, Wu et al. 2005). The performance of MAPE as a compatibilizer was determined by its molecular structure (Lu, Wu et al. 2005). However, as in the case of MAPP, this relationship between the MAPE structure and its compatibilizer effect is also poorly understood.

a

b
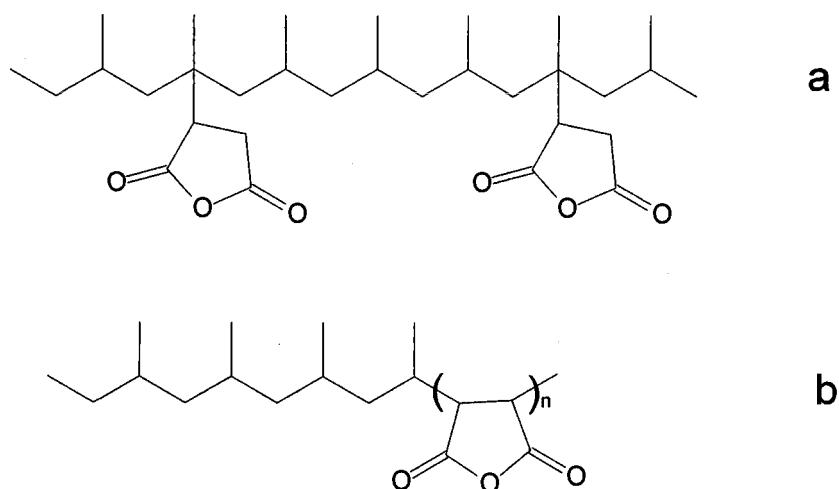
Figure 1.3 Different molecular structures of MAPP.

MA-SEBS was investigated as a compatibilizer for wood-PE composites, wood-PP composites and wood-PE-PS composites (Gatenholm, Hedenberg et al. 1995; Hedenberg and Gatenholm 1995; Oksman and Clemons 1998; Oksman and Lindberg 1998; Oksman, Lindberg et al. 1998; Nitz, Reichert et al. 2000). In wood-PP composites with 40 wt% wood flour, the addition of 3 wt% MA-SEBS increased the tensile strength of the composites from 30.1 MPa to 42.3 MPa. The impact strength was increased by 30%. However, the addition of MA-SEBS decreased the tensile modulus from 4165 MPa to 3665 MPa (Nitz, Reichert et al. 2000). Similar behavior

was observed in wood-PE composites with MA-SEBS as a compatibilizer (Oksman and Lindberg 1998; Oksman, Lindberg et al. 1998).

Acrylic acid-grafted polyethylene was found to be able to improve the strength of wood-PE composites (Li and Matuana 2003). However, acrylic acid-grafted polyethylene as a compatibilizer was less effective than MAPE (Li and Matuana 2003). The anhydride group in MAPE can form ester linkages with hydroxyl groups of wood faster and more efficiently than the carboxylic acid group in acrylic acid-grafted polyethylene.

Another important group of compatibilizers is isocyanates (Kokta, Maldas et al. 1990b; Bledzki, Reihmane et al. 1998; Lu, Wu et al. 2000). Isocyanates have been widely used as wood adhesives. When used as wood adhesives, isocyanates first react with moisture to form an amine that further reacts with isocyanates to form an adhesive network. Isocyanates are also able to form urethane linkages with wood hydroxyl groups. Both hydrogen bonding and covalent bonding contribute to the adhesion between isocyanates and wood (Wendler and Frazier 1996; Frazier and Ni 1998; Ni and Frazier 1998). However, little information is available about the relative contributions of the hydrogen bonding and the covalent linkages to the adhesive strength.

Effects of four isocyanates, including poly(methylene diphenyl diisocyanate) (PMPIC or PMDI), toluene 2,4-diisocyanate (TDIC), hexamethylene diisocyanate (HMDIC) and ethyl isocyanate (EIC), were investigated as compatibilizers for wood-PVC composites (Kokta, Maldas et al. 1990b). The compatibilization effects of these

four isocyantes decreased in the following order: PMDI>TDIC>HMDIC>EIC. In PMDI- and TDIC-compatibilized wood-PVC composites, there might exist interaction between the delocalized π-electrons of the benzene rings of the isocyanates and the opposite polarity of PVC due to the presence of electronegative chlorine (Maldas, Kokta et al. 1989a; Kokta, Maldas et al. 1990b). This interaction did not exist in HMDIC- and EIC-compatibilized wood-PVC composites.

Polystyrene

—CH —CH₂— CH —CH₂— CH —CH₂—
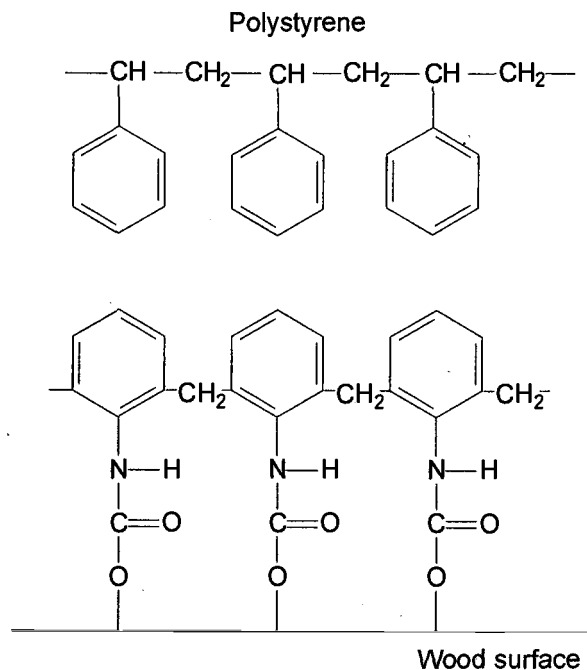
Figure 1.4 PMDI as a compatibilizer for wood-PS composites.

In PMDI-compatibilized wood-PS composites, the delocalized π-electrons of the benzene rings in PMDI and PS interact with each other, thus improving the adhesion between the compatibilizer and the PS matrix (Figure 1.3) (Maldas, Kokta et al. 1988; Maldas, Kokta et al. 1989b; Maldas, Kokta et al. 1989c; Maldas and Kokta 1990c; Maldas and Kokta 1990a). PMDI also improved the mechanical properties of

the wood-PE and wood-PP composites (Raj, Kokta et al. 1989; Djiporovic, Dingova et al. 2003; Pickering and Ji 2004). The improvement of the mechanical properties supposedly result from the strengthening and stiffening of wood fibers by PMDI because adhesion between PMDI and PE or PP is supposed to be weak.

The following chemicals were also investigated as compatibilizers: dichlorotriazine and its derivatives, m-phenylene bismaleimide and stearic acid (Zadorecki and Flodin 1985a; Zadorecki and Flodin 1985b; Sain and Kokta 1994; Joly, Kofman et al. 1996) (Raj and Kokta 1991b). In dichlorotriazine-compatibilized cellulose-polyester composites, the highest increase in tensile modulus was only about 9%, when compared to the composites without a compatibilizer. Stearic acid was much less effective than MAPE in terms of enhancing the strengths ofwood-PE composites (Raj and Kokta 1991b). Wood-PP composites with m-phenylene bismaleimide-treated wood fibers had moderately higher tensile strengths than those with untreated wood fibers (Sain and Kokta 1994). Therefore, these chemicals were not considered as effective compatibilizers for WPCs.

Theoretically, an effective compatibilizer should be able to bond both wood and plastics, i.e., at least contain two domains: a plastic-binding domain and a wood-binding domain. Extensive literature review reveals that most published studies except those related to MAPP and MAPE focused on chemicals that can effectively bond wood. These chemicals are typically poor compatibilizers because they lack the capacity of bonding plastics. Therefore, the choices for effective compatibilizers are still very limited even though extensive efforts have been devoted to develop effective

compatibilizers. As a matter of fact, the ideal structure and functionality of an effective compatibilizer are still poorly understood.

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A Novel Wood-binding Domain of a Wood-Plastic Coupling Agent: Development and Characterization

Cheng Zhang, Kaichang Li and John Simonsen

2 A NOVEL WOOD-BINDING DOMAIN OF A WOOD-PLASTIC COUPLING AGENT: DEVELOPMENT AND CHARACTERIZATION

Cheng Zhang, Kaichang Li and John Simonsen
Department of Wood Science and Engineering
Oregon State University, Corvallis, Oregon 97331, U.S.A.

ABSTRACT

Poly(N-acryloyl dopamine) (PAD) was successfully synthesized through free radical homopolymerization of N-acryloyl-O,O'-diphenylmethyldopamine and subsequent deprotection. The adhesive ability of PAD to wood was studied in detail. PAD underwent substantial oxidation and cross-linking reactions at about 80 °C. Therefore, maple veneer samples bonded with PAD powder at the press temperature of 120 °C had high shear strengths and high water resistance. In contrast to conventional wood adhesives such as phenol-formaldehyde and urea-formaldehyde resins, PAD resulted in the increase, rather than the decrease, in the shear strengths of 2-ply laminated maple veneer test specimens after the test specimens underwent a water-soaking-and-drying treatment. A mixture of PAD and polyethylenimine (PEI) resulted in much higher shear strengths than PAD alone. To achieve high shear strengths and high water resistances, the maple specimens bonded with PAD/PEI mixtures had to be cured above 150 °C because reactions between PAD and PEI occurred at about 150 °C. Water resistances of the maple specimens bonded with

PAD/PEI mixtures were dependent upon the PDA/PEI weight ratio and the curing temperature.

Keywords: adhesive, compatibilization, composites, marine adhesive

2.1 INTRODUCTION

Various fillers such as glass fibers and mineral fillers are extensively used to increase the strength and stiffness of thermoplastics in the plastics industry. Wood fibers are currently gaining popularity because they are inexpensive, readily available, and their low abrasiveness causes low machine wear and reduced damage to processing equipment. Wood-filled plastics, also called wood-plastic composites (WPCs), are one of the fastest growing sectors in wood composite industry (Sellers, Miller et al. 2000). The most commonly used thermoplastics in a WPC are polyethylene (PE) and polypropylene (PP). The most common filler used in WPCs is ground wood waste. In addition, cellulosic natural fiber materials such as bagasse, corncobs, and cereal straw, have also been used as fillers (Seymour and Carraher 1981). WPCs are used as outdoor decking materials, interior door panels, window moldings, interior automobile parts, and a large variety of other molded products (Youngquist 1995). WPCs have many advantages over traditional wood products such as reduced water absorbance, reduced thickness swelling, and enhanced

durability against biodeterioration. When compared to unfilled thermoplastics, WPCs exhibit higher strength and stiffness, higher resistance to ultraviolet degradation, and higher thermal stability.

The final performance of WPCs is greatly dependent upon the properties of the interface between the thermoplastic matrix and the wood filler. This interface is normally weak and fails to transfer stress between the phases because the wood is hydrophilic and the thermoplastic is hydrophobic. To address this problem, a coupling agent (commonly called a compatibilizer) that can bridge the interface and improve the stress transfer between phases is often added to the composite formulation during the manufacture of WPCs.

Extensive studies suggest that an ideal compatibilizer should contain two domains: one domain able to form entanglements or segmental crystallization with the polymer matrix and the other able to form a strong adhesive bond with wood. In the example of wood-filled polypropylene composites, a di-block copolymer with one block being PP and the other block containing wood-binding functional groups would be an ideal compatibilizer. Maleic anhydride (MA)-grafted polypropylene (MAPP) is by far the most effective compatibilizer for wood-filled PP composites. In MAPP, the succinic anhydride groups bind to wood via ester linkages while the PP chains form adhesion with the PP matrix (Kishi, Yoshioka et al. 1988; Gauthier, Joly et al. 1998). MAPP is normally produced through grafting of MA to PP via a free radical process. Succinic anhydride groups in MAPP are irregularly distributed along the PP chain (Gauthier, Joly et al. 1998). Therefore, MAPP does not have an optimum structure for

compatibilization. Maleic anhydride is also not a good material to make PP-(poly-MA) di-block copolymer because maleic anhydride is known to have a low tendency to form a homopolymer (Russell and Kelusky 1988; Lu and Chung 1998). Therefore, improvement of WPC properties would benefit from the development of a new wood-binding domain that is able to form a di-block copolymer with PP.

In this study, a novel wood-binding domain was developed through mimicking the strong adhesion of mussels to rock and other substances in seawater. To cope with tides and strong turbulence, mussels secret adhesive proteins, typically called marine adhesives. Extensive studies have revealed that marine adhesives contain 8-18 mol% L-3,4-dihydroxyphenylalanine (DOPA) (Rzepecki, Chin et al. 1991; Rzepecki, Hansen et al. 1992). To further determine the specific functions of individual amino acid such as tyrosine, DOPA, lysine and cysteine in marine adhesive proteins, various polypeptides have been chemically synthesized and studied for their binding abilities to various substrates (Yamamoto 1987b; Yamamoto 1987a; Yu and Deming 1998; Tatehata, Mochizuki et al. 2000). Several key conclusions are apparent from these studies: a) "Functionality, and not amino acid sequence, was the only feature necessary for moisture-resistant adhesion;" (Yu and Deming 1998) b) DOPA residues appear to play an essential role in both adhesion and cross-liking in marine adhesives; c) Other amino acids such as lysine significantly improved the binding of marine adhesives.

Inspired by the strong binding of marine adhesives, poly (N-acryloyl dopamine), a polymer that contains DOPA-like phenolic hydroxyl groups, was

investigated as a good candidate for the wood-binding domain of a di-block copolymer compatibilizer.

2.2 EXPERIMENTAL

2.2.1 General Information

All IR samples were recorded on a Nexus 470 FTIR spectrometer equipped with a Golden Gate heated diamond ATR (attenuated total reflectance) accessory. ^{1}H NMR spectra were recorded on a 300-MHz spectrometer. All chemicals and NMR solvents were purchased from commercial sources and used as received. Polyethylenimine was purchased from the Sigma-Aldrich Co., Milwaukee, Wisconsin. Thin-layer chromatography (TLC) was performed with AlugramSil-G/UV$_{254}$ plates (Fisher Scientific, Pittsburgh, PA) with UV light. Column chromatography was performed with Whatman silica 60 [230-400 mesh (63-38 μm), Fisher Scientific, Pittsburgh, PA] using a standard flash chromatography apparatus (Ace Glass, Vineland, NJ).

2.2.2 Synthesis of *O, O'*-diphenylmethyldopamine hydrochloride (2)

O, O'-diphenylmethyldopamine hydrochloride (2) was synthesized according to a literature procedure. (Liu and Li 2002)

2.2.3 Synthesis of *N*-acryloyl-*O, O'*-diphenylmethyldopamine (3)

Triethylamine (5.15 g, 50.91 mmol) was added to a suspension of 2 (6 g, 16.96 mmol) in CH_2Cl_2 (150 mL). The reaction mixture was chilled in an ice-water bath and acryloyl chloride (2 g, 22.07 mmol) in CH_2Cl_2 (10 mL) was then added dropwise over 30 min. The cooling bath was removed and the mixture was stirred for 3 h at 25 °C. The solvents were removed under vacuum and the residues dissolved in EtOAc. The residual solids were removed by filtration and the EtOAc solution washed three times with 1 M NH_4Cl, then three times with 5% $NaHCO_3$ and once with brine. The organic layer was processed in a standard fashion to afford crude 3 that was subsequently purified by silica gel chromatography ($CHCl_3$/EtOAc 9:1) to provide 3 (5.01 g, 80%). 1H NMR (CD_3SOCD_3): 8.15 (1H, t), 7.54 (4H, m), 7.46 (6H, m), 6.93 (2H, t), 6.70 (1H, d), 6.20 (1H, q), 6.09 (1H, d), 5.56 (1H, d), 3.35 (2H, q), 2.69 (2H, t).

2.2.4 Synthesis of poly(*N*-acryloyl-*O, O'*-diphenylmethyldopamine)(4)

Compound 3 (4.46 g, 12.01 mmol) and 2,2'-azobisisobutyronitrile (0.02 g, 0.122 mmol) were dissolved in acetonitrile (30 mL) in a 100-mL flask. The solution was degassed by bubbling N_2 for 3 min. The flask was sealed and heated to 70 °C for 3 days. The polymerized product 4 was then washed with ethyl ether (Et_2O) and dried under vacuum (4.40 g, 98%). 1H NMR (CD_3SOCD_3): 7.41 (4H, broad), 7.22 (6H,

broad), 6.74 (2H, broad), 6.47 (1H, broad), 3.35 (2H, broad), 3.15 (2H, broad), 2.00

(1H, broad), 1.58 (2H, broad).

2.2.5 Synthesis of poly(*N*-acryloyldopamine) (PAD) (5)

To a suspension of 4 (4.2 g) in trifluoroacetic acid (TFA) (30 mL) was added

33 wt % HBr in acetic acid with stirring. The mixture was stirred for 3 h at 25 °C.

The product was washed with Et$_2$O and dried under vacuum (2.29 g, 98%).

2.2.6 The differential scanning calorimetry (DSC) analysis

Calorimetric measurements were obtained on a DSC-2920 (TA Instruments,

Inc, New Castle, DE) with argon as a purge gas. Argon flow was adjusted to a rate of

40 mL/min. The calorimeter was calibrated against indium (m.p. 156.6 °C, ΔH=28.45

J/g) at 10 °C/min. Test samples of ca. 2-5 mg were weighed in standard aluminum

pans with lid closures. An empty aluminum pan with the lid was used as a reference.

The samples were first cooled to 5-8 °C with ice and the thermograms were then

recorded at a heating rate of 10 °C/min between 5 to 300 °C. For the DSC analysis of

a preheated sample, the sample was heated quickly to a pre-set temperature (120 °C or

180 °C), and held at that temperature for 5 min. The hot sample was cooled to 8 °C

with ice at an approximate rate of 50 °C/min. The thermograms were then recorded at

a heating rate of 10°C/min between 5 to 300 °C. If the sample was the mixture of

PAD and polyethylenimine (PEI) (1:1 weight ratio), PEI was first dried under high

vacuum to completely remove water prior to mixing with PAD. The Universal Analysis V3.3B software supplied by TA Instruments, Inc. was used to plot and analyze the thermal data. The DSC spectra have been normalized to represent 1 g of sample.

2.2.7 Adhesion test specimen preparation

Maple veneer 0.6 mm thick was cut into 100×60 mm pieces. When only PAD was used, the PAD powder was brushed directly onto maple veneer surfaces. When mixtures of PAD and PEI were used, PAD was first added to an aqueous PEI solution with a pre-determined weight ratio between PAD and PEI and then mixed well. The PAD/PEI mixtures were brushed onto the veneer surfaces. The bonded area of each piece of veneer was 100×10 mm. The adhesive spread rate was 40 g/m^2 (dry weight).

One piece of PAD- or PAD/PEI mixture-brushed veneer and another piece of unaltered veneer were mated with the wood grain in the samples parallel and hot-pressed to form two-ply wood composites. The press time and temperature varied with the requirements of the experiment. After pressing, the bonded two-ply wood composite was cut into 10 specimens. Each specimen had a bonded area of 10×10 mm.

2.2.8 Determination of shear strength

The shear strength of a bonded wood specimen was tested with an Instron TTBML testing machine with the specimen in tension. The crosshead speed was 1 mm/min. The maximum shear strength at breakage was recorded and the degree of cohesive or adhesive failure observed.

2.2.9 Determination of water resistance

Water resistance of the wood composites was determined by soaking the bonded specimen in water at room temperature for 24 h, then drying at room temperature in a fume hood for 24 h, then measuring the shear strength. This water soaking and drying cycle (WSAD) was repeated up to three times. A separate boil test was performed in accordance with U. S. Voluntary Product Standard PS 1-95 for Construction and Industrial Plywood (published by the U.S. Department of Commerce through APA—The Engineered Wood Association, Tacoma, WA), i.e. test specimens were boiled in water for 4 h and then dried for 20 h at 63 ± 3 °C. The specimens were boiled in water again for 4 h, cooled down with tap water and evaluated for the shear strengths while the specimens were wet. The shear strengths were also measured after the specimens were dried again at room temperature in a fume hood for 24 h.

2.3 RESULTS AND DISCUSSION

Synthesis of poly (*N*-acryloyl dopamine) (PAD) 5 is shown in Figure 2.1. Protection of phenolic hydroxyl groups in 1 with dicholorodiphenylmethane readily yielded 2 in 73% yield. Reaction of 2 with acryloyl chloride in the presence of triethylamine afforded 3 in 80% yield. Polymerization of 3 provided 4 that was readily deprotected to give 5. Deprotection of 4 was verified through Fourier Transform Infrared (FTIR) spectrometry (spectra not shown).
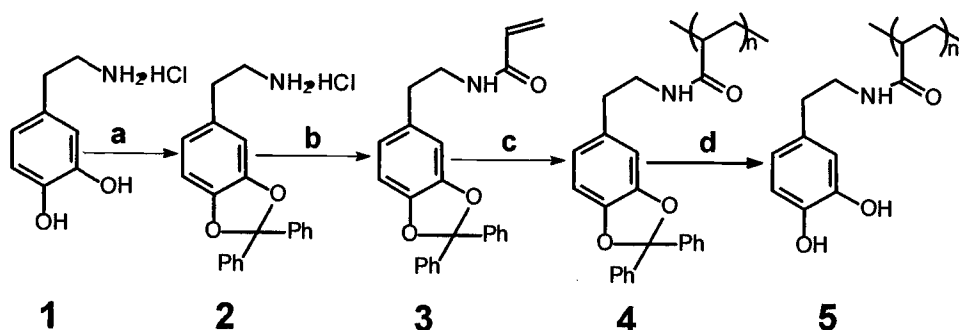
Figure 2.1 Synthesis of PAD. Reaction conditions: a, Ph_2CCl_2; b, acryloyl chloride/Et_3N; c, AIBN/CH_3CN; d, HBr/AcOH/TFA.

PAD powder bonded maple veneers strongly (Figure 2.2). Shear strengths of PAD powder wood composites at curing times of 2 and 5 min were comparable to each other and slightly higher than those at curing times of 10 and 20 min. Most interestingly, the shear strengths significantly increased after the specimens underwent the WSAD cycle. The gain in shear strengths was highest at a cure time of 5 min. Reported shear strengths of specimens bonded with conventional wood adhesives such

as phenol-formaldehyde and urea-formaldehyde resins typically decrease after a WSAD cycle (Sellers and McSween 1985; Pizzi 1994). Therefore, this big strength gain is an unprecedented phenomenon in wood adhesion.

Visual inspection revealed an even distribution of PAD on the veneer surfaces for those specimens cured at 120 °C. Optical microscopic inspection showed that the adhesive could penetrate up to 4 woody cells (microscopic image not included). We conclude that the PAD flowed well and penetrated the wood substrate at 120 °C.
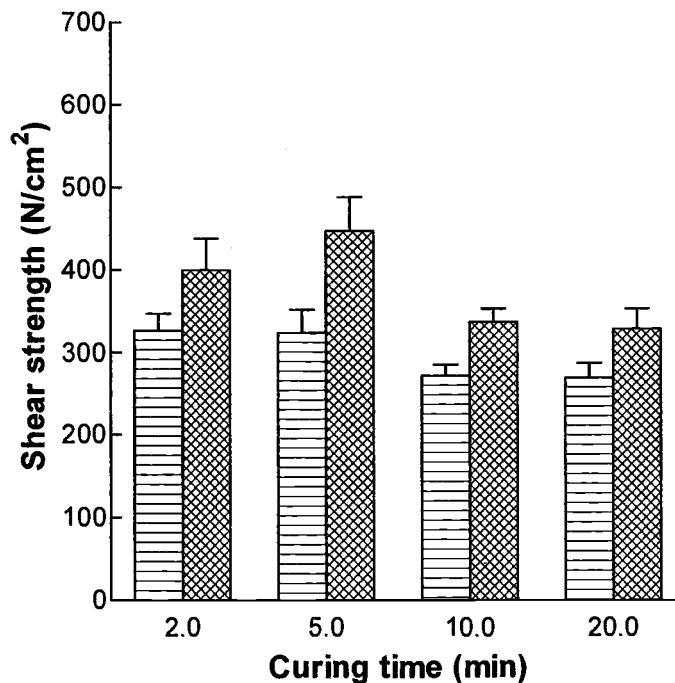
Figure 2.2 Effects of the curing time on the shear strengths of wood composites bonded with PAD at the curing temperature of 120 °C. Without a WSAD test (▤), after a WSAD test (▦). Error bars show the standard deviation of the data (minimum of eight independent measurements).

The gain in shear strength occurred only after the first WSAD cycle, i.e., the shear strength did not further increase after the specimens underwent a second or third WSAD cycle, but instead decreased slightly. However, the shear strength values after soaking always remained higher than that of an un-soaked specimen (Figure 2.3). We concluded that the PAD adhesive was very water-resistant.
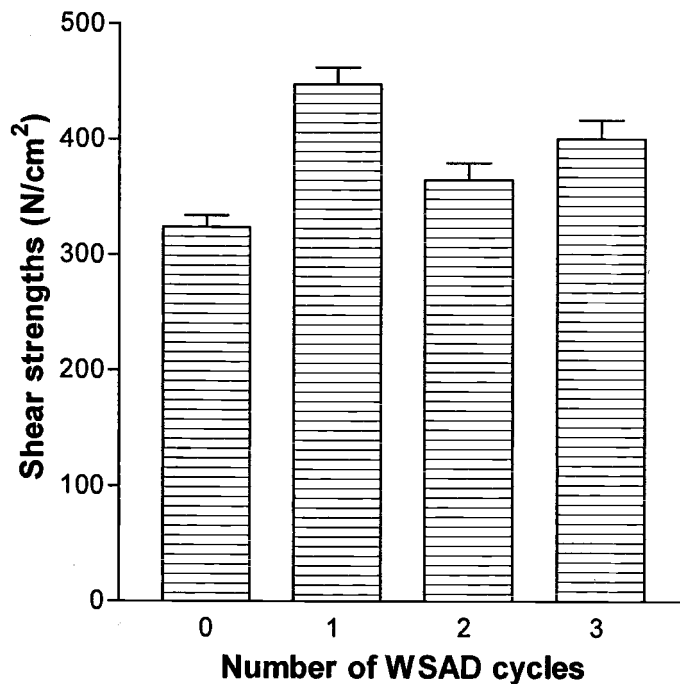
Figure 2.3 Effects of the number of WSAD cycles on the shear strengths of wood composites bonded with PAD at a curing temperature of 120 °C for 5 min. Error bars show the standard deviation of the data (minimum of eight independent measurements).

Results from the boil test indicated the wood composites did not delaminate, although the shear strengths of wet specimens were significantly lower than those of unexposed (and dry) wood composites (Figure 2.4). However, when the exposed

wood composites were subsequently dried the shear strengths increased greatly and became higher than the original unexposed specimens. The gain in shear strength was larger for specimens cured at 180 °C than for those cured at 120 °C (Figure 2.4).
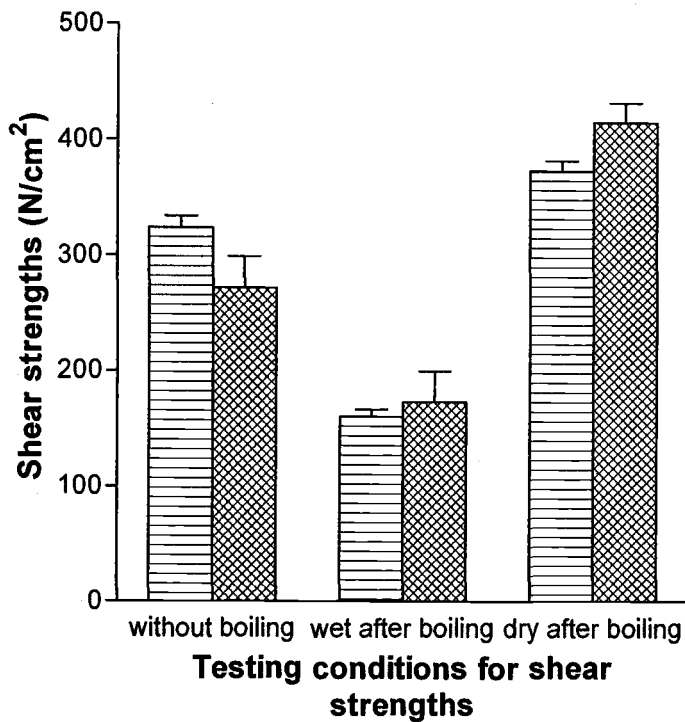
Figure 2.4 Effects of the boil test on the shear strengths of wood composites bonded with PAD. Cure temperature of 120 °C (▤), cure temperature of 180 °C (▨). Error bars show the standard deviation of the data (minimum of eight independent measurements).

Results of the DSC measurements on PAD showed a strong heat absorbance peak around 80 °C (Figure 2.5). When PAD was pre-heated at 120 °C for five min and then analyzed by DSC, the strong peak at 80 °C was greatly reduced, which indicated

that a chemical reaction of PAD, presumably with itself, had occurred. Possible

reactions of PAD at elevated temperatures will be discussed in detail later.
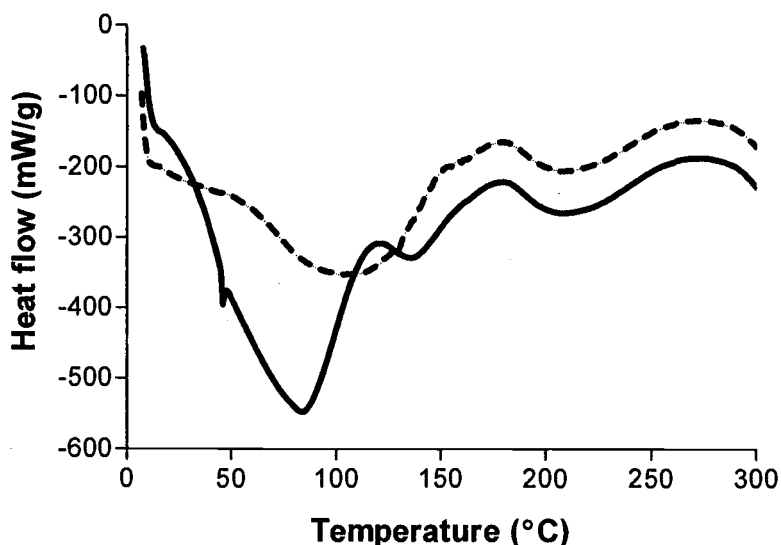
Figure 2.5 DSC characterization of PAD. Unheated before
testing (—), preheated at 120°C for 5 min. (- - -).

In addition to phenolic hydroxyl groups, an amino group is also one of the

major functional groups in mussel adhesive proteins (Waite 1990a). Polyethylenimine

(PEI) was combined with PAD to mimic marine adhesives. When mixed, PAD

dispersed well in an aqueous PEI (50% wt) solution, although it did not completely

dissolve. Under the same press conditions as those shown in Figure 2.2, a mixture of

PAD and PEI (1:1 wt ratio, dry basis) resulted in much higher shear strengths than

PAD alone (Figure 2.6), reaching 600 N/cm^2 when the press time was 20 min.

However, the shear strengths decreased significantly after the specimens bonded with

PAD/PEI mixtures underwent a WSAD treatment. Increasing the press times from 5

to 20 min had little impact on the shear strength after a WSAD treatment. Comparison of the data in Figure 2.6 with those in Figure 2.2 reveals that the water resistances of the wood composites bonded with a PAD/PEI (1:1 wt ratio) mixture at a press temperature of 120 °C were lower than those bonded with PAD alone.
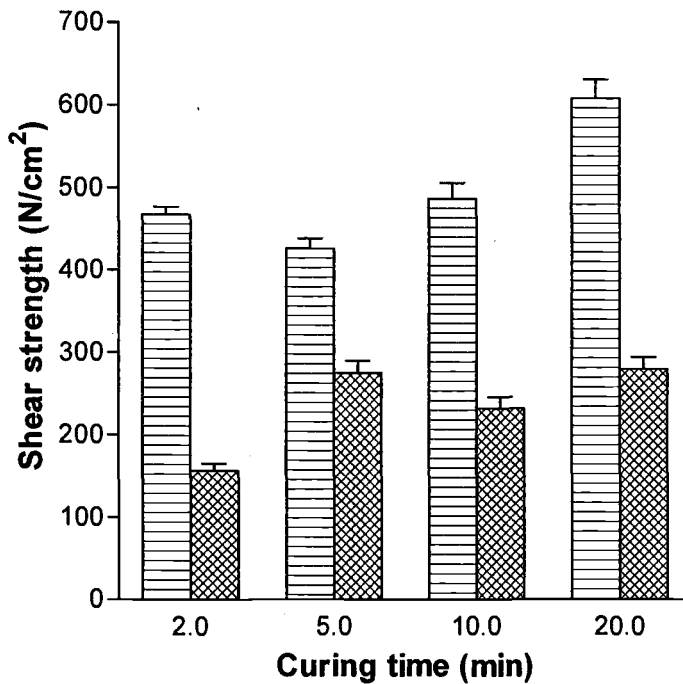
Figure 2.6 Effects of the cure time on the shear strengths of wood composites bonded with PAD/PEI (1:1 wt ratio) at the cure temperature of 120 °C. Without a WSAD test (▤), after a WSAD test (▨). Error bars show the standard deviation of the data (minimum of eight independent measurements).

Because PEI is soluble in water, the amount of PEI in the PAD/PEI mixtures is expected to have a large impact on the water resistance of the wood composites

bonded with PAD/PEI mixtures. The shear strengths of wood composites bonded

with PAD/PEI mixtures at the press temperature of 180 °C are shown in Figure 2.7.
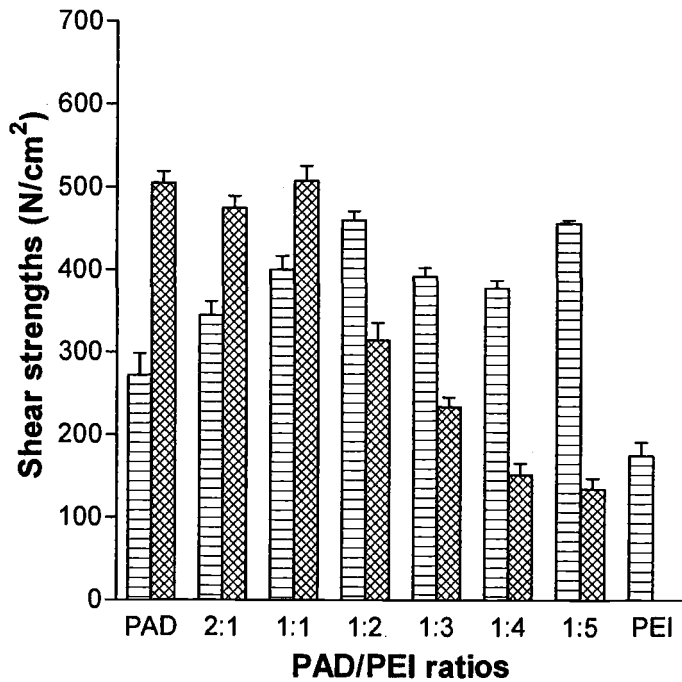
Figure 2.7 Effects of PAD/PEI weight ratios on the shear
strengths of wood composites bonded with PAD/PEI mixtures at
the cure temperature of 180 °C for 5 min. Without a WSAD test
(▤), after a WSAD test (▨). Error bars show the standard
deviation of the data (minimum of eight independent
measurements).

When the wood composites were evaluated without the WSAD treatment, the

highest shear strength was reached when the weight ratio of PAD to PEI was 1:2.

Shear strengths of wood composites bonded with PAD alone or PEI alone were much

lower than those bonded with PAD/PEI mixtures. When the wood composites were

evaluated after one WSAD cycle, the PAD/PEI weight ratio of 1:1 resulted in the

maximum shear strength. At the PAD/PEI weight ratios of 1:2, 1:3, and 1:4, the WSAD treatment decreased the shear strengths of the wood composites. However, when the PAD/PEI weight ratios were 2:1 or 1:1, the WSAD treatment increased the shear strengths of the wood composites. It appears that the higher the PAD contents in the PAD/PEI mixtures the higher the gain in shear strengths after a WSAD treatment.

Comparison of Figure 2.2 to Figure 2.7 reveals that the gain in the shear strength after WSAD treatment of the wood composites bonded with PAD alone were higher at the press temperature of 180 °C than at 120 °C. In contrast to the reduction of the shear strengths for the composites bonded with PAD/PEI mixtures (1:1 wt ratio) at 120 °C for 5 min after a WSAD treatment (Figure 2.6), a press temperature of 180 °C resulted in an increase in shear strengths for the wood composites bonded with PAD/PEI mixtures (1:1 wt ratio) (Figure 2.7). The press temperature had an important impact on the shear strength of the wood composites.

In an effort to better understand the effects of the press temperatures on the strength properties and water resistances, PAD/PEI mixtures were analyzed using a DSC. PAD/PEI mixtures showed a heat absorbance peak around 150 °C (Figure 2.8). When the PAD/PEI mixtures were pre-heated at 120 °C for 5 min and then analyzed with the DSC, the heat absorption peak remained, but became very sharp. However, this heat absorption peak at 150 °C disappeared when the PAD/PEI mixtures were pre-heated at 180 °C for 5 min. Thus it appears that there is a reaction between PAD and PEI occurring at 150 °C. These DSC results suggest that the PAD/PEI mixture has a cure temperature of about 150 °C. This is consistent with the shear strength data of the

wood composites. The wood composites prepared at 120 °C were weaker and less water resistant than those prepared at 180 °C. The DSC results and the strong adhesive bond data suggest that the PAD reacted with PEI to form a highly cross-linked polymer network.
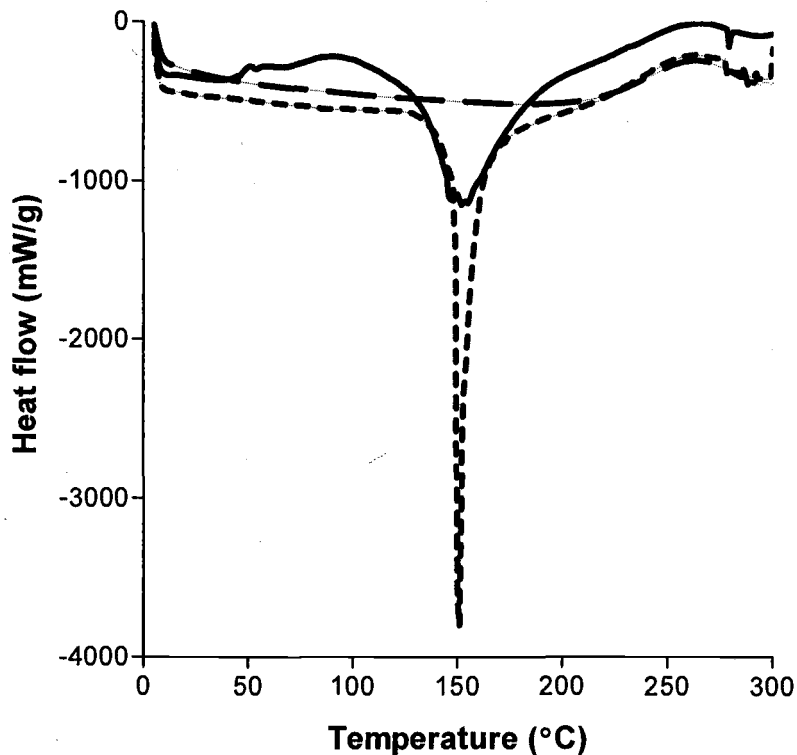
Figure 2.8 DSC characterization of PAD/PEI (1:1 wt ratio) mixtures. Unheated before testing (▬), preheated at 120 °C for 5 min (- - -), preheated at 180 °C for 5 min (▬ ▬ ▬).

The reactions that take place here may be similar to those in the byssal threads secreted by the mussel feet, which are initially soft and colorless and then gradually harden and turn brown. This process is called quinone-tanning (Lindner and Dooley

1976; Lindner 1984; Waite 1990b). Quinone-tanning is a very complex process that includes various oxidation reactions and cross-linking reactions among phenolic structures and between phenolic structures of DOPA/tyrosine and amino groups of lysine (Waite 1990b). Some possible reactions of PAD and PAD/PEI mixtures at elevated temperatures are outlined in Figure 2.9.
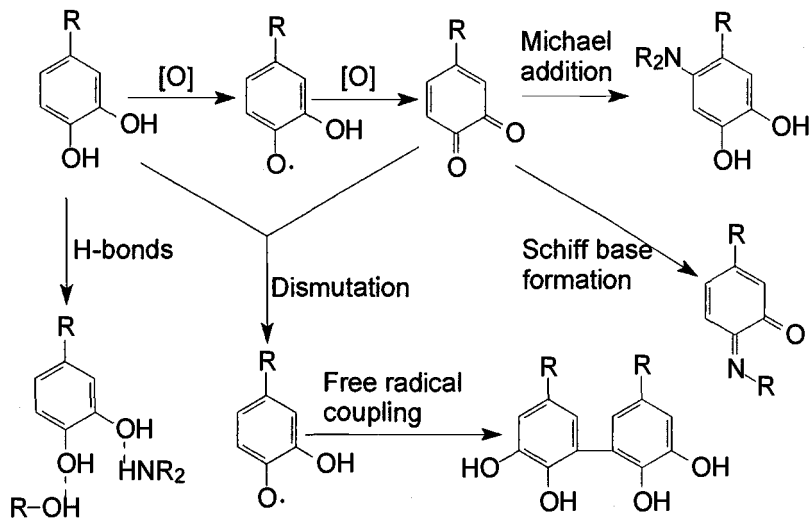
Figure 2.9 Possible reactions of PAD and PAD/PEI mixtures at elevated temperatures.

Phenolic hydroxyl groups in PAD and imino groups in PEI could form hydrogen bonds with each other and with the hydroxyl groups on the wood surface. The phenolic hydroxyl groups in PAD should be easily oxidized to phenolic free radicals and quinones. A redox pair (one catechol and one quinone) dismutate to form two free radicals. These free radicals can couple in many ways to form various cross-links. One of the coupling reactions is shown in Figure 2.9. DSC characterization of PAD reveals that oxidation reactions and crosslinking reactions of

PAD would occur at 80 °C or higher. Imino groups might react with *o*-quinones through Michael reaction and Schiff-base formation reactions (Figure 2.9). DSC spectra of PAD/PEI mixtures indicate that these reactions between PAD and PEI would primarily occur at about 150 °C.

2.4 CONCLUSIONS

PAD was successfully synthesized. PAD powder yielded high adhesive strengths for parallel laminated, 2-ply maple veneer specimens. PAD should be able to serve as a wood-binding domain for a wood-plastic compatibilizer since *N*-acryloyl-*O, O*'-diphenyldopomine can be used to prepare a PP-PAD di-block copolymer.

Curing reactions of PAD occurred at about 80 °C. The curing temperature for PAD/PEI mixtures was about 150 °C. A combination of PAD and PEI had higher adhesive strengths than PAD alone. The shear strengths were related to the curing time and temperature. The adhesion mechanisms of PAD and PAD/PEI mixtures are not fully understood, but are believed to be similar to those of mussel protein adhesives. The curing mechanisms of PAD and PAD/PEI mixtures are presumably very complex and are believed to be similar to the natural quinone-tanning process. A strength increase, rather than decrease, of wood composites bonded with PAD or PAD/PEI mixtures at 180 °C were observed when the 2-ply maple veneer laminated specimens were soaked in water and then dried. The strength gains were related to the PAD/PEI ratio and to the curing temperature.

2.5 ACKNOWLEDGMENT

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Terminally Functionalized Polyethylenes as Compatibilizers for Wood-Polyethylene Composites

Cheng Zhang, Kaichang Li and John Simonsen

3 TERMINALLY FUNCTIONALIZED POLYETHYLENES AS COMPATIBILIZERS FOR WOOD-POLYETHYLENE COMPOSITES

Cheng Zhang, Kaichang Li and John Simonsen
Department of Wood Science and Engineering
Oregon State University, Corvallis, Oregon 97331, U.S.A.

ABSTRACT

Isocyanate-terminated polyethylenes (PE), PE-MDI and PE-PMDI, were synthesized by reacting polyethylene monoalcohol (PEA) with 4, 4'-methylenediphenyl diisocyanate (MDI) and polymeric methylene diphenyl diisocyanate (PMDI), respectively. Effects of PEA, PE-MDI and PE-PMDI on the mechanical properties and water resistance of wood-PE composites were investigated. All three compatibilizers increased the strength of the wood-PE composites. Composites containing PE-MDI or PE-PMDI exhibited a higher modulus of rupture (MOR) than those with PEA. The addition of PE-MDI and PE-PMDI decreased the water uptake rate of the composites while PEA increased this rate. The superior compatibilization effects of PE-MDI and PE-PMDI were attributed to the formation of covalent bonding between isocyanate and wood. This covalent bonding was demonstrated by the FTIR spectra of the wood residues after a *p*-xylene extraction.

Scanning electron microscope (SEM) images revealed that isocyanate-terminated PE samples improved the interfacial adhesion between wood and PE.

3.1 INTRODUCTION

Wood-plastic composites (WPCs) have experienced rapid growth due to various advantages of wood, such as low cost, low specific gravity, renewability, and reduced wear on processing equipment. However, poor compatibility between hydrophilic wood and hydrophobic plastic is still an unsolved issue that limits the further application of WPCs. This poor compatibility causes agglomeration of wood fibers and weak interfacial adhesion between wood and plastic. As a result, mechanical properties of the composites are often unsatisfactory. To address this problem, a coupling agent (usually called a compatibilizer) is added to WPCs. Different compatibilizers, especially maleic anhydride modified polyethylene (MAPE) and maleic anhydride modified polypropylene (MAPP), have been extensively studied (Maldas, Kokta et al. 1989; Raj, Kokta et al. 1989; Kokta, Maldas et al. 1990; Gauthier, Joly et al. 1998; Coutinho and Costa 1999; Lu, Wu et al. 2000; Nitz, Reichert et al. 2000; Bledzki and Faruk 2003; Djiporovic, Dingova et al. 2003; Geng, Li et al. 2004; Pickering and Ji 2004; Zhang, Li et al. 2004). The basic function of a compatibilizer is to form linkages between wood and the plastic, i.e., an effective compatibilizer should have the capability of bonding both wood and plastic.

Therefore, an ideal compatibilizer should contain two different domains: a wood-binding domain and a plastic-binding domain. At present, while the basic concepts of compatibilization are understood, the optimized chemical structure of an effective compatibilizer, including the ideal structures of the wood-binding domain and the plastic-binding domain, are still poorly understood. Published results suggest that the wood-binding domain may be a functional group such as the succinic anhydride group in MAPP and MAPE, or a polymer such as the polyaminoamide-epichlorohydrin (PAE) resins in the PAE-stearic anhydride compatibilizer system (Gauthier, Joly et al. 1998; Geng, Li et al. 2004; Zhang, Li et al. 2004). It is still not known whether a polymer is superior to a functional group as a wood-binding domain. Since the plastics (PP or PE) are chemically inert, the bonding of a plastic-binding domain to the plastics relies on the formation of entanglements/co-crystallization between the plastic-binding domain and the plastic matrix. Therefore, an ideal compatibilizer should have a plastic-binding domain whose structure is identical to the plastic, i.e., PE as a plastic-binding domain for wood-PE composites and PP as a plastic-binding domain for wood-PP composites. The molecular structures of most compatibilizers that have been studied so far are not well defined. For example, MAPE is manufactured by grafting maleic anhydride to PE. The grafting reaction is a free radical process; the distribution of the resulting succinic anhydride group on the PE chain is difficult to control and is poorly defined. Thus the PE chain length between two adjacent succinic anhydride groups on the same PE chain is variable and may not be the optimum for effective entanglements/co-crystallization. In this study,

terminally functionalized polyethylenes were prepared and investigated as compatibilizers for wood-PE composites. These compatibilizers had well-defined structures with a linear PE chain as a PE-binding domain and a hydroxyl group or an isocyanate group as a wood-binding domain. Contributions of the PE-binding domain and different wood-binding domains to the strength and water-resistance of the resulting wood-PE composites were investigated in detail.

3.2 EXPERIMENTAL

3.2.1 Materials and analytical instruments

Wood flour (pine, 40 mesh) was donated by American Wood Fibers (Schofield, WI). It was vacuum-dried at 103 °C for at least 12 h before use. Fortiflex HP54-60-FLK high density polyethylene (density, 954 kg/m^3; melt flow index, 0.50 g/10 min) was donated by BP Solvay Polymers North America (Houston, TX). Polyethylene monoalcohol (PEA, Mn = 700) and 4, 4'-methylenediphenyl diisocyanate (MDI) were purchased from Aldrich (Milwaukee, WI). Polymeric methylene diphenyl diisocyanate (PMDI) was provided by Huntsman Group (Salt Lake City, UT). All chemicals and solvents were purchased from commercial sources and used as received. All FTIR spectra were obtained with a Nexus 470 FTIR spectrometer (Thermo Nicolet Corporation, Madison, WI) using the KBr pellet method, and were recorded as an average of 32 scans at a resolution of 4 cm^{-1}. The

fractured surface of the wood-PE specimens from the bending test was examined by an AmRay 1000A Scanning electron microscope (SEM). All specimens were coated with an Au-Pd film (8-10 nm) before imaging. The SEM was operated at 10 kV on a Polaroid-type 55 positive-negative film.

3.2.2 Synthesis of PE-MDI

MDI (71.5 g, 0.57 mole NCO) was dissolved in chlorobenzene (300 mL) in a 500 ml flask. PEA (20.0 g) was added to the MDI solution and the resulting mixture was stirred at 80 °C for 18 h. After the reaction, the solution was poured into ice-water cooled CH_2Cl_2 (500 mL) with stirring and precipitation occurred. The precipitate was collected by centrifugation. After being washed three times with CH_2Cl_2, the precipitate was centrifuged again and dried under vacuum to get the PE-MDI (26.8 g).

3.2.3 Synthesis of PE-PMDI

Using the same procedure as described above for making PE-MDI, PMDI (75.4 g, 0.57 mole NCO) and PEA (20 g) were dissolved in 300 ml chlorobenzene in a 500 ml flask at 80 °C. The solution was stirred at 80 °C for 18 h. The reaction product (PE-PMDI) was precipitated in CH_2Cl_2. After being washed three times with CH_2Cl_2, the PE-PMDI (27.1 g) was collected by centrifugation and dried under vacuum.

3.2.4 Blending procedure for wood-PE composites

Wood flour, PE powder and a compatibilizer were mixed at room temperature with mechanical stirring. Then the mixture was poured into the mixing bowl of a Brabender Plasticorder that was preheated to 150 °C. The speed of the rotors in the bowl was set to 40 rpm. The mixture was blended for 10 min. The contents were then removed from the Brabender and stored for subsequent compression molding. Compositions of wood-PE composites are summarized in Table 3.1.

Table 3.1 The composition of wood-PE composites.

Sample code	Composite Composition (wt%)						
	PE	Wood Flour	PEA	MDI	PE-MDI	PMDI	PE-PMD
Control	60	40	0	0	0	0	0
PEA-1	59	40	1	0	0	0	0
PEA-2	58	40	2	0	0	0	0
MDI-1	59	40	0	1	0	0	0
MDI-2	58	40	0	2	0	0	0
PE-MDI-1	59	40	0	0	1	0	0
PE-MDI-2	58	40	0	0	2	0	0
PE-MDI-4	56	40	0	0	4	0	0
PMDI-1	59	40	0	0	0	1	0
PMDI-2	58	40	0	0	0	2	0
PE-PMDI-1	59	40	0	0	0	0	1
PE-PMDI-2	58	40	0	0	0	0	2
PE-PMDI-4	56	40	0	0	0	0	4

3.2.5 Press procedure for wood-PE composites

A steel mold with the dimensions of 101.6 mm x 101.6 mm x 2 mm was used to compression mold the wood-PE composites into boards. The platens of an automatic benchtop press (Carver, Inc., Wabash, IN) were preheated to 185 °C. The mold was filled with the well-mixed wood-PE composite, placed on the lower platen of the Carver press and heated for 10 min at 185 °C. The press was closed slowly allowing the blended wood-plastic mixture to flow into the mold shape. The press pressure was raised from 35 to 345 kPa over two min and the mold was pressed at 345 kPa for an additional 10 min. The mold was then removed from the hot press and cooled under pressure under ambient conditions. The resulting wood-PE board was cut into 9 small test specimens. Each specimen had dimensions of 54 mm x 13.00-14.45 mm x 2.51-2.73 mm.

3.2.6 Flexural tests of the wood-PE composites

Three-point bending tests were performed on a Sintech testing machine (MTS Systems Corporation, Enumclaw, WA) in accordance with ASTM D790-02. The load-deflection curves were recorded. The support span was 43 mm and the crosshead speed was 1.0 mm/min. At least 10 specimens (five each from two different boards) were tested for each wood-PE composite sample. The modulus of rupture (MOR) and modulus of elasticity (MOE) were calculated from the load-deflection data. MOR was defined as maximum stress in the outer fibers at midspan. It is an accepted criterion of

strength, although it is not a true stress because the formula by which it is computed is valid only to the elastic limit. The MOE was determined from the slope in the initial elastic region of the load-deflection curve. It is accepted as a criterion of stiffness.

3.2.7 Removal of PE from the wood-PE composites

Wood-PE composite samples were cut into small pieces (about 2 mm in diameter) and wrapped with filter paper. Then the wrapped samples were put in a thimble and extracted with p-xylene in a modified Soxhlet extraction apparatus for 48 h. The thimble holder of the Soxhlet was wrapped with a heating tape and heated during the extraction to keep the p-xylene in the thimble boiling. After the extraction, the wood residue was dried and examined by FTIR.

3.2.8 Water sorption of the wood-PE composites

The water sorption of the wood-PE composites with and without compatibilizers was measured by soaking the composite specimens in water at room temperature. The weight gain of the specimens at pre-determined times were used to determine the water uptake of the samples.

3.3 RESULTS

The representative reaction between PEA and MDI is shown in Figure 3.1. MDI and chlorobenzene are soluble in dichloromethane, and no precipitation occurred when a solution of PEA and chlorobenzene was poured into dichloromethane. After the precipitation and three washings with dichloromethane, the product PE-MDI was free of MDI, PEA, and chlorobenzene.
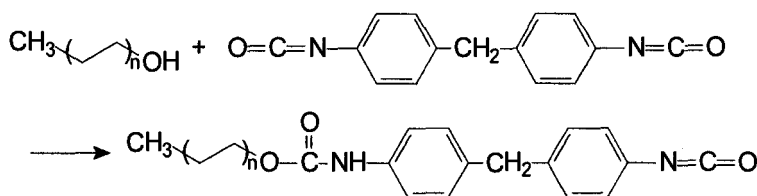
Figure 3.1 A representative reaction between PEA and MDI

FTIR spectra of PEA, MDI and PE-MDI are shown in Figure 3.2. The FTIR spectrum of PE-MDI had a new absorbance peak at 1720 cm^{-1} that is the characteristic peak of the urethane group, which demonstrated that PEA did react with MDI. The isocyanate peak at 2260 cm^{-1} in the FTIR spectrum of PE-MDI implied that PE-MDI contained free isocyanate groups. The FTIR spectrum of PE-PMDI was very similar to that of PE-MDI except that PE-PMDI had a stronger isocyanate absorbance peak.
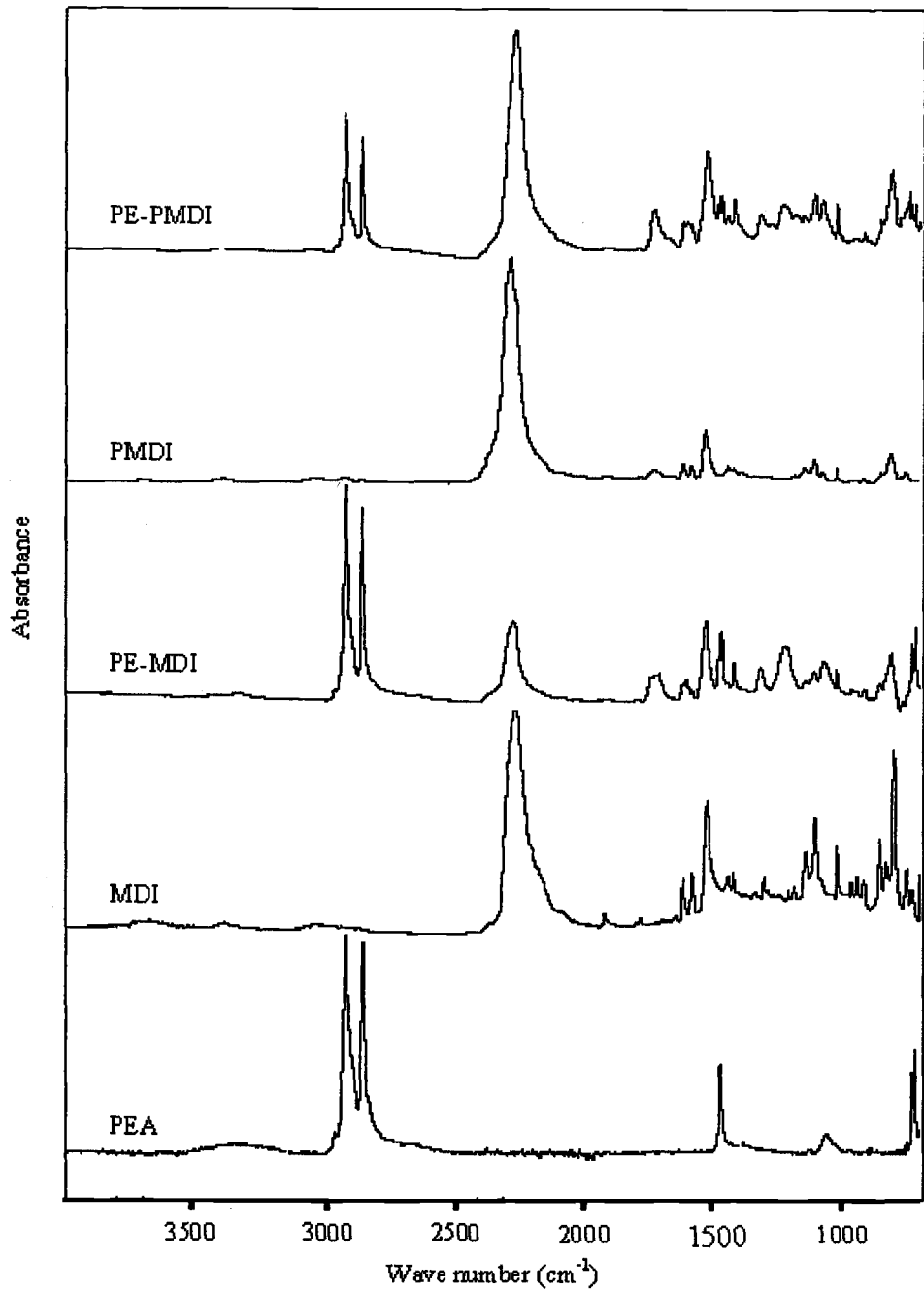
Figure 3.2 FTIR spectra of PEA, MDI, PE-MDI, PMDI and PE-PMDI .

The effect of PEA on the flexural properties of wood-PE composites is shown in Figure 3.3. Wood-PE composites with 1 wt% PEA as a compatibilizer (PEA-1 in Figure 3.3) had a higher MOR than the control, i.e., the wood-PE composites without a compatibilizer. Increasing the dosage of PEA to 2 wt% (PEA-2) did not further increase the MOR. The addition of PEA had little effect on the MOE.
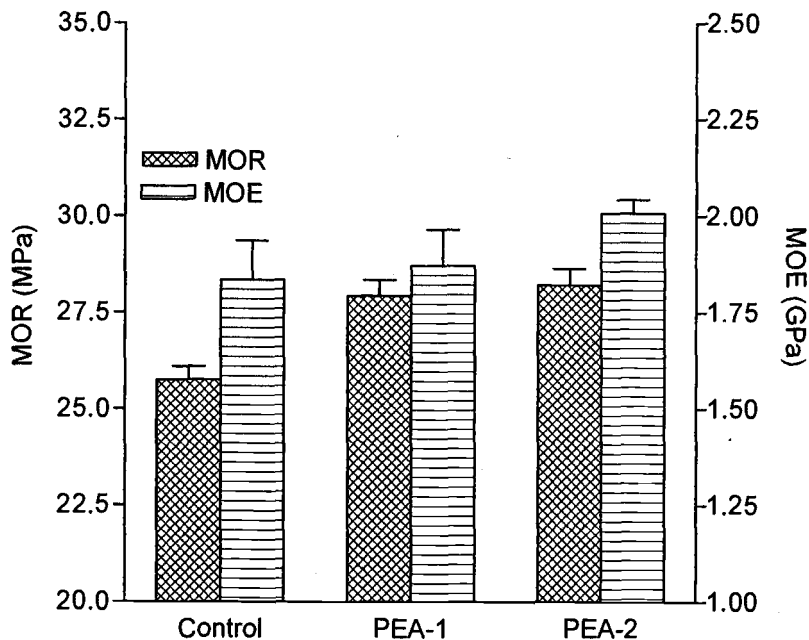
Figure 3.3 Effect of PEA on the flexural properties of wood-PE composites. Data are the mean of at least 10 replicates and the error bars represent one standard error of the means.

The effects of MDI and PE-MDI on the flexural properties of wood-PE composites are shown in Figure 3.4. Wood-PE composites with MDI as a compatibilizer had higher MORs than the control (Figure 3.3 and 3.4). The MOR and

MOE of the composites with 1 wt% MDI (MDI-1 in Figure 3.4) were statistically the same as those with 2 wt% MDI (MDI-2 in Figure 3.4). The composites with 1 wt% PE-MDI (PE-MDI-1 in Figure 3.4) had statistically the same MOR and MOE as those with MDI (either MDI-1 or MDI-2 in Figure 3.4). However, the MOR significantly increased when the PE-MDI dosage was increased from 1 wt% to 2 wt%. Further increasing the PE-MDI dosage to 4 wt% greatly decreased the MOR (Figure 3.4).
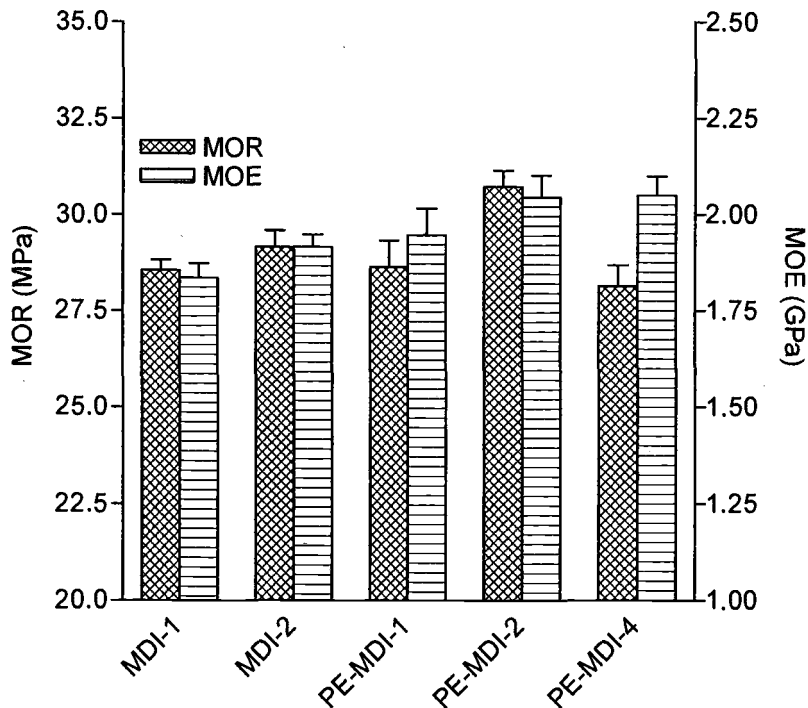
Figure 3.4 Effects of MDI and PE-MDI on the flexural properties of wood-PE composites. Data are the mean of at least 10 replicates and the error bars represent one standard error of the means.
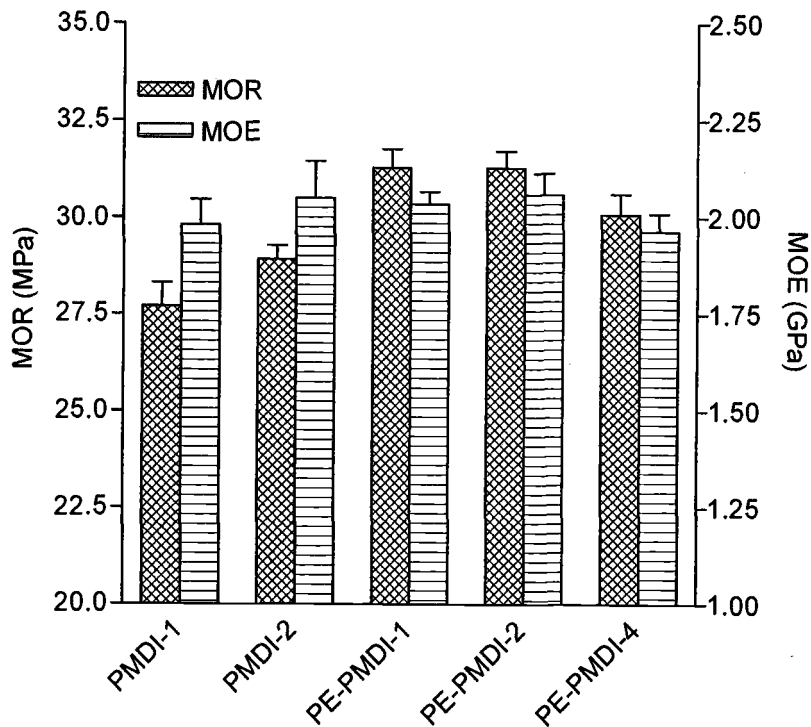
Figure 3.5 Effects of PMDI and PE-PMDI on the flexural properties of wood-PE composites. Data are the mean of at least 10 replicates and the error bars represent one standard error of the means.

When compared with the control (Figure 3.2), the addition of either 1 wt% PMDI or 2 wt% PMDI (PMDI-1 or PMDI-2 in Figure 3.5) increased the MOR of the wood-PE composites (Figure 3.5). PMDI-2 resulted in slightly higher MOR than PMDI-1. When compared with PMDI-1 or PMDI-2, PE-PMDI-1 (1 wt% PE-PMDI) resulted in much higher MOR (Figure 3.5). The wood-PE composites with PMDI-1 (1 wt% PE-PMDI) had the same MOR as those with 2 wt% PE-MDI. In other words,

increasing the dosage of PE-PMDI from 1 wt% to 2 wt% did not change the strength

of the composites. Further increase in the dosage of PE-PMDI to 4 wt% decreased the

MOR.

Four wood-PE composites (control, PEA-2, PE-MDI-2, PE-PMDI-2) were

extracted with *p*-xylene to remove the PE. The wood residues after extraction were

characterized with FTIR. The spectrum of the control was selected as a reference and

subtracted from the other three spectra (Figure 3.6).
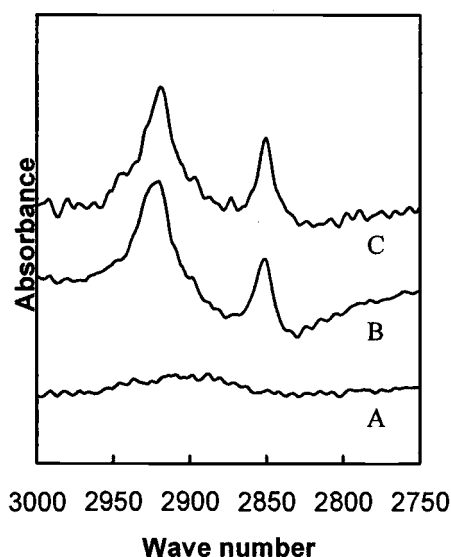
Figure 3.6 Subtracted FTIR spectra of wood residues after *p*-xylene extraction [A, (PEA-2)-control; B, (PE-MDI-2)-control, and C, (PE-PMDI-2)-control].

The subtracted spectra B and C, i.e., the spectra of (PE-MDI-2)-(control) and

(PE-PMDI-2)-(control), respectively, had two peaks at 2915 cm^{-1} and 2850 cm^{-1}

(Figure 3.6) that are the characteristic peaks of PE aliphatic hydrocarbons. The

subtracted spectrum A, i.e., the spectrum of (PEA-2)-(control), lacked these two

characteristic peaks. Since PE, PEA, PE-MDI and PE-PMDI are soluble in p-xylene, they were removed during the extraction. Thus these two peaks must be from the PE chains of the compatibilizers that were covalently bonded to the wood. Such peaks were not observed in the subtracted FTIR spectrum of (PEA-2)-(control), suggesting that PEA did not form covalent linkages with wood.

The SEM images of the fractured surfaces of the wood-PE specimens are shown in Figure 3.7. For the wood-PE specimen without a compatibilizer, gaps between the wood fibers and PE matrix could be clearly observed. The surfaces of the wood fibers were fairly clean, i.e., there was little plastic sticking to the wood fiber. This implied poor interfacial adhesion between wood and PE. For the wood-PE composites with PE-MDI as a compatibilizer, wood fibers were tightly embedded in the PE matrix. No obvious gap could be seen between two phases. For the wood-PE composites with PE-PMDI as a compatibilizer, it was difficult to differentiate the wood fibers from the PE because surfaces of the wood flour appeared to be covered by PE. Taken together, these images suggest that when PE-MDI or PE-PMDI is used as a compatibilizer, the interfacial adhesion is improved. The fracture was observed to occur mainly in the PE matrix rather than in the interface between wood fibers and the PE matrix.
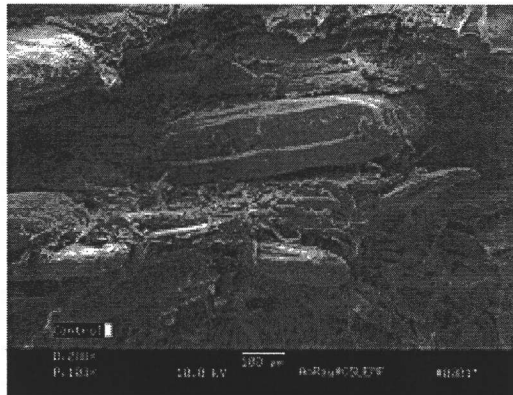
Control
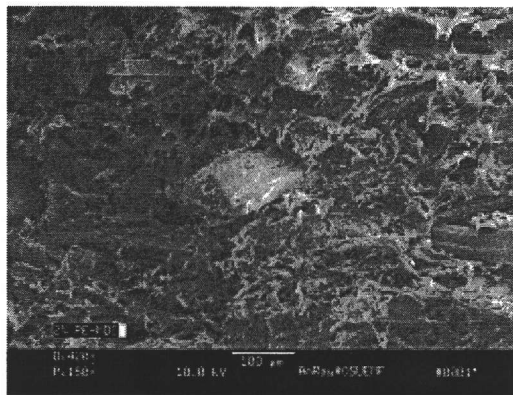
PE-MDI-2
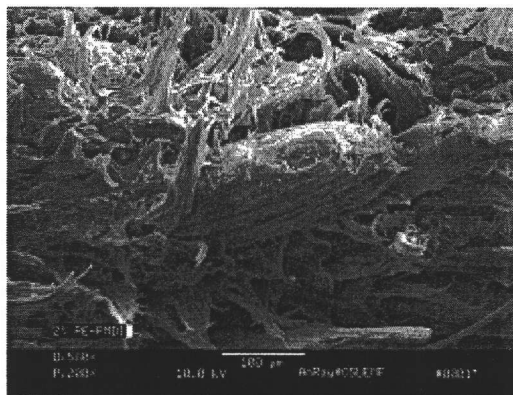
PE-PMDI-2

Figure 3.7 SEM images of fractured surfaces of the wood-PE composites.

The results of the water soaking test are shown in Figure 3.8. Wood-PE composites with PEA as a compatibilizer absorbed more water than the composites without a compatibilizer for equal soaking times. Both PE-MDI and PE-PMDI lowered the water uptake rate significantly and PE-PMDI was more effective than PE-MDI in terms of reducing the water uptake rate of the resulting wood-PE composites.
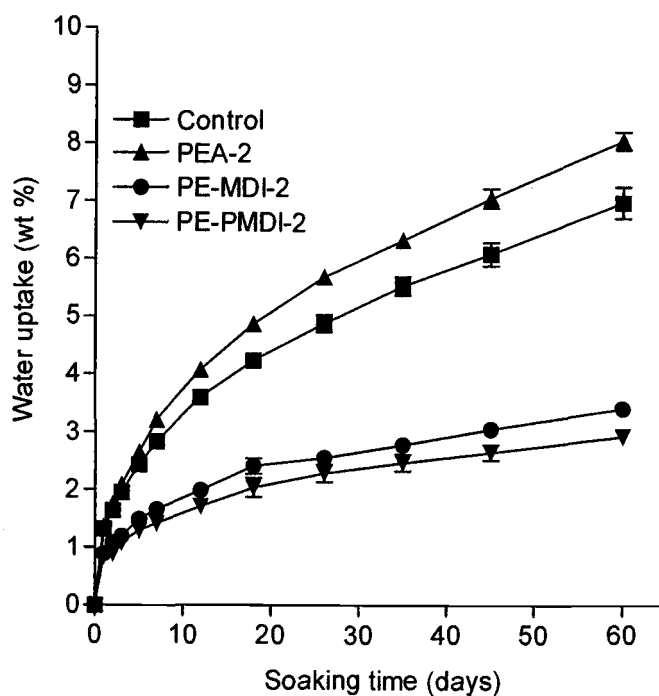
Figure 3.8 Effects of compatibilizers on the water-uptake rate of the wood-PE composites. Data are the mean of at least 3 replicates and the error bars represent one standard error of the means.

3.4 DISCUSSION

All of the three compatibilizers, PEA, PE-MDI and PE-PMDI, have similar molecular structures. At one end of the molecule is a linear PE chain. At the other end is a wood-binding domain. The PE end bonds with the PE matrix through entanglements or segmental crystallization. The wood-binding domain of PEA is a hydroxyl group. The hydroxyl group can form hydrogen bonds with wood components. PEA was thus able to improve the interfacial adhesion between wood and PE matrix, thereby increasing the strength of the wood-PE composites. The results in Figure 3.3 indeed indicated that PEA enhanced the MOR. Probably because the hydrogen bonding was weak, the strength increase by PEA was actually quite small. MDI and PMDI are known to be able to bond with wood. As a mater of fact, PMDI is widely used as a wood adhesive. Therefore, MDI and PMDI can strengthen and stiffen the wood fibers. We hypothesize that as the filler becomes stronger, the resulting composites become stronger. Results in Figure 3.4 and Figure 3.5 appeared to support this hypothesis because the composites with MDI and PMDI as compatibilizers showed higher MOR than the control. PEA and PE-MDI had the same PE-binding domain, but the isocyanate group in PE-MDI could form covalent linkages with wood. The FTIR spectra of the extracted wood-PE composites also confirmed the presence of covalent linkages between PE-MDI and wood, and the lack of covalent linkages between PEA and wood. The covalent linkages between PE-MDI and wood might account for the better compatibilization effect of PE-MDI-2 than

PEA-2 (Figsure 3.3 and 3.4). The bonding between PE-PMDI and wood was expected to be more efficient and stronger than that between PE-MDI and wood because a PE-PMDI molecule should contain multiple isocyanate groups whereas PE-MDI contains only a maximum of one isocyanate group. That the composites with 1 wt% PE-PMDI had a higher MOR than those with 1 wt% PE-MDI supports the contention of more efficient bonding for PE-PMDI than PE-MDI. Increasing the PE-MDI dosage should increase the amount of PE-MDI bonded to wood, thereby increasing the strength of the resulting wood-PE composites. This explanation appeared to be supported by the fact that the MOR of the composites with 2 wt% PE-MDI was higher than that with 1 wt% PE-MDI and was comparable with that with 1 wt% PE-PMDI (Figure 3.4 and 3.5). The bonding between wood and compatibilizers was limited by the amount of available hydroxyl groups on the wood surface. The amount of isocyanate groups in 1 wt% PE-PMDI was presumably enough to react with most of the hydroxyl groups on the wood surface. Thus, increasing the PE-PMDI dosage to 2 wt% did not further increase the MOR and MOE. In composites with 4 wt% PE-MDI or 4 wt% PE-PMDI, the excess compatibilizers might penetrate into the PE matrix and lower the strength and stiffness of the matrix. The excess PE-MDI or PE-PMDI might also interfere with effective entanglements or segmental crystallization between compatibilizers and PE matrix. Therefore, increasing the dosage of PE-MDI or PE-PMDI to 4 wt% decreased the MOR and MOE.

It was observed that the interaction between wood and compatibilizers had a significant impact on the water resistance of the wood-PE composites. The hydrogen

bonding between PEA and wood can be disrupted by water, which explains the higher water uptake of the composites that were compatibilized with PEA. On the other hand, isocyanate groups reacted with the hydroxyl groups of the wood, thus blocking the water sorption sites. The hydrophobic PE chains of PE-MDI and PE-PMDI also prevented water from penetrating the wood. These two factors might account for the lower water-uptake rates of the composites with PE-MDI and PE-PMDI.

3.5 CONCLUSIONS

Isocyanate-terminated polyethylene polymers were successfully synthesized through reactions between PEA and isocyanates. PE-MDI and PE-PMDI were more effective compatibilizers than PEA in terms of increasing the strength and water resistance of the wood-PE composites. *p*-Xylene extraction studies suggested that PE-MDI and PE-PMDI covalently bonded to wood while covalent bonding was not observed between PEA and wood. SEM pictures of the fractured composites surfaces revealed that PE-MDI and PE-PMDI improved the interfacial adhesion between wood and PE.

3.6 ACKNOWLEDGMENTS

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Improvement of Interfacial Adhesion between Wood and Polypropylene in Wood-Polypropylene Composites

Cheng Zhang, Kaichang Li and John Simonsen

4 IMPROVEMENT OF INTERFACIAL ADHESION BETWEEN WOOD AND POLYPROPYLENE IN WOOD-POLYPROPYLENE COMPOSITES

Cheng Zhang, Kaichang Li and John Simonsen
Department of Wood Science and Engineering
Oregon State University, Corvallis, Oregon 97331, U.S.A.

ABSTRACT

N-vinylformamide grafted polypropylene (VFPP) was successfully synthesized through a free radical grafting reaction. Both polymeric methylene diphenyl diisocyanate (PMDI) and VFPP were effective compatibilizers for increasing both the strength and stiffness of the resulting wood-PP (polypropylene) composites. Both the modulus of rupture (MOR) and the modulus of elasticity (MOE) of the resulting wood-PP composites were further increased when PMDI and VFPP were used together as an integrated compatibilizer system. This new PMDI-VFPP compatibilizer system was comparable to maleic anhydride grafted polypropylene in terms of enhancing the strength and stiffness of the wood-PP composites. Study of the fractured surfaces of the wood-PP composites with scanning electron microscopy revealed that this new PMDI-VFPP compatibilizer system greatly improved the interfacial adhesion between wood and PP. This PMDI-VFPP compatibilizer system also greatly reduced the water absorption of the resulting wood-PP composites. In this

PMDI-VFPP compatibilizer system, PMDI is proposed to function as a wood-binding domain and VFPP to function as a PP-binding domain. PMDI reacted with the amide group in VFPP, thus forming covalent linkages between PMDI and VFPP.

Keywords: interfacial adhesion, wood, polypropylene, wood-plastic composites, compatibilizer

4.1 INTRODUCTION

In recent years, much attention has been directed to the development of wood-filled thermoplastics, commonly called wood-plastic composites (WPCs), due to their economic and ecological advantages (Schneider 1994; Youngquist 1995; Bledzki, Reihmane et al. 1998; Coutinho and Costa 1999; Wolcott and Englund 1999). WPCs are normally produced by mixing wood fibers with thermoplastics and extruding or molding under high pressure and high temperature. The thermoplastics suitable for making WPCs include polypropylene (PP), high or low-density polyethylene (PE), polystyrene and poly (vinyl chloride). The wood fillers used for the production of WPCs can be wood flour or wood fibers. WPCs have many property advantages when compared with wood or plastics alone (Wolcott and Englund 1999). However, the interfacial adhesion between the thermoplastic matrix and the wood filler is normally weak because of the incompatibility of hydrophilic wood and hydrophobic

thermoplastics. A chemical coupling agent (commonly called a compatibilizer) is normally used to improve the interfacial adhesion in the WPCs. A number of coupling agents have been investigated for the improvement of WPC strength properties (Karnani, Krishnan et al. 1997; Bledzki, Reihmane et al. 1998; Lu, Wu et al. 2000; Nitz, Reichert et al. 2000). However, the number of coupling agents that can effectively improve the interfacial adhesion is still limited. In this study, we developed and characterized a novel compatibilizer system that contained polymeric methylene diphenyl diisocyanate (PMDI) as a wood-binding domain and N-vinylformamide grafted PP (VFPP) as a PP-binding domain.

4.2 EXPERIMENTAL

4.2.1 Materials and analytical instruments

Wood flour (pine, 40 mesh) was donated by American Wood Fibers (Schofield, WI). Wood flour was vacuum dried at 70 °C for at least 2 days before use. Fortilene HB1602 Polypropylene (density, 900 kg/m^3, melt flow index, 12 g/10 min) was donated by BP Solvay Polymers North America (Houston, TX). N-vinylformamide and dicumyl peroxide were purchased from Acros (Morris Plains, NJ). MAPP (maleic anhydride grafted polypropylene, A-C OptiPak$^{(TM)}$ 210) was a gift from Honeywell International, Inc. (Morristown, NJ). PMDI was provided by Huntsman Group (Salt Lake City, UT). All chemicals and solvents were obtained

from commercial sources and used as received. FTIR spectra were recorded on a Nexus 470 FTIR spectrometer (Thermo Nicolet Corporation, Madison, WI) equipped with a golden gate heated diamond ATR (attenuated total reflectance) accessory. The nitrogen content analysis was performed on a LECO CNS 2000 Analyzer (LECO Corporation, St. Joseph, MI). Differential scanning calorimetry (DSC) measurements were obtained on a DSC-2920 (TA Instruments, Inc, New Castle, DE) at a heating rate of 10 °C/min under a nitrogen atmosphere (55 ml/min) (Zhang, Li et al. 2003). The fractured surfaces of the samples from the bending test were examined by an AmRay 1000A Scanning electron microscope (SEM). All samples were coated with an Au-Pd film (8-10 nm) before imaging.

4.2.2 Synthesis of N-vinylformamide grafted PP

The grafting reaction of N-vinylformamide with PP was conducted in a Brabender Plasticorder (C. W. Brabender Instruments, Inc., South Hackensack, NJ) fitted with a mixing bowl containing roller blades. The mixing bowl was initially heated to 180 °C under a nitrogen atmosphere. PP (30.0 g) was added into the bowl while the speed of the rotors was fixed at 150 rpm. After 3 min, dicumyl peroxide (0.2 g) was added and mixed for another 3 min. N-vinylformamide (10.0 g) was then added and the resulting mixture was mixed for 10 min. The whole procedure was performed under a nitrogen atmosphere. After reaction, the product was removed and ground into small particles that were extracted with water in a Soxhlet extractor for 48

h to remove unreacted N-vinylformamide and poly (N-vinylformamide). The extracted product was vacuum-dried at 70 °C for at least 48 h to obtain N-vinylformamide grafted PP (VFPP) (31.0 g, 77.5%).

4.2.3 Blending procedures for wood-PP composites

Wood flour, PP pellets and the compatibilizers were mixed in a Brabender Plasticorder. The bowl of the Brabender Plasticorder was preheated to 180 °C and the speed of the rotors in the bowl was set to 100 rpm. PP pellets with or without VFPP were added and blended for 10 min. Then wood flour with or without PMDI was added and mixed for another eight minutes. The contents were then removed from the Brabender Plasticorder and stored for subsequent compression molding. When PMDI was used, wood flour was first mixed with PMDI under nitrogen atmosphere with a mechanical stirrer for 10 min. When MAPP was used, MAPP was added into the mixing bowl soon after the addition of wood flour. The compositions of the wood-PP composites produced are summarized in Table 4.1.

4.2.4 Press procedure for wood-PP composites

A steel mold with the dimensions of 101.6 mm x 101.6 mm x 2 mm was used to compression mold the wood-PP composites into boards. The platens of an automatic benchtop press (Carver, Inc., Wabash, IN) were preheated to 180 °C. The mold was filled with the well-mixed wood-PP composites, placed on the lower platen

of the Carver press and heated for 10 min at 180 °C. The press was closed slowly allowing the blended wood-plastic mixture to flow into the mold shape. The press pressure was raised from 34.5 to 344.8 kPa over two minutes and the mold was pressed at 344.8 kPa for an additional 10 min. The mold was then removed from the hot press and cooled under pressure at ambient conditions. The resulting wood-PP composite board was cut into 9 small test specimens. Each specimen had dimensions of 54 mm x 13.71-14.22 mm x 2.17-2.56 mm.

Table 4.1 Composition (in wt%) of wood-PP composites.

Sample code	PP	Wood Flour	MAPP	PMDI	VFPP
Control	60	40			
M2	58	40	2		
M4	56	40	4		
P2	58	40		2	
P3	57	40		3	
V2	58	40			2
V3	57	40			3
P2V2	56	40		2	2
P3V2	55	40		3	2
P4V2	54	40		4	2
P5V2	53	40		5	2
P4V3	53	40		4	3

4.2.5 Flexural tests on the wood-PP composites

Three-point bending tests were performed on a Sintech machine (MTS Systems Corporation, Enumclaw, WA) in accordance with ASTM D790-02. The load-deflection curves were recorded. The support span was 43 mm and the crosshead

speed was 1.0 mm/min. At least 12 specimens were tested for each wood-PP composite sample. Brittle fracture was observed for all samples. The modulus of rupture (MOR) and modulus of elasticity (MOE) were calculated from the load-deflection data. MOR was defined as the maximum stress in the outer fibers at midspan. It is an accepted criterion of strength, although it is not a true stress because the formula by which it is computed is valid only to the elastic limit. The MOE was determined from the slope in the initial elastic region of the load-deflection curve.

4.2.6 Water absorption of the wood-PP composites

The water absorption of the wood-PP composites with and without compatibilizers was measured by soaking the composite specimens in water at room temperature. The weight gain of the specimens at pre-determined times was used to determine the water uptake by the samples.

4.3 RESULTS

VFPP was synthesized by grafting N-vinylformamide onto PP via a free radical reaction. The comparison of the FTIR spectra of PP with VFPP showed a new amide absorption band at 1664 cm^{-1} (spectra not shown). This indicates that N-vinylformamide was grafted onto the PP chain. Differential scanning calorimetry thermograms also showed that PP and VFPP had different melting points (163.1 °C for

PP and 159.2 °C for VFPP). The total nitrogen content in VFPP was 0.79 wt%, which

means that 0.042 g N-vinylformamide was grafted to 1 g PP. Unlike maleic

anhydride, N-vinylformamide can readily form homopolymers. (Chang and

McCormick 1993) Thus VFPP might contain long poly (N-vinylformamide) branches

stretching out from the PP backbone.

The effect of PMDI on the flexural properties of wood-PP composites is shown

in Figure 4.1.
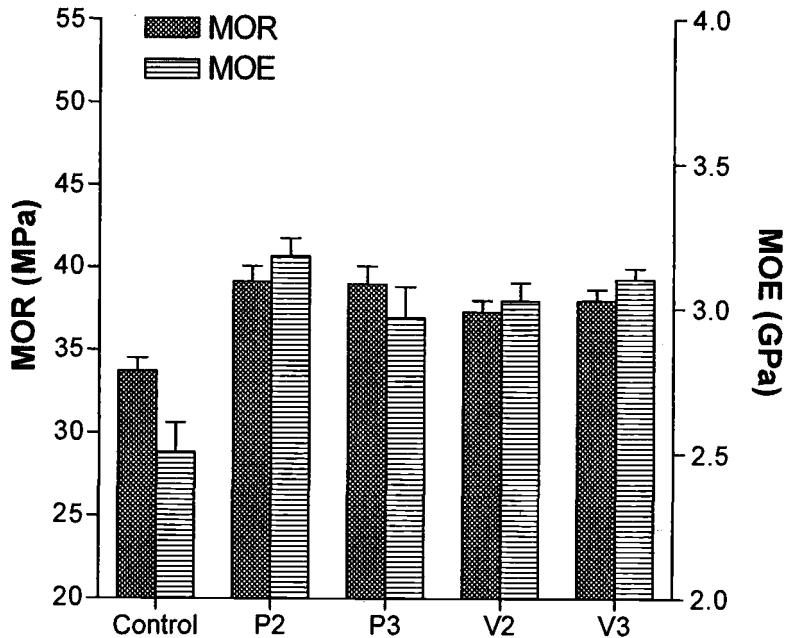
Figure 4.1 Effect of PMDI and VFPP on the flexural properties of
wood-PP composites. MOR represents the modulus of rupture and
MOE represents the modulus of elasticity.

Wood-PP composites with PMDI as a compatibilizer had higher MOR and

MOE than the control, i.e., the wood-PP composites without a compatibilizer.

Increasing the dosage of PMDI from 2 wt% to 3 wt% had little effects on the MOR

and MOE. When compared with the control, VFPP also increased the MOR and MOE

(Figure 4.1). There was no significant difference in MOR and MOE between 2 wt%

or 3 wt% VFPP.

When PMDI and VFPP were used together, the MOR increased, i.e., the MOR

with a combination of 2 wt% PMDI and 2 wt% VFPP was higher than that with 2 wt%

PMDI or 2 wt% VFPP alone (Figures 4.1-4.2).

Figure 4.2 Effect of PMDI-VFPP compatibilizers on the flexural properties of wood-PP composites. MOR represents the modulus of rupture and MOE represents the modulus of elasticity.

The MOE remained statistically the same. When the dosage of PMDI in the PMDI-VFPP combination was increased from 2 wt% to 4 wt%, the MOR greatly increased (Figure 4.2). Similarly, the MOE greatly increased when the dosage of PMDI was increased from 2 wt% to 3 wt%, and then flattened out when the dosage of PMDI was further increased from 3 wt% to 4 wt%. Further increase in the PMDI dosage from 4 wt% to 5 wt% greatly decreased both MOR and MOE.
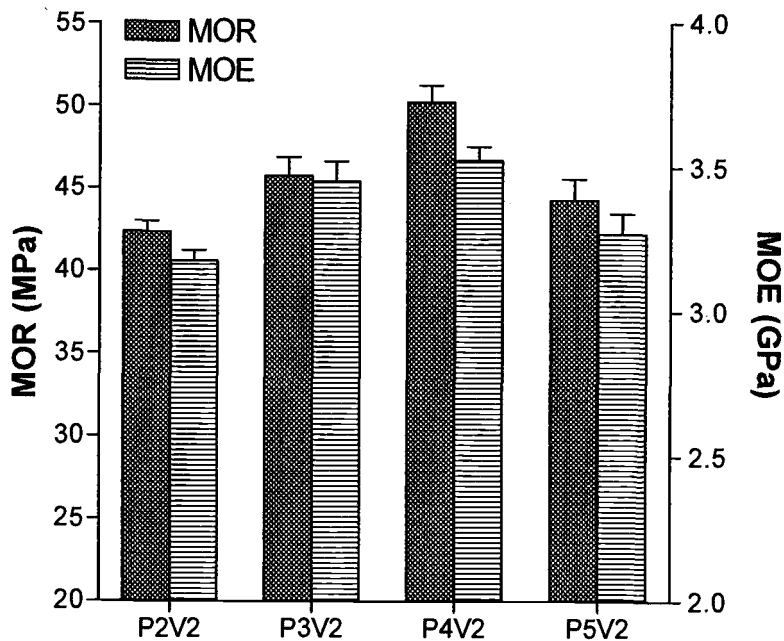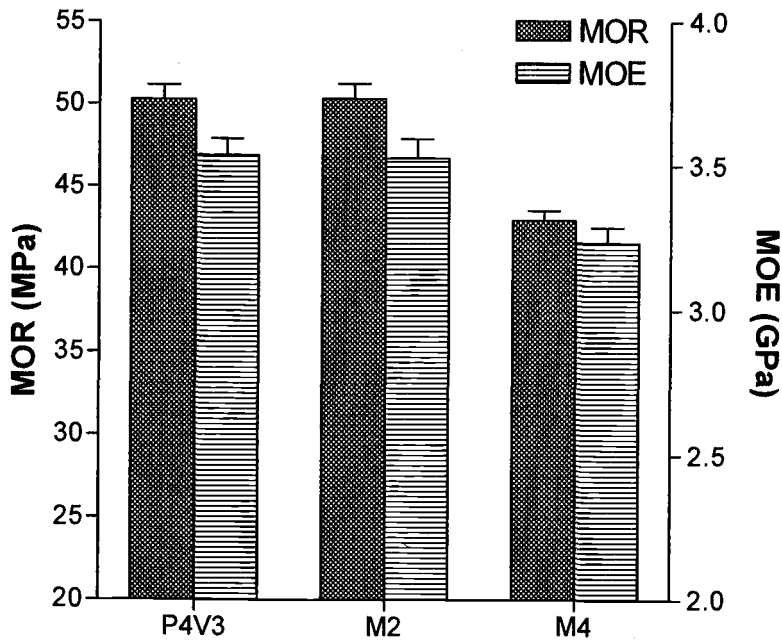

Figure 4.3 Effect of MAPP and PMDI-VFPP on the flexural properties of wood-PP composites. MOR represents the modulus of rupture and MOE represents the modulus of elasticity.

At 4 wt% PMDI, increasing the dosage of VFPP from 2 wt% to 3 wt% did not further increase the MOR and MOE (Figures 4.2-4.3). The MOR and MOE at 4 wt%

PMDI and 2 wt% VFPP or 4 wt% PMDI and 3 wt% VFPP were comparable with those with 2 wt% MAPP (Figures 4.2-4.3). Increase in MAPP dosage from 2 wt% to 4 wt% greatly decreased both the MOR and MOE (Figure 4.3), which is consistent with reports that MAPP was more effective at a low dosage (Bledzki, Faruk et al. 2002; Bledzki and Faruk 2003).

The SEM images of the fractured surfaces of the wood-PP specimens are shown in Figure 4.4. For the wood-PP composite specimen without a compatibilizer (Figure 4.4-a), the fiber pullout was observed on the fractured surface. The surface of the wood fiber was fairly clean, i.e., there was little plastic sticking on the wood fiber, and the surface of the void, which was created by the fiber pullout, was also very smooth (Figure 4.4-a). All these observations imply that the failure mainly occurred at the interface of the wood fiber and the PP matrix. In other words, the interfacial adhesion between the wood fiber and the PP matrix was very poor. For the wood-PP composite with MAPP as a compatibilizer, less fiber pullout was found (Fiure 4.4-b), which indicated that the interfacial adhesion between wood fibers and the PP matrix was good. For the wood-PP composite with a combination of PMDI and VFPP as a compatibilizer, little fiber pullout could be found (Figure 4.4-c). There were small voids on the fractured surface and it was difficult to differentiate the wood fiber from the PP because the surface of the wood fiber appeared to be covered by the PP. All these observations suggested that the fracture mainly occurred in the PP matrix rather than in the interface between wood fibers and the PP matrix.

(a)
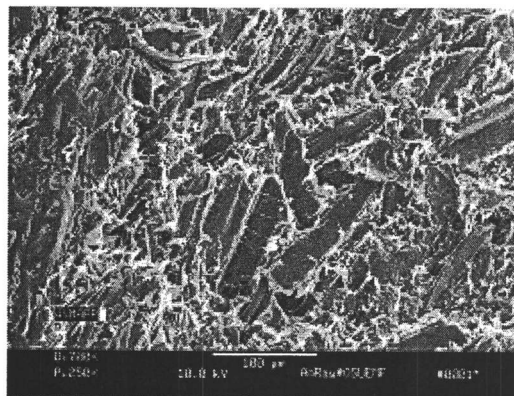
(b)
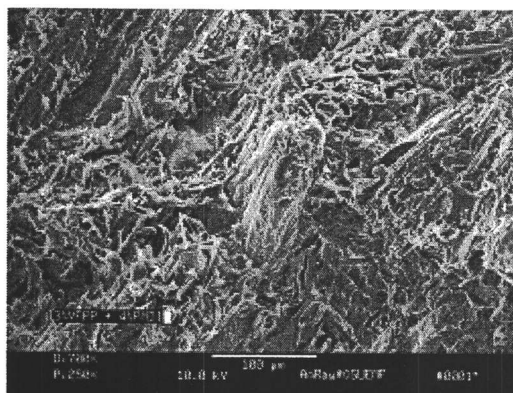
(c)

Figure 4.4 SEM pictures of fractured surfaces of wood-PP composites. (a): wood-PP composite without a compatibilizer. (b): wood-PP composite with MAPP (4 wt%) as a compatibilizer. (c): wood-PP composite with a combination of PMDI (4 wt%) and VFPP (3 wt%) as a compatibilizer.

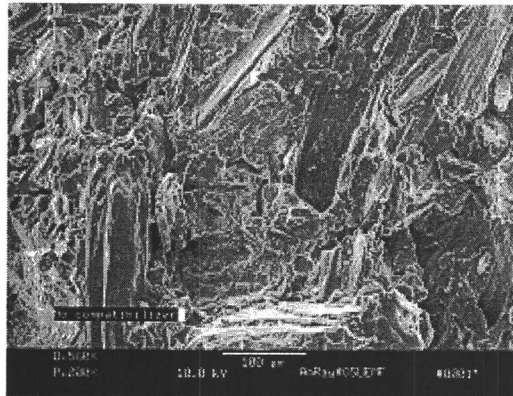The wood-PP composites without a compatibilizer absorbed more water than the composites with a compatibilizer at the same soak time (Figure 4.5). P3V2 (a combination of 3 wt% PMDI and 2 wt% VFPP) was comparable to MAPP in terms of reducing the water absorption (Figure 4.5). PMDI alone lowered the water uptake to a greater extent than P3V2. However, P4V2 (a combination of 4 wt% PMDI and 2 wt% VFPP) was more effective than P3, P3V2 and MAPP in terms of reducing the water uptake of the resulting wood-PP composites. The water uptake decreased with increasing the dosage of PMDI for the PMDI-VFPP compatibilizers.
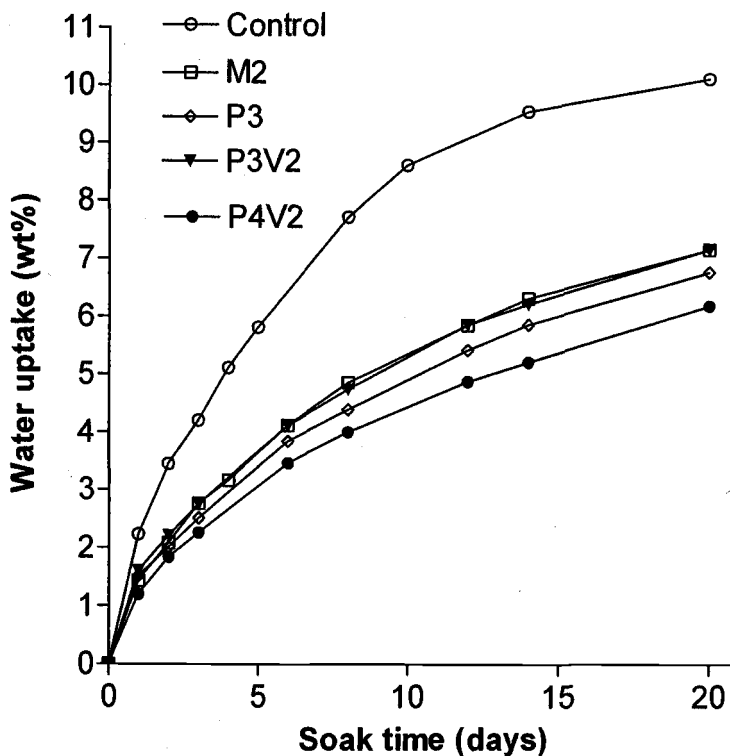
Figure 4.5 Effect of compatibilizers on the water-uptake of the wood-PP composites.

4.4 DISCUSSION

PMDI is a very good wood adhesive, which implies that PMDI can strengthen and stiffen the wood fibers. Given similar interfacial stress transfer, the theory predicts that as the filler becomes stronger, the resulting composites become stronger. The results shown in Figure 4.1 appear to support this theory. The poly (N-vinylformamide) branches in VFPP contained amide groups that were capable of forming hydrogen bonds with various wood components, and the PP backbone in VFPP was capable of forming entanglements or co-crystalline structures with the PP matrix. VFPP was thus able to improve the interfacial adhesion between wood and the PP matrix, thereby increasing the strength and stiffness of the wood-PP composites. The results in Figure 4.1 indeed indicate that VFPP enhanced both the MOR and MOE.

The results in Figure 4.2 demonstrated that PMDI and VFPP had synergistic effect in terms of increasing the strength and stiffness of the resulting wood-PP composites. The amide group in VFPP is capable of reacting with PMDI to form covalent linkages (Bao, Daunch et al. 2003). Such a reaction would further improve the interfacial adhesion between wood and the PP matrix. The compatibilization mechanisms by which this PMDI-VFPP compatibilizer system enhances the interfacial adhesion between wood and PP are proposed as follows: PMDI consolidates wood fibers, thus strengthening and stiffening wood fibers and also reacts with the amide group in VFPP to covalently link VFPP to PMDI-consolidated wood. The PP

backbone in VFPP forms entanglements or co-crystalline structures with the PP matrix. The amide group in VFPP also forms hydrogen bonds with the PMDI-consolidated wood. SEM images also confirmed that a combination of PMDI and VFPP greatly improved the interfacial adhesion (Figures 4.4-a and 4.4-c).

It appeared that the PMDI dosage had significant impact on the water absorption (Figure 4.5). PMDI penetrated the wood particles well and bonded the wood fibers strongly during mixing and compression molding. This would limit the penetration of water into wood, thus reducing the water-uptake. We speculated that P3V2 resulted in less well consolidated wood flour than P3 because a part of PMDI would react with the amide groups in VFPP in the wood-PP composites with P3V2 as a compatibilizer, which accounts for a higher water-uptake with P3V2 than P3. That P4V2 had a much lower water-uptake than P3V2 probably resulted from the increase in the PMDI dosage in the PMDI-VFPP system.

4.5 CONCLUSIONS

VFPP was successfully synthesized. Both PMDI and VFPP enhanced the strength and stiffness of the resulting wood-PP composites. Combinations of PMDI and VFPP were much more effective compatibilizers than PMDI or VFPP alone. The compatibilization effect of the PMDI-VFPP system was comparable to MAPP. SEM pictures suggested that the improvement of the strength and stiffness of the resulting wood-PP composites by a combination of PMDI and VFPP was due to the

improvement of interfacial adhesion between wood and PP. The PMDI-VFPP system also significantly reduced the water-uptake of the resulting wood-PP composites.

4.6 ACKNOWLEDGEMENTS

4.7 REFERENCES

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5 GENERAL CONCLUSIONS

The bonding between an effective compatibilizer and the wood in wood-plastic composites should be strong and water-resistant. Poly (*N*-acryloyl dopamine) (PAD) powder yielded high adhesive strengths for parallel laminated, 2-ply maple veneer specimens. A combination of PAD and polyethylenimine (PEI) had higher adhesive strengths than PAD alone. A strength increase, rather than decrease, of wood composites bonded with PAD or PAD/PEI mixtures at 180 °C were observed when the 2-ply maple veneer laminated specimens were soaked in water and then dried. *N*-acryloyl-*O, O'*-diphenyldopomine can be used to prepare a PAD-polypropylene (PP) di-block copolymer or PAD grafted PP. Therefore, PAD should be able to serve as a wood-binding domain for a wood-plastic compatibilizer.

The curing mechanisms of PAD and PAD/PEI mixtures are presumably very complex and are believed to be similar to the natural quinone-tanning process. More research work is expected to investigate the curing mechanisms of PAD and PAD/PEI mixtures.

Isocyanate-terminated polyethylenes were successfully synthesized through the reactions between polyethylene monoalcohol (PEA) and 4, 4'-methylenediphenyl diisocyanate (MDI) or polymeric methylene diphenyl diisocyanate (PMDI). The reaction products, PE-MDI and PE-PMDI, were more effective compatibilizers than PEA in terms of increasing the strength and water resistance of the wood-polyethylene

(PE) composites. *p*-Xylene extraction studies suggested that PE-MDI and PE-PMDI covalently bonded to wood while covalent bonding was not observed between PEA and wood. The better performance of PE-MDI and PE-PMDI as wood-PE compatibilizers could be attributed to the covalent bonding between isocyanates and wood. SEM pictures of the fractured composites surfaces revealed that PE-MDI and PE-PMDI improved the interfacial adhesion between wood and PE.

Both PMDI and N-vinylformamide grafted polypropylene (VFPP) enhanced the strength and stiffness of the resulting wood-PP composites. Combinations of PMDI and VFPP were much more effective compatibilizers than PMDI or VFPP alone. The compatibilization effect of the PMDI-VFPP system was comparable to maleic anhydride grafted polypropylene (MAPP). SEM pictures suggested that the improvement of the strength and stiffness of the resulting wood-PP composites by a combination of PMDI and VFPP was due to the improvement of interfacial adhesion between wood and PP. The PMDI-VFPP system also significantly reduced the water-uptake of the resulting wood-PP composites.

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