

AN ABSTRACT OF THE DISSERTATION OF

Yu Geng for the degree of Doctor of Philosophy in Wood Science presented on June 8, 2005.

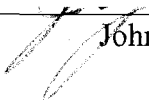
Title: Investigation of New Compatibilizer Systems for Wood-Polyethylene Composites

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Wood-plastic composites (WPCs) are one of the fastest-growing sectors of the wood composites industry. However, the strengths of WPCs are typically low because of the poor interfacial adhesion between hydrophilic wood and hydrophobic thermoplastics. A compatibilizer that can form bridges between wood and plastics is required to give WPCs desirable strength properties. At present, the choice of effective compatibilizers is limited and the compatibilization mechanisms are not fully understood. In this study, three novel compatibilizer systems were investigated for wood-polyethylene composites.

A widely used paper wet-strength agent polyaminoamide-epichlorohydrin (PAE) combined with stearic anhydride was applied as a compatibilizer system for wood-polyethylene composites. It was found that the pH value of the PAE solution

had a significant impact on the modulus of rupture (MOR) and the modulus of elasticity (MOE) of the resulting wood-polyethylene composites. The dosages of PAE and stearic anhydride were optimized in terms of the enhancement of MOR and MOE. Under optimal conditions, the PAE-stearic anhydride compatibilizer resulted in a higher MOR and MOE than commercially available maleic anhydride-grafted polyethylene (MAPE). Fourier Transform Infrared Spectroscopy (FTIR) analysis revealed that PAE and stearic anhydride formed covalent bondings with wood flour. Water-resistance tests indicated that PAE-stearic anhydride compatibilizer system increased the water-resistance of the resulting composites.

A combination of poly(diphenylmethane diisocyanate) (PMDI), and stearic anhydride was also studied as a compatibilizer system. PMDI alone increased the MOR and MOE of the resulting WPCs to some extent. Stearic anhydride alone had limited effects on the enhancement of MOR and MOE of the WPCs. A combination of PMDI and stearic anhydride resulted in higher MOR and MOE than PMDI. The PMDI-stearic anhydride compatibilizer system was even superior to commercially available MAPE in terms of increasing strengths (MOR and MOE) and water-resistance. The compatibilization mechanism of the PMDI-stearic anhydride compatibilizer system was investigated and proposed as follows: PMDI bonded wood and stearic anhydride, and the hydrocarbon chain of stearic anhydride bonded polyethylene through secondary bonds, entanglements and/or co-crystallization with the polyethylene matrix.

We later discovered that the mixing order for PMDI, wood and PE dramatically affected the MOR and MOE of the resulting wood-PE composites. When PMDI was first mixed with PE and then mixed with wood, the resulting wood-PE composites had much higher MOR and MOE than those composites that were made by adding PMDI to wood followed by PE. On top of already very high MOR of the wood-PE-PMDI composites, stearic acid further increased the MOR. A combination of PMDI and stearic acid resulted in much higher MOR and MOE than MAPE, one of the most effective compatibilizers for wood-PE composites. More importantly, the PMDI-stearic acid compatibilizer system is cost-competitive to MAPE. PMDI is readily available and stearic acid is inexpensive, abundant, and readily available. Therefore, this new PMDI-stearic acid compatibilizer system may be viable for commercial application.

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INVESTIGATION OF NEW COMPATIBILIZER SYSTEMS FOR
WOOD-POLYETHYLENE COMPOSITES

by
Yu Geng

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CONTRIBUTION OF AUTHORS

Dr. Kaichang Li and Dr. John Simonsen were involved in experimental design and revising of each manuscript.

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DEDICATIONS

I wish to dedicate this work to my mother, Ping Gao.

INVESTIGATION OF NEW COMPATIBILIZER SYSTEMS FOR WOOD-POLYETHYLENE COMPOSITES

CHAPTER 1: GENERAL INTRODUCTION

1.1 BRIEF HISTORY

Wood-plastic composites (WPCs) have become one of the fastest growing composite materials in the wood composites industry. WPCs are normally made from a mixture of wood particles (generally wood flour), plastics (thermoplastics or thermosets) and small amounts of process and property modifiers. The first commercially WPCs were made of phenol-formaldehyde and wood flour, named “Bakelite”, which was used as a gearshift knob for Rolls Royce in 1916 (Clemons 2002). But the WPC industry did not flourish in the US until the 1980s. In 1983, American Woodstock (Sheboygan, WI) began producing automotive interior substrates by using injection molding technology with a mixture of polypropylene and wood flour. This was one of the first large applications of wood-plastics technology in the United States (Schut 1999). From then on, the WPC industry has shown significant growth. Since 1998, the market growth of WPCs has averaged 16 % annually (Wolcott and Smith 2004). The total North American and European market for WPCs was about 0.59 million tons in 2002, and was valued at over \$0.75 billion (Morton, Quarmley et al. 2003; Wolcott and Smith 2004).

WPCs have many advantages compared with either wood fiber or plastics. Compared with wood, WPCs have lower water absorbance and lower thickness

swell. They are more durable against biodeterioration than wood (Wolcott and Englund 1999). The processing of WPCs can eliminate many post-manufacturing steps, such as machining and assembly, thus reducing the cost of the final product. Compared with plastics, WPCs have higher strength and stiffness, higher thermal stability, higher resistance to degradation, and higher resistance to ultraviolet light. Wood flour, which provides the reinforcement in WPCs, is much less expensive than synthetic or glass fibers; therefore, the final cost is reduced. WPCs also reduce machine wear and abrasion of processing equipment when compared to synthetic or inorganic fillers (Sellers, Miller et al. 2000).

While WPC production in the US began with automotive interior parts, the largest market growth occurred in building products. In the early 1990s, Advanced Environmental Recycling Technologies (AERT, Junction, TX) and Trex (Winchester, VA) began producing WPCs for deck boards, landscape timbers, picnic tables, and industrial flooring, which is now the largest and fastest growing WPC market in the United States (Youngquist 1995). WPCs can also be used for window and door profiles and a large variety of other molded products.

1.2 WPC COMPONENTS

1.2.1 WOOD FIBERS

The most commonly used wood species in WPCs are pine, maple and oak. Based on the processing procedure, different forms of wood particles can be used in

WPCs, such as sawmill chips, sawdust, wood flour or powder, cutter shavings, pulp or wood residues. Compared with wood fibers or other longer natural fibers, wood flour has relatively high bulk density and free-flowing nature, low cost, familiarity, and availability, which has made it more attractive to WPC manufacturers and users. The typical particle size of wood flour used in WPCs is 10 to 80 mesh.

1.2.2 PLASTICS

There are two major classifications in plastics: thermoplastics and thermosets. Both of them can be used in the production of WPCs and will be considered separately.

1.2.2.1 THERMOPLASTICS

Thermoplastics soften when heated and harden again when cooled. Thermoplastics can generally go through many melt/freeze cycles without appreciable chemical changes, which make them suitable for recycling. Since the thermal degradation temperature of wood is around 210 °C, thermoplastics used in the preparation of WPCs should have processing temperatures lower than 210 °C (Wolcott and Englund 1999). Thermoplastics that meet this requirement include low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC). Among these polymers, PP and polyethylene (PE), including HDPE and LDPE, are the most popular in the production of WPCs. WPCs made with PE are generally manufactured with

extrusion profile technology and used in exterior building components, while WPCs with PP are typically manufactured with injection molding technology and used in automotive applications, consumer products and building products (Clemons 2002).

1.2.2.2 THERMOSETS

Thermosets are network polymers formed by crosslinking reactions. They cannot be remelted. Once these polymers are formed, reheating will cause them to scorch. Thermosets are generally used in structures that require higher mechanical properties or elevated temperatures. Resins, such as epoxies, phenolics, and polyesters are all thermosets. Phenolics are commonly used in the chipboard industry, while polyesters are the most widely used resin systems, especially in the marine industry for fiberglass reinforced composites for boat hulls, tanks and the like (Mali, Sarsama et al. 2003). The WPCs considered in this project were all based on thermoplastics.

1.2.3 ADDITIVES

In order to improve performance and processing properties of the WPCs, additives are added during the production of WPCs. These include lubricants, colorants, coupling agents, antioxidants, UV-absorbers, antimicrobial agents, fire retardants, and foaming agents, among others (Mali, Sarsama et al. 2003).

1.2.3.1 LUBRICANTS

Lubricants are the most common additives in WPCs. They are used to improve the flow ability and surface properties of WPCs during the processing. The functions of lubricant can be divided into two parts, external and internal lubrication. External lubrication prevents polymers from sticking to the metallic processing machine, while internal lubrication facilitates the formation of homogeneous mixtures of wood, polymer and additives. It is believed that external lubricants form a multimolecular layer between the polymers and the metallic processing machine. The internal lubricants generally reduce both viscosity and heat of the polymer in the melt state by their good affinity for each other (Štepek and Daoust 1983). The application of lubricants may reduce the modulus of rupture (MOR) of the resulting composites because lubricants will interfere with the interaction between wood and plastic matrix and thereby reduce the stress transfer between them (Wolcott 2003). The most commonly used lubricant in WPCs is the combination of zinc stearate and EBS (Ethylene Bis-stearamide) wax (Laver 1996).

1.2.3.2 COLORANTS

WPCs without colorants typically weather to a grey color similar to that of weathered solid wood. Also, as with solid wood, rust and black iron stains can discolor WPCs. When WPCs are exposed to exterior conditions, photodegradation may occur due to solar ultraviolet radiation, rain, snow, and pollutants. Therefore, both the mechanical properties and the color of WPCs can suffer serious

deterioration. Pigments and other colorants can be added to the WPC formulation to prevent discoloration and also to impart a specific color to the end product (Markarian 2002). For example, rutile titanium dioxide was applied during the formation of PVC/wood-fiber composites. The light stability of the resulting composites improved significantly (Matuana, Kamdem et al. 2001).

1.2.3.3 COUPLING AGENTS

Coupling agents are essential ingredients for WPCs. They can build a bridge between the two unlikely components: the hydrophilic wood and the hydrophobic plastic. Coupling agents can help disperse the wood fiber in the polymer matrix and transfer the stress from the plastic matrix to the wood filler. Therefore, they can increase the tensile, flexural and impact strengths of the resulting WPCs. They can also reduce water sorption and provide better retention of mechanical properties upon aging (Mali, Sarsama et al. 2003).

1.2.3.4 ANTIOXIDANTS

Antioxidants are used to prevent degradation during processing and service. They can consume oxygen by chemical reactions. They are especially important and routinely used in PVC processes (Markarian 2002).

1.2.3.5 UV-ABSORBERS

UV-absorbers reduce the damaging effect of ultraviolet light. They therefore prevent the degradation of wood and/or plastic components and increase the useful life of the product in exterior environments (Clemons 2002; Markarian 2002).

1.2.3.6 ANTIMICROBIAL AGENTS

Mold is a serious issue for many WPC products and decay can be an issue in certain wet environments. Antimicrobial agents are used to minimize mold growth or decay of the wood in WPCs in outdoor applications. The type and amount of antimicrobial agents varies with the susceptibility of the wood type, the percentage of wood fibers, the compressibility of the wood fibers, the type of microbes in the product's environment, and the moisture level of the exposure condition (Markarian 2002). Zinc borate is a widely used antimicrobial agent, which is believed to be effective in preventing rot, but not in mold or algae growth. Ciba Company has developed a series of biostabilizers, named Ciba® Irgaguard® F 3000, which can protect WPCs against various fungi, molds, and other microorganisms (Jiang and Kamdem 2004).

1.2.3.7 FIRE RETARDANTS

Both wood flour and the plastic matrix are flammable materials. Therefore, fire retardants are used in WPCs to reduce the flammability or to retard the spread of fire over the surface of WPCs. At present, there are many fire retardants available for plastics. Considering environmental problems, halogen-free fire retardants are

expected to experience promising growth in the market (Mali, Sarsama et al. 2003). For example, ammonium polyphosphate (APP) is a popular fire retardant in linear low density polyethylene (LLDPE)-wood-fiber composites (Li and He 2004).

1.2.3.8 FOAMING AGENTS

WPCs are generally heavier than pure plastics or natural wood. The ductility and impact resistance of WPCs are also worse than those of pure plastics. To overcome these drawbacks, a foaming agent is applied in WPCs. The addition of foaming agents can reduce part density; improve stiffness and performance with woodworking tools and fasteners. There are two types of foaming agents: physical and chemical agents. Physical agents include carbon dioxide, nitrogen, argon, chlorofluorocarbons (CFCs), etc (Jiang and Kamdem 2004; Matuana, Park et al. 1998; Rizvi, Matuana et al. 2000; Zhang, Rizvi et al. 2004). Chemical agents include azodicarbonamide and sodium bicarbonate, etc (Jiang and Kamdem 2004; Li and Matuana 2003).

1.3 COMPATIBILIZER

WPCs are generally produced by mixing wood flour with a polymer. The major components of wood are cellulose, hemicellulose and lignin, which contain many hydroxyl groups. Therefore, wood is hydrophilic. Most polymers, especially thermoplastics, are hydrophobic substances that are not compatible with hydrophilic wood. This results in poor interfacial adhesion between the wood and

plastic. To overcome this problem, a chemical coupling agent, generally called a compatibilizer, needs to be added to build a bridge between them, which can transfer the stress from the plastic matrix to the wood filler. By this means, the adhesion between the wood and plastic phases can be improved.

The first compatibilizer was developed in 1963, which was a catalyst system that contained ferrous cations and hydrogen peroxide. It was used to graft unsaturated monomers onto wood fibers (Bridgeford 1963). This system was further developed by other researchers (Dimov and Pavlov 1969; Faessinger and Conte 1967; Hornof, Kokta et al. 1976; Kokta and Valade 1972). However, the application of compatibilizers in WPCs did not grow significantly until the 1980s, when isocyanate and maleic anhydride were used as compatibilizers in WPCs (Goettler 1983; Woodhams 1984). Currently, over forty compatibilizers have been developed for application in WPCs. They can be classified as organic, inorganic and organic-inorganic types.

1.3.1 ORGANIC-BASED COMPATIBILIZERS

Organic compatibilizers include acrylates, amides, anhydrides, chlorotriazines, epoxides, imides, isocyanates, organic acids, polymers, and copolymers. Generally, there are two ways for these compatibilizers to reinforce WPCs; one is that there are bi- or multifunctional groups in their molecular structures, such as the anhydride groups in maleic anhydride, isocyanate groups in isocyanates, and

chloro-groups in dichlorotriazine. All of these functional groups can react with the hydroxyl groups in cellulose, hemicelluloses, or lignin to form covalent or hydrogen bonds (Chtourou, Riedl et al. 1992; Maldas and Kokta 1989; Raj and Kokta 1991; Raj, Kokta et al. 1988; Zadorecki and Flodin 1985a). As a result, the resulting composites typically show improved mechanical properties. The second way for these compounds to reinforce WPCs is to graft to the polymer matrix, thus resulting in strong adhesion through covalent bonding and even crosslinking at the interface between the phases.

1.3.1.1 ACRYLATES, METHACRYLATES AND ACRYLIC ACIDS

Acrylates, methacrylates and acrylic acids contain an α , β -unsaturated carbonyl group, which can form crosslinking or interfacial adhesion when applied in WPCs. This class of compatibilizers is represented in WPCs by methacrylic acid, methyl methacrylate, butyl acrylate, epoxypentyl methacrylate, glycidyl methacrylate (GMA), hydroxyethyl methacrylate (HEMA), etc (Daneault, Kokta et al. 1989; Kent, Winston et al. 1962; Maldas and Kokta 1990a; Maldas, Kokta et al. 1988, 1989a; Meyer 1965, 1981; Takase and Shiraishi 1989). For example, when HEMA-modified polypropylene was mixed with refiner ground pulp (RGP), the resulting composites showed both higher tensile strength and higher Young's modulus than the composites with only polypropylene and RGP. It was believed that the effect of HEMA in composites was due to the hydrogen bonding formed at

the interface between HEMA modified polypropylene and RGP (Takase and Shiraishi 1989).

1.3.1.2 AMIDES AND IMIDES

The representative for this kind of compatibilizer is N, N'-*m*-phenylenedimaleimide (PDM). With the presence of a free radical initiator, it can graft to polypropylene by opening the carbon-carbon double bond on the maleimide ring; while, at the same time, it can also bond to the wood surface through polar interaction such as hydrogen bonding. When PDM was compounded with polypropylene before compounding with wood flour, the tensile strength of the resulting composites increased by 32% (Xanthos 1983).

1.3.1.3 ANHYDRIDES

Anhydrides are the most popular compatibilizer used in WPCs. They have been shown to modify the wood surface by esterification and hydrogen bonding. As a result, the interaction between wood and plastics is improved.

Acetic anhydride has been used to modify the wood surface and can reduce the surface polarity of the wood fiber and consequently improve the interfacial adhesion between wood and polymer. The use of acetylated chemico-thermomechanical pulp (CTMP) fiber in WPCs improved the tensile properties,

especially the Young's moduli of the resulting composites (Chtourou, Riedl et al. 1992).

Medium density fiberboard (MDF) prepared by succinic anhydride-modified thermomechanical pulp (TMP) fiber showed significant improvement in thickness swelling, strength properties and lower water absorption compared to a control of phenol-formaldehyde-treated MDF board (Rozman, Banks et al. 1994).

Phthalic anhydride was used as a compatibilizer for wood-polystyrene and wood-polyvinyl chloride composites. The resulting composites showed improvements in mechanical properties, but the performance of phthalic anhydride was inferior to that of isocyanate (Maldas and Kokta 1989, 1990b).

Maleic anhydride is the most popular compatibilizer among all the anhydrides. It is an α , β -unsaturated carbonyl compound with one carbon-carbon double bond and two carboxylate groups. The carbon-carbon double bond in maleic anhydride is easily polymerized by free radical initiators. This results in crosslinking or strong adhesion across the interface of WPCs (Morrison and Boyd 1992). However, the hydrocarbon chain in maleic anhydride is perhaps not long enough to form either entanglement or co-crystallization with the plastic matrix, which makes it less effective in improving the interfacial adhesion in WPCs (Maldas and Kokta 1990a). Therefore, some adjustments were made on maleic anhydride to overcome

this drawback. It was grafted to polyethylene, polypropylene, and polystyrene, respectively, to form copolymers, such as maleic anhydride-grafted polyethylene (MAPE) (Sanadi, Rowell et al. 1992), maleic anhydride-grafted polypropylene (MAPP) (Dalvåg, Klason et al. 1985; Han, Ichinose et al. 1989; Kishi, Yoshioka et al. 1988; Myers, Chahyadi et al. 1991, 1993; Olsen 1991; Takase and Shiraishi 1989), styrene-maleic anhydride copolymers (Simonsen, Jacobsen et al. 1998), and maleic-anhydride-grafted styrene-ethylene-butylene-styrene triblock copolymers (SEBS-MA) (Oksman, Lindberg et al. 1998). Among them, MAPE and MAPP have been proven to significantly improve the mechanical properties of WPCs and thereby, become commercial products in the marketplace.

1.3.1.4 CHLOROTRIAZINES

Chlorotriazines and their derivatives were used as compatibilizers in wood-polyester composites (Zadorecki and Flodin 1985a, b). The active chlorine in chlorotriazines and their derivatives reacted with the hydroxyl groups in wood fibers to form ether linkages, while the carbon-carbon double bonds on their alkyl chains were thought to graft to the polymer matrix by forming covalent bonds. Therefore, chlorotriazines and their derivatives could build a bridge between wood fiber and polyester matrix, resulting in higher mechanical properties.

1.3.1.5 EPOXIDES

Propylene and butylene oxide have been proven to react with the hydroxyl groups in wood under mildly alkaline condition at 120 °C and 150 psi (Rowell, Moisuk et al. 1982). The reaction formed an ether bond and produced a new hydroxyl group, which could further react to form a polymer. The resulting polymer may form entanglements or co-crystallization with the polymer matrix in WPCs and thereby, increase the mechanical properties of the composites.

1.3.1.6 ISOCYANATES

Isocyanate is a very active functional group. It can react with the hydroxyl groups in wood to form a urethane or a carbamate, which is much more stable to hydrolysis than esterification (Johns 1982; Maldas and Kokta 1990b). The reactivity of isocyanates as a compatibilizer depends on its backbone structure. Poly(diphenylmethane diisocyanate) (Maldas and Kokta 1989, 1990c, d, 1991a; Maldas, Kokta et al. 1989a, b; Raj, Kokta et al. 1988) and toluene 2,4-diisocyanate (Kokta, Maldas et al. 1990a; Raj, Kokta et al. 1988) both have aromatic rings in their structures, in which the delocalized π -electrons can form strong interactions with a polymer matrix, such as polystyrene or polyvinyl chloride. However, ethyl isocyanate (Maldas and Kokta 1991b; Raj, Kokta et al. 1988) and hexamethylene diisocyanate (Gatenholm, Felix et al. 1992; Maldas and Kokta 1991b; Raj, Kokta et al. 1988) do not have such effect on plastics. Therefore, their effect as compatibilizers in WPCs was observed to be inferior to those with aromatic rings (Maldas, Kokta et al. 1988).

1.3.1.7 ORGANIC ACIDS

Abietic acid (ABAC) and linoleic acid (LAC) are organic acids that can be used as compatibilizers in WPCs (Kokta, Maldas et al. 1990b). They both contain carboxylate group, which can react with the hydroxyl groups in wood. On the other hand, the diene group in ABAC and the long hydrocarbon chain in LAC have the potential to form strong interactions with the polymer matrix. When ABAC or LAC was applied in wood-PVC composites, they both increased the strength, ultimate elongation, and breaking energy of the resulting composites. LAC had better effect than ABAC. It is believed that LAC is linear, while ABAC has a ring structure. The allylic structure in LAC has better reactivity in grafting to PVC, while too much ABAC may act as an inhibitor in composites (Kokta, Maldas et al. 1990b).

1.3.1.8 POLYMERS AND COPOLYMERS

Polymers and copolymers used as compatibilizers in WPCs can be divided into two groups; one is resins, such as mono- and dimethylolmelamine resin (Hua, Zadorecki et al. 1987), phenol-formaldehyde resin (Chtourou, Riedl et al. 1992; Simonsen and Rials 1992, 1996), the other is functional groups that are grafted onto the polymer matrix, such as maleic anhydride-grafted polymers, which have been introduced previously.

Resins can penetrate and crosslink in the wood fiber cells and thereby consolidate and strengthen the wood fibers. On the other hand, they can improve the interfacial adhesion of WPCs through secondary bonds, entanglements, or co-crystallization with polymer matrix.

Functional group-grafted polymers that have been used as compatibilizers also include N, N'-m-phenylene bismaleicimide modified polypropylene (BPP) (Sain, Kokta et al. 1993), polystyrene/polymethacrylic acid (Liang, Mott et al. 1994), polymethacrylic acid (Liang, Mott et al. 1994), and polyvinyl acetate (Liang, Mott et al. 1994). These compatibilizers all have polymer chain backbones which can form secondary bonds, entanglement or co-crystallization with polymer matrix. Moreover, they also have functional groups that can react with the hydroxyl groups in wood to form covalent bonds. This can increase the interfacial adhesion between the wood filler and the polymer matrix. For example, when BPP was applied in wood-polypropylene composites, its polymer chain part can form entanglement or co-crystallization with polypropylene. On the other hand, the imide functional groups in BPP can react with the hydroxyl groups in wood and thereby build a bridge between wood and polypropylene (Sain, Kokta et al. 1993).

1.3.2 INORGANIC-BASED COMPATIBILIZERS

Sodium silicate was studied as an inorganic compatibilizer in WPCs. It did not improve the mechanical properties of the resulting composites. However, when

combined with poly (diphenylmethane diisocyanate), increases in Izod impact strength were observed compared to the pure polymer (Maldas and Kokta 1990d).

1.3.3 ORGANIC-INORGANIC COMPATIBILIZERS

Organic-inorganic compatibilizers include silanes and titanates, both of which are hybrid compounds in structure. In other words, the compound has an inorganic center, which is either silicon or titanium, with a surrounding organic part. The coupling effectiveness of these kinds of agents appears to be determined by the functionality of the organic part in these agents.

Titanium di(dioctylpyrophosphate)oxyacetate was grafted to inorganic fillers such as calcium carbonate, calcium metasilicate, and barium sulfate. The grafted titanate was reported to form a nonextractable organic monomolecular layer between the interface of the inorganic filler and the organic polyolefin matrix. It therefore built a bridge between them, and improved the impact strength of the resulting system (Monte and Sugerman 1981). But the results of another research group showed that a titanate compound did not result in a positive effect on the properties of WPCs when wood or cellulose was used as a filler (Dalvåg, Klason et al. 1985).

There are several silanes that can be used as compatibilizers in WPCs. Their effects vary with the functional groups that are attached to them. Both vinyltri(2-

methoxyethoxy) silane (Beshay, Kokta et al. 1985; Kokta, Maldas et al. 1990c; Maldas, Kokta et al. 1988, 1989a; Raj, Kokta et al. 1989, 1990) and γ -methacryloxypropyltrimethoxy silane (Bataille, Ricard et al. 1989; Beshay, Kokta et al. 1985; Kokta, Maldas et al. 1990c; Maldas, Kokta et al. 1989a; Raj, Kokta et al. 1988, 1989; Xanthos 1983) contain vinyl groups, which might form a network among the wood particles and thereby increase the interfacial adhesion between wood filler and polymer matrix. β -(3,4-Epoxy cyclohexyl)ethyltrimethoxy silane (Kokta, Maldas et al. 1990c) and γ -glycidoxy propyltrimethoxy silane (Kokta, Maldas et al. 1990c) can also form ether bonds with wood fibers via their epoxy groups, which may be the mechanism by which they act as compatibilizers. The functionality of aminopropyltriethoxy silane (Bataille, Ricard et al. 1989; Kokta, Maldas et al. 1990c; Maldas, Kokta et al. 1988, 1989a; Raj, Kokta et al. 1989) comes from its amino group, which can form hydrogen bonds with wood. This compatibilizer showed the weakest effect among all the silanes that were tested.

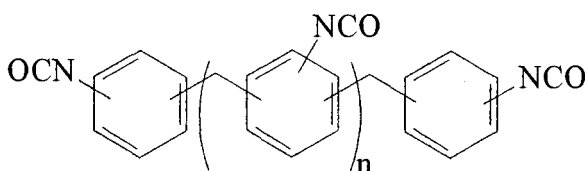
1.4 POLY(DIPHENYLMETHANE DIISOCYANATE) (PMDI)

Poly(diphenylmethane diisocyanate) (PMDI) is one of the most popular wood adhesives in the wood industry. It has been used in the wood-based panel industry for more than thirty years. PMDI was first used as a wood adhesive for particleboard by H.-J. Deppe in 1971 (Frisch and Rumaou 1983). Commercial production of PMDI bonded particleboard started in Germany in 1975. In the United States, PMDI was first used for the manufacture of multilayer panels by

Ellingson Timber Company in 1975 (Shoemaker and McQueary 1975a, b). Nowadays, the market for PMDI and other isocyanate adhesives in the wood industry is surpassed only by urea-formaldehyde (UF), phenol-formaldehyde (PF) and melamine-urea-formaldehyde (MUF) (Dunky and Pizzi 2002). In 1998, the consumption of isocyanate in North America was around 90 kilotons, which represented 5.1% of the total adhesive consumed (Sellers 2001).

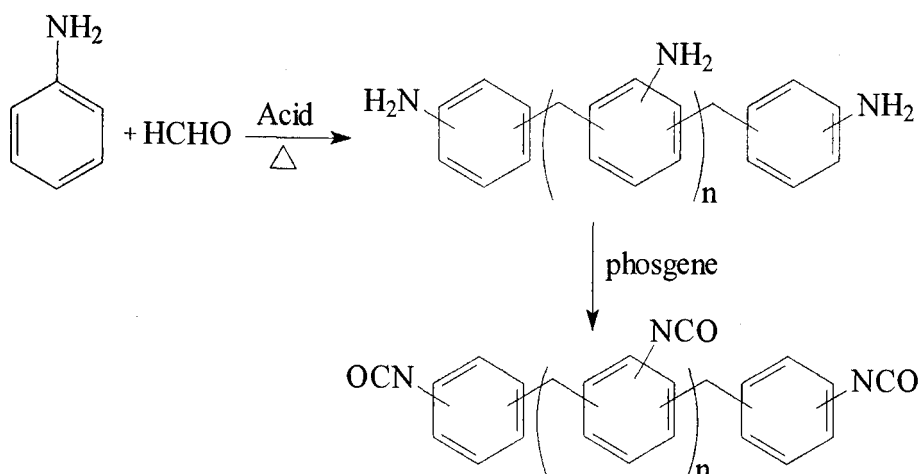
1.4.1 SYNTHESIS OF PMDI

The generalized structure of PMDI is shown in scheme 1.1. The commercial product is a mixture of molecules with different n values, with n varying from 2 to 8.



Scheme 1.1 Structure of PMDI

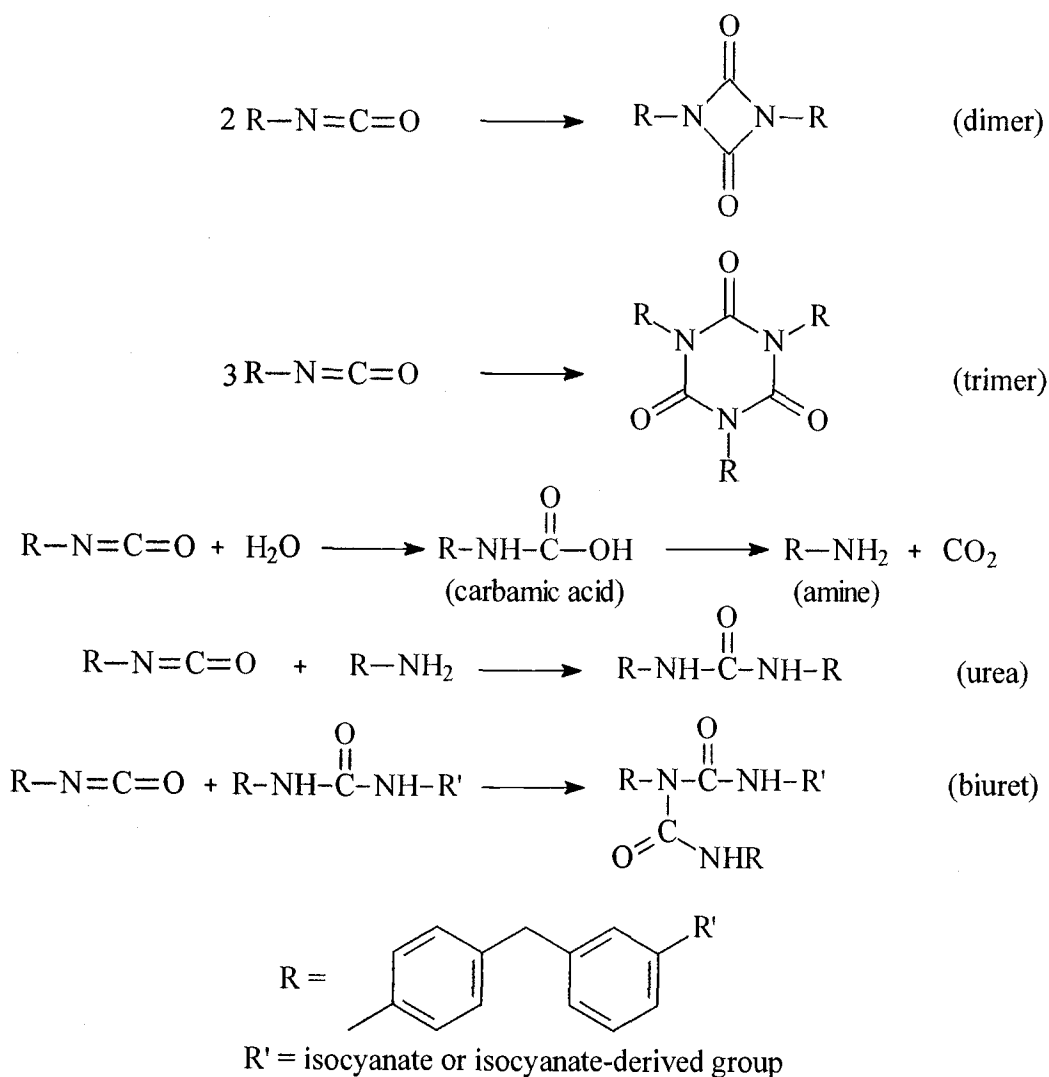
The synthesis of PMDI begins with aniline. With acid catalysis, aniline reacts with formaldehyde and forms polymerized methane-connected aminobenzene rings. Then, the amino groups in the polymer react with phosgene to form isocyanate groups. The reaction route is shown in scheme 1.2.



Scheme 1.2 Synthesis of PMDI

1.4.2 REACTIONS OF PMDI

The isocyanate groups in PMDI are very reactive. They react with hydroxyl groups, amino groups, water, or even with PMDI itself. It was found that when PMDI was applied in wood, about 1/4 to 1/3 of the PMDI reacted with water contained in the wood (Frink and Sachs 1981). When PMDI reacts with water, it first forms an unstable carbamic acid, then immediately loses carbon dioxide and forms an amine. The amine further reacts with PMDI to form a urea structure. The urea can further react with PMDI to form biurets. At elevated temperatures, PMDI crosslinks with itself forming dimers and trimers (Scheme 1.3).



Scheme 1.3 Reaction of PMDI

1.4.3 PROPERTIES OF PMDI

PMDI used as a wood adhesive has many advantages compared to other wood adhesives. First, PMDI is a formaldehyde-free wood adhesive. This is advantageous because formaldehyde has been designated as a human carcinogen and is a known pollutant in the environment. Second, PMDI has an excellent

wetting ability on wood surfaces compared to UF or PF, which makes it suitable for gluing surfaces with poor wettability, such as straw, bagasse, rice shells and sugar cane bagasse (Dunky and Pizzi 2002). Third, PMDI has very good penetrating ability because its molecular weight is much smaller than that of UF and PF. This property helps it penetrate 5 to 10 times further into wood than PF resin (Marcinko, Phanopoulos et al. 2000). The penetration of PMDI was observed to be not only through wood cell lumens, but also through the wood cell wall, which resulted in very good mechanical interlocking. Finally, PMDI spreads very easily on wood surfaces, which results in lower application amounts compared to other wood adhesives, such as PF resin. The low spread rates are due to PMDI's low viscosity and low surface tension (Johns 1989).

However, the lower market share of PMDI reveals that PMDI does have some disadvantages compared to other wood adhesives. First of all, the price of PMDI is much higher than that of UF and PF resins. This is due to the synthesis route and the raw materials used. The price of aniline and phosgene used for producing PMDI are much more expensive than that of formaldehyde, phenol and urea, which are used for producing UF and PF resin. Additionally, since PMDI is very reactive, it can even stick to the surface of metal platens, thus release agents are required for the use of PMDI in wood products. Isocyanates are very toxic. Special protection equipment has to be used for the commercial application of PMDI as wood adhesives.

1.4.4 APPLICATION OF PMDI IN WPCS

PMDI has been used as a compatibilizer in WPCs for over twenty years. It has been used in different WPC systems, such as wood-polyethylene, wood-polypropylene, wood-polystyrene, and wood-polyvinyl chloride composites. Due to the strong adhesion of PMDI to wood fibers, all the resulting WPCs coupled by PMDI had improved mechanical properties compared to WPCs coupled by other compatibilizers or no compatibilizer (Coran and Patel 1982; Goettler 1983; Maldas and Kokta 1989, 1990a, b, c, d, 1991a, b; Maldas, Kokta et al. 1989a, b; Nakamura, Okamura et al. 1983; Raj, Kokta et al. 1988).

PMDI as a compatibilizer in polystyrene composites showed better mechanical property improvements than when coupled with other polymer matrices. It was concluded that since both PMDI and polystyrene have aromatic rings in their structure properties, the π -electrons in the aromatic rings were delocalized and formed strong interactions between PMDI and polystyrene, which then caused strong bonding between them. Since the isocyanate groups in PMDI also formed strong interactions with the wood surface, PMDI therefore built a bridge between the wood particles and polystyrene, resulting in composites with much improved mechanical properties (Maldas, Kokta et al. 1988, 1989a, b).

1.5 OBJECTIVES

WPCs have undergone great development during the past ten years. However, the choice of compatibilizers is limited. Among all the compatibilizers mentioned previously in this chapter, most of them are only effective at a very low level and only a few of them have been commercialized. Moreover, the mechanism of compatibilization is still obscure. In this study, our research is focused on development of new compatibilizer systems for wood-polyethylene composites. The new compatibilizer systems will be based on either polyaminoamide-epichlorohydrin resins or PMDI combined with stearic anhydride or stearic acid.

1.6 REFERENCES

- Bataille, P., L. Ricard, and S. Sapieha (1989). "Effects of Cellulose Fibers in Polypropylene Composites." Polym. Comp. **10**(2): 103-108.
- Beshay, A. D., B. V. Kokta, and C. Daneault (1985). "Use of Wood Fibers in Thermoplastic Composites II: Polyethylene." Polym. Comp. **6**(4): 261-271.
- Bridgeford, D. J. (1963). "Method of Depositing a Polymer of Olefinically Unsaturated Monomer within a Polymeric Material and the Resulting Product." US Patent 3,083,118: 45 pp.
- Chtourou, H., B. Riedl, and A. Ait-Kadi (1992). "Reinforcement of Recycled Polyolefins with Wood Fibers." J. Reinf. Plast. Comp. **11**: 372-394.
- Clemons, C. (2002). "Wood-Plastic Composites in the United States: The Interfacing of Two Industries." For. Prod. J. **52**(6): 10-18.
- Coran, A. Y. and R. Patel (1982). "Composites of Grafted Olefin Polymers and Cellulose Fibers." US Patent 4,323,625: 7 pp.
- Dalvåg, H., C. Klason, and H.-E. Strömvall (1985). "The Efficiency of Cellulosic Fillers in Common Thermoplastics. Part II. Filling with Processing Aids and Coupling Agents." Int. J. Polym. Mater. **11**: 9-38.
- Daneault, C., B. V. Kokta, and D. Malda (1989). "The Xanthate Method of Grafting. XII. Effect of Operating Conditions on the Grafting of Vinyl Monomers onto Wood Pulp." J. Appl. Polym. Sci. **38**: 841-848.
- Dimov, K. and P. Pavlov (1969). "Grafting with Acrylonitrile with the Redox System Cellulose Xanthogenate-Hydrogen Peroxide." J. Polym. Sci. **7**: 2775-2792.
- Dunky, M. and A. Pizzi (2002). "Wood adhesives." in: Adhesion Science and Engineering. D. A. Dillard and A. V. Pocius (Ed.), Amsterdam, Neth, Elsevier Science B.V. **2(Surfaces, Chemistry and Applications)**: 1039-1103.
- Faessinger, R. W. and J. S. Conte (1967). "Thioated Cellulosic/Amylaceous Substrate-Ethylenically Unsaturated Monomer Graft Copolymer." US Patent 3,359,224: 21 pp.
- Frink, J. W. and H. I. Sachs (1981). "Isocyanate Binders for Wood Composite Boards." in: Urethane Chemistry and Application, K. N. Edwards (Ed.), Washington, DC, Am. Chem. Soc., 285-309.

- Frisch, K. C. and L. P. Rumao (1983). "Diisocyanates as Wood Adhesives." in: Wood Adhesives: Chemistry and Technology, A. Pizzi (Ed.), New York, Marcel Dekker., 289-317.
- Gatenholm, P., J. Felix, C. Klason, and J. Kubát (1992). "Cellulose-Polymer Composites with Improved Properties." in: Polymer Science: Advances in New Materials. J. C. Salamone and J. S. Riffle (Ed.), New York, NY, Plenum Press. 7: 75-82.
- Goettler, L. (1983). "Treated Fibers and Bonded Composites of Cellulose Fibers in Vinyl Chloride Polymer Characterized by an Isocyanate Bonding Agent." US Patent 4,376,144: 8 pp.
- Han, G.-S., H. Ichinose, S. Takase, and N. Shiraishi (1989). "Composites of Wood and Polypropylenes III." Mokuzai Gakkaishi **35**(12): 1100-1104.
- Hornof, V., B. V. Kokta, and J. L. Valade (1976). "The Xanthate Method of Grafting. IV. Grafting of Acrylonitrile onto High-Yield Pulp." J. Appl. Polym. Sci. **20**: 1543-1554.
- Hua, L., P. Zadorecki, and P. Flodin (1987). "Cellulose Fiber-Polyester Composites with Reduced Water Sensitivity (1)-Chemical Treatment and Mechanical Properties." Polym. Comp. **8**(3): 199-202.
- Jiang, H. and D. P. Kamdem (2004). "Development of Poly(vinyl chloride)/Wood Composites. A Literature Review." J. Vinyl & Additive Technol. **10**(2): 59-69.
- Johns, W. E. (1982). "Isocyanates as Wood Binders-A Review." J. Adhes. **15**: 59-67.
- Johns, W. E. (1989). "The Chemical Bonding of Wood." in: Wood Adhesives: Chemistry and Technology. A. Pizzi (Ed.), New York, Marcel Dekker Inc. **2**: 75-96.
- Kent, J. A., A. Winston, and W. R. Boyle (1962). "Preparation of Wood-Plastic Combinations Using Gamma Radiation to Induce Polymerization: Effects of Gamma Radiation on Wood." Washington, DC, Annual Report ORO-600, U.S. Atomic Energy Commission.
- Kishi, H., M. Yoshioka, A. Yamanoi, and N. Shiraishi (1988). "Composites of Wood and Polypropylenes I." Mokuzai Gakkaishi **34**(2): 133-139.

- Kokta, B. V., D. Maldas, C. Daneault, and P. Béland (1990a). "Composites of Polyvinyl Chloride-Wood Fibers. I. Effect of Isocyanate as a Bonding Agent." Polym.-Plast. Technol. Eng. **29**(1&2): 87-118.
- Kokta, B. V., D. Maldas, C. Daneault, and P. Béland (1990b). "Composites of Poly(Vinyl Chloride) and Wood Fibers. Part II: Effect of Chemical Treatment." Polym. Comp. **11**(2): 84-89.
- Kokta, B. V., D. Maldas, C. Daneault, and P. Béland (1990c). "Composites of Polyvinyl Chloride-Wood Fibers. III: Effect of Silane as Coupling Agent." J. Vinyl Technol. **12**(3): 146-153.
- Kokta, B. V. and J. L. Valade (1972). "Effect of Acrylonitrile on Grafting of Styrene with the Redox System Cellulose Xanthate-Hydrogen Peroxide." TAPPI **55**(3): 366-369.
- Laver, T. C. (1996). "Extruded synthetic wood composition and method for making same." US Patent 5,516,472: 21 pp.
- Li, B. and J. He (2004). "Investigation of mechanical property, flame retardancy and thermal degradation of LLDPE-wood-fiber composites." Polymer Degradation and Stability **83**(2): 241-246.
- Li, Q. and L. M. Matuana (2003). "Foam Extrusion of High Density Polyethylene/Wood-Flour Composites Using Chemical Foaming Agents." J. Appl. Polym. Sci. **88**: 3139-3150.
- Liang, B.-H., L. Mott, S. M. Shaler, and G. T. Caneba (1994). "Properties of Transfer-Molded Wood-Fiber/Polystyrene Composites." Wood Fiber Sci. **26**(3): 382-389.
- Maldas, D. and B. V. Kokta (1989). "Improving Adhesion of Wood Fiber with Polystyrene by the Chemical Treatment of Fiber with a Coupling Agent and the Influence on the Mechanical Properties of Composites." J. Adhesion Sci. Technol. **3**(7): 529-539.
- Maldas, D. and B. V. Kokta (1990a). "Influence of Polar Monomers on the Performance of Wood Fiber Reinforced Polystyrene Composites. I. Evaluation of Critical Conditions." Int. J. Polym. Mater. **14**: 165-189.
- Maldas, D. and B. V. Kokta (1990b). "Influence of Phthalic Anhydride as a Coupling Agent on the Mechanical Behavior of Wood Fiber-Polystyrene Composites." J. Appl. Polym. Sci. **41**: 185-194.

- Maldas, D. and B. V. Kokta (1990c). "Effects of Coating Treatments on the Mechanical Behavior of Wood-Fiber-Filled Polystyrene Composites. I. Use of Polyethylene and Isocyanate as Coating Components." J. Appl. Polym. Sci. **40**: 917-928.
- Maldas, D. and B. V. Kokta (1990d). "Effects of Coating Treatments on the Mechanical Behavior of Wood Fiber-Filled Polystyrene Composites. II. Use of Inorganic Salt/Polyvinyl Chloride and Isocyanate as Coating Components." J. Reinf. Plast. Comp. **8**: 2-12.
- Maldas, D. and B. V. Kokta (1991a). "Surface Modification of Wood Fibers Using Maleic Anhydride and Isocyanate as Coating Components and Their Performance in Polystyrene Composites." J. Adhesion Sci. Technol. **5**(9): 727-740.
- Maldas, D. and B. V. Kokta (1991b). "Influence of Maleic Anhydride as a Coupling Agent on the Performance of Wood Fiber-Polystyrene Composites." Polym. Eng. Sci. **31**(18): 1351-1357.
- Maldas, D., B. V. Kokta, and C. Daneault (1989a). "Influence of Coupling Agents and Treatments on the Mechanical Properties of Cellulose Fiber-Polystyrene Composites." J. Appl. Polym. Sci. **37**: 751-775.
- Maldas, D., B. V. Kokta, and C. Daneault (1989b). "Thermoplastic Composites of Polystyrene: Effect of Different Wood Species on Mechanical Properties." J. Appl. Polym. Sci. **38**: 413-439.
- Maldas, D., B. V. Kokta, R. G. Raj, and C. Daneault (1988). "Improvement of the Mechanical Properties of Sawdust Wood Fibre-Polystyrene Composites by Chemical Treatment." Polymer **29**: 1255-1265.
- Mali, J., P. Sarsama, L. Suomi-Lindberg, S. Metsä-Kortelainen, J. Peltonen, M. Vilkki, T. Koto, and S. Tiisala (2003). "Woodfibre-plastic composites." http://www.vtt.fi/rte/uutta/wpc_final_%20report.pdf: 84 pp.
- Marcinko, J., C. Phanopoulos, and P. Teachey (2000). "Why Does Chewing Gum Stick To Hair and What Does This Have to Do With Lignocellulosic Structural Composite Adhesion?" Wood Adhesives 2000, Madison, WI, Forest Products Society, 111-121.
- Markarian, J. (2002). "Additives in Food Packaging." Plastics, Additives & Compounding **4**(4): 16-21.

- Matuana, L. M., D. P. Kamdem, and J. Zhang (2001). "Photoaging and Stabilization of Rigid PVC/Wood-Fiber Composites." J. Appl. Polym. Sci. **80**: 1943-1950.
- Matuana, L. M., C. B. Park, and J. J. Balatinecz (1998). "Cell Morphology and Property Relationships of Microcellular Foamed PVC/Wood-Fiber Composites." Polym. Eng. Sci. **38**(11): 1862-1872.
- Meyer, J. A. (1965). "Treatment of Wood-Polymer Systems Using Catalyst-Heat Techniques." For. Prod. J. **15**(9): 362-364.
- Meyer, J. A. (1981). "Wood-Polymer Materials: State of the Art." Wood Sci. **14**(2): 49-54.
- Monte, S. J. and G. Sugerman (1981). "United States and Japanese Application of Titanate Coupling Agents in Polyolefins." Polym.-Plast. Technol. Eng. **17**(1): 95-122.
- Morrison, R. T. and R. N. Boyd (1992). Organic Chemistry, 6th ed. Englewood Cliffs, NJ, Prentice-Hall, Inc., 971-985.
- Morton, J., J. Quarmley, and L. Rossi (2003). "Current and Emerging Applications for Natural and Woodfiber-Plastic Composites." The Seventh International Conference on Woodfiber-Plastic Composites, Madison, WI, 3-6.
- Myers, G. E., I. S. Chahyadi, C. A. Coberly and D. S. Ermer (1991). "Wood Flour/Polypropylene Composites: Influence of Maleated Polypropylene and Process and Composition Variables on Mechanical Properties." Int. J. Polym. Mater. **15**: 21-44.
- Myers, G. E., I. S. Chahyadi, C. Gonzalez, and C. A. Coberly (1993). "Wood Flour and Polypropylene or High-Density Polyethylene Composites: Influence of Maleated Polypropylene Concentration and Extrusion Temperature on Properties." in: Wood Fiber/Polymer Composites: Fundamental Concepts, Processes, and Materials Options. M. P. Wolcott (Ed.), Proc. 1st Wood Fiber-Plastic Composite Conference, Wisconsin, MI, 49-56.
- Nakamura, T., M. Okamura, Y. Moriguchi, and T. Hayase (1983). "Polyisocyanate Cross-linked Polymers Containing Cellulosic Component." US Patent 4,404,347: 7 pp.
- Oksman, K., H. Lindberg, and A. Holmgren (1998). "The Nature and Location of SEBS-MA Compatibilizer in Polyethylene-Wood Flour Composites." J. Appl. Polym. Sci. **69**: 201-209.

- Olsen, D. J. (1991). "Effectiveness of Maleated Polypropylenes as Coupling Agents for Wood Flour/Polypropylene Composites." ANTEC, Proc. 49th Annual Technical Conference, Montreal, Canada, Society of Plastics Engineers, Brookfield, CT, 1886-1891.
- Raj, R. G. and B. V. Kokta (1991). "Improving the Mechanical Properties of HDPE-Wood Fiber Composites with Additives/Coupling Agents." ANTEC, Proc. 49th Annual Technical Conference, Montreal, Canada, Society of Plastics Engineers, Brookfield, CT, 1883-1885.
- Raj, R. G., B. V. Kokta, G. Grouleau, and C. Daneault (1990). "The Influence of Coupling Agents on Mechanical Properties of Composites Containing Cellulosic Fillers." Polym.-Plast. Technol. Eng. **29**(4): 339-353.
- Raj, R. G., B. V. Kokta, D. Maldas, and C. Daneault (1988). "Use of Wood Fibers in Thermoplastic Composites: VI. Isocyanate as a Bonding Agent for Polyethylene-Wood Fiber Composites." Polym. Comp. **9**(6): 404-411.
- Raj, R. G., B. V. Kokta, D. Maldas, and C. Daneault (1989). "Use of Wood Fibers in Thermoplastics. VII. The Effect of Coupling Agents in Polyethylene-Wood Fiber Composites." J. Appl. Polym. Sci. **37**: 1089-1103.
- Rizvi, G., L. M. Matuana, and C. B. Park (2000). "Foaming of PS/Wood Fiber Composites Using Moisture as a Blowing Agent." Polym. Eng. Sci. **40**(10): 2124-2132.
- Rowell, R. M., R. Moisuk, and J. A. Meyer (1982). "Wood-Polymer Composites: Cell Wall Grafting With Alkylene Oxides and Lumen Treatments With Methyl Methacrylate." Wood Sci. **15**(2): 90-96.
- Rozman, H. D., W. B. Banks, and M. L. Lawther (1994). "Improvements of Fiberboard Properties Through Fiber Activation and Subsequent Copolymerization with Vinyl Monomer." J. Appl. Polym. Sci. **54**: 191-200.
- Sain, M. M., B. V. Kokta, and D. Maldas (1993). "Effect of Reactive Additives on the Performance of Cellulose Fiber-Filled Polypropylene Composites." J. Adhesion Sci. Technol. **7**(1): 49-61.
- Sanadi, A. R., R. M. Rowell, and R. A. Young (1992). "Estimation of Fiber-Matrix Interfacial Shear Strengths in Lignocellulosic-Thermoplastic Composites." in: Materials Interactions Relevant to Recycling of Wood-Based Materials. R. M. Rowell, T. L. Laufenberg and J. K. Rowell (Ed.), Pittsburgh, PA, Materials Research Society. **266**: 81-92.

- Schut, J. H. (1999). "For Compounding, Sheet & Profile: Wood is Good." Plastics Technology March: 46-52.
- Sellers, T., Jr. (2001). "Wood Adhesive Innovations and Applications in North America." For. Prod. J. **51**(6): 12-22.
- Sellers, T., Jr., G. D. Miller, Jr., and M. Katabian (2000). "Recycled Thermoplastics Reinforced with Renewable Lignocellulosic Materials." For. Prod. J. **50**(5): 24-28.
- Shoemaker, P. D. and H. O. McQueary (1975a). "Polyisocyanate: Formaldehyde Binder System for Cellulosic Materials." US Patent 3,919,017: 5 pp.
- Shoemaker, P. D. and H. O. McQueary (1975b). "Manufacture of Multilayer Panels Using Polyisocyanate: Formaldehyde Binder System." US Patent 3,930,110: 5 pp.
- Simonsen, J., R. Jacobsen, and R. Rowell (1998). "Wood-Fiber Reinforcement of Styrene-Maleic Anhydride Copolymers." J. Appl. Polym. Sci. **68**: 1567-1573.
- Simonsen, J. and T. Rials (1992). "Enhancing the Interfacial Bond Strength of Lignocellulosic Fiber Dispersed in Synthetic Polymer Matrices." in: Materials Interactions Relevant to Recycling of Wood-Based Materials, R. M. Rowell, T. L. Laufenberg, and J. K. Rowell (Eds), Pittsburgh, PA, Materials Research Society, 105-111.
- Simonsen, J. and T. Rials (1996). "Morphology and Properties of Wood-Fiber Reinforced Blends of Recycled Polystyrene and Polyethylene." J. Thermoplastic Comp. Mater. **9**: 292-302.
- Štepek, J. and H. Daoust (1983). "Lubricants and Mold-Release Agents," Additives for Plastics, Springer-Verlag New York Inc., 34-49.
- Takase, S. and N. Shiraishi (1989). "Studies on Composites from Wood and Polypropylenes. II." J. Appl. Polym. Sci. **37**: 645-659.
- Wolcott, M. P. (2003). "Formulation and process development of flat-pressed wood-polyethylene composites." For. Prod. J. **53**(9): 25-32.
- Wolcott, M. P. and K. Englund (1999). "A Technology Review of Wood-Plastic Composites." the 33rd Proceedings of the Washington State University International Particleboard/Composite Materials Symposium, Pullman, WA, 103-111.

- Wolcott, M. P. and P. M. Smith (2004). "Opportunities and Challenges for Wood-Plastic Composites in Structural Applications." Progress in Woodfibre-Plastic Composites Conference, Toronto, Canada, 1-10.
- Woodhams, R. T. (1984). "Reinforced Resin Composites." US Patent 4,442,243: 6 pp.
- Xanthos, M. (1983). "Processing Conditions and Coupling Agent Effects in Polypropylene/Wood Flour Composites." Plast. Rubber Process. Appl. 3(3): 223-228.
- Youngquist, J. A. (1995). "Unlikely Partners? The Marriage of Wood and Nonwood Materials." For. Prod. J. 45(10): 25-30.
- Zadorecki, P. and P. Flodin (1985a). "Surface Modification of Cellulose Fibers. II. The Effect of Cellulose Fiber Treatment on the Performance of Cellulose-Polyester Composites." J. Appl. Polym. Sci. 30: 3971-3983.
- Zadorecki, P. and P. Flodin (1985b). "Surface Modification of Cellulose Fibers. I. Spectroscopic Characterization of Surface-Modified Cellulose Fibers and Their Copolymerization with Styrene." J. Appl. Polym. Sci. 30: 2419-2429.
- Zhang, H., G. Rizvi, and C. B. Park (2004). "Development of an Extrusion System for Producing Fine-Celled HDPE/Wood-Fiber Composite Foams Using CO₂ as a Blowing Agent." Adv. Polym. Technol. 23(4): 263-276.

CHAPTER 2: EFFECTS OF A NEW COMPATIBILIZER SYSTEM ON THE FLEXURAL PROPERTIES OF WOOD-POLYETHYLENE COMPOSITES

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2.1 SYNOPSIS

A novel wood-plastic compatibilizer system containing a paper wet-strength agent as a wood-binding domain and stearic anhydride as a polyethylene (PE) binding domain was investigated. Treatment of wood flour with a commercial paper wet strength agent Kymene® 557H (simply called Kymene) prior to the mixing of PE and the wood flour increased the modulus of rupture (MOR) and the modulus of elasticity (MOE) of the resulting wood-PE composites. Addition of stearic acid in the mixing of PE and the wood-Kymene mixture further increased the MOR and MOE. Stearic anhydride was even more effective than stearic acid in the increase of the MOR and MOE. When compared to wood-PE composites without a compatibilizer, the stearic anhydride-Kymene compatibilizer system increased the MOR by about 33%, and the MOE by about 40%. The stearic anhydride-Kymene compatibilizer system gave a slightly lower MOR, but higher MOE than the commercially used compatibilizer (maleic anhydride-grafted polypropylene). The compatibilization mechanisms were proposed as follows: Kymene not only bound to wood fibers, but also strengthened and stiffened the wood fibers. Stearic anhydride formed covalent linkages such as ester and amide with the kymene-consolidated wood fibers and the long hydrocarbon chain of the stearic anhydride bonded to the PE matrix through entanglements and/or co-crystallization.

2.2 KEYWORDS

Compatibilizer, Kymene, stearic anhydride, paper wet-strength agent, polyethylene, wood, wood-plastic composites.

2.3 INTRODUCTION

Over the past 50 years, plastics have become a regular part of our daily lives. From containers to car parts, plastics can be shaped and made into almost anything. Fillers are often added to the plastic as a means to lower costs and increase the strength and stiffness of the resulting material(Wolcott 1996; Wolcott and Englund 1999). Wood has been used by the plastics industry as an inexpensive filler for thermoplastics(Wolcott and Englund 1999). These wood-filled thermoplastics, commonly called wood-plastic composites (WPCs) have many property advantages when compared with wood or plastics alone(Wolcott and Englund 1999). However, WPCs also have some disadvantages over pure plastics, including water absorption and thickness swell(Wolcott 1996; Wolcott and Englund 1999). The bond between the wood filler and the thermoplastic matrix is very limited, allowing wood fibers to slip and pull out from the thermoplastic when stressed(Gauthier, Joly et al. 1998).

The inability of wood fibers to produce effective bonds with thermoplastics is a major impediment to the continued development of WPCs. Wood fibers and particles are not compatible with thermoplastics because wood is hydrophilic and the plastic is hydrophobic. One approach to overcome this problem is to add a coupling agent (commonly called a compatibilizer) to improve the interfacial adhesion between the wood fibers and the plastic, thereby increasing the strength properties of the resulting WPC.

Polyethylene (PE) is one of the most commonly used thermoplastics for WPCs. At present, the choice of an effective compatibilizer for wood-PE composites is limited. In this study, we developed and characterized a novel compatibilizer system that contained a paper wet-strength agent as a wood-binding domain and stearic anhydride as a PE-binding domain. The compatibilization mechanism of this new compatibilizer system was discussed in detail.

2.4 EXPERIMENTAL

2.4.1 MATERIALS

Wood flour (pine flour, 0.425 mm, moisture content, 2.04%) was donated by American Wood Fibers (Schofield, WI). HDPE (high density polyethylene) (melt flow index, 0.55 g/10 min) was donated by BP Solvey Polyethylene North America (Houston, TX). Stearic acid was purchased from Acros (Morris Plains, NJ). Stearic anhydride was purchased from Aldrich (Milwaukee, WI). MAPP (maleic anhydride grafted polypropylene, A-C OptiPakTM 210) was a gift from Honeywell International, Inc. (Morristown, NJ). Kymene® 557H (12.5 % aqueous solution) was provided by Hercules Inc. (Wilmington, DE).

2.4.2 PREPARATION OF WOOD-PE COMPOSITES

Wood flour, HDPE powder and the compatibilizer were mixed in a Brabender Plasticorder with roller blade mixing bowl attached (C. W. Brabender Instruments,

Inc., South Hackensack, NJ). The weight ratio of the components and the blending procedure used are listed in Table 2.1.

Table 2.1 Components and their ratio of wood-PE composites

Labels of wood-PE composites	Components of wood-PE composites	Weight ratio of the components	Blending procedures
Control	Wood/HDPE	40/60	A
MAPP	Wood/MAPP/HDPE	40/2/58	B
SA	Wood/stearic acid/HDPE	40/1/59	B
SAN	Wood/stearic anhydride/HDPE	40/1/59	B
K-1	Wood/Kymene/HDPE	40/2/58	C
K-2	Wood/Kymene/HDPE	40/2/58	D
K-3	Wood/Kymene/HDPE	40/2/58	E
K+SA	Wood/Kymene/stearic acid/HDPE	40/2/1/57	F
K+SAN	Wood/Kymene/stearic anhydride/HDPE	40/2/1/57	F

2.4.2.1 BLENDING PROCEDURES FOR WOOD-PE COMPOSITES

A: The bowl of the Brabender Plasticorder was preheated to 120 °C and the speed of the rotors in the bowl set to 100 rpm. Wood flour (17.96 g) was added and

blended for 10 min. The bowl temperature was then raised to 170 °C and HDPE (26.40 g) was added and blended for 5 min. The contents were then removed from the Brabender and stored for compression molding.

B: As described in **A**, the bowl was preheated to 120 °C and the rotor speed was set to 100 rpm. Wood flour (17.96 g) was then added to the bowl. After the bowl temperature returned to 120 °C, one of the following materials, stearic acid (0.44 g), stearic anhydride (0.44 g), or MAPP (0.88 g) was added and mixed for 10 min. The bowl temperature was then raised to 170 °C and HDPE (25.96 g for stearic acid and stearic anhydride, 25.52 g for MAPP) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

C: As described in **A**, the bowl was preheated to 120 °C and the rotor speed was set to 100 rpm. Wood flour (17.96 g) was then added to the bowl. After the bowl temperature returned to 120 °C, Kymene (7.04 g, 0.88 g dry solids) was added and mixed for 10 min. The bowl temperature was then raised to 170 °C, and HDPE (25.52 g) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

D: Kymene (7.04 g, 0.88 g oven-dry solids) was diluted with de-ionized water (36.96 mL) to form a 2% aqueous solution. Wood flour (17.96 g) was added to

the diluted Kymene solution (44 mL) and mixed well by mechanical stirring. The resulting wood-Kymene mixture was dried at 104 °C for about 20 h. The oven-dry wood-Kymene mixture (18.48 g) was added to the preheated Brabender bowl at 120 °C and 100 rpm, and mixed for 10 min. The bowl temperature was then raised to 170 °C and HDPE (25.52 g) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

E: Kymene (7.04 g, 0.88 g oven-dry solids) was added dropwise to wood flour (17.96g) in a 400 mL beaker with mechanical stirring and mixed well. The wood-Kymene mixture was added to the preheated Brabender bowl at 120 °C and 100 rpm and mixed for 10 min. The bowl temperature was then raised to 170 °C, and HDPE (25.52 g) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

F: The Brabender bowl was preheated to 120 °C and the rotor speed was set to 100 rpm. The oven-dry wood-Kymene mixture (18.48 g) as prepared in **D** was added. After the bowl temperature returned to 120 °C, stearic acid (0.44 g) or stearic anhydride (0.44 g) was added and mixed for 10 min. The bowl temperature was then raised to 170 °C and HDPE (25.08 g) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

2.4.2.2 PRESS PROCEDURE

A steel mold with the dimensions of 101.6 x 101.6 x 2 mm was used to compression mold the wood-PE WPC into stock test samples. 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 sample, placed on the lower platen of the Carver press and pre-heated for 10 min. The press was closed slowly allowing the wood-plastic to flow into the mold shape. The press pressure was raised from 34.5 to 344.8 kPa in two min 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-PE sample was cut into 10 small test specimens. Each specimen had dimensions of 52.46-55.16 mm of length, 10.70-14.28 mm of width, and 2.32-3.10 mm of thickness.

2.4.3 DETERMINATION OF THE STRENGTH AND STIFFNESS OF THE WOOD-PE COMPOSITES

The small specimens were tested on a Sintech machine (MTS Systems Corporation, Enumclaw, WA) and the load-deflection curve determined. The support span was 43 mm and the crosshead speed was 1.0 mm/min. At least 10 specimens were tested for each wood-PE composite in accordance with ASTM D790-86. All specimens showed a yielding fracture mode. The modulus of rupture (MOR) and modulus of elasticity (MOE) were calculated from the load-deflection data. The MOR was defined as the first point on the load-deflection curve to show a slope of

zero. The MOE was determined from the slope in the initial elastic region of the load-deflection curve.

2.5 RESULTS

When a Kymene solution was added directly to wood flour in the preheated Brabender bowl (blending procedure C), the resulting wood-PE composites had a lower MOR than the control, i.e., wood-PE composite without a compatibilizer (Fig. 2.1). When wood flour was pre-mixed with a diluted Kymene solution and dried in an oven (blending procedure D), the resulting composite had a higher MOR than the control (Fig. 2.1). Mixing of PE and wet wood-Kymene mixture in the preheated Brabender (blending procedure E) resulted in a composite with a lower MOR than the control (Fig. 2.1).

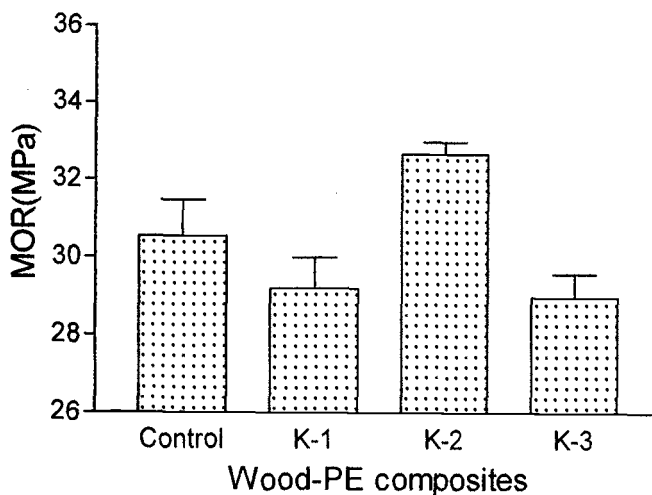


Fig. 2.1 Effects of blending procedures on MOR of wood-Kymene-PE composites. Data are the mean of at least ten replicates and the error bars represent one standard deviation

Compared with the control, addition of Kymene, regardless of the blending procedures, increased the MOE of the resulting wood-PE composites (Fig. 2.2). Mixing of PE with the oven-dry wood-Kymene mixture gave the highest MOE (Fig. 2.2).

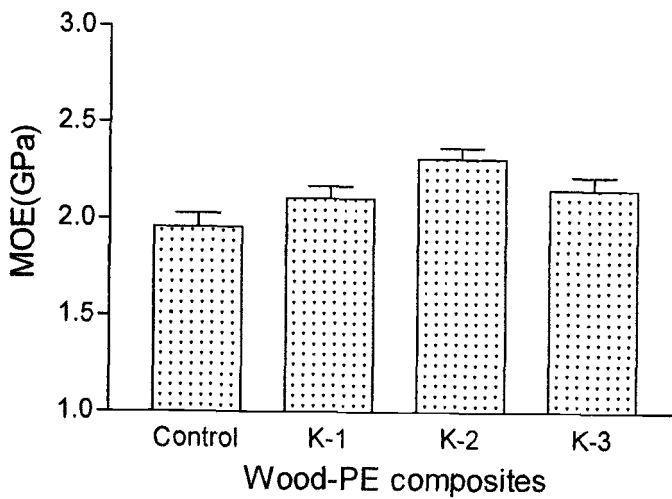


Fig. 2.2 Effects of blending procedures on MOE of wood-Kymene-PE composites. Data are the mean of at least ten replicates and the error bars represent one standard deviation

Compared to the control, stearic acid had little effects on the MOR of the resulting wood-PE composites (Fig. 2.3). However, when both Kymene and stearic acid were present, the MOR of the wood-PE composites was much higher than that of the control and the composites containing either Kymene or stearic acid only (Fig. 2.3). Addition of Kymene and stearic acid increased the MOR by about 14% compared to the control. In the contrast to the little effect of stearic acid on the

MOR, the presence of stearic acid slightly increased the MOE of the composites compared to the control (Fig. 2.4). The MOE of the composites containing both Kymene and stearic acid was about 33% higher than those of the control and about 12% higher than those of the composites containing only Kymene (Fig. 2.4).

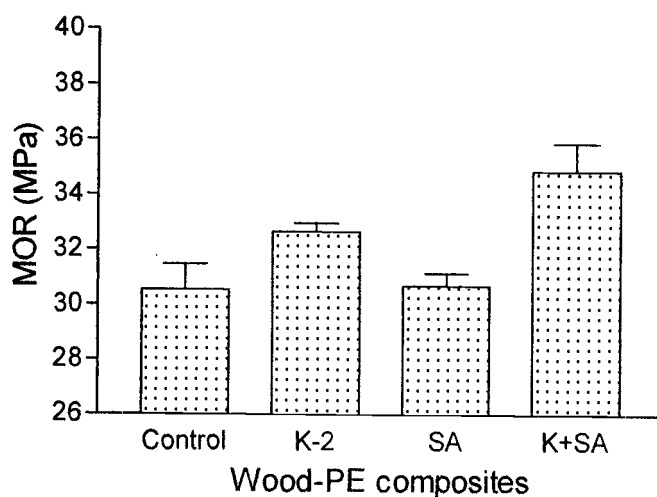


Fig. 2.3 Effects of stearic acid and a combination of stearic acid and Kymene on MOR. Data are the mean of at least ten replicates and the error bars represent one standard deviation.

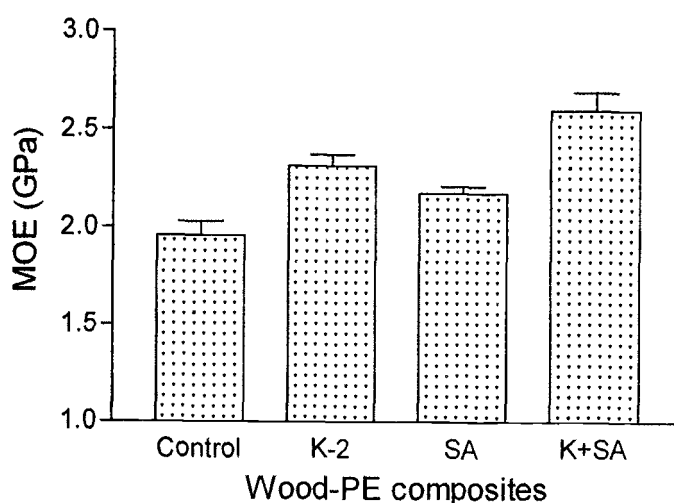


Fig. 2.4 Effects of stearic acid and a combination of stearic acid and Kymene on MOE. Data are the mean of at least ten replicates and the error bars represent one standard deviation.

Stearic anhydride increased the MOR by about 12% when compared to the control (Fig. 2.5). A combination of stearic anhydride and Kymene had a much greater compatibilization effect than stearic anhydride or Kymene alone. The wood-PE composites containing both stearic anhydride and Kymene had about 33% higher MOR than the control (Fig. 2.5). However, a combination of stearic anhydride and Kymene gave slightly lower MOR than MAPP (Fig. 2.5).

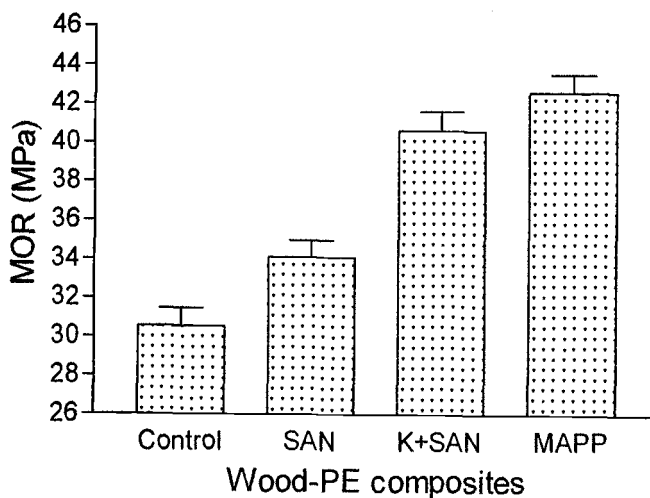


Fig. 2.5 Effects of stearic anhydride, a combination of stearic acid and Kymene, and MAPP on MOR. Data are the mean of at least ten replicates and the error bars represent one standard deviation.

The MOE of the wood-PE composites containing stearic anhydride as a compatibilizer was higher than that of the control. A combination of stearic anhydride and Kymene further increased the MOE, as compared to stearic anhydride alone (Fig. 2.6). When both stearic anhydride and Kymene were used together, the MOE was about 40% higher than that of the control. Interestingly, a combination of stearic anhydride and Kymene resulted in a higher MOE than MAPP (Fig. 2.6).

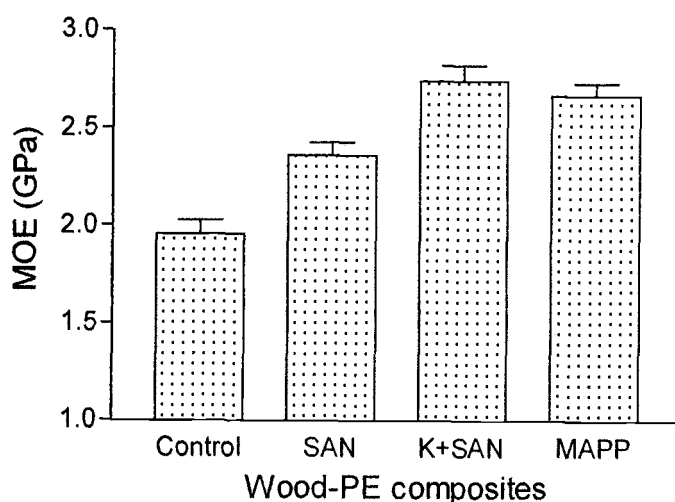
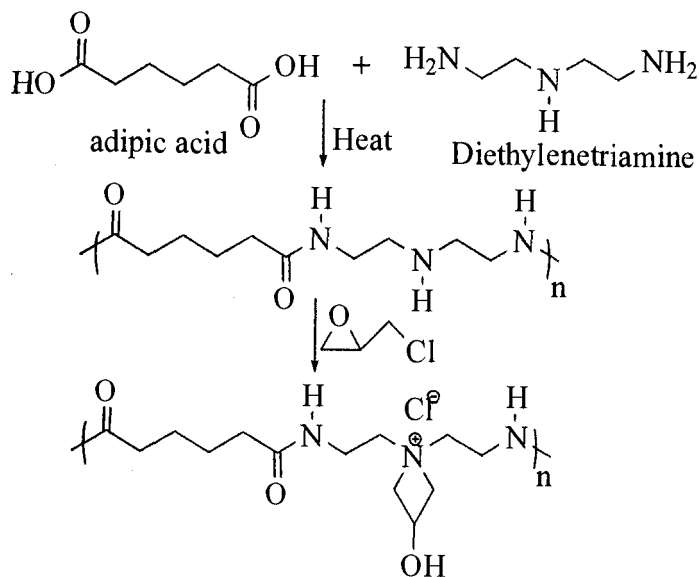


Fig. 2.6 Effects of stearic anhydride, a combination of stearic acid and Kymene, and MAPP on MOE. Data are the mean of at least ten replicates and the error bars represent one standard deviation.

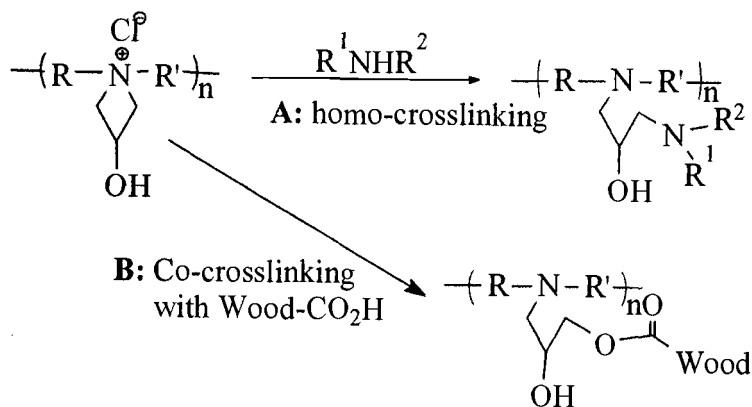
2.6 DISCUSSION

The Kymene® 557 (simply called Kymene) is the most widely used paper wet strength agent. Kymene is a polyaminoamide-epichlorohydrin (PAE) adduct whose representative structure is shown in Scheme 2.1 (Keim 1960a, b). It has been well established that hydroxy-azetidium (the cationic four-membered ring structure) is the key functional group for wet strength development in paper (Espy 1995; Espy and Rave 1988). The characteristic four-membered azetidium structure is fairly stable in water at room temperature. However, the azetidium undergoes various reactions at elevated temperatures. The chemistry and wet-strength mechanisms of PAE resins have been extensively studied and reviewed (Dunlop-Jones 1996; Espy 1994, 1995; Espy and Rave 1988; Linhart 1995). Based on these studies in paper, we speculate that the key reactions between Kymene and wood

flour are similar to those shown in Scheme 2.2. When wood flour is added to a diluted Kymene solution and mixed well, the PAE polymers are readily absorbed to the wood fibers due to the positive charges in the PAE polymers. Due to their low molecular weight, the PAE polymers may even diffuse into the cell walls of the wood fibers. Upon drying, the PAE polymers react with themselves, as shown in reaction A in Scheme 2.2, to form a highly cross-linked insoluble network around and through the fibers. One effect of this reaction is that the highly crosslinked network could consolidate fine and loose fibers on the wood flour surfaces. The PAE polymers could also form covalent linkages between fibers (as in reaction B in Scheme 2.2), thus reinforcing the natural hydrogen bonding in the wood flour. Therefore, treatment of wood flour with Kymene is expected to strengthen and stiffen the wood fibers. The results in Fig. 2.2 indeed show that Kymene increased the MOE values. When wood flour was stirred in a diluted Kymene solution and then dried, the PAE polymers are expected to be well absorbed and well distributed in the wood fibers, resulting in significant strengthening and stiffening of the wood flour. This would explain why blending procedure D (thoroughly mixing the wood flour in a diluted Kymene solution following by oven-drying the mixture) gave rise to higher MOR and MOE than blending procedure C (mixing wood flour and Kymene in the Brabender bowl), or E (mixing wood flour and concentrated Kymene).



Scheme 2.1 A synthetic scheme for industrial production of PAE resins



Scheme 2.2 Proposed key reactions in the binding of Kymene to wood flour

Extensive studies suggest that effective wood-plastic compatibilizers contain two domains with one domain able to bind to wood and the other able to bind to plastic (Bledzki and Gassan 1999; de Roover, Slavons et al. 1995; Felix and

Gatenholm 1991, 1993; Garg, Lenk et al. 1996; Gassan and Bledzki 1997; Gauthier, Joly et al. 1998; Heinen, Rosenmüller et al. 1996; Joly, Kofman et al. 1996; Minoura, Ueda et al. 1969; Raj and Kokta 1989; Rengarajan, Parameswaran et al. 1990; Russell 1995; Russell and Kelusky 1988; Sathe, Rao et al. 1994; Takase and Shiraishi 1989). This study suggests that Kymene is a good wood-binding domain. It appears to not only bind strongly to wood flour, but also seems to strengthen and stiffen the wood flour. For effective compatibilization, a plastic-binding domain bonded to the wood-binding domain is still needed. Stearic acid was first investigated as a PE-binding domain, hoping that the long hydrocarbon chain of stearic acid would form entanglements or co-crystallization with the PE matrix, and the carboxylic acid group would form ester or amide linkages with the wood-Kymene mixture at the high mixing temperature (170 °C). The data in Fig. 2.3 and 2.4 indeed show that addition of stearic acid in the mixing of PE and the oven-dry wood-Kymene mixture greatly increased the MOR and MOE. At the high mixing temperature (170 °C) ester or amide linkages between the carboxylic acid and the wood-Kymene mixture would be expected, but the formation rate might be slow. Therefore, we investigated the more reactive stearic anhydride to see if it could further increase the compatibilization effects. As expected, stearic anhydride gave a higher MOR and MOE than stearic acid, and a combination of stearic anhydride and Kymene was superior to a combination of stearic acid and Kymene in terms of MOR and MOE. (Fig. 2.5 and 2.6). That wood/stearic anhydride/Kymene/PE composites had higher MOE values than wood/MAPP/PE

composites suggests that a combination of an acid anhydride with a long hydrocarbon chain and Kymene is a promising compatibilizer system for wood-PE composites.

2.7 CONCLUSIONS

Treatment of wood fibers with Kymene increased the MOR and MOE of the resulting wood-PE composites. The combination of stearic acid and wood flour pre-treated with Kymene yielded a higher MOR and MOE than either stearic acid or Kymene alone. The combination of stearic anhydride and Kymene-pretreated wood flour had superior compatibilization effects, in terms of mechanical properties, compared to the combination of stearic acid and the Kymene-pretreated wood flour. A paper wet strength agent could serve as an effective wood-binding domain of a wood-plastic compatibilizer system. The combination of Kymene and carboxylic anhydride was a superior compatibilizer system for wood-plastic composites. This compatibilizer system is particularly attractive for reactive extrusion of WPCs.

2.8 ACKNOWLEDGMENTS

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respectively. This research was supported by a grant from the national research initiative competitive grants program of USDA.

2.9 REFERENCES

- Bledzki, A. K. and J. Gassan (1999). "Composites reinforced with cellulose based fibres" Progr. Polym. Sci. **24**(2): 221-274.
- de Roover, B., M. Sclavons, V. Carlier, J. Devaux, R. Legras and A. Momtaz (1995). "Molecular characterization of maleic anhydride-functionalized polypropylene" J. Polym. Sci., Part A: Polym. Chem. **33**(5): 829-842.
- Dunlop-Jones, N. (1996). "Wet-strength chemistry". in: Paper Chemistry, 2nd ed. J. C. Roberts (Ed.), New York, Blackie Academic & Professional: 98-119.
- Espy, H. H. (1994). "Alkaline-Curing Polymeric Amine-Epichlorohydrin Resins". in: Wet-Strength Resins and Their Application. L. L. Chan (Ed.), Atlanta, GA, Tappi Press. **Ch. 2**: 13-44.
- Espy, H. H. (1995). "The Mechanism of Wet-Strength Development in Paper: A Review" TAPPI J. **78**(4): 90-99.
- Espy, H. H. and T. W. Rave (1988). "The Mechanism of Wet-Strength Development by Alkaline-Curing Amino Polymer-Epichlorohydrin Resins" TAPPI J. **71**(5): 133-137.
- Felix, J. M. and P. Gatenholm (1991). "The nature of adhesion in composites of modified cellulose fibers and polypropylene" J. Appl. Polym. Sci. **42**: 609-620.
- Felix, J. M. and P. Gatenholm (1993). "Formation of entanglements at brushlike interfaces in cellulose-polymer composites" J. Appl. Polym. Sci. **50**: 699-708.
- Garg, D. H., W. Lenk, S. Berwald, K. Lunkwitz, F. Simon and K.-J. Eichhoun (1996). "Hydrophilization of microporous polypropylene Celgard membranes by the chemical modification technique" J. Appl. Polym. Sci. **60**(12): 2087-2104.
- Gassan, J. and A. K. Bledzki (1997). "The influence of fiber-surface treatment on the mechanical properties of jute-polypropylene composites" Compos. Part A: Applied Science and Manufacturing **28A**(12): 1001-1005.
- Gauthier, R., C. Joly, A. C. C. Coupas, H. Gauthier and M. Escoubes (1998). "Interfaces in polyolefin/cellulosic fiber composites: chemical coupling, morphology, correlation with adhesion and aging in moisture" Polym. Compos. **19**: 287-300.

- Heinen, W., C. H. Rosenmöller, C. B. Wenzel, H. J. M. de Groot, J. Lugtenburg and M. van Duin (1996). "¹³C NMR Study of the Grafting of Maleic Anhydride onto Polyethylene, Polypropene, and Ethene-Propene Copolymers" Macromol. **29**(4): 1151-1157.
- Joly, C., M. Kofman and R. Gauthier (1996). "Polypropylene/cellulosic fiber composites: chemical treatment of the cellulose assuming compatibilization between the two materials" J. Macro. Sci. - Pure Appl. Chem. **A33**: 1981-1996.
- Keim, G. I. (1960a). "Cationic Thermosetting Polyamide-Epichlorohydrin Resins and Process of Making Same." US Patent 2,926,154: 4 pp.
- Keim, G. I. (1960b). "Wet-Strength Paper and Method of Making Same." US Patent 2,926,116: 5 pp.
- Linhart, F. (1995). "The practical application of wet-strength resins." in: Applications of wet-end paper chemistry. C. O. Au and I. Thorn (Ed.), New York, Blackie Academic & Professional: 102-119.
- Minoura, Y., M. Ueda, S. Mizunuma and M. Oba (1969). "The reaction of polypropylene with maleic anhydride" J. Appl. Polym. Sci. **13**: 1625-1640.
- Raj, R. G. and B. V. Kokta (1989). "Compounding of cellulose fibers with polypropylene: Effect of fiber treatment on dispersion in the polymer matrix" J. Appl. Polym. Sci. **38**: 1987-1996.
- Rengarajan, R., V. R. Parameswaran, S. Lee and P. L. Rinaldi (1990). "NMR analysis of polypropylene-maleic anhydride copolymer" Polymer **31**: 1703-1706.
- Russell, K. E. (1995). "Grafting of maleic anhydride to hydrocarbons below the ceiling temperature" J. Polym. Sci., Part A: Polym. Chem. **33**(3): 555-561.
- Russell, K. E. and E. C. Kelusky (1988). "Grafting of maleic anhydride to n-eicosane" J. Polym. Sci.: Part A: Polym. Chem. **26**: 2273-2280.
- Sathe, S. N., G. S. S. Rao and S. Devi (1994). "Grafting of maleic anhydride onto polypropylene: Synthesis and characterization" J. Appl. Polym. Sci. **53**: 239-245.
- Takase, S. and N. Shiraishi (1989). "Studies on Composites from Wood and Polypropylenes. II" J. Appl. Polym. Sci. **37**: 645-659.

- Wolcott, M. P. (1996). "The role of thermoplastics in conventional wood composites". Proceeding of the 30th Washington State University International Particleboard/Composites Materials Symposium, Pullman, WA, 37-44.
- Wolcott, M. P. and K. Englund (1999). "A technology review of wood-plastic composites". Proceeding of the 33rd Washington State University International Particleboard/Composites Materials Symposium, Pullman, WA, 103-111.

CHAPTER 3: FURTHER INVESTIGATION OF POLYAMINOAMIDE-
EPICHLOROHYDRIN/STEARIC ANHYDRIDE COMPATIBILIZER SYSTEM
FOR WOOD-POLYETHYLENE COMPOSITES

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3.1 SYNOPSIS

The combination of a polyaminoamide-epichlorohydrin (PAE) resin (a paper wet strength agent) and stearic anhydride was recently reported as an effective compatibilizer system for wood-polyethylene composites. Further investigation of this new compatibilizer system revealed that the pH value of a PAE solution, dosages of PAE and stearic anhydride, and the weight ratio of PAE to stearic anhydride had significant impacts on the compatibilization effects of the compatibilizer system. Adjusting the pH value of the PAE solution from 5.0 to 10.4 increased the strength of the resulting wood-polyethylene composites. The highest strength of the resulting wood-polyethylene composites was obtained at 3 wt% PAE and 3 wt% stearic anhydride. At 4 wt% or 6 wt% of a compatibilizer, this PAE-stearic anhydride system was superior to maleic anhydride-grafted polyethylene (MAPE), one of the most effective compatibilizers, in terms of enhancing the strength of the resulting wood-polyethylene composites. Fourier Transform Infrared Spectroscopy (FTIR) analysis revealed that PAE and stearic anhydride formed covalent bonding with wood flour. The compatibilization mechanisms of this PAE-stearic anhydride compatibilizer system were investigated in detail. Water-resistance tests indicated that PAE-stearic anhydride compatibilizer system increased the water-resistance of the resulting composites.

3.2 KEYWORDS

Compatibilizer, polyaminoamide-epichlorohydrin, stearic anhydride, paper wet-strength agent, polyethylene, wood, wood-plastic composites.

3.3 INTRODUCTION

Wood as a filler for strengthening thermoplastics such as polyethylene (PE) has many advantages over commonly used inorganic fillers such as glass fibers. For example, wood is inexpensive and renewable. Wood-filled thermoplastics products can be burned after their useful lives, thus leaving much less solid waste than inorganic-based materials-filled thermoplastics. In the past several years, wood-filled thermoplastics, commonly called wood-plastic composites (WPCs) have become one of the fastest growing composite materials in the wood composites industry. More than 700 million lb of WPCs were produced in 2002. However, the amount of WPCs sold in 2002 was only about 5% of penetratable markets (Morton, Quarmley et al. 2003). One of the obstacles for preventing WPCs from gaining a bigger market share is that the strength of WPCs is still not high enough to meet strength requirements of many applications.

Wood is hydrophilic and thermoplastics are hydrophobic. Wood and thermoplastic are thus not compatible, i.e., the interphase between wood and plastics is typically weak, failing to transfer stress. A coupling agent, commonly called compatibilizer, is normally added in the production of WPCs for improving the interfacial adhesion. At present, maleic anhydride-grafted PE (MAPE) and maleic anhydride-grafted polypropylene (MAPP) are commonly used compatibilizers for WPCs. However, the compatibilization effect of MAPE or MAPP is still much lower than what is potentially achievable. Moreover, the

choice of compatibilizers for WPCs is still limited. In an effort to gain a better understanding of the interfacial chemistry of WPCs, we recently discovered a new compatibilizer system consisting of a polyaminoamide-epichlorohydrin (PAE) resin (a paper-wet strength agent) and stearic anhydride (Geng, Li et al. 2004). In this study this new compatibilizer system was further investigated for improvements of its compatibilization effect on wood-PE composites.

3.4 EXPERIMENTAL

3.4.1 MATERIALS

Wood flour (pine flour, 0.425 mm, moisture content, 2.04%) was donated by American Wood Fibers (Schofield, WI). High density polyethylene (PE) (melt flow index, 0.55 g/10 min) was donated by BP Solvay Polyethylene North America (Houston, TX). Stearic anhydride was purchased from Aldrich (Milwaukee, WI). MAPE (maleic anhydride grafted polyethylene, A-C OptiPakTM 200) was a gift from Honeywell International, Inc. (Morristown, NJ). The PAE resin used in this study was Kymene® 557H (12.5 % aqueous solution) that was donated by Hercules Inc. (Wilmington, DE).

3.4.2 PREPARATION OF WOOD-PE COMPOSITES

Wood-PE composites were prepared by mixing wood flour and PE powder in the presence or absence of a compatibilizer in a Brabender Plasticorder with roller blade mixing bowl attached (C. W. Brabender Instruments, Inc., South

Hackensack, NJ) followed by compression molding of the mixed material in a stainless steel mold. Mixing procedures varied with the compatibilizer used. The composition of wood-PE composites and the mixing procedure are listed in Table 3.1.

Table 3.1 The composition of wood-PE composites

Mixing Procedure	Composite	Wood flour (wt%)	MAPE (wt%)	PAE (wt%)	Stearic anhydride (wt%)	HDPE (wt%)
A	Control	40	-	-	-	60
B	MAPE2	40	2	-	-	58
	MAPE4	40	4	-	-	56
	MAPE6	40	6	-	-	54
C	PAE1S1	40	-	1	1	58
	PAE2S1	40	-	2	1	57
	PAE3S1	40	-	3	1	56
	PAE5S1	40	-	5	1	54
	PAE3S2	40	-	3	2	55
	PAE3S3	40	-	3	3	54
	PAE3S4	40	-	3	4	53
	PAE3S5	40	-	3	5	52
	PAE2S2	40	-	2	2	56

Mixing procedure A: The mixing procedure A was for mixing wood flour and PE without a compatibilizer. The bowl of the Brabender Plasticorder was preheated to 120 °C and the speed of the rotors in the bowl set to 100 rpm. Wood flour (17.96 g) was added and blended for 10 min. The bowl temperature was then raised to 170 °C and HDPE (26.40 g) was added and blended for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Mixing procedure B. The mixing procedure B was for mixing wood flour, PE and MAPE. The Brabender bowl was preheated to 120 °C and the rotor speed was set to 100 rpm. Wood flour (17.96 g) was then added to the bowl. After the bowl temperature was returned to 120 °C, MAPE was added and mixed for 10 min. The bowl temperature was then raised to 170 °C and PE was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Mixing procedure C. The mixing procedure C was used for preparing wood-PE composites with a PAE-stearic anhydride compatibilizer. The following was an example of the mixing procedure for preparing wood-PE composites with wood/PAE/stearic anhydride/PE weight ratio of 40/2/1/57. The PAE solution (7.04 mL, 0.88 g dry weight) was diluted with de-ionized water (36.96 mL). The diluted PAE solution was adjusted to the predetermined pH value by adding 1.5 M aqueous

sodium hydroxide solution. Then, wood flour (17.96 g) was added to the diluted PAE solution and mixed well by mechanical stirring. The resulting wood-PAE mixture was dried at 104 °C for about 20 h. The oven-dry wood-PAE mixture was added to the preheated Brabender bowl at 120 °C. After the bowl temperature was returned to 120 °C, stearic anhydride was added and mixed for 10 min. The bowl temperature was then raised to 170 °C and PE was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Press procedure (Geng, Li et al. 2004). A stainless steel mold with the dimensions of 101.6 x 101.6 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 sample, placed on the lower platen of the Carver press and pre-heated for 10 min. The press was closed slowly allowing the wood-plastic to flow into the mold shape. The press pressure was raised from 34.5 to 344.8 kPa in two min 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 clamps at ambient conditions. The resulting wood-PE sample was cut into 10 small test specimens. Each specimen had dimensions of 52.46-56.46 mm of length, 10.70-14.28 mm of width, and 2.10-3.10 mm of thickness.

3.4.3 DETERMINATION OF THE STRENGTH AND STIFFNESS OF THE WOOD-PE COMPOSITES

This test method was basically the same as described in our previous paper (Geng, Li et al. 2004). The small specimens were tested on a Sintech machine (MTS Systems Corporation, Enumclaw, WA) and the load-deflection curves determined. The support span was 43 mm and the crosshead speed was 1.0 mm/min. At least 10 specimens were tested for each wood-PE composite in accordance with ASTM D790-02. All specimens showed a yielding fracture mode. The modulus of rupture (MOR) and modulus of elasticity (MOE) were calculated from the load-deflection data. The MOR was defined as the first point on the load-deflection curve to show a slope of zero. The MOE was determined from the slope in the initial elastic region of the load-deflection curve.

3.4.4 WATER-RESISTANCE TEST

Five specimens of each wood-PE composite were used for the water-resistance test. All specimens were pre-weighed and then soaked in water at room temperature. The specimens were taken out of water, wiped with tissue paper, weighed once every 24 h for the first five days, and then weighed at a longer time interval until day 65. The water uptake percentage was determined from the weight gain divided by the dry weight of the specimens.

3.4.5 REMOVAL OF PE FROM WOOD-PE COMPOSITES

Four wood-PE composites were investigated in this set of experiments: 1. The composite without any compatibilizer; 2. The composite with 3 wt% PAE at pH 10.4. 3. The composite with 3 wt% stearic anhydride, and 4. The composite with 3 wt% stearic anhydride and 3 wt% PAE at pH 10.4. The wood-PE composites were cut into small pieces by a fodder chopper, and wrapped in filter paper. The wrapped wood-PE composite specimens were extracted with *p*-xylene in a modified Soxhlet extractor for 48 h. The thimble holder of the Soxhlet extractor was wrapped with heating tape and heated to maintain the temperature of the solution in the thimble at about 120 °C. The extracted wood residue was dried and characterized with FTIR.

3.5 RESULTS

The effect of the pH value of the PAE solution on the MOR and MOE of the resulting wood-PE was investigated at the 40/2/1/57 wood/PAE/stearic anhydride/PE weight ratio (Fig. 3.1). At all pH values studied, both MOR and MOE were higher than those of the control, i.e., without the PAE-stearic anhydride compatibilizer. There were no statistically significant changes in either MOR or MOE of the resulting composites when the pH value of the PAE solution was adjusted from 5.0 (the original pH value of the PAE solution) to 9.0 (Fig. 3.1). When the pH value was further increased to 10.4, the MOR at pH 10.4 was significantly higher than that at pH 5.0, whereas the MOE at pH 10.4 was still statistically the same as that at pH 5.0 (Fig. 3.1). However, both MOR and MOE

decreased with a further increase in the pH value from 10.4 to 11.7 (Fig. 3.1). pH 10.4 thus appeared to be the optimal pH value for the compatibilization effect.

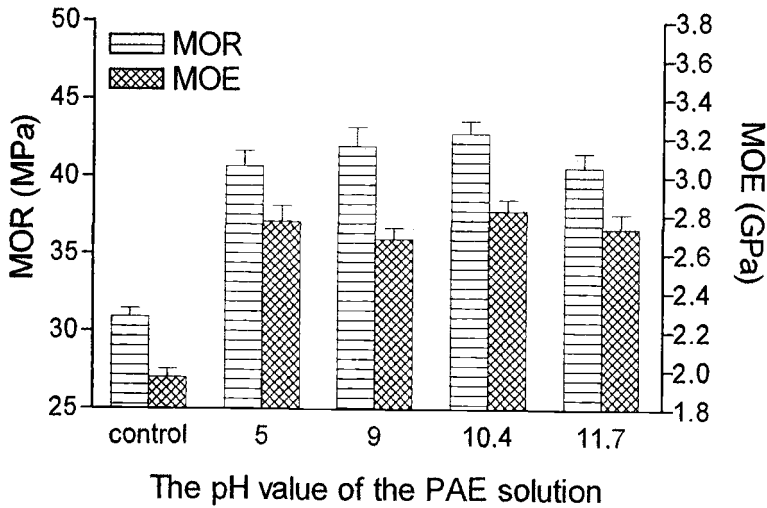


Fig. 3.1 Effect of the pH value of the PAE solution on MOR and MOE of wood-PE composites (Control: wood/PE weight ratio = 40/60; the weight ratio in other wood-PE composites: wood/PAE/stearic anhydride/PE = 40/2/1/57). Data are the mean of at least ten replicates and the error bars represent one standard error of the mean.

With a pH 10.4 PAE solution and a loading of 1.0 wt % stearic anhydride (the weight percentage based on the wood-PE composite), both MOR and MOE gradually increased with increasing PAE dosage from 1 wt% to 3 wt% (Fig. 3.2). When the PAE dosage was further increased from 3 wt% to 5 wt%, the MOE further increased, but the MOR significantly decreased (Fig. 3.2). Therefore, 3 wt% PAE was determined to be the optimal dosage of PAE given that adding 5 wt% PAE reduced the MOR (Fig. 3.2).

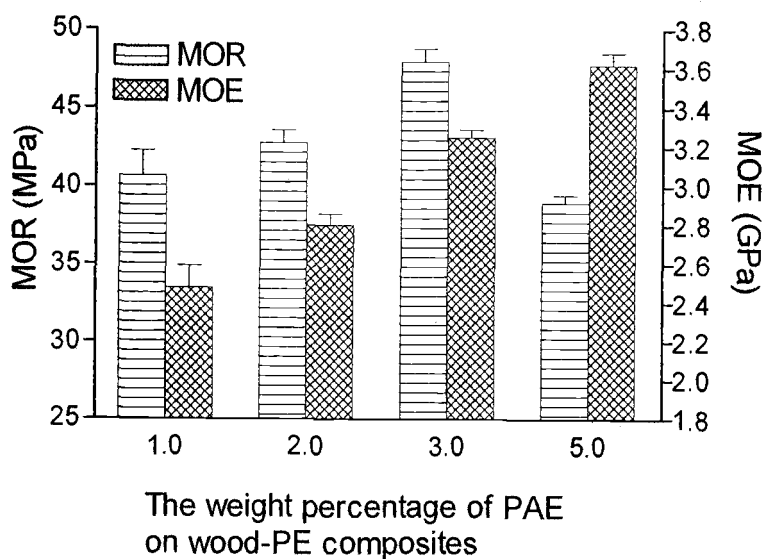


Fig. 3.2 Effect of the PAE dosage on MOR and MOE of wood-PE composites (Wood/PAE/stearic anhydride/PE weight ratio = 40/X/1/Y (X + Y = 59)). Data are the mean of at least ten replicates and the error bars represent one standard error of the mean.

For the wood-PE composites containing 3 wt% PAE, the MOR gradually increased with increasing stearic anhydride dosage from 1.0 wt % to 3.0 wt% (Fig. 3.3). The MOE at 1.0 wt% stearic anhydride was basically the same as that at 2.0 wt% stearic anhydride, and the MOE at 3.0 wt% stearic anhydride was higher than that at 1 wt% or 2 wt% (Fig. 3.3). However, the MOR of the wood-PE composites gradually decreased when the stearic anhydride dosage further increased from 3 wt% to 5 wt%. The MOE values at 3 wt% and 4 wt% stearic anhydride were statistically the same and were slightly higher than those at 5 wt%. Therefore, the PAE-stearic anhydride compatibilizer with 3 wt% PAE and 3 wt% stearic anhydride resulted in the highest MOR and MOE (Fig. 3.3).

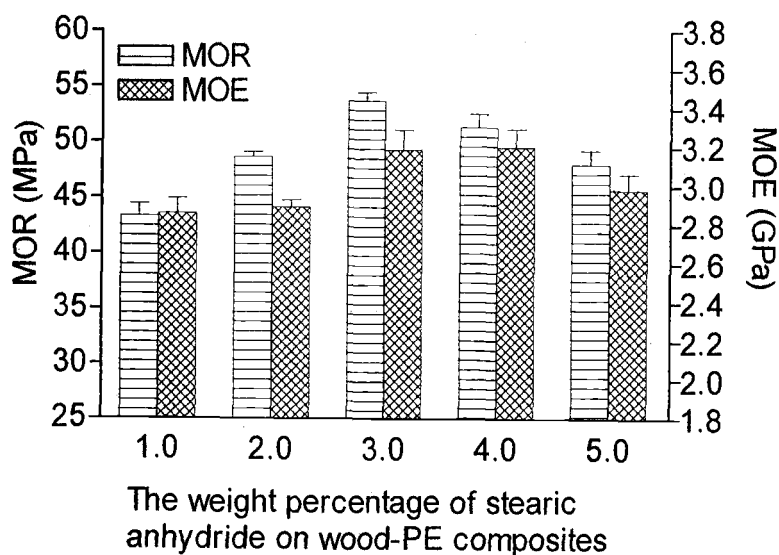


Fig. 3.3 Effect of stearic anhydride dosage on MOR and MOE of wood-PE composites (Wood/PAE/stearic anhydride/PE weight ratio = 40/3/X/Y ($X + Y = 57$)). Data are the mean of at least ten replicates and the error bars represent one standard error of the mean.

The PAE-stearic anhydride compatibilizer system was compared with MAPE for its compatibilization effects on wood-PE composites (Fig. 3.4). At a 2 wt% level, i.e., 1 wt% PAE plus 1 wt% stearic anhydride vs. 2 wt% MAPE, MAPE resulted in higher MOR and MOE than the PAE-stearic anhydride system (Fig. 3.4). However, at the 4 wt% level, i.e., 2 wt% PAE plus 2 wt% stearic anhydride vs. 4 wt% MAPE, the MOR with the PAE-stearic anhydride system was higher than that with MAPE, and the MOE values were statistically the same (Fig. 3.4). The MOR value of the PAE-stearic anhydride sample was much higher than that of MAPE when the two compatibilizers were compared at the 6 wt% level (Fig. 3.4). The MOR and MOE were much higher at 4 wt% MAPE than those at 2 wt% or 6

wt% MAPE. The MOR and MOE at 2 wt% PAE and 2% stearic anhydride were comparable to those at 3 wt% PAE and 3 wt% stearic anhydride (Fig. 3.4).

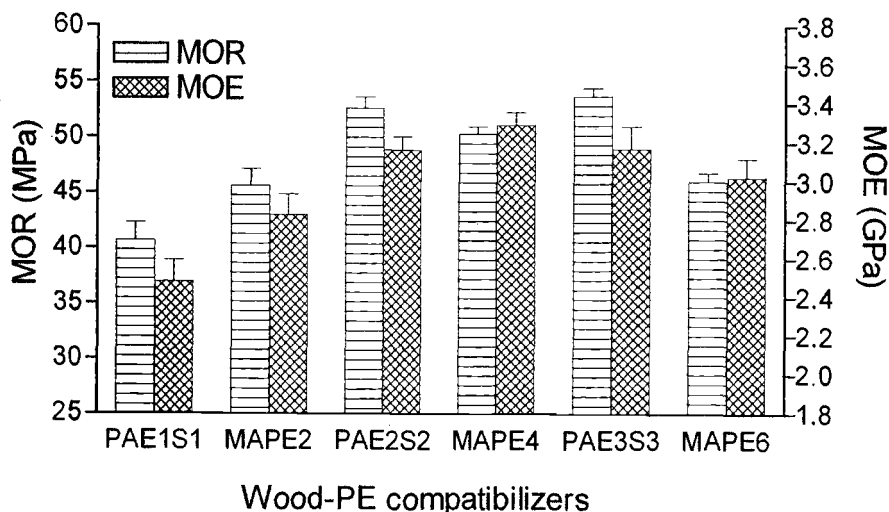


Fig. 3.4 Comparison of the PAE-stearic anhydride compatibilizer system with MAPE (Data are the mean of at least ten replicates and the error bars represent one standard error of the mean).

The water uptake of all the samples increased with increasing soaking time (Fig. 3.5). The wood-PE composites with 3 wt% PAE had the highest water-uptake percentages among all wood-PE composites studied (Fig. 3.5). However, a combination of PAE and stearic anhydride dramatically reduced the water-uptake percentages when compared with PAE alone. The wood-PE composites with the stearic anhydride and PAE-stearic anhydride compatibilizer system had similar water-uptake percentages and were more water-resistant than the control, i.e. the composites without any compatibilizer. MAPE resulted in the lowest water-uptake percentages.

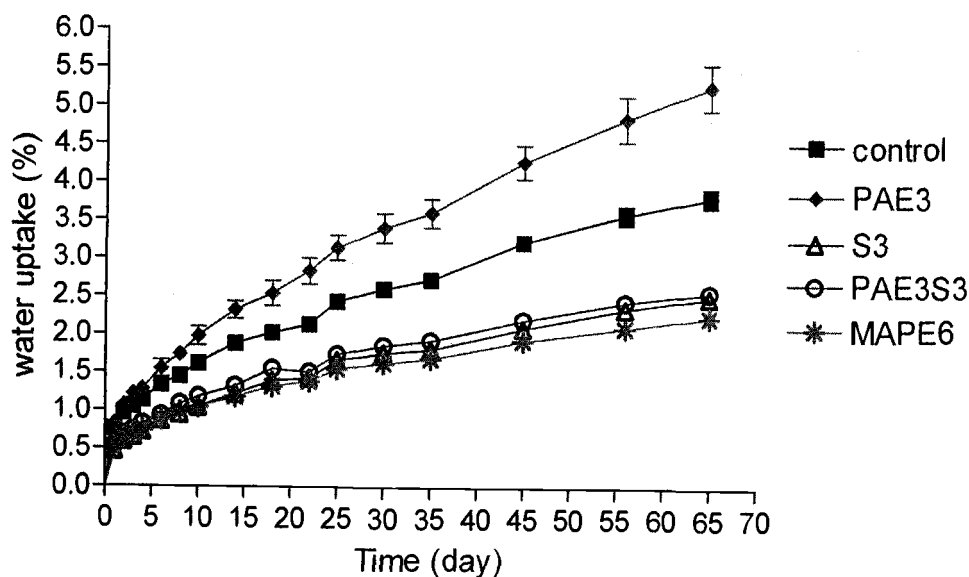


Fig. 3.5 Water-resistance test (Data are the means of five duplicates and the error bars present one standard error of the mean).

The HDPE used in this study was completely soluble in *p*-xylene above 100 °C. The modified Soxhlet extractor efficiently removed the PE in the wood-PE composites. Extensive studies revealed that the extraction for 48 h completely removed non-chemically bonded PE and stearic anhydride-related products (stearic anhydride, stearic acid, and stearic acid esters with low molecular weights) from the wood-PE composites. FTIR spectra of the extracted wood residues are shown in Fig. 3.6. The effects of compatibilizers on the properties of the extracted wood residues were better understood from subtracted FTIR spectra (Fig. 3.7). After subtracting the control, the FTIR spectrum of the residues with 3 wt% PAE (PAE3-control spectrum in Fig. 3.7) had weak absorbance peaks at 2920 cm^{-1} and 2850 cm^{-1} . The absorbance peaks at 2920 cm^{-1} and 2850 cm^{-1} in the S3-control FTIR

spectrum were stronger than those in the PAE3-control FTIR spectrum (Fig. 3.7). The PAE3S3-control FTIR spectrum had stronger absorbance peaks at 2920 cm^{-1} and 2850 cm^{-1} than the S3-control spectrum and the PAE3-control spectrum (Fig. 3.7). The expanded spectra between 1500 cm^{-1} and 1800 cm^{-1} from Fig. 3.7 are shown in Fig. 3.8. All three spectra (PAE3-control, S3-control, and PAE3S3-control) had weak absorbance peaks for the carbonyl group ($\text{C}=\text{O}$) of esters (Fig. 3.8). The S3-control spectrum lacked an absorbance peak for the carbonyl group ($\text{C}=\text{O}$) of amides. The absorbance peak of the amide $\text{C}=\text{O}$ for the PAE3S3-control spectrum was stronger than that for the PAE3-control spectrum (Fig. 3.8).

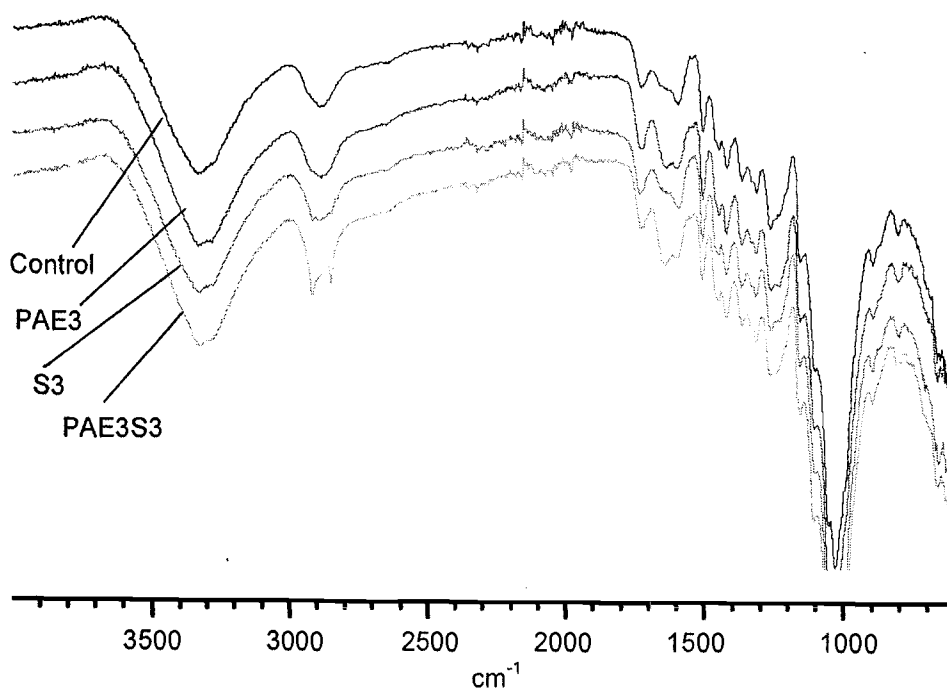


Fig. 3.6 FTIR spectra of extracted samples

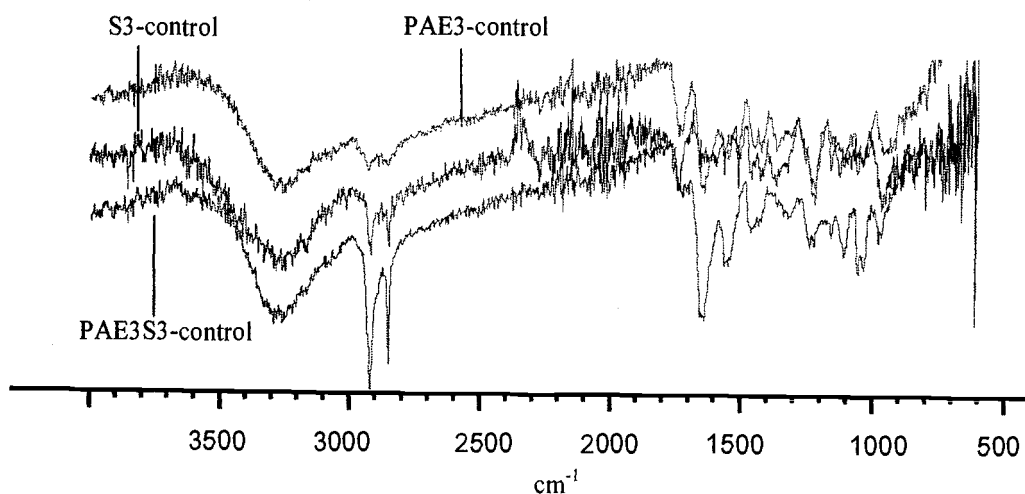


Fig. 3.7 FTIR spectra of extracted samples with control spectrum subtracted

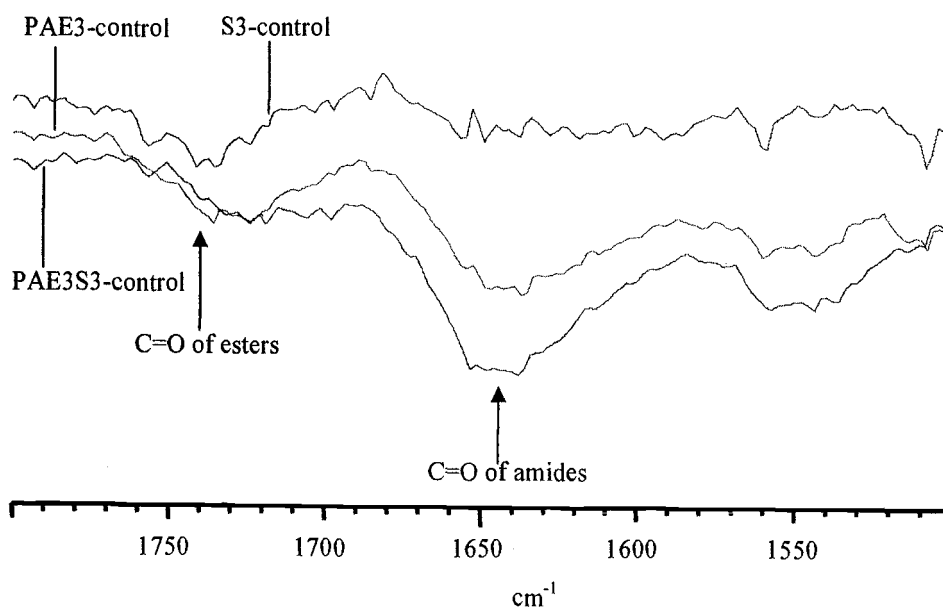


Fig. 3.8 Expanded FTIR spectra of extracted samples with control spectrum subtracted

3.6 DISCUSSION

As proposed in our previous study, the ability of the PAE-stearic anhydride system to improve the interfacial adhesion between wood and PE results from the following actions: 1) the PAE resin strengthens and stiffens wood fibers and serves as a wood-bonding domain; 2) the hydrocarbon chain of stearic anhydride forms entanglements or co-crystallizes with the matrix, serving as a PE-bonding domain; 3) the anhydride functional group of stearic anhydride reacts with PAE-bonded wood, thus linking the two domains together (Geng, Li et al. 2004).

When compared to the control, the *p*-xylene-extracted wood residues containing PAE as a compatibilizer had an additional relatively strong absorbance peak at $1600\text{--}1650\text{ cm}^{-1}$, representing the C=O group of the amide linkages in the PAE resin, and additional weak absorbance peaks at 2920 cm^{-1} and 2850 cm^{-1} , representing hydrocarbon (CH_2) groups from PAE resins (Figs. 3.7 and 3.8) (Crews, Rodríguez et al. 1998). These results indicated that PAE resins indeed bonded to wood, which is also consistent with results from the application of PAE as a paper wet-strength agent (Espy 1994, 1995). The extracted wood residues with stearic anhydride as a compatibilizer had additional absorbance peaks at 2920 cm^{-1} and 2850 cm^{-1} from the hydrocarbon groups of stearic anhydride and an additional absorbance peak of the carbonyl group of esters. This implies that stearic anhydride formed ester linkages with wood (see S3-control spectra in Figs. 3.7 and 3.8). The PAE3S3-control spectrum had stronger absorbance peaks for

hydrocarbon at 2920 cm^{-1} and 2850 cm^{-1} and stronger absorbance peaks for the C=O group of amides than the S3-control spectrum, which demonstrated that the extracted wood residues with PAE3S3 as a compatibilizer contained higher amount of covalently bonded stearic-anhydride-based products than those with S3 as a compatibilizer. The stronger absorbance of the carbonyl group of amides in the PAE3S3 FTIR spectrum suggested that amide linkages were likely formed from the reactions between stearic anhydride and PAE-bonded wood. All these results support the previously proposed compatibilization mechanism, except that there was no direct evidence of entanglement/co-crystallization between the hydrocarbon chain of stearic anhydride and the HDPE matrix.

In our previous study, the PAE solution was directly mixed with wood flour without adjusting its pH value. Our results in this study indeed showed that the resulting wood-PE composites had the highest strength at pH 10.4 (Fig. 3.1), which was consistent with results that the highest paper wet strength for the PAE resins develops around pH 10 (Espy 1994, 1995). As proposed in our previous study, the PAE resin evidently strengthens and stiffens the wood fibers through homopolymerization and covalent linkages with wood, thereby increasing the strength of the resulting composites. The hydroxy-azetidium (the cationic four-membered ring structure) is the key functional group for wet strength development in paper (Espy 1994, 1995; Espy and Rave 1988). The characteristic four-membered azetidium structure is fairly stable under acidic conditions at room temperature, but can react

with various nucleophiles at elevated temperatures to form various ring-opening structures. When the pH value is increased, the nucleophilicity of some nucleophiles also increases, resulting in faster reactions between the azetidium structure and the nucleophiles. However, the rate of the undesirable reaction between the azetidium structure and the hydroxyl group of sodium hydroxide would also increase with increasing pH values, which may explain the lower MOR and MOE at pH 11.7 when compared those at pH 10.4.

According to the previously proposed compatibilization mechanism, the dosage of the PAE resin and stearic anhydride would have a significant impact on the strength of the wood-PE composites. The amount of wood fibers being strengthened and stiffened would increase with increasing PAE dosage, which may explain why the strength (MOR) and the stiffness (MOE) of the wood-PE composites increased with increasing PAE dosage (Fig. 3.2). However, if too much PAE resin is added, the excess PAE resin might remain on the wood flour surface and become a weak interphase between wood and PE, resulting in lower strength. The results from Fig. 3.2 suggested that 3 wt% of PAE was optimal for strength.

The quantity of covalent linkages between stearic anhydride and the PAE-bonded wood should increase with increasing stearic anhydride dosage, thus increasing the interfacial strength, which may explain why the MOR and MOE

increased when the stearic anhydride dosage increased from 1 wt% to 3 wt%. However, if too much stearic anhydride is added, the excess stearic anhydride may serve as a plasticizer for the PE matrix or concentrate in and weaken the interphase between the PAE-bonded wood and PE, thus lowering the strength and stiffness of the wood-PE composites. That both MOR and MOE significantly decreased with increasing the stearic anhydride dosage appears to be in accord with this explanation (Fig. 3.3). It has generally been observed in our work on composites containing 40% wood filler that the loading becomes optimal somewhere in the range of 2 to 4%. Our hypothesis for this effect is that somewhere in this range the surface of the wood becomes saturated with the compatibilizer. The behavior of PAE and stearic anhydride confirms to this general hypothesis. Both PAE and stearic anhydride show improved performance up to 3% when added independently (Fig 3.2 and 3.3). Yet the combination of 3% PAE plus 3% stearic anhydride does not show a significant improvement over the 2% PAE + 2% stearic anhydride compatibilizer system. That both show improvement independently suggests that they are interacting with the wood surface up to this loading. However, the 3% PAE + 3% stearic anhydride system is higher than the optimum loading generally observed for compatibilizers. This suggests that both the PAE and SA are competing for sites on the wood surface, in addition to reacting with each other, and that the 3% PAE + 3% stearic anhydride system is “overloaded” in this sense.

PAE resin is a water-soluble polymer. It is plausible that the surface of PAE-bonded wood became more hydrophilic than wood, thus being able to adsorb more water than wood, which might explain why the water-uptake percentage for the wood-PE composites with PAE was higher than the control. Stearic anhydride was able to react with the hydroxyl groups and amino groups on the surface of the PAE-bonded wood, thus greatly reducing the water-uptake of the resulting wood-PE composites. The wood-PE composites with PAE3S3 indeed had much lower water-uptake percentages than the control and the composites with PAE3.

3.7 CONCLUSIONS

Adjustment of the pH value of the PAE solution from 5.0 to 10.4 increased the MOR of the resulting wood-PE composites. Optimization of the PAE and stearic anhydride dosages revealed that the MOR and MOE of the resulting wood-PE composites were the highest at 3 wt% PAE and 3 wt% stearic anhydride. At a low dosage level, i.e., 2 wt%, MAPE was superior to the PAE-stearic anhydride system. At the 4 wt% or 6 wt% levels, the PAE-stearic anhydride system resulted in the higher strengths for the resulting wood-PE composites. The MOR and MOE were higher at 4 wt% MAPE than those at 2 wt% or 6 wt% MAPE. An extraction method was successfully developed to remove PE from the wood-PE composites. Characterization of the *p*-xylene-extracted wood-PE composites demonstrated that stearic anhydride covalently bonded to wood and the PAE-bonded wood. The PAE-stearic anhydride compatibilizer system increased the water-resistance of the

resulting composites. However, this compatibilizer system was still slightly less effective than MAPE in increasing the water-resistance.

3.8 ACKNOWLEDGMENTS

We thank American Wood Fibers (Schofield, WI), BP Solvay Polyethylene North America (Houston, TX), and Hercules Inc. (Wilmington, DE) for donating wood flour, high-density polyethylene, and Kymene® 557H wet strength resin, respectively. This research was supported by a grant from the national research initiative competitive grants program of USDA.

3.9 REFERENCES

- Crews, P., J. Rodríguez and M. Jaspars (1998). Organic Structure Analysis, Oxford University Press, New York.
- Espy, H. H. (1994). "Alkaline-Curing Polymeric Amine-Epichlorohydrin Resins". in: Wet-Strength Resins and Their Application. L. L. Chan (Ed.), Tappi Press. Atlanta, GA **Ch. 2**: 13-44.
- Espy, H. H. (1995). "The Mechanism of Wet-Strength Development in Paper: A Review." TAPPI J. **78**(4): 90-99.
- Espy, H. H. and T. W. Rave (1988). "The Mechanism of Wet-Strength Development by Alkaline-Curing Amino Polymer-Epichlorohydrin Resins." TAPPI J. **71**(5): 133-137.
- Geng, Y., K. Li and J. Simonsen (2004). "Effects of a New Compatibilizer System on the Flexural Properties of Wood-Polyethylene Composite." J. Appl. Polym. Sci. **91**: 3667-3672.
- Morton, J., J. Quarmley and L. Rossi (2003). "Current and Emerging Applications for Natural and Woodfiber-Plastic Composites". The Seventh International Conference on Woodfiber-Plastic Composites, Forest Products Society, Madison, WI, 3-6.

CHAPTER 4: A COMBINATION OF POLY(DIPHENYLMETHANE
DIISOCYANATE) AND STEARIC ANHYDRIDE AS A NOVEL
COMPATIBILIZER FOR WOOD-POLYETHYLENE COMPOSITES

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4.1 ABSTRACT

A combination of poly(diphenylmethane diisocyanate) (PMDI) and stearic anhydride was investigated as a new compatibilizer system for improving the interfacial adhesion between wood and polyethylene (PE). The treatment of wood flour with PMDI increased both the modulus of rupture (MOR) and the modulus of elasticity (MOE) of the resulting wood-PE composites. The combination of stearic anhydride and PMDI further increased both MOR and MOE of the resulting composites. Compared with the commercially used compatibilizer maleic anhydride-grafted polyethylene (MAPE), the PMDI-stearic anhydride compatibilizer system resulted in significantly higher MOR and MOE. The moisture content of wood flour affected the compatibilization of both the PMDI-stearic anhydride compatibilizer system and MAPE. The compatibilization mechanisms of PMDI-stearic anhydride system were investigated in detail. Water-resistance tests indicated that the composites with the PMDI-stearic anhydride system were statistically more water-resistant than those with MAPE.

4.2 KEYWORDS

Compatibilizer; PMDI; wood; polyethylene; stearic anhydride; wood-plastic composites

4.3 INTRODUCTION

Wood-plastic composites (WPCs) have many superior properties when compared with wood or plastics (Clemons 2002; Morton, Quarmley et al. 2003). WPCs have become one of the fastest growing sectors in the wood composites industry. However, WPCs are made from two incompatible partners: hydrophilic wood and hydrophobic plastics. A coupling agent (commonly called compatibilizer) is normally added in the production of WPCs. An effective compatibilizer should have capacity of bonding both wood and plastic. In other words, an effective compatibilizer should contain two domains: a wood-binding domain able to bond to wood and a plastic-binding domain able to bond to plastic. A number of compatibilizers have been investigated (Bledzki and Faruk 2003; Coutinho and Costa 1999; Djiporovic, Dingova et al. 2003; Geng, Li et al. 2004; Lu, Wu et al. 2000; Maldas, Kokta et al. 1989; Nitz, Reichert et al. 2000; Raj, Kokta et al. 1989; Zhang, Li et al. 2004). However, most compatibilizers studied so far are not very effective in improving the strength and stiffness of the resulting WPCs, and some compatibilizers only have wood-binding capacities. Overall, the number of effective compatibilizers is limited.

Poly(diphenylmethane diisocyanate) (PMDI) is a widely used adhesive in the wood composites industry (Frink and Sachs 1981; Frisch and Rumao 1983; Johnson 2000; Sellers 2001). PMDI penetrates wood well. The isocyanate group in PMDI is reactive to nucleophiles such as hydroxyl groups, amino groups and

carboxylic acid groups (Bao, Daunch et al. 2003; Frink and Sachs 1981; Frisch and Rumao 1983). When reacted with water, the isocyanate group in PMDI decomposes to form an amine that can further react with additional isocyanate groups to form a urea structure. The isocyanate group also can react with hydroxyl groups in wood to form urethane structures. When it is mixed with wood flour, PMDI penetrates and forms a highly crosslinked network, which strengthens the wood particles. Therefore, PMDI should be able to serve as a wood-binding domain. Stearic anhydride contains a long hydrocarbon chain that has the identical structure as polyethylene (PE) and may form co-crystalline structure and/or entanglements with PE. The hydrocarbon chain of stearic anhydride may be able to serve as effective PE-binding domain. The anhydride group of stearic anhydride may bond to wood or PMDI-treated wood, thus linking the wood-binding domain and the PE-binding domain together.

In this study, we investigated a combination of PMDI and stearic anhydride as a compatibilizer for wood-PE composites. The compatibilization mechanisms of this new compatibilizer were investigated in detail.

4.4 EXPERIMENTAL

4.4.1 MATERIALS

Pine flour (40 mesh and 2.04 wt% moisture content) was provided by American Wood Fibers (Schofield, WI). This flour was re-dried under reduced pressure (60

kPa, absolute) at 60 °C for 20 h prior to use. The moisture content of the re-dried wood flour was 1.0%. HDPE (high density polyethylene) (melt flow index: 0.55 g/10 min) was provided by BP Solvay Polyethylene North America (Houston, TX). PMDI was provided by Huntsman Polyurethanes (West Deptford, NJ). MAPE (maleic anhydride-grafted polyethylene, A-C OptiPakTM 200) was donated by Honeywell International, Inc. (Morristown, NJ). Stearic anhydride and *p*-xylene were purchased from Acros Organics (Morris Plains, NJ).

4.4.2 PREPARATION OF WOOD-PE BLENDS

Dry wood flour and HDPE powder with or without a compatibilizer were mixed in a Brabender Plasticorder with a mixing bowl attached (C. W. Brabender Instruments, Inc., South Hackensack, NJ). The blending procedure depended on the composition being prepared.

Blending procedure A: This procedure was used for making wood-PE blends without a compatibilizer. The bowl of the Brabender Plasticorder was preheated to 120 °C and the speed of the rotor in the bowl was set to 100 rpm. Wood flour (17.60 g) was added and mixed for 10 min. The bowl temperature was then raised to 170 °C and HDPE (26.40 g) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Blending procedure B: This procedure was used for making wood-stearic anhydride-PE and wood-MAPE-PE blends. The following is an example used to prepare wood-PE composites with a wood/stearic anhydride/PE weight ratio of 40/0.5/59.5. The bowl was preheated to 120 °C and the rotor speed was set to 100 rpm. Wood flour (17.60 g) was then added to the bowl. After the bowl temperature returned to 120 °C, stearic anhydride (0.22 g) was added and mixed for 10 min. The bowl temperature was then raised to 170 °C and HDPE (26.18 g) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Blending procedure C: This procedure was used for preparing wood-PE blends with PMDI. The following is an example used to prepare wood-PE composites with a wood/PMDI/PE weight ratio of 40/0.5/59.5. PMDI (0.22 g) was added dropwise into wood flour (17.60 g) under a nitrogen atmosphere and mixed well by mechanical stirring. The resulting wood-PMDI mixture was added to the preheated Brabender bowl at 120 °C and 100 rpm, and mixed for 10 min. The bowl temperature was then raised to 170 °C and HDPE (26.18 g) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Blending procedure D: This procedure was used for preparing wood-PE blends with a PMDI-stearic anhydride compatibilizer. The following is an example

used to prepare wood-PE composites with a wood/PMDI/stearic anhydride/PE weight ratio of 40/1.5/0.5/58. Wood flour (17.60 g) and stearic anhydride (0.22 g) were mixed together. PMDI (0.66 g) was added dropwise to the mixture of wood and stearic anhydride under a nitrogen atmosphere and mixed well by mechanical stirring. The resulting wood-stearic anhydride-PMDI mixture was added to the preheated Brabender bowl at 120 °C and 100 rpm, and mixed for 10 min. The bowl temperature was then raised to 170 °C and HDPE (25.52 g) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

4.4.3 PROCEDURE FOR MOLDING COMPOSITES FROM BLENDS

A stainless steel mold with dimensions of 101.6 x 101.6 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 a well-mixed wood-PE sample, placed on the lower platen of the Carver press and pre-heated for 10 min. The press was closed slowly allowing the wood-plastic to flow into the mold shape. The press pressure was raised from 35 to 345 kPa in 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 in a cold press at 345 kPa under ambient conditions. The resulting wood-PE board was cut into 10 small test specimens. Each specimen was 54.50-56.50 mm long, 13.00-14.30 mm wide, and 2.10-2.40 mm thick.

4.4.4 MECHANICAL TESTS

Twenty specimens were tested for each wood-PE composite prepared in section 4.4.3 in accordance with ASTM D790-02. Three-point bending test was applied on all of the specimens. The specimens were tested on a Sintech 1/G machine (MTS Systems Corporation, Enumclaw, WA) and the load-deflection curves determined. The support span was 43 mm and the crosshead speed was 1.0 mm/min. The modulus of rupture (MOR) and modulus of elasticity (MOE) were calculated from the load-deflection data. The MOR was defined as the first point on the load-deflection curve to show a slope of zero. The MOE was determined from the slope in the initial elastic region of the load-deflection curve.

4.4.5 WATER-RESISTANCE TEST

Five specimens of each WPC sample were used for the water-resistance test. All the specimens were pre-weighed and then soaked in deionized water at room temperature. The specimens were removed from the water, wiped with a tissue paper, and then weighed every 24 h for the first five days. The specimens were resoaked in the water right after weighed. And then they were weighed at longer time intervals until day 100. The water uptake percentage was determined as the weight gain divided by the dry weight of the specimen.

4.4.6 INVESTIGATION OF COVALENT LINKAGES BETWEEN COMPATIBILIZERS AND WOOD IN WOOD-PE COMPOSITES

The following four wood-PE composites were investigated: the composite without any compatibilizer (control), the composite with 1.5 wt% PMDI, the composite with 0.5 wt% stearic anhydride, and the composite with 1.5 wt% PMDI and 0.5 wt% stearic anhydride. The wood-PE composites were cut into small pieces by a fodder chopper and then wrapped in a piece of filter paper. Soluble constituents were extracted from the wrapped wood-PE composites by *p*-xylene in a modified Soxhlet extractor for 48 h. The thimble holder of the Soxhlet extractor was wrapped with a heating tape and heated to maintain the temperature of the solution in the holder at about 120 °C. The extracted residue was dried at 103 °C for 24 h and then was characterized by Fourier Transform Infrared spectrometry (FTIR). 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.

4.4.7 ANALYSIS OF THE FRACTURED SURFACES OF WOOD-PE COMPOSITES WITH SCANNING ELECTRON MICROSCOPY (SEM)

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

4.5 RESULTS

4.5.1 EFFECTS OF TREATMENT ON PROCESSING

At higher PMDI dosages, the wood-PE composite material did not flow well during the compression molding, and thus a uniform composite board could not be obtained when the PMDI dosage was 2 wt%.

4.5.2 MECHANICAL PROPERTIES

Both MOR and MOE of the resulting composites gradually increased when the PMDI dosage was increased from 0.5 wt% to 1.5 wt% (Fig. 4.1).

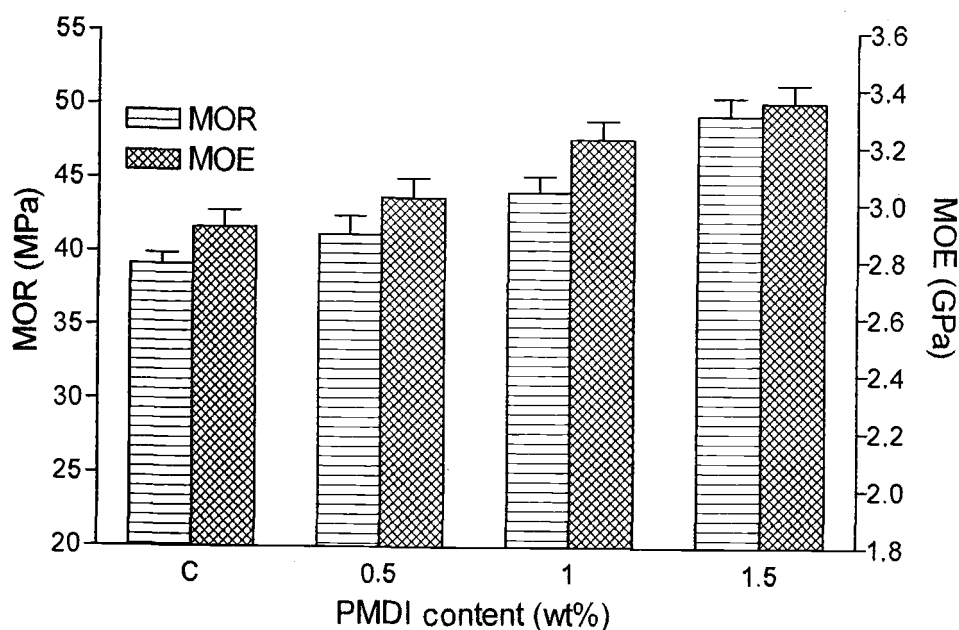


Fig. 4.1 Effect of the PMDI dosage on MOR and MOE of wood-PE composites (C: wood/PE weight ratio = 40/60; wood/PMDI/PE weight ratio = 40/X/Y ($X+Y=60$)). Data are the means of twenty replicates and the error bars represent one standard error of the means.

The MOR of the wood-PE composites increased when the stearic anhydride dosage was increased from 0.5 wt% to 2 wt% (Fig. 4.2). The MOR of the wood-PE composites with 0.5 wt% and 1.0 wt% stearic anhydride was statistically the same as that of the control at a 95% confidence level (Fig. 4.2). The MOR of the wood-PE composite with 2.0 wt% stearic anhydride was higher than that of the control (Fig. 4.2). There was no statistically significant change in the MOE values of any of the wood-PE composites when the stearic anhydride dosage was increased from 0.5 wt% to 2 wt% (Fig. 4.2).

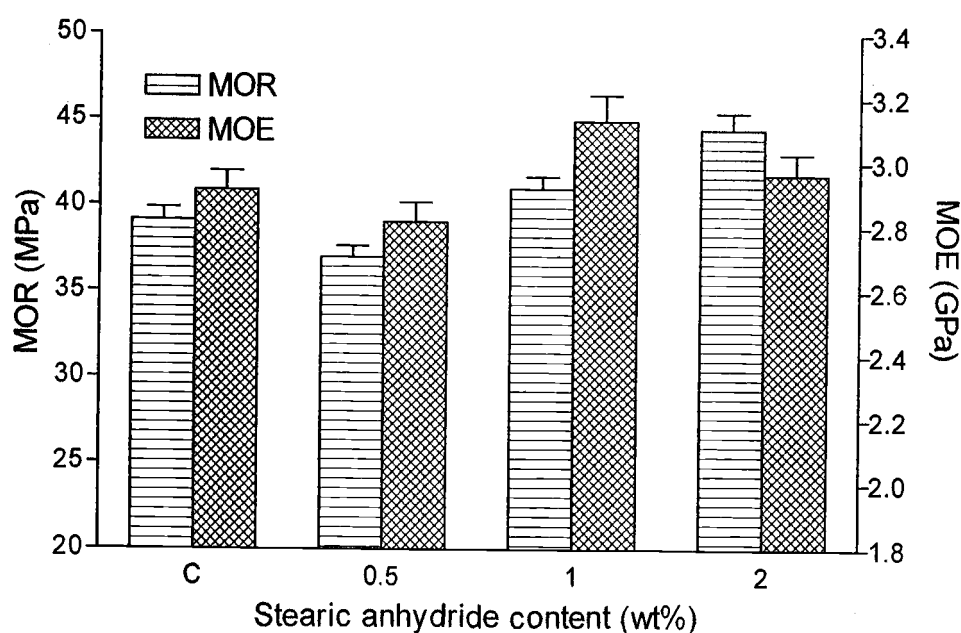


Fig. 4.2 Effect of the stearic anhydride dosage on MOR and MOE of wood-PE composites (C: wood/PE weight ratio = 40/60; wood/stearic anhydride/PE weight ratio = 40/X/Y ($X+Y=60$)). Data are the means of twenty replicates and the error bars represent one standard error of the means.

For the wood-PE composites containing 1.5 wt% PMDI, both MOR and MOE gradually increased when the stearic anhydride dosage was increased from 0.25 wt% to 0.5 wt% (Fig. 4.3). When the stearic anhydride dosage was further increased from 0.5 wt% to 2 wt%, the MOR gradually decreased. The MOE decreased when the stearic anhydride dosage was increased from 0.5 wt% to 1.0 wt%. However, the MOE remained the same when the stearic anhydride dosage was further increased from 1.0 wt% to 2.0 wt%. The highest MOR and the highest MOE were obtained when a combination of 1.5 wt% PMDI and 0.5 wt% stearic anhydride was used.

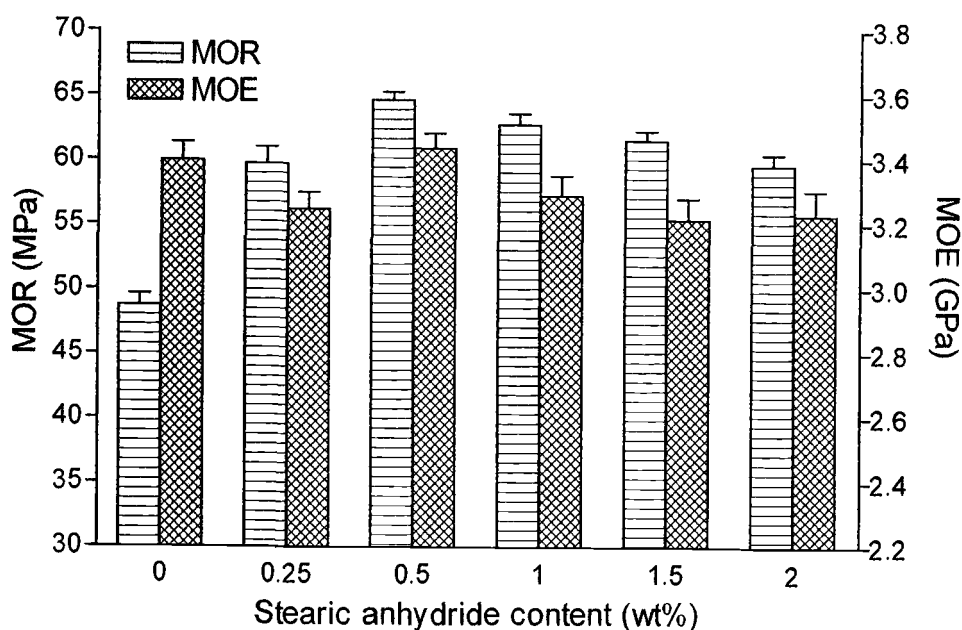


Fig. 4.3 Effect of the stearic anhydride dosage on MOR and MOE of wood-PE composites (Wood/PMDI/stearic anhydride/PE weight ratio = 40/1.5/X/Y (X + Y = 58.5)). Data are the means of twenty replicates and the error bars represent one standard error of the means.

When the wood flour was used as received, the resulting wood-PE composites (C-a, PS-a, and M-a in Fig. 4.4) had much lower strength and stiffness than those made from the re-dried wood flour (C-b, PS-b, and M-b in Fig. 4.4), i.e., $C-b > C-a$, $PS-b > PS-a$, and $M-b > M-a$. More specifically, for the wood-PE composites without a compatibilizer (C-a vs. C-b in Fig. 4.4), re-drying of the wood flour increased the MOR by 20% and the MOE by 33%. For wood-PE composites containing PMDI-stearic anhydride as a compatibilizer system (PS-a vs. PS-b in Fig. 4.4), re-drying of the wood flour also increased the MOR by 32%, whereas the MOE remained statistically the same. For wood-PE composites with MAPE (M-a vs. M-b in Fig. 4.4), re-drying of the wood flour increased the MOR by 12% and the MOE by 10%. When the wood flour was used as received, the combination of 1.5 wt% PMDI and 0.5 wt% stearic anhydride (PS-a in Fig. 4.4) resulted in statistically the same MOR as 2 wt% MAPE (M-a in Fig. 4.4). However, the MOE for the combination of 1.5 wt% PMDI and 0.5 wt% stearic anhydride (PS-a in Fig. 4.4) was significantly higher than that of 2 wt% MAPE (M-a in Fig. 4.4).

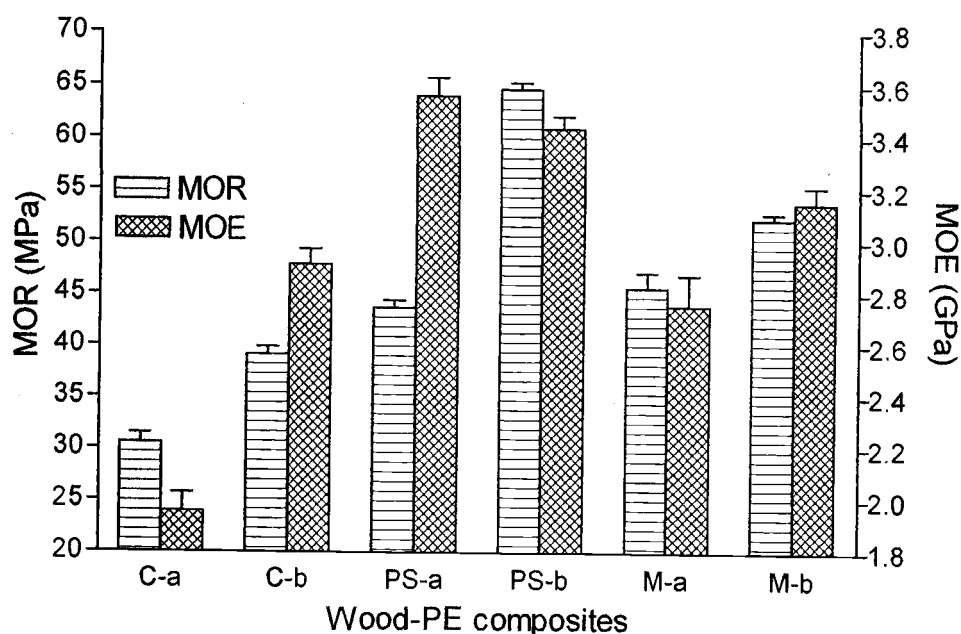


Fig. 4.4 Effect of moisture content on wood-PE composites (a: wood flour was not re-dried before use; b: wood flour was re-dried before use. C: wood/PE weight ratio = 40/60; PS: wood/PMDI/stearic anhydride/PE weight ratio = 40/1.5/0.5/58; M: wood/MAPE/PE weight ratio = 40/2/58). Data are the means of twenty replicates and the error bars represent one standard error of the means.

At the 2 wt% level, the combination of 1.5 wt% PMDI and 0.5 wt% stearic anhydride (PS-b in Fig. 4.4) resulted in an approximately 20% higher MOR and about a 10% higher MOE than 2 wt% MAPE (M-b in Fig. 4.4). When compared to the control (C-b), the combination of 1.5 wt% PMDI and 0.5 wt% stearic anhydride (PS-b in Fig. 4.4) increased the MOR by 60 % and the MOE by 15 %.

4.5.3 WATER-RESISTANCE TEST

The water-uptake percentages of all wood-PE composites increased with increased soaking time (Fig. 4.5). The wood-PE composite without a compatibilizer, i.e., the

control, had the highest water-uptake percentage at the same soaking time among all wood-PE composites investigated. At the same soaking time, wood-PE composites with stearic anhydride (S0.5 in Fig. 4.5) had a lower water-uptake percentage than the control. When PMDI was used alone, the water-uptake percentage of the resulting composites (P1.5 in Fig. 4.5) at the same soaking time was much lower than that of the composites with stearic anhydride (S0.5 in Fig. 4.5). The combination of PMDI and stearic anhydride (P1.5S0.5 in Fig. 4.5) resulted in slightly lower water-uptake percentage at the same soaking time than PMDI alone (P1.5 in Fig. 4.5). Both PMDI (P1.5 in Fig. 4.5) and the combination of PMDI and stearic anhydride (P1.5S0.5 in Fig. 4.5) yielded slightly lower water uptake percentages than MAPE2.

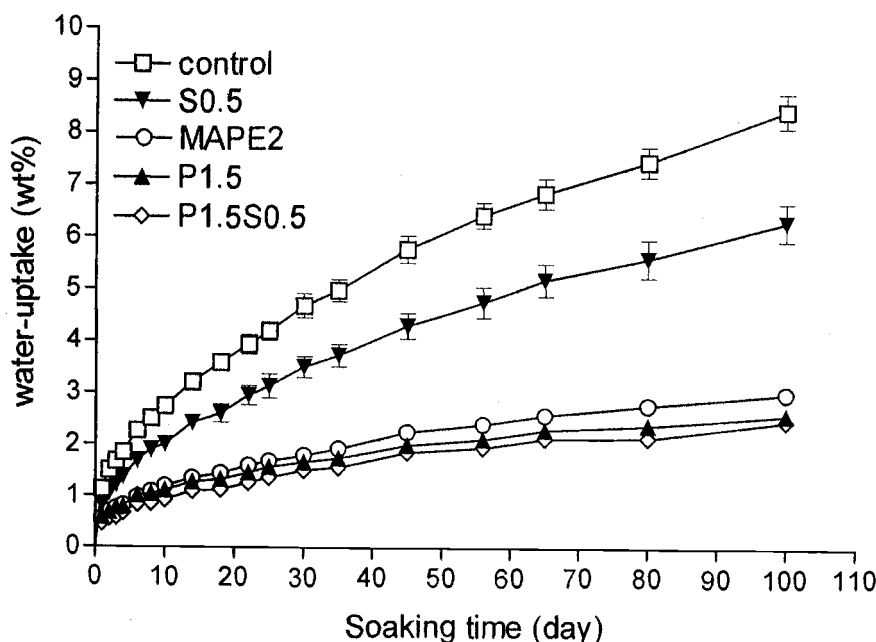


Fig. 4.5 Water-resistance test (Control: wood/PE weight ratio = 40/60; S0.5: wood/stearic anhydride/PE weight ratio = 40/0.5/59.5; MAPE2: wood/MAPE/PE weight ratio = 40/2/58; P1.5: wood/PMDI/PE weight ratio = 40/1.5/58.5; P1.5S0.5: wood/PMDI/stearic anhydride/PE weight ratio = 40/1.5/0.5/58). Data are the means of five duplicates and the error bars represents two standard errors of the means.

4.5.4 INVESTIGATION OF COVALENT LINKAGES BETWEEN COMPATIBILIZERS AND WOOD

p-Xylene dissolves the PE used in this study at temperature above 100 °C. Initial studies on the wood-PE composites without a compatibilizer revealed that extraction of the composites with *p*-xylene using a modified Soxhlet extractor for 48 h completely removed the PE from the composites. FTIR spectra of the extracted wood residues are shown in Fig. 4.6. The evidence for possible covalent linkages between the compatibilizer and wood is more apparent in the subtracted FTIR spectra (Fig. 4.7). Hydrocarbons (CH₃, CH₂ or CH) have characteristic

absorbance peaks at 2920 and 2860 cm^{-1} (Crews, Rodríguez et al. 1998). The FTIR spectrum of S0.5-control (the spectrum of the 0.5% stearic anhydride composite with control spectrum subtracted) showed weak absorbance peaks at 2920 and 2860 cm^{-1} , indicating that some stearic anhydride had bonded to wood in the S0.5 sample and could not be removed in the hot *p*-xylene extraction. Stronger absorbance peaks at 2920 and 2860 cm^{-1} were observed when 2 wt% rather than 0.5 wt% stearic anhydride was used (spectrum not shown). The FTIR spectrum of P1.5S0.5-control had much stronger absorbance peaks at 2920 and 2860 cm^{-1} , implying that the more stearic hydride had bonded to wood in the P1.5S0.5 sample than in the S0.5 sample (Fig. 4.7). Both S0.5-control and P1.5S0.5-control showed a strong absorbance peak at 1730 cm^{-1} , representing the C=O ester group. Both P1.5-control and P1.5S0.5-control had strong absorbance peaks at 1700 and 1600 cm^{-1} , representing C=O urea and urethane groups (Crews, Rodríguez et al. 1998).

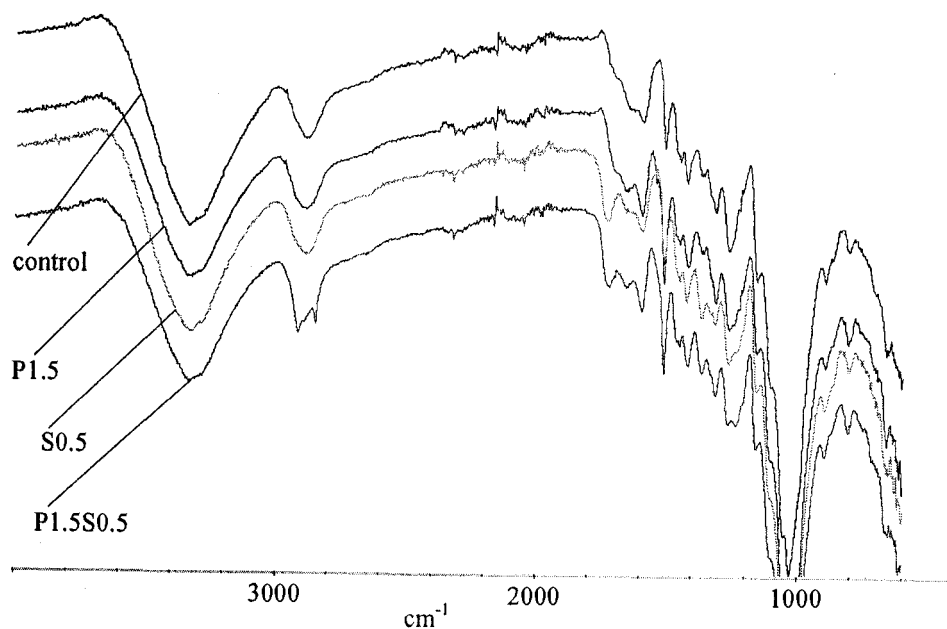


Fig. 4.6 FTIR spectra of extracted samples (Control: wood/PE weight ratio = 40/60; P1.5: wood/PMDI/PE weight ratio = 40/1.5/58.5; S0.5: wood/stearic anhydride/PE weight ratio = 40/0.5/59.5; P1.5S0.5: wood/PMDI/stearic anhydride/PE weight ratio = 40/1.5/0.5/58).

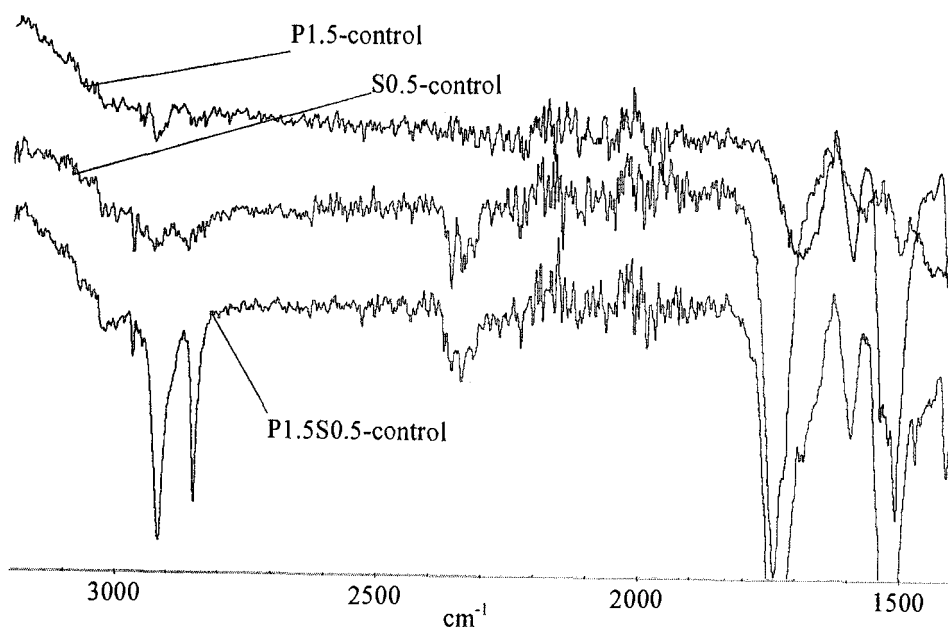


Fig. 4.7 FTIR spectra of extracted samples with control spectrum subtracted (P1.5: wood/PMDI/PE weight ratio = 40/1.5/58.5; S0.5: wood/stearic anhydride/PE weight ratio = 40/0.5/59.5; P1.5S0.5: wood/PMDI/stearic anhydride/PE weight ratio = 40/1.5/0.5/58).

4.5.5 MICROSCOPY ANALYSIS

Objective interpretation of SEM images can be complicated due to the difficulty of observing a truly representative portion of the sample. We have included SEM images in Figure 4.8 which we feel are representative of our observations in the SEM. Presenting detailed images of the entire surface that was examined would require too much space. The images included herein are not intended to be conclusive proof, simply examples of what was observed in the SEM. Our discussion of these images is based upon the examination of the total fractured area of the sample, not just the images presented here. We include SEM images only as supporting data. An SEM picture of the fractured surface of the control is shown in

Fig 4.8a. Large gaps were observed between the wood particles and the PE matrix, indicating poor adhesion between wood particles and the PE matrix. For the S0.5 sample, a protruding wood fiber was observed to be fairly clean, i.e. free of adhered plastic (Fig. 4.8b). There were also voids and surface depressions that presumably resulted from fiber pullout. For the P1.5 sample, large gaps between wood particles and the PE matrix were also observed, along with voids created by fiber pullout (Fig. 4.8c). For the P1.5S0.5 sample, no visible gaps between wood particles and the PE matrix were found, and only a few voids were observed on the fractured surface (Fig. 4.8d).

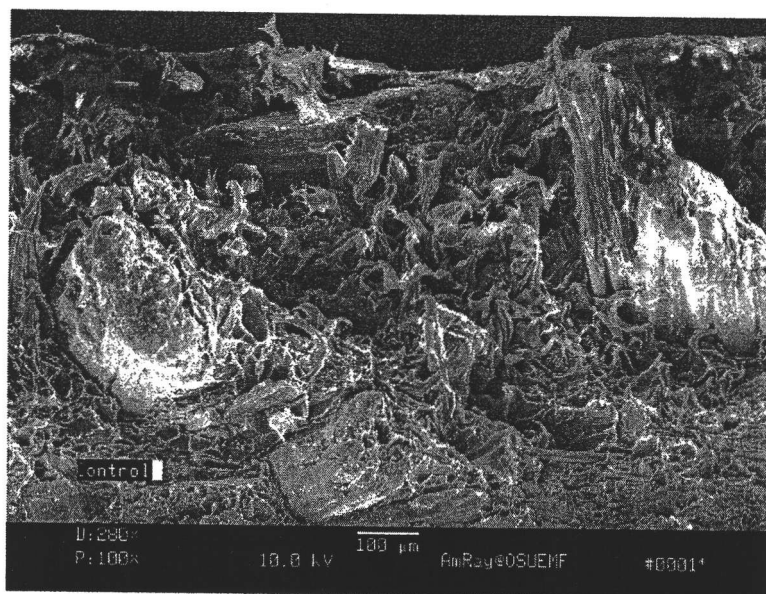


Fig. 4.8a SEM pictures of fractured surfaces of wood-PE composite samples (Control: wood/PE weight ratio = 40/60)

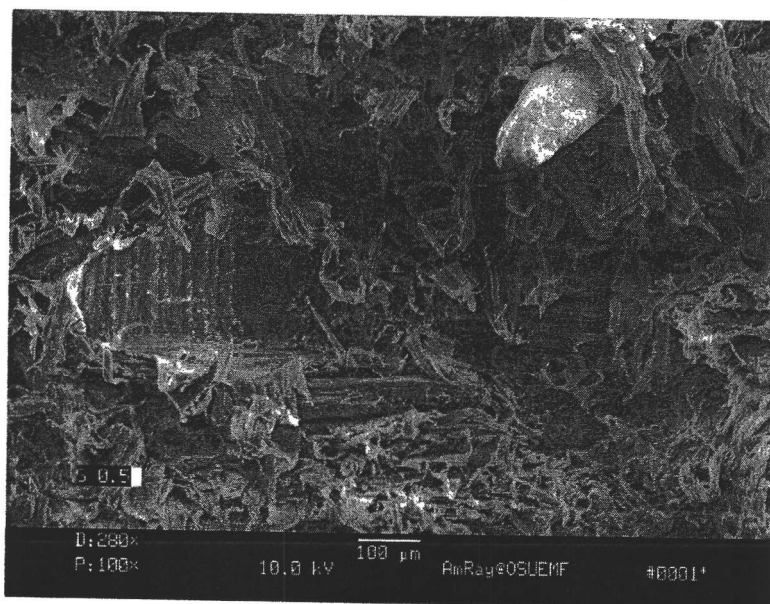


Fig. 4.8b SEM pictures of fractured surfaces of wood-PE composite samples (S0.5: wood/stearic anhydride/PE weight ratio = 40/0.5/59.5)

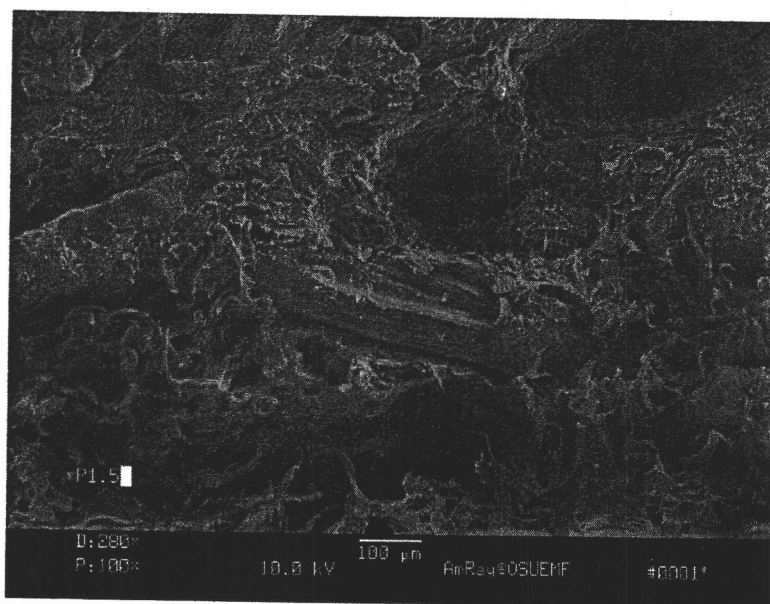


Fig. 4.8c SEM pictures of fractured surfaces of wood-PE composite samples (P1.5: wood/PMDI/PE weight ratio = 40/1.5/58.5)

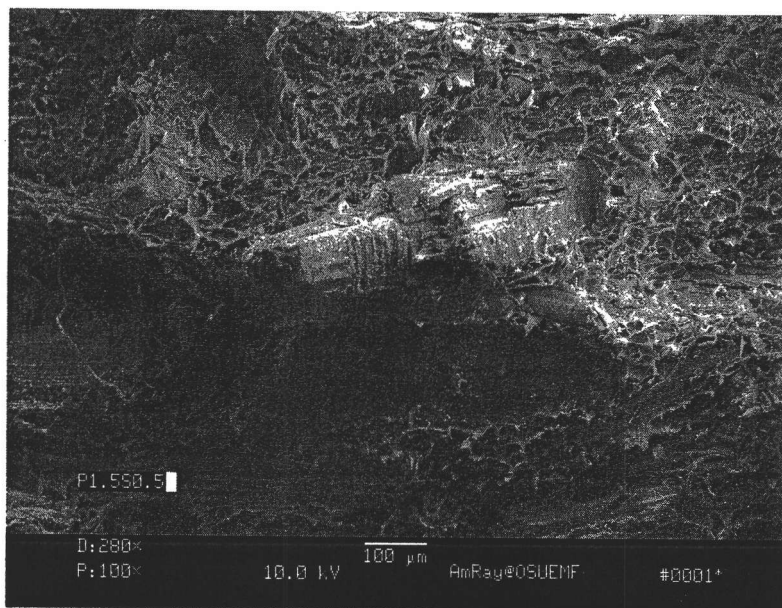


Fig. 4.8d SEM pictures of fractured surfaces of wood-PE composite samples (P1.5S0.5: wood/PMDI/stearic anhydride/PE weight ratio = 40/1.5/0.5/58)

4.6 DISCUSSION

The FTIR spectrum of the *p*-xylene-extracted P1.5-control sample had two extra peaks at 1600 and 1700 cm^{-1} that correspond to C=O groups of urea or urethane. These peaks indicate that PMDI had bonded to wood. Theory predicts that stronger fillers enable stronger composites. The ability of PMDI to bond to wood and thereby strengthen wood particles might explain why both MOR and MOE increased when PMDI was used (Fig. 4.1). When the dosage of PMDI increased, the amount of wood particles that were consolidated and strengthened might also increase. This would explain the further increase in both MOR and MOE of the wood-PE composites. The SEM picture of the fractured P1.5 sample shows poor adhesion between wood particles and the PE matrix. Therefore, the improvement

of the strength and stiffness of the wood-PE composites by PMDI might be mainly due to the strengthening of the wood particles rather than the improvement of the interfacial adhesion between the wood particles and the PE matrix. The cured PMDI networks might prevent water from penetrating the wood. This would account for the improved water resistance of the wood-PE composites containing PMDI.

The additional absorbance peak at 1730 cm^{-1} ($\text{C}=\text{O}$ group of esters) and the weak absorbance peaks at 2920 cm^{-1} and 2860 cm^{-1} (characteristic hydrocarbon absorbance peaks) in the FTIR spectrum of S0.5-control suggest that some stearic anhydride had formed ester linkages with wood (Fig. 4.7). The hydrocarbon chain of the wood-bonded stearate might form entanglements or co-crystalline structures with the PE matrix, and thereby improve the interfacial adhesion. The weak hydrocarbon absorbance peaks (S0.5-control in Fig. 4.7) suggest that the amount of stearate bonded to wood was small, and the SEM picture of the fractured S0.5 sample also indicates poor adhesion between the wood particles and the PE matrix. All these agree with the fact that 0.5 wt% stearic anhydride resulted in little increase in the MOR and MOE when compared with the control. Stronger hydrocarbon peaks were observed for the wood-PE composites with 2 wt% stearic anhydride (spectrum not shown), indicating that more stearic anhydride had bonded to wood. This may explain why the wood-PE composites with 2 wt% stearic anhydride had a slightly higher MOR and MOE than the control. The stearate

bonded to wood makes the wood more hydrophobic, thus preventing water from penetrating the wood. This may explain why the wood-PE composites containing stearic anhydride absorbed less water than the control at the same soaking time.

The hydrocarbon absorbance peaks at 2920 cm^{-1} and 2860 cm^{-1} in the P1.5S0.5-control FTIR spectrum were much stronger than those in the S0.5-control FTIR spectrum (Fig. 4.7). This implies that the amount of the bonded stearate in the P1.5S0.5 sample was much higher than that in the S0.5 sample. Why more stearic anhydride had reacted with wood in the presence of PMDI is still poorly understood. One of the possible explanations is that PMDI absorbed residual moisture in the wood, thus preventing stearic anhydride from hydrolysis by moisture, thereby making it more available for reaction with wood hydroxyls. This explanation is consistent with the observation that re-drying of the wood flour prior to use greatly increased the strength of the resulting wood-PE composites for the same compatibilizer system (Fig. 4.4). The increased concentration of wood-bonded stearate would be expected to improve the interfacial adhesion between wood and the PE matrix, and this was indeed observed. The SEM picture of the fractured surface of the P1.5S0.5 sample showed strong interfacial adhesion. Therefore, the superior strength and stiffness of the P1.5S0.5 sample was a result of the strong interfacial adhesion and the strengthening of wood particles by the compatibilizer system.

In the presence of 1.5 wt% PMDI, the amount of the wood-bonded stearate increased with increasing stearic anhydride dosage. This may explain why both the MOR and MOE increased when the stearic anhydride dosage increased from 0.25 wt% to 0.5 wt% (Fig. 4.3). However, if too much stearic anhydride is added, the excessive stearic anhydride may concentrate in the interphase between the wood particles and the PE matrix, thus weakening the interfacial adhesion. Free stearic anhydride may also serve as a plasticizer for the PE matrix. These suppositions may explain why the MOR gradually decreased when the stearic anhydride dosage was increased from 0.5 wt% to 2 wt% (Fig. 4.3).

4.7 CONCLUSIONS

Treatment of wood flour with PMDI slightly increased both MOR and MOE of the resulting wood-PE composites. Combinations of PMDI and stearic anhydride further increased the MOR and MOE of the composites. At the 2 wt% dosage level, a PMDI-stearic anhydride compatibilizer system was superior to commercially available MAPE with respect to increasing strength and stiffness. The improved strength and stiffness of the wood-PE composites by a PMDI-stearic anhydride compatibilizer system likely resulted from both improved interfacial adhesion and strengthened wood particles. Analysis of *p*-xylene-extracted wood-PE composites with FTIR revealed that stearic anhydride formed ester linkages with wood and PMDI-treated wood. The fractured surface of the composites revealed the strong interfacial adhesion between wood particles and the PE matrix

in the wood-PE composites containing a PMDI-stearic anhydride compatibilizer. Moisture in the wood flour reduced the efficacy of the compatibilizers. The PMDI-stearic anhydride compatibilizer system significantly reduced the water-uptake of the resulting wood-PE composites when compared with MAPE.

4.8 ACKNOWLEDGMENTS

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4.9 REFERENCES

- Bao, S., W. A. Daunch, Y. Sun, P. L. Rinaldi, J. J. Marcinko, and C. Phanopoulos (2003). "Solid state two-dimensional NMR studies of polymeric diphenylmethane diisocyanate (PMDI) reaction in wood." *For. Prod. J.* **53**(6): 63-71.
- Bledzki, A. K. and O. Faruk (2003). "Wood fibre reinforced polypropylene composites: Effect of fibre geometry and coupling agent on physico-mechanical properties." *Appl. Compos. Mat.* **10**(6): 365-379.
- Clemons, C. (2002). "Wood-plastic composites in the united states: The interfacing of two industries." *For. Prod. J.* **52**(6): 10-18.
- Coutinho, F. M. B. and T. H. S. Costa (1999). "Performance of polypropylene-wood fiber composites." *Polymer Testing* **18**(8): 581-587.
- Crews, P., J. Rodríguez, and M. Jaspars (1998). *Organic structure analysis*, Oxford University Press, New York.
- Djiporovic, M., E. Dingova, J. Miljkovic, and K. Popov-Pergal (2003). "The influence of different coupling agents on some properties of polypropylene-wood composites." *Mater. Sci. Forum* **413**: 219-223.
- Frink, J. W. and H. I. Sachs (1981). "Isocyanate Binders for Wood Composite Boards." in: *Urethane Chemistry and Application*, K. N. Edwards (Ed.), Washington, DC, Am. Chem. Soc., 285-309.
- Frisch, K. C. and L. P. Rumao (1983). "Diisocyanates as wood adhesives." in: *Wood adhesives: Chemistry and technology*. A. Pizzi (Ed.), New York, Marcel Dekker: 289-317.
- Geng, Y., K. Li and J. Simonsen (2004). "Effects of a new compatibilizer system on the flexural properties of wood-polyethylene composite." *J. Appl. Polym. Sci.* **91**: 3667-3672.
- Johnson, R. S. (2000). "An overview of north american wood adhesive resins." *Wood Adhesives 2000*, Madison, WI, Forest Products Society. 41-49.
- Lu, J. Z., Q. Wu and H. S. J. McNabb (2000). "Chemical coupling in wood fiber and polymer composites: A review of coupling agents and treatments." *Wood Fiber Sci.* **32**(1): 88-104.

- Maldas, D., B. V. Kokta, and C. Daneault (1989). "Influence of coupling agents and treatments on the mechanical properties of cellulose fiber-polystyrene composites." J. Appl. Polym. Sci. **37**: 751-775.
- Morton, J., J. Quarmley, and L. Rossi (2003). "Current and Emerging Applications for Natural and Woodfiber-Plastic Composites." The Seventh International Conference on Woodfiber-Plastic Composites, Forestry Products Society, Madison, WI, 3-6.
- Nitz, H., P. Reichert, H. Romling, and R. Mulhaupt (2000). "Influence of compatibilizers on the surface hardness, water uptake, and the mechanical properties of poly(propylene) wood flour composites prepared by reactive extrusion." Macromol. Mater. Eng. **276/277**: 51-58.
- Raj, R. G., B. V. Kokta, D. Maldas, and C. Daneault (1989). "Use of Wood Fibers in Thermoplastics. VII. The Effect of Coupling Agents in Polyethylene-Wood Fiber Composites." J. Appl. Polym. Sci. **37**: 1089-1103.
- Sellers, T. J. (2001). "Wood adhesive innovations and application in north america." For. Prod. J. **51**(6): 12-22.
- Zhang, C., K. Li and J. Simonsen (2004). "Improvement of interfacial adhesion between wood and polypropylene in wood-polypropylene composites." J. Adhesion Sci. Technol. **18**(14): 1603-1612.

CHAPTER 5: A COMMERCIALY VIABLE COMPATIBILIZER SYSTEM
FOR WOOD-POLYETHYLENE COMPOSITES

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5.1 ABSTRACT

A commercially viable compatibilizer system containing poly(diphenylmethane diisocyanate) (PMDI) and stearic acid was developed for improving the interfacial adhesion between wood and polyethylene (PE). The treatment of PE with PMDI before mixing with wood increased both the modulus of rupture (MOR) and the modulus of elasticity (MOE) of the resulting wood-PE composites. Addition of stearic acid further increased both MOR and MOE of the resulting composites. The PMDI-stearic acid compatibilizer system was more effective in increasing both the MOR and MOE of the resulting wood-PE composites than maleic anhydride-grafted polyethylene (MAPE), a commonly used commercial compatibilizer. The compatibilization mechanisms of the PMDI-stearic acid system were investigated by Fourier Transform Infrared (FTIR) Spectrometry. A water-resistance test revealed that the composites with the PMDI-stearic acid system were statistically more water-resistant than those with MAPE.

5.2 KEYWORDS

Compatibilizer; PMDI; wood; polyethylene; stearic acid; wood-plastic composites

5.3 INTRODUCTION

Wood-plastic composites (WPCs) have been a rapidly developing field during the past fifteen years. They have attracted increasing attention from both the academic and industrial communities. WPCs have many advantages when compared with either wood or plastics. However, the interfacial adhesion between hydrophilic wood and hydrophobic plastic is very poor due to their dissimilar properties. Therefore, a coupling agent, generally called a compatibilizer, is added during the production of WPCs. At present, a number of compatibilizers have been investigated for wood-polyethylene composites, and maleic anhydride-grafted polyethylene (MAPE) is one of the most commonly used commercial compatibilizers (Balasuriya, Ye et al. 2002; Frink and Sachs 1981; Geng, Li et al. 2004, 2005; Li and Matuana 2003; Liao, Huang et al. 1997; Lu, Wu et al. 2005; Oksman and Lindberg 1998; Oksman, Lindberg et al. 1998; Raj, Kokta et al. 1989; Sedlackova, Lacik et al. 2001; Wang, Yeh et al. 2003). But the cost of MAPE is much higher than either wood or polyethylene. This has limited its widespread application in industry. In our previous paper, we described a new effective compatibilizer system that consists of PMDI and stearic anhydride (Geng, Li et al. 2005). However, the PMDI-stearic anhydride compatibilizer system has limited commercial value because stearic anhydride is not readily available in a large quantity for commercial application. In this study, we disclosed a very effective and commercially viable compatibilizer system that is composed of PMDI and stearic acid.

5.4 EXPERIMENTAL

5.4.1 MATERIALS

Pine flour (40 mesh and 2.04% moisture content) was provided by American Wood Fibers (Schofield, WI). It was re-dried at 104 °C for 20 h prior to use. The moisture content of the re-dried pine flour was 0.50%. HDPE (high density polyethylene) (melt flow index: 0.55 g/10 min) was provided by BP Solvay Polyethylene North America (Houston, TX). PMDI was provided by Huntsman Polyurethanes (West Deptford, NJ). MAPE (maleic anhydride-grafted polyethylene, A-C OptiPak^(TM) 200) was donated by Honeywell International, Inc. (Morristown, NJ). Stearic acid and *p*-xylene were purchased from Acros Organics (Morris Plains, NJ).

5.4.2 PREPARATION OF WOOD-PE BLENDS

Dry wood flour and HDPE powder with or without a compatibilizer were mixed in a Brabender Plasticorder with a mixing bowl attached (C. W. Brabender Instruments, Inc., South Hackensack, NJ).

The blending procedure varied with the different components in the composites.

Blending procedure A: This procedure was used for preparing wood-PE-PMDI blends by mixing wood flour with PMDI first followed by mixing the wood-PMDI blend with PE. This example blending procedure was used to prepare wood-

PE composites with a wood/PMDI/PE weight ratio of 40/0.5/59.5. PMDI (0.22 g) was added dropwise into wood flour (17.60 g) under a nitrogen atmosphere and mixed well by mechanical stirring. The resulting wood-PMDI mixture was added to the preheated Brabender bowl at 120 °C and 100 rpm, and mixed for 10 min. The bowl temperature was then raised to 170 °C and HDPE (26.18 g) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Blending procedure B: This procedure was used for preparing wood-PE-PMDI blends by mixing PE with PMDI first followed by mixing the PE-PMDI blend with wood flour. The following example procedure was used to prepare wood-PE composites with a wood/PMDI/PE weight ratio of 40/0.5/59.5: PMDI (0.22 g) was added dropwise into HDPE (26.18 g) under a nitrogen atmosphere and mixed for 2 min with mechanical stirring. Then, pine flour (17.60 g) was added and mixed for additional 2 min. The resulting wood-PMDI-HDPE mixture was added to the preheated Brabender bowl at 170 °C and 100 rpm, and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Blending procedure C: This procedure was used for making wood-PE composites without a compatibilizer. Pine flour (17.60 g) and HDPE (26.40 g) was mixed in a 400 mL beaker by mechanical stirring for 2 min. The bowl of the

Brabender Plasticorder was preheated to 170 °C and the speed of the rotors in the bowl was set to 100 rpm. The mixture of pine flour and HDPE was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Blending procedure D: This procedure was used for making wood-MAPE-PE and wood-stearic acid-PE blends. The following example procedure was used to prepare wood-PE composites with a wood/MAPE/PE weight ratio of 40/2/58: Pine flour (17.60 g), MAPE (0.88 g) and HDPE (25.52 g) were mixed in a 400 mL beaker with mechanical stirring for 2 min. The bowl of the Brabender Plasticorder was preheated to 170 °C and the speed of the rotor in the bowl was set to 100 rpm. The mixture of pine flour, MAPE and HDPE was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Blending procedure E: This procedure was used for preparing wood-PE blends with a PMDI-stearic acid compatibilizer. The following is an example used to prepare wood-PE composites with a wood/PMDI/stearic acid/PE weight ratio of 40/1.5/0.5/58: HDPE (25.52 g) and stearic acid (0.22 g) were mixed together. PMDI (0.66 g) was added dropwise to the mixture of HDPE and stearic acid under a nitrogen atmosphere and mixed for 2 min with mechanical stirring. Then pine flour (17.60 g) was added and mixed for additional 2 min. The resulting wood-

stearic anhydride-PMDI-HDPE mixture was added to the preheated Brabender bowl at 170 °C and 100 rpm, and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

5.4.3 PRESS PROCEDURE

A stainless steel mold with dimensions of 101.6 x 101.6 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 a well-mixed wood-PE sample, placed on the lower platen of the Carver press and pre-heated for 10 min. The press was closed slowly allowing the wood-plastic to flow into the mold shape. The press pressure was raised from 34.5 to 344.8 kPa over two min 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 in a cold press at 344.8 kPa under ambient conditions. The resulting wood-PE board was cut into 10 small test specimens. Each specimen was 54.50-56.50 mm long, 13.00-14.30 mm wide, and 2.10-2.40 mm thick.

5.4.4 DETERMINATION OF THE STRENGTH AND STIFFNESS OF THE WOOD-PE COMPOSITES

Ten specimens were tested for each wood-PE composite in accordance with ASTM D790-02. Three-point bending test was applied on all the specimens. The small specimens were tested on a Sintech machine (MTS Systems Corporation, Enumclaw, WA) and the load-deflection curve determined. The support span was

43 mm and the crosshead speed was 1.0 mm/min. The modulus of rupture (MOR) and modulus of elasticity (MOE) were calculated from the load-deflection data. The MOR was defined as the first point on the load-deflection curve to show a slope of zero. The MOE was determined from the slope in the initial elastic region of the load-deflection curve.

5.4.5 WATER-RESISTANCE TEST

Five specimens of each wood-PE composite were used for the water-resistance test. All the specimens were pre-weighed and then soaked in water at room temperature. The specimens were taken out of the water, wiped with tissue paper, and then weighed every 24 h for the first five days. The specimens were re-soaked in water right after weighing. After that, the specimens were weighed at longer time intervals until day 150. The water uptake percentage was determined as the weight gain divided by the dry weight of the specimen.

5.4.6 INVESTIGATION OF COVALENT LINKAGES BETWEEN A COMPATIBILIZER AND WOOD IN WOOD-PE COMPOSITES

The following five wood-PE composites were investigated: the composite without any compatibilizer, the composite made with the blending procedure **A** and with 1.5 wt% PMDI, the composite made with the blending procedure **B** and with 1.5 wt% PMDI, the composite with 0.5 wt% stearic acid, and the composite with 1.5 wt% PMDI and 0.5 wt% stearic acid. The wood-PE composites were cut into small pieces by a fodder chopper, and then wrapped with a piece of filter paper. The

wrapped wood-PE composites were extracted by *p*-xylene in a modified Soxhlet extractor for 48 h. The thimble holder of the Soxhlet extractor was wrapped with heating tape and heated to maintain the temperature of the solution in the holder around 120 °C. The extracted wood-PE composites residue was dried at 103 °C for 24 h and then characterized by Fourier Transform Infrared (FTIR) spectrometry. 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.

5.4.7 STATISTICAL ANALYSIS OF RESULTS

All data were analyzed with standard two-tail t-test using S-plus statistical software (Insightful Corp., Seattle, WA).

5.5 RESULTS

5.5.1 EFFECTS OF BLENDING PROCEDURES ON THE MECHANICAL PROPERTIES OF THE RESULTING WOOD-PE COMPOSITES

At 0.5 wt% PMDI, the MOR values of the wood-PE composites made from blending procedure **A** and blending procedure **B** were statistically the same while the MOE from blending procedure **B** was slightly higher than that from blending procedure **A** (Fig. 5.1). At 1.0 wt% PMDI and 1.5 wt% PMDI, blending procedure **B** resulted in much higher MOR and MOE than blending procedure **A**. For blending procedure **A**, the MOR and MOE gradually increased when the PMDI dosage was increased from 0.5 wt% to 1.0 wt% (Fig. 5.1). For blending procedure

B, the MOR of the resulting composites significantly increased when the PMDI dosage was increased from 0.5 wt% to 1.5 wt% (Fig. 5.1). The MOE of the resulting composites increased when the PMDI dosage was increased from 0.5 wt% to 1.0 wt% and remained statistically the same when the PMDI dosage was further increased from 1.0 wt% to 1.5 wt% (Fig. 5.1).

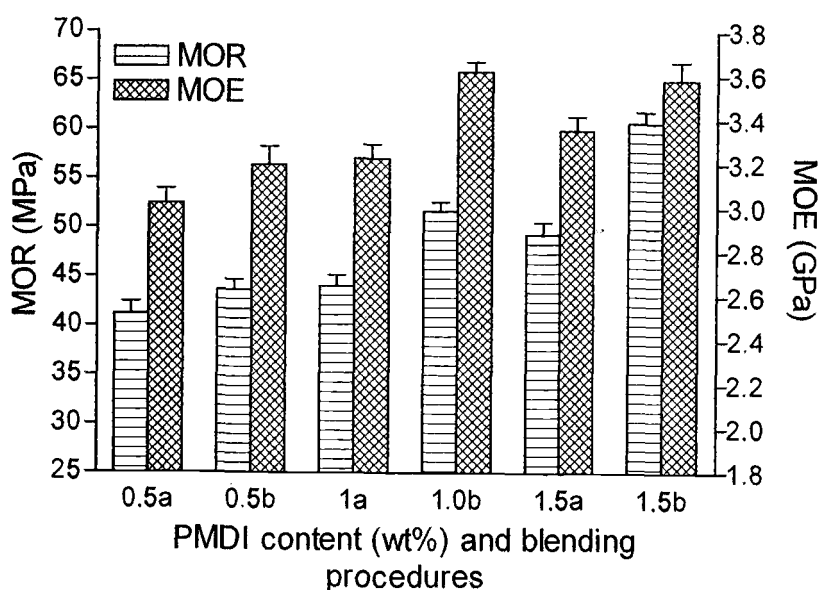


Fig. 5.1 Effect of the addition order on MOR and MOE of wood-PE composites (a: blending procedure A, i.e., the mixing of PMDI with wood first; b: blending procedure B, i.e., the mixing of PMDI with PE first; the numbers (0.5, 1.0, and 1.5) before the letters a and b in the X axis represent the dosage of PMDI. wood/PMDI/PE weight ratio = 40/X/Y ($X+Y=60$)). Data are the means of ten replicates and the error bars represent one standard error of the means.

5.5.2 EFFECT OF STEARIC ACID ON MECHANICAL PROPERTIES OF THE RESULTING WOOD-PE COMPOSITES

When compared with the control, 0.5 wt% stearic acid resulted in a slightly lower MOR, whereas the MOE remained statistically the same. When the dosage of

stearic acid was increased from 0.5 wt% to 1.0 wt%, neither the MOR nor the MOE of the resulting composites were statistically different at a 95% confidence level (Fig. 5.2).

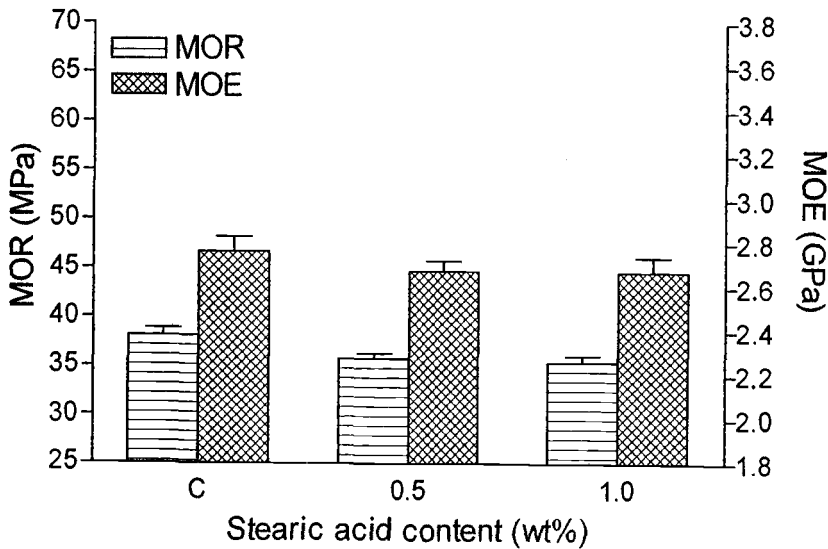


Fig. 5.2 Effect of the stearic acid dosage on MOR and MOE of wood-PE composites (C: wood/PE weight ratio = 40/60; wood/stearic acid/PE weight ratio = 40/X/Y (X+Y=60)). Data are the means of ten replicates and the error bars represent one standard error of the means.

5.5.3 Effect of combinations of PMDI and stearic acid on mechanical properties of the resulting wood-PE composites

When compared with 1.5 wt% PMDI, combinations of 1.5 wt% PMDI and 0.11 wt% or 0.25 wt% stearic acid did not result in statistically different MORs or MOEs (Fig. 5.3). However, the composite with a combination of 1.5 wt% PMDI and 0.5 wt% stearic acid had a significantly higher MOR than those with 1.5 wt% PMDI, whereas the combination did not increase the MOE (Fig. 5.3).

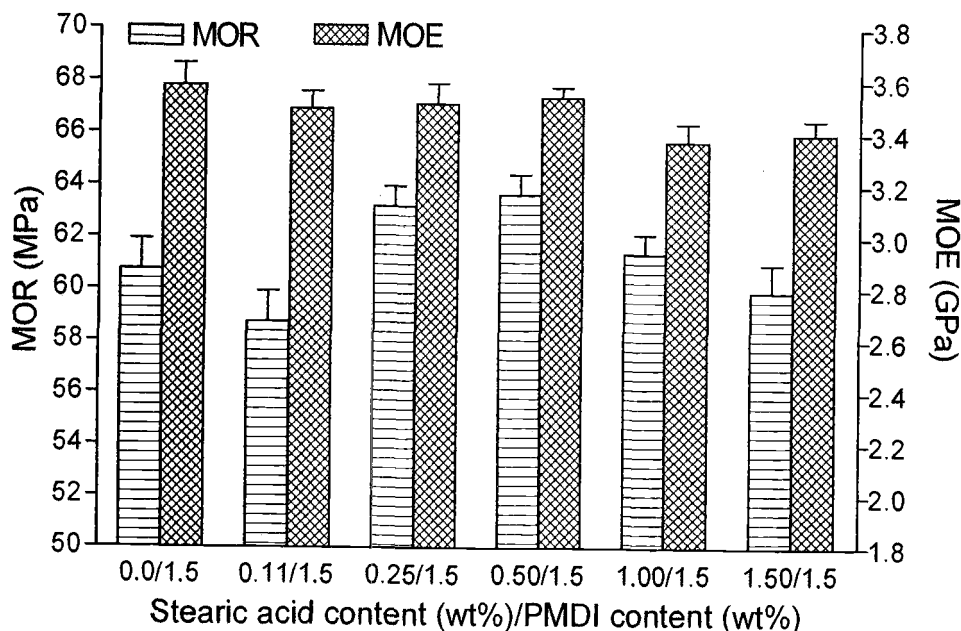


Fig. 5.3 Effect of combinations of PMDI-stearic acid compatibilizer on MOR and MOE of wood-PE composites (Wood/PMDI/stearic acid/PE weight ratio = 40/1.5/X/Y ($X + Y = 58.5$)). Data are the means of ten replicates and the error bars represent one standard error of the means.

At 1.5 wt% PMDI, the MOR of the resulting composites significantly increased and the MOE remained statistically the same when the dosage of stearic acid increased from 0.11 wt% to 0.25 wt% (Fig. 5.3). Both MOR and MOE remained statistically the same when the dosage of stearic acid was further increased from 0.25 wt% to 0.50 wt%. Further increase in the dosage of stearic acid from 0.5 wt% to 1.0 wt% resulted in a slight decrease in both MOR and MOE of the resulting composites. When the dosage of stearic acid was increased from 1.0 wt% to 1.5 wt%, both MOR and MOE were statistically the same although the

average value of the MOR with 1.0 wt% stearic acid was higher than that with 1.5 wt% stearic acid.

5.5.4 COMPARISON OF PMDI-STEARIC ACID COMPATIBILIZER SYSTEM WITH MAPE

When the dosage of the compatibilizers was 2 wt% in wood-PE composites, the MOR of the composites with P1.5SA0.5 (1.5 wt% PMDI and 0.5 wt% stearic acid) was about 20% higher than that of the composites with MAPE2 (2 wt% MAPE) (Fig. 5.4). The MOE values of these two systems were not statistically different. When compared to the control, the MOR of the composites with the PMDI-stearic acid increased by over 60%, while the MOE increased by around 20 % (Fig. 5.4).

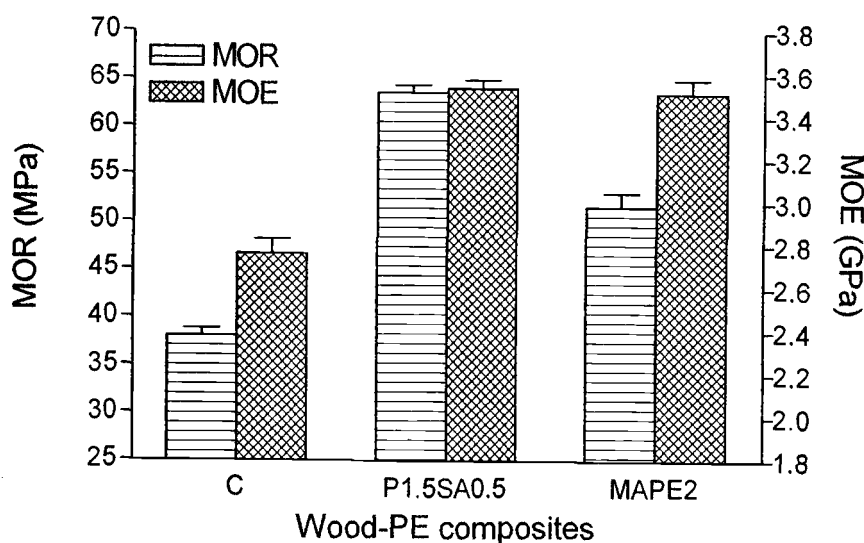


Fig. 5.4 Comparison of PMDI-stearic acid compatibilizer system with MAPE (C: wood/PE weight ratio = 40/60; P1.5SA0.5: wood/PMDI/stearic acid/PE weight ratio = 40/1.5/0.5/58; MAPE2: wood/MAPE/PE weight ratio = 40/2/58). Data are the means of ten replicates and the error bars represent one standard error of the means.

5.5.5 WATER-RESISTANCE TEST

The water uptake percentage of all wood-PE composites increased with increasing soaking time (Fig. 5.5). The wood-PE composites without any compatibilizer and with 0.5 wt% stearic acid both had the highest water-uptake percentage. There was no statistical difference between them. The wood-PE composites with 2 wt% MAPE had much lower water uptake percentage than the control and the composites with 0.5 wt% stearic acid. Both composites with 1.5 wt% PMDI alone and with the combination of 1.5 wt% PMDI and 0.5 wt% stearic acid had lower water-uptake percentage than those with MAPE. The water uptake percentages for both composites with 1.5 wt% PMDI alone and with the combination of 1.5 wt% PMDI and 0.5 wt% stearic acid were statistically the same (Fig. 5.5).

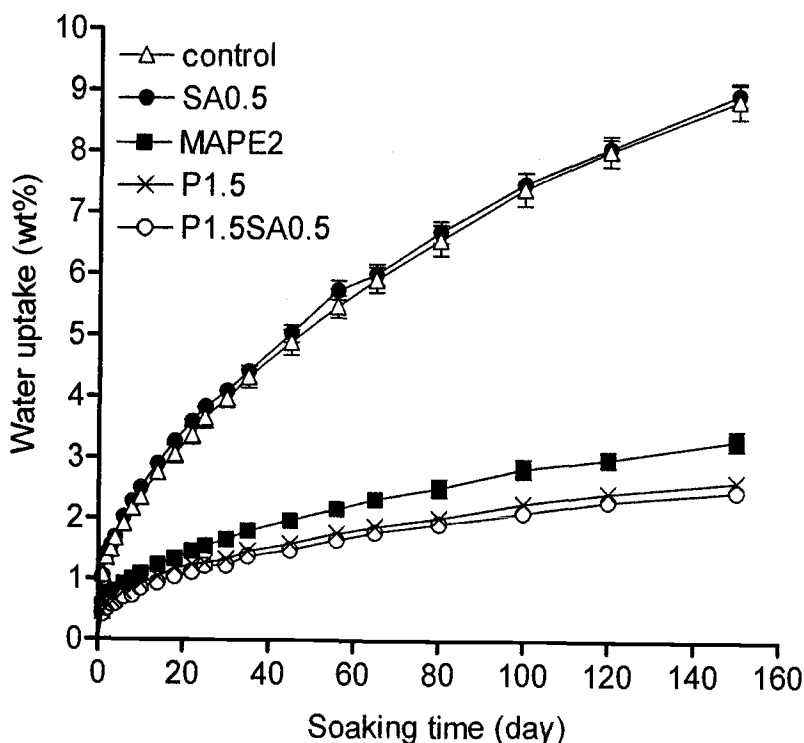


Fig. 5.5 Water-resistance test (Control: wood/PE weight ratio = 40/60; SA0.5: wood/stearic acid/PE weight ratio = 40/0.5/59.5; MAPE2: wood/MAPE/PE weight ratio = 40/2/58; P1.5: wood/PMDI/PE weight ratio = 40/1.5/58.5; P1.5SA0.5: wood/PMDI/stearic acid/PE weight ratio = 40/1.5/0.5/58). Data are the means of five duplicates and the error bars represents two standard errors of the means.

5.5.6 FTIR ANALYSIS OF COVALENT LINKAGES BETWEEN COMPATIBILIZERS AND WOOD

PE dissolves well in *p*-xylene at temperatures > 100 °C. Therefore, the PE in wood-PE composites should be completely removed by a modified Soxhlet extractor after 48 h. The residue obtained from this procedure was analyzed by FTIR spectroscopy. The interactions between the compatibilizers and the wood fiber were better illustrated by viewing subtracted FTIR spectra (Fig. 5.6). There was a strong absorbance peak around 1740 cm^{-1} in the FTIR spectrum of SA0.5-

control, which was from the carbonyl groups of the ester linkages that formed between stearic acid and the hydroxyl groups in wood. The strong absorbance peaks at 1600-1740 cm^{-1} in P1.5-control (blending procedure **A**), P1.5-control (blending procedure **B**), and P1.5SA0.5-control were from the carbonyl groups in esters, urea and urethane structures. The spectrum of the P1.5-control (blending procedure **A**) had no hydrocarbon absorbance peaks at 2850 and 2920 cm^{-1} , whereas the spectrum of the P1.5-control (blending procedure **B**) had two strong hydrocarbon absorbance peaks at 2850 and 2920 cm^{-1} . The spectrum of the P1.5SA0.5 also had two strong hydrocarbon absorbance peaks at 2850 and 2920 cm^{-1} .

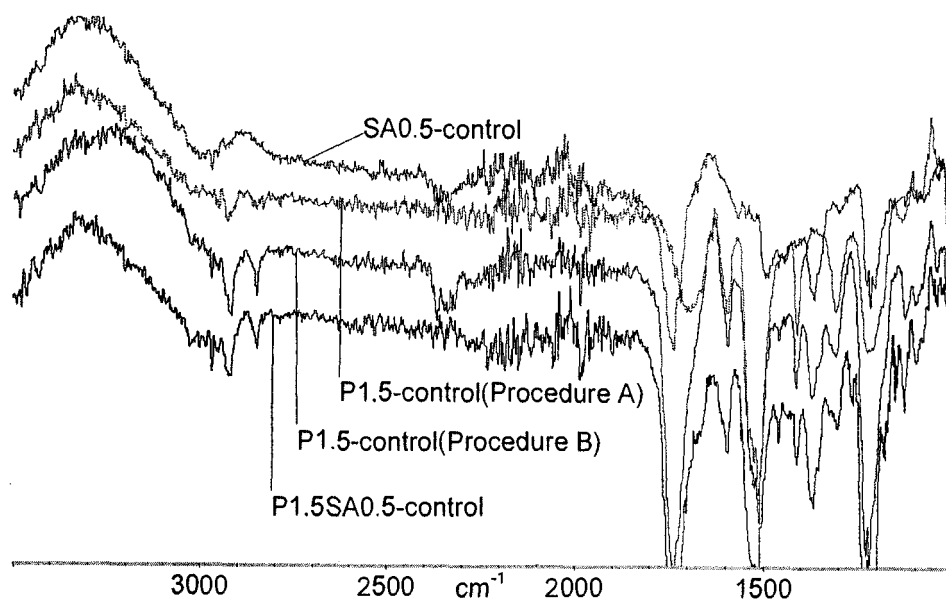


Fig. 5.6 FTIR spectra of extracted residues with control spectrum subtracted (control: wood/PE weight ratio = 40/60; SA0.5: wood/stearic acid/PE weight ratio = 40/0.5/59.5; P1.5: wood/PMDI/PE weight ratio = 40/1.5/58.5; P1.5SA0.5: wood/PMDI/stearic acid/PE weight ratio = 40/1.5/0.5/58).

5.6 DISCUSSION

Mixing of PMDI with PE first resulted in much higher MOR and MOE than mixing of PMDI with wood first (Fig. 5.1). It is somewhat surprising and still poorly understood why the mixing order makes such a large difference in the strength and stiffness of the resulting wood-PE composites. Comparison of P1.5-control FTIR spectra from two different blending procedures (the procedures **A** and **B**) revealed that some PE could not be removed from wood-composites made from the blending procedure **B** using the *p*-xylene extraction method. Presumably, the PE was covalently bonded to wood. We speculate that PE contains a very small amount of functional groups such as hydroxyl groups that can react with PMDI, thus covalently bonding the PE to wood. Because the functional groups are at such a small amount that efficient bonding of the PE to wood can only be realized when PMDI and PE are mixed first.

When stearic acid was incorporated into wood-PE composites, it formed ester linkages with hydroxyl groups in wood. The absorbance peak at 1740 cm^{-1} in the FTIR spectrum of SA0.5-control indeed indicates the existence of ester linkages (Fig. 5.6). However, the amount of the covalently linked stearic acid may be very low because the formation of esters between a carboxylic acid and hydroxyl groups in wood is slow in the absence of a catalyst, which may explain why addition of

stearic acid resulted in little increase in the MOR and MOE of the resulting composites (Fig. 5.2).

At 1.5 wt% PMDI, addition of stearic acid at certain dosages further increased the MOR. Stearic acid can react with both PMDI and wood. Theoretically, stearic acid can be bonded to wood more efficiently when stearic acid is used with PMDI than when stearic acid is used alone. The long hydrocarbon chain of the covalently bonded stearic acid may form secondary bonds, entanglements or co-crystallizes with the PE matrix. Therefore, increasing amounts of covalently bonded stearic acid would further improve the interfacial adhesion. However, if too much stearic acid is added, the excess stearic acid may act as a plasticizer for PE, thus decreasing the strength of the resulting composites. This may explain why both MOR and MOE slightly decreased when the dosage of stearic acid increased from 0.5 wt% to 1.0 wt% (Fig. 5.3). The gain in the MOR value by addition of stearic acid may appear to be small; however, the gain is in addition to an already very high MOR value. Stearic acid is thus an essential component of this new compatibilizer system.

PMDI is widely used as a wood adhesive and is readily available. Stearic acid is inexpensive, abundant, and readily available for commercial application. This PMDI-stearic acid compatibilizer system is more effective than the most commonly used compatibilizer for wood-PE composites, MAPE. This new compatibilizer is

also cost-competitive with MAPE. Therefore, this compatibilizer should be viable in commercial applications.

5.7 CONCLUSIONS

Mixing PMDI with PE first was more effective than mixing PMDI with wood first in terms of increasing the strength and stiffness of the resulting wood-PE composites. Combinations of PMDI and stearic acid further increased both MOR and MOE of the resulting composites. At the 2 wt% dosage level, the PMDI-stearic acid compatibilizer system resulted in significantly higher MOR and MOE value for wood-PE composites than commercially available MAPE. Analysis of *p*-xylene-extracted wood-PE composites indicated that both stearic acid and PMDI formed covalent bonds with wood. The PMDI-stearic acid compatibilizer system greatly improved the water resistance of the resulting wood-PE composites. The price of the PMDI-stearic acid compatibilizer system should be less than that of commercially available MAPE.

5.8 ACKNOWLEDGEMENTS

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5.9 REFERENCES

- Balasuriya, P. W., L. Ye, Y. W. Mai and J. Wu (2002). "Mechanical properties of wood flake-polyethylene composites. II. Interface modification." J. Appl. Polym. Sci. **83**(12): 2505-2521.
- Frink, J. W. and H. I. Sachs (1981). "Isocyanate Binders for Wood Composite Boards." in: Urethane Chemistry and Application, K. N. Edwards (Ed.), Washington, DC, Am. Chem. Soc., 285-309.
- Geng, Y., K. Li and J. Simonsen (2004). "Effects of a New Compatibilizer System on the Flexural Properties of Wood-Polyethylene Composites." J. Appl. Polym. Sci. **91**: 3667-3672.
- Geng, Y., K. Li and J. Simonsen (2005). "A combination of poly(diphenylmethane diisocyanate) and stearic anhydride as a novel compatibilizer for wood-polyethylene composites." J. Adhesion Sci. Technol.: accepted.
- Li, Q. and L. M. Matuana (2003). "Surface of cellulosic materials modified with functionalized polyethylene coupling agents." J. Appl. Polym. Sci. **88**(2): 278-286.
- Liao, B., Y. Huang and G. Cong (1997). "Influence of modified wood fibers on the mechanical properties of wood fiber-reinforced polyethylene." J. Appl. Polym. Sci. **66**(8): 1561-1568.
- Lu, J. Z., Q. Wu and I. I. Negulescu (2005). "Wood-fiber/high-density-polyethylene composites: coupling agent performance." J. Appl. Polym. Sci. **96**(1): 93-102.
- Oksman, K. and H. Lindberg (1998). "The influence of a SBS compatibilizer in polyethylene-wood flour composites." Holzforschung **52**(6): 661-666.
- Oksman, K., H. Lindberg and A. Holmgren (1998). "The nature and location of SEBS-MA compatibilizer in polyethylene-wood flour composites." J. Appl. Polym. Sci. **69**(1): 201-209.
- Raj, R. G., B. V. Kokta, D. Maldas and C. Daneault (1989). "Use of Wood Fibers in Thermoplastics. VII. The Effect of Coupling Agents in Polyethylene-Wood Fiber Composites." J. Appl. Polym. Sci. **37**: 1089-1103.
- Sedlackova, M., I. Lacik and I. Chodak (2001). "Poly(ethylene-co-methacrylic acid) as an effective compatibilizer of LDPE/wood flour composite."

Macromolecular Symposia **170**(Property Tailoring of Thermoplastics-Based Blends and Composites): 157-164.

Wang, Y., F.-C. Yeh, S.-M. Lai, H.-C. Chan and H.-F. Shen (2003). "Effectiveness of functionalized polyolefins as compatibilizers for polyethylene/wood flour composites." Polymer Engineering and Science **43**(4): 933-945.

CHAPTER 6: GENERAL CONCLUSIONS

The wood-plastic composites (WPC) industry has made great progress during the past ten years, but the application of WPCs is still limited due to poor interfacial adhesion between two unlikely components: hydrophilic wood and hydrophobic plastic. Compatibilizers have historically been used in WPCs to facilitate the interfacial adhesion between wood and plastics. However, to date the variety and efficacy of compatibilizers has not been sufficient to allow penetration of significant new markets.

In this study, three novel compatibilizer systems were developed for wood-polyethylene composites: polyaminoamide-epichlorohydrin (PAE)-stearic anhydride, poly(diphenylmethane diisocyanate) (PMDI)-stearic anhydride and PMDI-stearic acid.

In the PAE-stearic anhydride compatibilizer system, adjustment of the pH value of PAE, the dosage of PAE and stearic anhydride all affected the mechanical properties (MOR and MOE) of the resulting wood-polyethylene composites. Under optimal conditions, the PAE-stearic anhydride system was comparable to commercially available MAPE. Characterization of *p*-xylene-extracted wood-PE composites demonstrated that stearic anhydride covalently bonded to wood and the

PAE-bonded wood. The PAE-stearic anhydride compatibilizer system increased the water-resistance of the resulting composites.

In the PMDI-stearic anhydride compatibilizer system, the dosages of both PMDI and stearic anhydride affected the mechanical properties of the resulting wood-polyethylene composites. At the 2 wt% dosage level, a PMDI-stearic anhydride compatibilizer system was superior to a commercially available MAPE-compatibilized system in terms of increased strength and stiffness of the resulting composites. The improvement of the strength and stiffness of the wood-PE composites by a PMDI-stearic anhydride compatibilizer system resulted from the improvement of the interfacial adhesion and the strengthening of the wood particles. Analysis of *p*-xylene-extracted wood-PE composites with FTIR revealed that stearic anhydride formed ester linkages with wood and PMDI-treated wood. The investigation of the fractured surface of the composites revealed a strong interfacial adhesion between wood particles and the PE matrix in the wood-PE composites containing a PMDI-stearic anhydride compatibilizer. Moisture in the wood flour had negative impacts on the efficacy of the compatibilizers. The PMDI-stearic anhydride compatibilizer system greatly reduced the water-uptake of the resulting wood-PE composites.

In the PMDI-stearic acid compatibilizer system, treatment of polyethylene with PMDI before mixing with wood increased both MOR and MOE of the resulting

wood-PE composites. Addition of stearic acid to PE before treating with PMDI further increased both MOR and MOE of the resulting composites. At the 2 wt% dosage level, PMDI-stearic acid compatibilizer system resulted in significantly higher strength and stiffness for the wood-PE composites compared to commercially available MAPE. Analysis of *p*-xylene-extracted wood-PE composites indicated that both stearic acid and PMDI formed covalent bonds with wood. The PMDI-stearic acid compatibilizer system greatly improved the water-resistance of the wood-PE composites. The price of the PMDI-stearic acid compatibilizer system should be less than that of MAPE. This compatibilizer system may be a feasible alternative to current products in various industrial applications.

BIBLIOGRAPHY

- Bao, S., W. A. Daunch, Y. Sun, P. L. Rinaldi, J. J. Marcinko, and C. Phanopoulos (2003). "Solid state two-dimensional NMR studies of polymeric diphenylmethane diisocyanate (pmdi) reaction in wood." For. Prod. J. 53(6): 63-71.
- Balasuriya, P. W., L. Ye, Y. W. Mai and J. Wu (2002). "Mechanical properties of wood flake-polyethylene composites. II. Interface modification." J. Appl. Polym. Sci. 83(12): 2505-2521.
- Bataille, P., L. Ricard, and S. Sapieha (1989). "Effects of Cellulose Fibers in Polypropylene Composites." Polym. Comp. 10(2): 103-108.
- Beshay, A. D., B. V. Kokta, and C. Daneault (1985). "Use of Wood Fibers in Thermoplastic Composites II: Polyethylene." Polym. Comp. 6(4): 261-271.
- Bledzki, A. K. and O. Faruk (2003). "Wood fibre reinforced polypropylene composites: Effect of fibre geometry and coupling agent on physico-mechanical properties." Appl. Compos. Mat. 10(6): 365-379.
- Bledzki, A. K. and J. Gassan (1999). "Composites reinforced with cellulose based fibres" Progr. Polym. Sci. 24(2): 221-274.
- Bridgeford, D. J. (1963). "Method of Depositing a Polymer of Olefinically Unsaturated Monomer within a Polymeric Material and the Resulting Product." US Patent 3,083,118: 45 pp.
- Chtourou, H., B. Riedl, and A. Ait-Kadi (1992). "Reinforcement of Recycled Polyolefins with Wood Fibers." J. Reinf. Plast. Comp. 11: 372-394.
- Clemons, C. (2002). "Wood-Plastic Composites in the United States: The Interfacing of Two Industries." For. Prod. J. 52(6): 10-18.
- Coran, A. Y. and R. Patel (1982). "Composites of Grafted Olefin Polymers and Cellulose Fibers." US Patent 4,323,625: 7 pp.
- Coutinho, F. M. B. and T. H. S. Costa (1999). "Performance of polypropylene-wood fiber composites." Polymer Testing 18(8): 581-587.
- Crews, P., J. Rodríguez and M. Jaspars (1998). Organic Structure Analysis, Oxford University Press, New York.

- Dalvåg, H., C. Klason, and H.-E. Strömwall (1985). "The Efficiency of Cellulosic Fillers in Common Thermoplastics. Part II. Filling with Processing Aids and Coupling Agents." Int. J. Polym. Mater. **11**: 9-38.
- Daneault, C., B. V. Kokta, and D. Maldas (1989). "The Xanthate Method of Grafting. XII. Effect of Operating Conditions on the Grafting of Vinyl Monomers onto Wood Pulp." J. Appl. Polym. Sci. **38**: 841-848.
- de Roover, B., M. Slavovs, V. Carlier, J. Devaux, R. Legras and A. Momtaz (1995). "Molecular characterization of maleic anhydride-functionalized polypropylene" J. Polym. Sci., Part A: Polym. Chem. **33**(5): 829-842.
- Djiporovic, M., E. Dingova, J. Miljkovic, and K. Popov-Pergal (2003). "The influence of different coupling agents on some properties of polypropylene-wood composites." Mater. Sci. Forum **413**: 219-223.
- Dimov, K. and P. Pavlov (1969). "Grafting with Acrylonitrile with the Redox System Cellulose Xanthogenate-Hydrogen Peroxide." J. Polym. Sci. **7**: 2775-2792.
- Dunlop-Jones, N. (1996). "Wet-strength chemistry". in: Paper Chemistry, 2nd ed. J. C. Roberts (Ed.), New York, Blackie Academic & Professional: 98-119.
- Dunky, M. and A. Pizzi (2002). "Wood adhesives." in: Adhesion Science and Engineering. D. A. Dillard and A. V. Pocius (Ed.), Amsterdam, Neth, Elsevier Science B.V. **2**(Surfaces, Chemistry and Applications): 1039-1103.
- Espy, H. H. (1994). "Alkaline-Curing Polymeric Amine-Epichlorohydrin Resins". in: Wet-Strength Resins and Their Application. L. L. Chan (Ed.), Atlanta, GA, Tappi Press. **Ch. 2**: 13-44.
- Espy, H. H. (1995). "The Mechanism of Wet-Strength Development in Paper: A Review" TAPPI J. **78**(4): 90-99.
- Espy, H. H. and T. W. Rave (1988). "The Mechanism of Wet-Strength Development by Alkaline-Curing Amino Polymer-Epichlorohydrin Resins" TAPPI J. **71**(5): 133-137.
- Faessinger, R. W. and J. S. Conte (1967). "Thioated Cellulosic/Amylaceous Substrate-Ethylenically Unsaturated Monomer Graft Copolymer." US Patent 3,359,224: 21 pp.

- Felix, J. M. and P. Gatenholm (1991). "The nature of adhesion in composites of modified cellulose fibers and polypropylene" J. Appl. Polym. Sci. **42**: 609-620.
- Felix, J. M. and P. Gatenholm (1993). "Formation of entanglements at brushlike interfaces in cellulose-polymer composites" J. Appl. Polym. Sci. **50**: 699-708.
- Frink, J. W. and H. I. Sachs (1981). "Isocyanate Binders for Wood Composite Boards." in: Urethane Chemistry and Application, K. N. Edwards (Ed.), Washington, DC, Am. Chem. Soc., 285-309.
- Frisch, K. C. and L. P. Rumao (1983). "Diisocyanates as Wood Adhesives." in: Wood Adhesives: Chemistry and Technology, A. Pizzi (Ed.), New York, Marcel Dekker., 289-317.
- Garg, D. H., W. Lenk, S. Berwald, K. Lunkwitz, F. Simon and K.-J. Eichhoun (1996). "Hydrophilization of microporous polypropylene Celgard membranes by the chemical modification technique" J. Appl. Polym. Sci. **60**(12): 2087-2104.
- Gassan, J. and A. K. Bledzki (1997). "The influence of fiber-surface treatment on the mechanical properties of jute-polypropylene composites" Compos. Part A: Applied Science and Manufacturing **28A**(12): 1001-1005.
- Gatenholm, P., J. Felix, C. Klason, and J. Kubát (1992). "Cellulose-Polymer Composites with Improved Properties." in: Polymer Science: Advances in New Materials. J. C. Salamone and J. S. Riffle (Ed.), New York, NY, Plenum Press. **7**: 75-82.
- Gauthier, R., C. Joly, A. C. C. Coupas, H. Gauthier and M. Escoubes (1998). "Interfaces in polyolefin/cellulosic fiber composites: chemical coupling, morphology, correlation with adhesion and aging in moisture" Polym. Compos. **19**: 287-300.
- Geng, Y., K. Li and J. Simonsen (2004). "Effects of a New Compatibilizer System on the Flexural Properties of Wood-Polyethylene Composite." J. Appl. Polym. Sci. **91**: 3667-3672.
- Geng, Y., K. Li and J. Simonsen (2005). "A combination of poly(diphenylmethane diisocyanate) and stearic anhydride as a novel compatibilizer for wood-polyethylene composites." J. Adhesion Sci. Technol.: accepted.
- Goettler, L. (1983). "Treated Fibers and Bonded Composites of Cellulose Fibers in Vinyl Chloride Polymer Characterized by an Isocyanate Bonding Agent." US Patent 4,376,144: 8 pp.

- Han, G.-S., H. Ichinose, S. Takase, and N. Shiraishi (1989). "Composites of Wood and Polypropylenes III." Mokuzai Gakkaishi **35**(12): 1100-1104.
- Heinen, W., C. H. Rosenmöller, C. B. Wenzel, H. J. M. de Groot, J. Lugtenburg and M. van Duin (1996). "¹³C NMR Study of the Grafting of Maleic Anhydride onto Polyethylene, Polypropene, and Ethene-Propene Copolymers" Macromol. **29**(4): 1151-1157.
- Hornof, V., B. V. Kokta, and J. L. Valade (1976). "The Xanthate Method of Grafting. IV. Grafting of Acrylonitrile onto High-Yield Pulp." J. Appl. Polym. Sci. **20**: 1543-1554.
- Hua, L., P. Zadorecki, and P. Flodin (1987). "Cellulose Fiber-Polyester Composites with Reduced Water Sensitivity (1)-Chemical Treatment and Mechanical Properties." Polym. Comp. **8**(3): 199-202.
- Jiang, H. and D. P. Kamdem (2004). "Development of Poly(vinyl chloride)/Wood Composites. A Literature Review." J. Vinyl & Additive Technol. **10**(2): 59-69.
- Johns, W. E. (1982). "Isocyanates as Wood Binders-A Review." J. Adhes. **15**: 59-67.
- Johns, W. E. (1989). "The Chemical Bonding of Wood." in: Wood Adhesives: Chemistry and Technology. A. Pizzi (Ed.), New York, Marcel Dekker Inc. **2**: 75-96.
- Johnson, R. S. (2000). "An overview of north american wood adhesive resins." Wood Adhesives 2000, Madison, WI, Forest Products Society, 41-49.
- Joly, C., M. Kofman and R. Gauthier (1996). "Polypropylene/cellulosic fiber composites: chemical treatment of the cellulose assuming compatibilization between the two materials" J. Macro. Sci. - Pure Appl. Chem. **A33**: 1981-1996.
- Keim, G. I. (1960a). "Cationic Thermosetting Polyamide-Epichlorohydrin Resins and Process of Making Same." US Patent 2,926,154: 4 pp.
- Keim, G. I. (1960b). "Wet-Strength Paper and Method of Making Same." US Patent 2,926,116: 5 pp.
- Kent, J. A., A. Winston, and W. R. Boyle (1962). "Preparation of Wood-Plastic Combinations Using Gamma Radiation to Induce Polymerization: Effects of Gamma Radiation on Wood." Washington, DC, Annual Report ORO-600, U.S. Atomic Energy Commission.

- Kishi, H., M. Yoshioka, A. Yamanoi, and N. Shiraishi (1988). "Composites of Wood and Polypropylenes I." Mokuzai Gakkaishi **34**(2): 133-139.
- Kokta, B. V., D. Maldas, C. Daneault, and P. Béland (1990a). "Composites of Polyvinyl Chloride-Wood Fibers. I. Effect of Isocyanate as a Bonding Agent." Polym.-Plast. Technol. Eng. **29**(1&2): 87-118.
- Kokta, B. V., D. Maldas, C. Daneault, and P. Béland (1990b). "Composites of Poly(Vinyl Chloride) and Wood Fibers. Part II: Effect of Chemical Treatment." Polym. Comp. **11**(2): 84-89.
- Kokta, B. V., D. Maldas, C. Daneault, and P. Béland (1990c). "Composites of Polyvinyl Chloride-Wood Fibers. III: Effect of Silane as Coupling Agent." J. Vinyl Technol. **12**(3): 146-153.
- Kokta, B. V. and J. L. Valade (1972). "Effect of Acrylonitrile on Grafting of Styrene with the Redox System Cellulose Xanthate-Hydrogen Peroxide." TAPPI **55**(3): 366-369.
- Laver, T. C. (1996). "Extruded synthetic wood composition and method for making same." US Patent 5,516,472: 21 pp.
- Li, B. and J. He (2004). "Investigation of mechanical property, flame retardancy and thermal degradation of LLDPE-wood-fiber composites." Polymer Degradation and Stability **83**(2): 241-246.
- Li, Q. and L. M. Matuana (2003). "Foam Extrusion of High Density Polyethylene/Wood-Flour Composites Using Chemical Foaming Agents." J. Appl. Polym. Sci. **88**: 3139-3150.
- Li, Q. and L. M. Matuana (2003). "Surface of cellulosic materials modified with functionalized polyethylene coupling agents." J. Appl. Polym. Sci. **88**(2): 278-286.
- Liang, B.-H., L. Mott, S. M. Shaler, and G. T. Caneba (1994). "Properties of Transfer-Molded Wood-Fiber/Polystyrene Composites." Wood Fiber Sci. **26**(3): 382-389.
- Liao, B., Y. Huang and G. Cong (1997). "Influence of modified wood fibers on the mechanical properties of wood fiber-reinforced polyethylene." J. Appl. Polym. Sci. **66**(8): 1561-1568.

- Linhart, F. (1995). "The practical application of wet-strength resins." in: Applications of wet-end paper chemistry. C. O. Au and I. Thorn (Ed.), New York, Blackie Academic & Professional: 102-119.
- Lu, J. Z., Q. Wu and H. S. J. McNabb (2000). "Chemical coupling in wood fiber and polymer composites: A review of coupling agents and treatments." Wood Fiber Sci. **32**(1): 88-104.
- Lu, J. Z., Q. Wu and I. I. Negulescu (2005). "Wood-fiber/high-density-polyethylene composites: coupling agent performance." J. Appl. Polym. Sci. **96**(1): 93-102.
- Maldas, D. and B. V. Kokta (1989). "Improving Adhesion of Wood Fiber with Polystyrene by the Chemical Treatment of Fiber with a Coupling Agent and the Influence on the Mechanical Properties of Composites." J. Adhesion Sci. Technol. **3**(7): 529-539.
- Maldas, D. and B. V. Kokta (1990a). "Influence of Polar Monomers on the Performance of Wood Fiber Reinforced Polystyrene Composites. I. Evaluation of Critical Conditions." Int. J. Polym. Mater. **14**: 165-189.
- Maldas, D. and B. V. Kokta (1990b). "Influence of Phthalic Anhydride as a Coupling Agent on the Mechanical Behavior of Wood Fiber-Polystyrene Composites." J. Appl. Polym. Sci. **41**: 185-194.
- Maldas, D. and B. V. Kokta (1990c). "Effects of Coating Treatments on the Mechanical Behavior of Wood-Fiber-Filled Polystyrene Composites. I. Use of Polyethylene and Isocyanate as Coating Components." J. Appl. Polym. Sci. **40**: 917-928.
- Maldas, D. and B. V. Kokta (1990d). "Effects of Coating Treatments on the Mechanical Behavior of Wood Fiber-Filled Polystyrene Composites. II. Use of Inorganic Salt/Polyvinyl Chloride and Isocyanate as Coating Components." J. Reinf. Plast. Comp. **8**: 2-12.
- Maldas, D. and B. V. Kokta (1991a). "Surface Modification of Wood Fibers Using Maleic Anhydride and Isocyanate as Coating Components and Their Performance in Polystyrene Composites." J. Adhesion Sci. Technol. **5**(9): 727-740.
- Maldas, D. and B. V. Kokta (1991b). "Influence of Maleic Anhydride as a Coupling Agent on the Performance of Wood Fiber-Polystyrene Composites." Polym. Eng. Sci. **31**(18): 1351-1357.

- Maldas, D., B. V. Kokta, and C. Daneault (1989a). "Influence of Coupling Agents and Treatments on the Mechanical Properties of Cellulose Fiber-Polystyrene Composites." J. Appl. Polym. Sci. **37**: 751-775.
- Maldas, D., B. V. Kokta, and C. Daneault (1989b). "Thermoplastic Composites of Polystyrene: Effect of Different Wood Species on Mechanical Properties." J. Appl. Polym. Sci. **38**: 413-439.
- Maldas, D., B. V. Kokta, R. G. Raj, and C. Daneault (1988). "Improvement of the Mechanical Properties of Sawdust Wood Fibre-Polystyrene Composites by Chemical Treatment." Polymer **29**: 1255-1265.
- Mali, J., P. Sarsama, L. Suomi-Lindberg, S. Metsä-Kortelainen, J. Peltonen, M. Vilkki, T. Koto, and S. Tiisala (2003). "Woodfibre-plastic composites." http://www.vtt.fi/rte/uutta/wpc_final_%20report.pdf: 84 pp.
- Marcinko, J., C. Phanopoulos, and P. Teachey (2000). "Why Does Chewing Gum Stick To Hair and What Does This Have to Do With Lignocellulosic Structural Composite Adhesion?" Wood Adhesives 2000, Madison, WI, Forest Products Society, 111-121.
- Markarian, J. (2002). "Additives in Food Packaging." Plastics, Additives & Compounding **4**(4): 16-21.
- Matuana, L. M., D. P. Kamdem, and J. Zhang (2001). "Photoaging and Stabilization of Rigid PVC/Wood-Fiber Composites." J. Appl. Polym. Sci. **80**: 1943-1950.
- Matuana, L. M., C. B. Park, and J. J. Balatinecz (1998). "Cell Morphology and Property Relationships of Microcellular Foamed PVC/Wood-Fiber Composites." Polym. Eng. Sci. **38**(11): 1862-1872.
- Meyer, J. A. (1965). "Treatment of Wood-Polymer Systems Using Catalyst-Heat Techniques." For. Prod. J. **15**(9): 362-364.
- Meyer, J. A. (1981). "Wood-Polymer Materials: State of the Art." Wood Sci. **14**(2): 49-54.
- Minoura, Y., M. Ueda, S. Mizunuma and M. Oba (1969). "The reaction of polypropylene with maleic anhydride" J. Appl. Polym. Sci. **13**: 1625-1640.
- Monte, S. J. and G. Sugerman (1981). "United States and Japanese Application of Titanate Coupling Agents in Polyolefins." Polym.-Plast. Technol. Eng. **17**(1): 95-122.

- Morrison, R. T. and R. N. Boyd (1992). Organic Chemistry, 6th ed. Englewood Cliffs, NJ, Prentice-Hall, Inc., 971-985.
- Morton, J., J. Quarmley, and L. Rossi (2003). "Current and Emerging Applications for Natural and Woodfiber-Plastic Composites." The Seventh International Conference on Woodfiber-Plastic Composites, Forestry Products Society, Madison, WI, 3-6.
- Myers, G. E., I. S. Chahyadi, C. A. Coberly and D. S. Ermer (1991). "Wood Flour/Polypropylene Composites: Influence of Maleated Polypropylene and Process and Composition Variables on Mechanical Properties." Int. J. Polym. Mater. **15**: 21-44.
- Myers, G. E., I. S. Chahyadi, C. Gonzalez, and C. A. Coberly (1993). "Wood Flour and Polypropylene or High-Density Polyethylene Composites: Influence of Maleated Polypropylene Concentration and Extrusion Temperature on Properties." in: Wood Fiber/Polymer Composites: Fundamental Concepts, Processes, and Materials Options. M. P. Wolcott (Ed.), Proc. 1st Wood Fiber-Plastic Composite Conference, Madison, WI, 49-56.
- Nakamura, T., M. Okamura, Y. Moriguchi, and T. Hayase (1983). "Polyisocyanate Cross-linked Polymers Containing Cellulosic Component." US Patent 4,404,347: 7 pp.
- Nitz, H., P. Reichert, H. Romling, and R. Mulhaupt (2000). "Influence of compatibilizers on the surface hardness, water uptake, and the mechanical properties of poly(propylene) wood flour composites prepared by reactive extrusion." Macromol. Mater. Eng. **276/277**: 51-58.
- Oksman, K. and H. Lindberg (1998). "The influence of a SBS compatibilizer in polyethylene-wood flour composites." Holzforschung **52**(6): 661-666.
- Oksman, K., H. Lindberg, and A. Holmgren (1998). "The Nature and Location of SEBS-MA Compatibilizer in Polyethylene-Wood Flour Composites." J. Appl. Polym. Sci. **69**: 201-209.
- Olsen, D. J. (1991). "Effectiveness of Maleated Polypropylenes as Coupling Agents for Wood Flour/Polypropylene Composites." ANTEC, Proc. 49th Annual Technical Conference, Montreal, Canada, Society of Plastics Engineers, Brookfield, CT, 1886-1891.

- Raj, R. G. and B. V. Kokta (1989). "Compounding of cellulose fibers with polypropylene: Effect of fiber treatment on dispersion in the polymer matrix" J. Appl. Polym. Sci. **38**: 1987-1996.
- Raj, R. G. and B. V. Kokta (1991). "Improving the Mechanical Properties of HDPE-Wood Fiber Composites with Additives/Coupling Agents." ANTEC, Proc. 49th Annual Technical Conference, Montreal, Canada, Society of Plastics Engineers, Brookfield, CT, 1883-1885.
- Raj, R. G., B. V. Kokta, G. Grouleau, and C. Daneault (1990). "The Influence of Coupling Agents on Mechanical Properties of Composites Containing Cellulosic Fillers." Polym.-Plast. Technol. Eng. **29**(4): 339-353.
- Raj, R. G., B. V. Kokta, D. Maldas, and C. Daneault (1988). "Use of Wood Fibers in Thermoplastic Composites: VI. Isocyanate as a Bonding Agent for Polyethylene-Wood Fiber Composites." Polym. Comp. **9**(6): 404-411.
- Raj, R. G., B. V. Kokta, D. Maldas, and C. Daneault (1989). "Use of Wood Fibers in Thermoplastics. VII. The Effect of Coupling Agents in Polyethylene-Wood Fiber Composites." J. Appl. Polym. Sci. **37**: 1089-1103.
- Rengarajan, R., V. R. Parameswaran, S. Lee and P. L. Rinaldi (1990). "NMR analysis of polypropylene-maleic anhydride copolymer" Polymer **31**: 1703-1706.
- Rizvi, G., L. M. Matuana, and C. B. Park (2000). "Foaming of PS/Wood Fiber Composites Using Moisture as a Blowing Agent." Polym. Eng. Sci. **40**(10): 2124-2132.
- Rowell, R. M., R. Moisuk, and J. A. Meyer (1982). "Wood-Polymer Composites: Cell Wall Grafting With Alkylene Oxides and Lumen Treatments With Methyl Methacrylate." Wood Sci. **15**(2): 90-96.
- Rozman, H. D., W. B. Banks, and M. L. Lawther (1994). "Improvements of Fiberboard Properties Through Fiber Activation and Subsequent Copolymerization with Vinyl Monomer." J. Appl. Polym. Sci. **54**: 191-200.
- Russell, K. E. (1995). "Grafting of maleic anhydride to hydrocarbons below the ceiling temperature" J. Polym. Sci., Part A: Polym. Chem. **33**(3): 555-561.
- Russell, K. E. and E. C. Kelusky (1988). "Grafting of maleic anhydride to n-eicosane" J. Polym. Sci.: Part A: Polym. Chem. **26**: 2273-2280.

- Sain, M. M., B. V. Kokta, and D. Maldas (1993). "Effect of Reactive Additives on the Performance of Cellulose Fiber-Filled Polypropylene Composites." J. Adhesion Sci. Technol. **7**(1): 49-61.
- Sanadi, A. R., R. M. Rowell, and R. A. Young (1992). "Estimation of Fiber-Matrix Interfacial Shear Strengths in Lignocellulosic-Thermoplastic Composites." in: Materials Interactions Relevant to Recycling of Wood-Based Materials. R. M. Rowell, T. L. Laufenberg and J. K. Rowell (Ed.), Pittsburgh, PA, Materials Research Society. **266**: 81-92.
- Sathe, S. N., G. S. S. Rao and S. Devi (1994). "Grafting of maleic anhydride onto polypropylene: Synthesis and characterization" J. Appl. Polym. Sci. **53**: 239-245.
- Schut, J. H. (1999). "For Compounding, Sheet & Profile: Wood is Good." Plastics Technology March: 46-52.
- Sedlackova, M., I. Lacik and I. Chodak (2001). "Poly(ethylene-co-methacrylic acid) as an effective compatibilizer of LDPE/wood flour composite." Macromolecular Symposia **170**(Property Tailoring of Thermoplastics-Based Blends and Composites): 157-164.
- Sellers, T., Jr. (2001). "Wood Adhesive Innovations and Applications in North America." For. Prod. J. **51**(6): 12-22.
- Sellers, T., Jr., G. D. Miller, Jr., and M. Katabian (2000). "Recycled Thermoplastics Reinforced with Renewable Lignocellulosic Materials." For. Prod. J. **50**(5): 24-28.
- Shoemaker, P. D. and H. O. McQueary (1975a). "Polyisocyanate: Formaldehyde Binder System for Cellulosic Materials." US Patent 3,919,017: 5 pp.
- Shoemaker, P. D. and H. O. McQueary (1975b). "Manufacture of Multilayer Panels Using Polyisocyanate: Formaldehyde Binder System." US Patent 3,930,110: 5 pp.
- Simonsen, J., R. Jacobsen, and R. Rowell (1998). "Wood-Fiber Reinforcement of Styrene-Maleic Anhydride Copolymers." J. Appl. Polym. Sci. **68**: 1567-1573.
- Simonsen, J. and T. Rials (1992). "Enhancing the Interfacial Bond Strength of Lignocellulosic Fiber Dispersed in Synthetic Polymer Matrices." in: Materials Interactions Relevant to Recycling of Wood-Based Materials, R. M. Rowell, T. L. Laufenberg, and J. K. Rowell (Ed.), Pittsburgh, PA, Materials Research Society, 105-111.

- Simonsen, J. and T. Rials (1996). "Morphology and Properties of Wood-Fiber Reinforced Blends of Recycled Polystyrene and Polyethylene." J. Thermoplastic Comp. Mater. **9**: 292-302.
- Štepek, J. and H. Daoust (1983). "Lubricants and Mold-Release Agents," Additives for Plastics, Srpinger-Verlag New York Inc., 34-49.
- Takase, S. and N. Shiraishi (1989). "Studies on Composites from Wood and Polypropylenes. II." J. Appl. Polym. Sci. **37**: 645-659.
- Wang, Y., F.-C. Yeh, S.-M. Lai, H.-C. Chan and H.-F. Shen (2003). "Effectiveness of functionalized polyolefins as compatibilizers for polyethylene/wood flour composites." Polymer Engineering and Science **43**(4): 933-945.
- Wolcott, M. P. (1996). "The role of thermoplastics in conventional wood composites". Proceeding of the 30th Washington State University International Particleboard/Composites Materials Symposium, Pullman, WA, 37-44.
- Wolcott, M. P. (2003). "Formulation and process development of flat-pressed wood-polyethylene composites." For. Prod. J. **53**(9): 25-32.
- Wolcott, M. P. and K. Englund (1999). "A Technology Review of Wood-Plastic Composites." the 33rd Proceedings of the Washington State University International Particleboard/Composite Materials Symposium, Pullman, WA, 103-111.
- Wolcott, M. P. and P. M. Smith (2004). "Opportunities and Challenges for Wood-Plastic Composites in Structural Applications." Progress in Woodfibre-Plastic Composites Conference, Toronto, Canada, 1-10.
- Woodhams, R. T. (1984). "Reinforced Resin Composites." US Patent 4,442,243: 6 pp.
- Xanthos, M. (1983). "Processing Conditions and Coupling Agent Effects in Polypropylene/Wood Flour Composites." Plast. Rubber Process. Appl. **3**(3): 223-228.
- Youngquist, J. A. (1995). "Unlikely Partners? The Marriage of Wood and Nonwood Materials." For. Prod. J. **45**(10): 25-30.
- Zadorecki, P. and P. Flodin (1985a). "Surface Modification of Cellulose Fibers. II. The Effect of Cellulose Fiber Treatment on the Performance of Cellulose-Polyester Composites." J. Appl. Polym. Sci. **30**: 3971-3983.

- Zadorecki, P. and P. Flodin (1985b). "Surface Modification of Cellulose Fibers. I. Spectroscopic Characterization of Surface-Modified Cellulose Fibers and Their Copolymerization with Styrene." J. Appl. Polym. Sci. **30**: 2419-2429.
- Zhang, C., K. Li and J. Simonsen (2004). "Improvement of interfacial adhesion between wood and polypropylene in wood-polypropylene composites." J. Adhesion Sci. Technol. **18**(14): 1603-1612.
- Zhang, H., G. Rizvi, and C. B. Park (2004). "Development of an Extrusion System for Producing Fine-Celled HDPE/Wood-Fiber Composite Foams Using CO₂ as a Blowing Agent." Adv. Polym. Technol. **23**(4): 263-276.