

CHEMICAL COUPLING IN WOOD FIBER AND POLYMER
COMPOSITES: A REVIEW OF COUPLING AGENTS AND
TREATMENTS¹

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ABSTRACT

Coupling agents in wood fiber and polymer composites (WFPC) play a very important role in improving the compatibility and adhesion between polar wood fibers and non-polar polymeric matrices. In this paper, we review coupling agents, pretreatment, and mixing technology for wood fiber and polymer currently used in the manufacture of WFPC. So far, over forty coupling agents have been used in production and research. These agents are classified as organic, inorganic, and organic-inorganic groups, among which organic agents are better than inorganic agents because of stronger interfacial adhesion. The most popular coupling agents currently being used include isocyanates, anhydrides, silanes, and anhydride-modified copolymers. Coupling agents are usually coated on the surface of wood fiber, polymer or both by compounding, blending, soaking, spraying, or other methods. Three basic processes suitable for coupling treatment are discussed: directly coating during mixing and fully or partly pretreating before mixing. The pretreatment of wood fiber and polymer by coating or grafting is the preferred method to improve the mechanical properties of WFPC.²

Keywords: Coating, coupling agents, grafting, polymer, thermoplastic matrix, WFPC, wood fiber.

INTRODUCTION

Wood fiber and polymer composites (WFPC) are normally produced by mixing wood fiber with polymer, or by adding wood

fiber as filler in a polymer matrix, and pressing or molding under high pressure and temperature. Most polymers, especially thermoplastics, are non-polar (hydrophobic) substances that are not compatible with polar (hydrophilic) wood fibers and, therefore, poor adhesion between polymer and wood fiber in WFPC can result (Geotler 1983; Klason et al. 1984). In order to improve the affinity and adhesion

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² See nomenclature following references.

between wood fibers and thermoplastic matrices in production, chemical coupling agents have been employed (Chun and Woodhams 1984; Woodhams et al. 1984; Dalvåg et al. 1985; Schneider and Brebner 1985). Coupling agents are substances that are used in small quantities to treat a surface so that bonding occurs between it and other surfaces, e.g., wood and thermoplastics (Pritchard 1998).

Generally, coupling agents comprise bonding agents and surfactants (surface-active agents), including compatibilizers and dispersing agents (Štepek and Daoust 1983; Radian Corporation 1987; Clint 1998). Bonding agents act as bridges that link wood fibers and thermoplastic polymers by one or more of the following mechanisms: covalent bonding, polymer chain entanglement, and strong secondary interactions as in the case of hydrogen bonding (Raj et al. 1988; Maldas et al. 1989a). Compatibilizers are used to provide compatibility between otherwise immiscible polymers through reduction of the interfacial tension (Pritchard 1998). Some compatibilizers, such as acetic anhydride and methyl isocyanate, are monofunctional reactants. They lower the surface energy of the fiber, and make it non-polar, more similar to the plastic matrix. Some bonding agents, such as maleated polypropylene (MAPP), maleated styrene-ethylene/butylene-styrene (SEBS-MA) and styrene-maleic anhydride (SMA), also act as compatibilizers in WFPC (Oksman and Lindberg 1998; Oksman et al. 1998; Simonsen et al. 1998). Dispersing agents reduce the interfacial energy at the wood fiber-matrix interface to help uniform dispersion of wood fiber in a polymer matrix without aggregation and thereby facilitate the formation of new interfaces (Rosen 1978; Porter 1994). For example, stearic acid and its metallic salts are used to improve the dispersibility of wood fibers in the matrix. In general, compatibilizers and dispersing agents do not form strong adhesion at the fiber-matrix interface (Štepek and Daoust 1983). Thus, a functional distinction between bonding agents, compatibilizers, and dispersing agents should be noticed. In this paper, however, all bonding

agents and surfactants are lumped together as coupling agents for the purpose of the review.

With the development of coupling agents, a number of pretreatment (i.e., fiber coating and graft co-polymerization) and mixing processes for improving mechanical properties of WFPC have been introduced. For example, Youngquist and colleagues (Krzysik et al. 1990; Krzysik and Youngquist 1991) conducted successful experiments on the bonding of air-formed wood fiber-polypropylene composites using MAPP as a coupling agent. They developed an excellent coating method to spray the emulsified Epolene E-43 on wood fiber before formation. As a result of these efforts, WFPC have been developed very rapidly during the last decade.

Several review articles on wood polymer composites have been published (e.g., Hamed and Coran 1978; Meyer 1981, 1982, 1984; Rowell and Konkol 1987; Schneider 1994; Youngquist 1995). These reviews cover from chemical modification and treatment of wood and plastics to production technologies and applications for various types of wood polymer composites. However, none of these reviews systematically dealt with coupling agents and treatments currently used in this field. The objective of this work is to provide a state-of-the-art review on coupling agents, pretreatment of wood fiber and polymer, and mixing technology for the manufacture of WFPC. The adhesion mechanism and coupling performance of various coupling agents will be discussed in future publications.

COUPLING AGENTS

Historical account

Bridgeford (1963) invented a method to graft olefinically unsaturated monomers onto wood fiber with a catalyst system containing ferrous cations and hydrogen peroxide to modify the compatibility between wood fiber and thermoplastic polymer. This method was further developed by other researchers (Gulina et al. 1965; Faessinger and Conte 1967; Dimov and Pavlov 1969; Kokta and Valade 1972; Hornof et al. 1976). Meyer (1968) was pos-

TABLE I. *Coupling agents used in WFPC.*

Coupling agent	Additive ^a	Reference
Organic agents		
1. Acrylates		
Glycidyl methacrylate (GMA)	TBPB	Takase and Shiraishi 1989
Hydroxyethyl methacrylate (HEMA)	TBPB	Takase and Shiraishi 1989
2. Amides and imides		
N,N'- <i>m</i> -Phenylene bismaleicimide (BMI)	DCP	Xanthos 1983; Sain and Kokta 1994
3. Anhydrides		
Acetic anhydride (AA)	—	Chtourou et al. 1992
Alkyl succinic anhydride (ASA)	—	Gatenholm et al. 1992, 1993
Succinic anhydride (SA)	BPO, pyridine	Rozman et al. 1994
Phthalic anhydride (PHA)	—	Maldas and Kokta 1989, 1990c
Maleic anhydride (MA)	BPO or TBPB	Maldas and Kokta 1990d, 1991a, b
4. Chlorotriazines and derivatives		
2-Diallylamino 4,6-dichloro- <i>s</i> -triazine (AACA)	BPO	Zadorecki and Flodin 1985
2-Octylamino 4,6-dichloro- <i>s</i> -triazine (OACA)	BPO	Zadorecki and Flodin 1985
Methacrylic acid, 3-((4,6-dichloro- <i>s</i> -triazine-2-yl) amino)propyl ester (MAA-CAAPE)	BPO	Zadorecki and Flodin 1985
5. Epoxides		
Butylene oxide (BO)	—	Rowell et al. 1982
Propylene oxide (PO)	—	Rowell et al. 1982
6. Isocyanates		
Ethyl isocyanate (EIC)	—	Raj et al. 1988; Maldas and Kokta 1991b
Hexamethylene diisocyanate (HMDIC)	—	Raj et al. 1988; Maldas and Kokta 1991b; Gatenholm et al. 1992
Poly[ethylene(polyphenyl isocyanate)] (PEPPIC)	—	Selke et al. 1990
Poly[methylene(polyphenyl isocyanate)] (PMPPIC)	DCP	Maldas et al. 1989a, b; Maldas and Kokta 1989, 1990a, b, 1991a; Raj et al. 1988
Toluene 2,4-diisocyanate (TDIC)	—	Raj et al. 1988; Kokta et al. 1990a
7. Organic acids		
Abietic acid (ABAC)	—	Kokta et al. 1990b
Linoleic acid (LAC)	—	Kokta et al. 1990b
8. Monomers		
Acrylonitrile (AN)	Vazo/ γ -ray	Kenaga et al. 1962; Kent et al. 1962;
Butyl acrylate (BA)	or	Ramalingam et al. 1963; Meyer 1965,
Epoxypropyl methacrylate (EPMA)	CS ₂ /H ₂ O ₂ /Fe ²⁺	1981; Ellwood et al. 1972; Maldas et
Methacrylic acid (MAA)	or	al. 1988; 1989a; Maldas and Kokta
Methyl methacrylate (MMA)	N ₂ /H ₂ O ₂ /(CH ₃) ₂ SO ₄	1990d; Daneault et al. 1989; Chen et
Styrene	or	al. 1995
Vinyl compounds	K ₂ S ₂ O ₈ /H ₂ O ₂	
9. Polymers and copolymers		
Ethyl/vinyl acetate (E/VAC)	—	Dalväg et al. 1985
Maleated polyethylene (MAPE)	—	Sanadi et al. 1992
Maleated polypropylene (MAPP)	DCP or TBPB, xylene	Dalväg et al. 1985; Kishi et al. 1988; Han et al. 1989; Takase and Shiraishi 1989; Myers et al. 1991, 1993; Olsen 1991

TABLE 1. Continued.

Coupling agent	Additive ^a	Reference
N,N'- <i>m</i> -Phenylene bismaleicimide modified polypropylene (BPP)	—	Sain et al. 1993
Polymethacrylic acid (PMAA)	—	Liang et al. 1994
Polystyrene/polymethacrylic acid (PS-PMAA)	—	Liang et al. 1994
Polyvinyl acetate (PVAC)	—	Liang et al. 1994
Mono- and dimethylolmelamine resin (DMM)	CH ₂ O, CH ₃ OH (or C ₂ H ₅ OH)	Hua et al. 1987
Phenol-formaldehyde resin (PF)	CH ₃ OH or H ₂ O	Coran and Patel 1982; Chtourou et al. 1992; Simonsen and Rials 1992, 1996
Styrene-ethylene-butylene-styrene/maleic anhydride (SEBS-MA)	—	Gatenholm et al. 1995; Hedenberg and Gatenholm 1995; Oksman et al. 1998
Styrene/maleic anhydride (SMA)	—	Simonsen et al. 1998
Inorganic agents		
1. Sodium silicate (Na ₂ SiO ₃)	MA or PMPPIC	Maldas and Kokta 1990a, d
Organic-inorganic agents		
1. Silanes		
Vinyltri(2-methoxyethoxy) silane (A-172)	CCl ₄ , DCP	Beshay et al. 1985; Maldas et al. 1988, 1989a; Raj et al. 1989, 1990; Kokta et al. 1990c
γ-Methacryloxypropyltrimethoxy silane (A-174)	CCl ₄ , DCP, CH ₃ OH	Xanthos 1983; Beshay et al. 1985; Bataille et al. 1989; Maldas et al. 1989a; Raj et al. 1988, 1989; Kokta et al. 1990c
β-(3,4-Epoxy cyclohexyl)ethyltrimethoxy silane (A-186)	LPO or DTBPO	Kokta et al. 1990c
γ-Glycidoxy propyltrimethoxy silane (A-187)	LPO or DTBPO	Kokta et al. 1990c
γ-Aminopropyltrimethoxy silane (A-1100)	DCP or BPO, MA, <i>p</i> -xylene	Maldas et al. 1988, 1989a; Bataille et al. 1989; Raj et al. 1989; Kokta et al. 1990c
2. Titanates		
Titanium di(dioctylpyrophosphate)oxyacetate (KR 138S)	CH ₂ Cl ₂	Dalvåg et al. 1985

^a BPO—benzoyl peroxide, DCP—dicumyl peroxide, LPO—lauroyl peroxide, TBPB—*tert*-butyl peroxide benzoate, DTBPO—di-*tert*-butyl peroxide.

sibly the first person who suggested using a coupling agent (which he called a crosslinking agent) to improve the mechanical properties of wood-polymer materials. Gaylord (1972) patented maleic anhydride (MA) as a coupling agent to combine cellulose and polyethylene (PE) or polyvinyl chloride (PVC) in the presence of a free radical initiator.

However, little attention had been paid to the applications of coupling agents in WFPC until the 1980s. From 1980 to 1985, a series of patents was issued for the application of

isocyanate and MA coupling agents in WFPC (Coran and Patel 1982; Geottler 1983; Nakamura et al. 1983; Woodhams 1984). Xanthos (1983) introduced γ-methacryloxypropyltrimethoxy silane (A-174) and N,N'-*m*-phenylene dimaleimide (BMI or PDM) as coupling agents to improve the mechanical properties of wood flour and polypropylene composites. Some coupling agents, such as silane A-174 and propylene oxide (PO), were also applied in wood and plastic composites (WPC) to improve their dimensional stability (Rowell et al.

1976; Rowell and Ellis 1978; Schneider and Brebner 1985).

As pioneers in the applications of coupling agents in WFPC, Klason and coworkers made an initial study on using MA as the coupling agent in the cellulose flour and polypropylene (PP) composites (Dalvåg et al. 1985). Woodhams et al. (1984) successfully introduced Epolene E-43, a kind of MAPP with low-molecular weight, as a coupling agent in thermomechanical pulp (TMP) and isotactic PP composites. These two articles have been the important references for the research on chemical coupling in WFPC.

The Kokta group in Canada made a number of investigations on isocyanate, alkoxysilane, and anhydride coupling agents. Through their efforts, poly[methylene(polyphenyl isocyanate)] (PMPPIC) has been successfully used as an important coupling agent in melt-blended composites. Kokta (1988) patented PMPPIC for cellulose fiber and PE composites. In Japan, the Shiraishi group focused on the application of MAPP with high-molecular weight (Kishi et al. 1988; Han et al. 1989). In the United States and Sweden, much work has been done on the application of MAPP and other coupling agents in the melt-blending process, such as injection molding, extrusion, and transfer molding (Myers et al. 1990, 1991, 1993; Olsen 1991; Liang et al. 1994; Gatenholm et al. 1995).

Classification and action of coupling agents

Over forty coupling agents have been used in WFPC (Table 1). Coupling agents are classified into organic, inorganic, and organic-inorganic groups. Organic agents include isocyanates, anhydrides, amides, imides, acrylates, chlorotriazines, epoxides, organic acids, monomers, polymers, and copolymers. Only a few inorganic coupling agents, such as silicates, are used in WFPC. Organic-inorganic agents include silanes and titanates.

Organic coupling agents in WFPC normally have bi- or multifunctional groups in their molecular structure. These functional groups,

such as (-N=C=O) of isocyanates, $[-(\text{CO})_2\text{O}-]$ of maleic anhydrides, and (-Cl-) of dichlorotriazine derivatives, interact with the polar groups [mainly hydroxyl groups (-OH)] of cellulose and lignin to form covalent or hydrogen bonding (Zadorecki and Flodin 1985; Raj et al. 1988; Maldas et al. 1989a; Raj and Kokta 1991; Chtourou et al. 1992). Alternatively, organic coupling agents can modify the polymer matrix by graft copolymerization, thus resulting in strong adhesion, even crosslinking, at the interface.

Inorganic coupling agents possibly act as dispersing agents to counteract the surface polarity of wood fiber and improve the compatibility between wood fiber and polymer (Dalvåg et al. 1985; Maldas and Kokta 1990a, b). Organic-inorganic agents are hybrid compounds in structure. For example, titanates usually contain a titanium center and an organic part surrounding this inorganic atom. The functionality of the organic part in these agents determines their coupling effectiveness in WFPC. Organic-inorganic coupling agents are between organic and inorganic agents in function.

Anhydrides such as MA, AA, SA, and PHA are popular coupling agents in WFPC. AA, SA, and PHA have two functional groups, i.e., carboxylate groups (-COO-), which can link wood fiber through esterification or hydrogen bonding. But MA is an α , β -unsaturated carbonyl compound, containing one carbon-carbon double bond (C=C) and two carboxylate groups (-COO-). This conjugated structure greatly increases the graft reactivity of the carbon-carbon double bond on the heterocyclic ring with the polymer matrix through the conjugate addition under a radical initiator (Morrison and Boyd 1992), resulting in crosslinking or strong adhesion at the interface. However, the molecular chain of MA is much shorter than that of polymer matrix and wood fibers. This discrete nature makes MA not so effective to improve the interfacial adhesion (Maldas et al. 1988; Maldas and Kokta 1990d). Accordingly, MA is usually used to modify the polymer matrix by graft copoly-

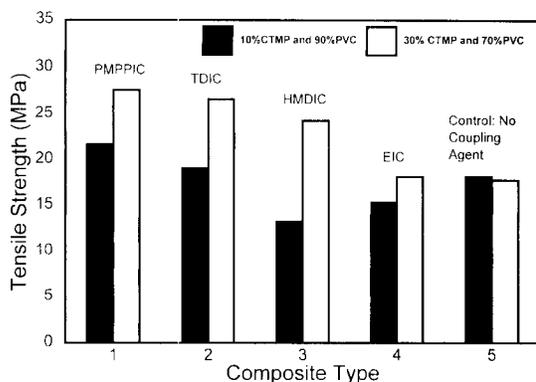


FIG. 1. Comparison of coupling effectiveness for different isocyanate coupling agents in PVC and CTMP (aspen) composites (plot made with test data published by Kokta et al. 1990a). Coupling agent used was: 1—PMPPIC, 2—TDIC, 3—HMDIC, 4—EIC, and 5—no coupling agent (control). Concentration of coupling agents was 0.5% based on weight of the polymer matrix.

merization. The formed copolymers, e.g., MAPE, MAPP, SEBS-MA, and SMA, are used as coupling agents (Raj et al. 1990; Olsen 1991; Sanadi et al. 1992; Sain et al. 1993; Hedenberg and Gatenholm 1995; Oksman et al. 1998; Simonsen et al. 1998).

Isocyanate links wood fiber through the urethane structure (or a carbamate), which is more stable to hydrolysis than esterification (John 1982; Maldas and Kokta 1990c). Due to the difference in molecular structure, the reactivity of isocyanate decreases in the following order: PMPPIC, TDIC, HMDIC, EIC (Kokta et al. 1990a). The delocalized π -electrons of the benzene rings in PMPPIC and TDIC lead to the stronger interaction with PS and other polymer matrices compared with HMDIC and EIC without π -electrons. Moreover, the cellulose phase and the polymer phase (PS or PVC) are continuously linked by PMPPIC at the interface, while the discrete nature of TDIC, HMDIC, and EIC makes them inferior in this respect (Maldas et al. 1988). A comparison of the performance of these coupling agents is shown in Fig. 1. As shown, composites with PMPPIC as a coupling agent had the highest tensile strength, compared with those made with other types of

coupling agents. Thus, PMPPIC is the best coupling agent in these isocyanates, while TDIC has better coupling effectiveness than HMDIC and EIC.

Silanes, represented as $R-Si(OR')_3$, have better performance in organic-inorganic coupling agents recently used in WFPC, because the attachment of silanes to hydroxy groups of cellulose or lignin is accomplished either directly to the alkoxy group ($-OR'$) attached to silicon or via its hydrolyzed products (i.e., silanol) by the hydrogen bonds or ether linkage (Kokta et al. 1990c). The functional group ($R-$) in silanes also influences the coupling action. Silane A-172 and A-174 both contain a vinyl group; silane A-186 and A-187, an epoxy group; while silane A-1100, an amino group. When in contact with PVC, polar methacryloxy groups in silane A-174 form a polar chain that is more hydrophilic than that of A-172, resulting in poor adhesion. But for other matrices, the α , β -unsaturated carbonyl structure of acrylic groups in A-174 may help form strong adhesion, even crosslinking, at the interface. Silane A-186 and A-187 with an epoxy group link cellulose and lignin by ether linkages, whereas NH_2 groups of A-1100 offer mostly hydrogen bonding, which is a weaker force (Kokta et al. 1990c).

Dichlorotriazines and derivatives have multifunctional groups in their molecular structure. These groups have different functions in the coupling reaction (Zadorecki and Flodin 1985). On the heterocyclic ring, the reactive chlorines react with the hydroxyl group ($-OH$) of wood fiber and give rise to the ether linkage between the cellulose phase and the coupling agent. The electronegative nitrogen may link the hydroxyl group through hydrogen bonding. On the alkyl chain, the carbon-carbon double bonds ($C=C$) form covalent bonds with the polymer matrix by grafting. At the same time, the electronegative nitrogen in the amino groups and oxygen in the carboxylate groups also link the cellulose phase through hydrogen bonding.

Some thermosetting resin adhesives, such as phenol-formaldehyde resin (PF) and mono-

dimethylolmelamine resin (DMM), have been introduced as a bonding agent in WFPC (Coran and Patel 1982; Hua et al. 1987; Simonsen and Rials 1992, 1996). PF and DMM resins can crosslink wood fibers with the methylene (-CH₂-) linkage resulting from the condensation reaction between their reactive methylol groups (-CH₂OH) and the hydroxyl groups (-OH) of wood fiber. Although these methylol groups can not react with the thermoplastic matrix, PF and DMM improve the interfacial adhesion through molecular entanglement with the matrix (Simonsen and Rials 1992, 1996).

Similar to MA, acrylic acids and methacrylates (e.g., MAA, MMA, EPMA, and GMA) also contain the α , β -unsaturated carbonyl structure, which may lead to crosslinking or strong interfacial adhesion. Organic acids such as abietic acid (ABAC) and linoleic acid (LAC) contain dienes and carboxylate groups in their molecular structure, which are helpful to form strong adhesion in the interfacial region. In addition, the reactive allylic group (-CH₂-) in LAC might graft to the polymer matrix (Kokta et al. 1990b). Lacking chemical bonding at the interface, KR 138S and Na₂SiO₃ perform poorly in WFPC (Dalvåg et al. 1985; Maldas and Kokta 1990a, b). Na₂SiO₃ is usually required to mix with organic coupling agents.

PRETREATMENT OF WOOD FIBER AND POLYMER

Pretreatment of wood fiber and polymer with coupling agents is extensively applied before mixing to improve the mechanical properties of WFPC. There are two pretreatment methods: 1) coating coupling agents on wood fiber, and 2) modifying wood fiber and polymer by graft co-polymerization (Maldas et al. 1988, 1989a).

Coating treatment

The compatibility between wood fiber and polymer is enhanced by coating wood fibers with coupling agents. This process can either cause the polar hydroxyl groups (-OH) of

wood fibers to react with coupling agents (such as PMPPIC) which have a linear molecular structure similar to the polymer matrix, or create a chemical interaction between coupling agents (such as MA) and the matrix (Maldas et al. 1989a; Kokta et al. 1990a).

Four kinds of coating methods have been used in WFPC production: compounding, blending, soaking, and spraying. The compounding method mixes coupling agents at high temperature with wood fibers and polymers in an extruder (Dalvåg et al. 1985; Myers et al. 1991). This method is mostly used in the melt-blending process. For the blending method, a coupling agent is coated on the surface of wood fiber, polymer or both in a roll mill or a magnetic stirrer at low or high temperature (Maldas et al. 1988). For the soaking method, wood fiber (such as cellulose fiber) can be first impregnated in the form of sheets of paper with a coupling agent solution containing initiators or other additives. Then the impregnated paper is removed from the solution and placed between two pieces of polymer release film for molding (Zadorecki and Flodin 1985; Sanadi et al. 1992). In the spraying process, coupling agents are emulsified and sprayed on to the surface of wood fibers (Krzysik et al. 1990; Krzysik and Youngquist 1991). Both blending and spraying are suitable for the precoating of wood fiber and polymer before mixing. Spraying and soaking are better than compounding and blending for coating processes because coupling agents are distributed at the interface more evenly and efficiently in the former two cases. However, it is difficult to accurately control the impregnating amount of coupling agents for the soaking method.

Graft co-polymerization

During graft co-polymerization, coupling agents either crosslink part of the polymer matrix to the wood surface to form a non-polar copolymer or modify the polarity of the polymer matrix by grafting it with polar monomers to form a graft copolymer. This results in the

improvement of the interfacial adhesion. Recently, several graft methods have been used in WFPC: 1) xanthation, 2) radiation, 3) maleation, 4) methacrylate graft co-polymerization, 5) acetylation, and 6) others.

In the xanthation process, wood fibers are first kept under carbon disulfide (CS_2) vapor in a peroxide-ferrous-ion initiation system for a certain period of time. Xanthated fibers are then mixed with monomers, such as styrene, butyl acrylate, or epoxy compounds, to form graft copolymers (Maldas et al. 1988, 1989a; Maldas and Kokta 1990d; Daneault et al. 1989). This method has been widely used for pretreating wood fiber in WFPC.

Another conventional method of grafting monomers on to wood cells is by using high-energy radiation sources (such as beta (β) and gamma (γ) rays) with or without a free radical catalyst. For example, the polymerization of vinyl or styrene monomers with wood components was generated by using Cobalt-60 (^{60}Co) gamma radiation (Kenaga et al. 1962; Kent et al. 1962; Ramalingam et al. 1963; Meyer 1965, 1981, 1984; Ellwood et al. 1972). Usually, at least 500,000 to 1,000,000 curies of Cobalt-60 are required for a production source (Meyer 1981).

In the maleation method, MA is used to modify the polymer matrix in the presence of a free radical initiator. It is then grafted on to wood fibers by a succinic half-ester bridge (Gaylord 1972; Chun and Woodhams 1984; De Vito et al. 1984; Kishi et al. 1988; Maldas and Kokta 1990d). Besides the graft application of MA in the PS matrix (Maldas and Kokta 1990d, 1991b), MA can modify PE, PP and SEBS to form graft copolymers (Maldas et al. 1989b; Gatenholm et al. 1992). Recently, maleic-anhydride-modified polypropylene or maleated polypropylene (MAPP) is a popular coupling agent for WFPC (Gaylord 1972; Chun and Woodhams 1984; Olsen 1991; Maldas and Kokta 1994). As mentioned before, two kinds of MAPP are used in WFPC. One is the MAPP with a high-molecular weight ($M_w > 30,000$) (Kishi et al. 1988; Han et al. 1989; Takase and Shiraishi 1989), such as

63H, 13H, and Hercoprime G (Olsen 1991; Gatenholm et al. 1992). The other type, such as Epolene E-43 (or 47L) and 15L, has a low-molecular weight ($M_w < 20,000$) (Woodhams et al. 1984; Olsen 1991; Myers et al. 1990, 1991, 1993). Maleated polymers are usually coated on to wood fiber before mixing.

The acid number, which represents the amount of functionality in a coupling agent, and molecular weight are two important properties influencing the coupling effectiveness of MAPP in WFPC (Olsen 1991). Generally, MAPP with a high-molecular weight and high acid number effectively improves the mechanical properties of WFPC. It was suggested that the Epolene E-43 probably acts as a dispersing agent instead of a true coupling agent in melt-blending formation because of its low-molecular weight (Wegner et al. 1992). Krzysik and coworkers (Krzysik et al. 1990; Krzysik and Youngquist 1991), however, reported that Epolene E-43 greatly improved the bonding of air-formed wood fiber and propylene composites.

Methacrylates can be used in graft reactions. For example, GMA and HEMA have been used to modify wood fiber and polymer (Maldas et al. 1989a; Takase and Shiraishi 1989). In a previous study, RGP was pretreated with an acetylating agent containing AA before mixing with MAPP (Kishi et al. 1988). For WPC, some epoxides [e.g., propylene oxide (PO) or butylene oxide (BO)] are grafted onto the cell wall before the impregnation of MMA into the cell lumen (Rowell et al. 1982). Other coupling agents, such as BMI (or PDM) and SA, are also applied in the graft copolymerization for PP matrix and TMP (Rozman et al. 1994; Sain and Kokta 1994).

MIXING TECHNOLOGY

Mixing processes

Based on the coating and grafting methods in WFPC, coupling treatments are generally divided into three basic processes (Fig. 2). Coupling agents can be directly coated on wood fiber and polymer during mixing

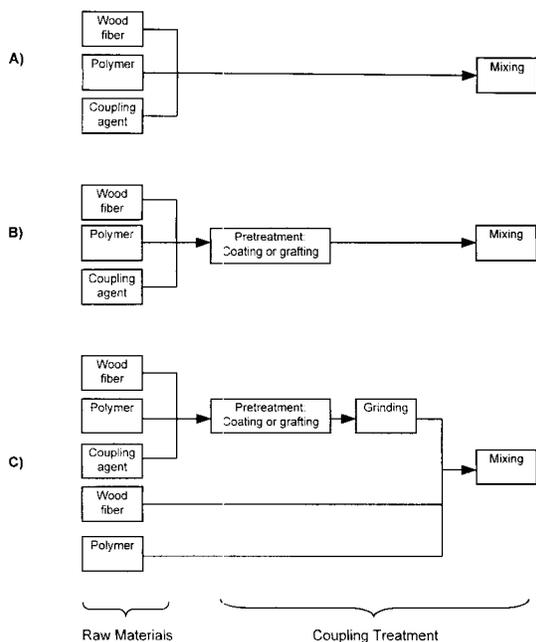


FIG. 2. Three basic coupling treatments in WFPC: A) directly coating during mixing, B) and C) pretreating before mixing. In (B) wood fiber, polymer, or both is coated or grafted with a coupling agent, but in (C) only part of fiber and polymer is pretreated by a coupling agent, then mixed with untreated fiber and polymer.

(Woodhams et al. 1984; Takase and Shiraishi 1989; Maldas et al. 1989a; Myers et al. 1991). This process (one-step process) is quite simple and cheap (Fig. 2a). In the two-step process, coating or grafting is carried out before mixing (Fig. 2b, c). Coupling agents are coated or grafted on the surface of wood fiber, polymer or both before mixing in the second process (Maldas et al. 1988; Krzysik et al. 1990; Maldas and Kokta 1990d; Krzysik and Youngquist 1991). In the third process, part of the polymer and wood fiber furnish is treated with a coupling agent, then mixed with untreated wood fiber and polymer (Maldas et al. 1989b; Kokta et al. 1990a). In the two-step process, the resulting mixtures are usually ground to mesh size 20 for melt-blending formation (Maldas et al. 1988, 1989b; Maldas and Kokta 1989, 1990a). All three processes are suitable for melt-blended composites. The second process

(Fig. 2b) is preferred for air-formed composites.

It has been suggested that a two-step process is better than a one-step process (Steppek and Daoust 1983). In the former case, less coupling agent and less mixing time are required to obtain good adhesion between wood fibers and polymers. Moreover, the two-step process helps increase the interface area (De Ruvo and Alfthan 1978; Maldas et al. 1989a), thus resulting in improving the mechanical properties of WFPC.

Mixing ratios

Coupling agents usually account for 2–8% by weight of wood fibers for melt-blending formation (wood fiber-to-matrix weight ratio is 50:50); and 1–4% for air-forming processes (wood fiber-to-matrix weight ratio is 70:30) (Maldas et al. 1989a, b; Krzysik et al. 1990; Krzysik and Youngquist 1991; Myers et al. 1991, 1993). Accordingly, a coupling agent accounts for only 1–3% of the total weight of a composite in WFPC. The mixing ratios of coupling agents, wood fibers, and thermoplastic polymers optimum to the mechanical properties of WFPC are shown in Table 2.

The concentration of coupling agents determines the coupling effectiveness in the composite. Generally, mechanical properties increase with increased concentration of a coupling agent (e.g., PMPPIC, MA, PHA, and MAPP) up to a certain limit, and then decline or level off at higher concentrations (Fig. 3). The reason that higher coupling agent concentrations result in lower mechanical properties of the composite possibly lies in 1) the formation of different by-products, 2) increase in concentration of unreacting or ungrafting coupling agents, and 3) interference with coupling reaction (John 1982; Beshay et al. 1985; Maldas et al. 1989a; Maldas and Kokta 1990d, 1991a, b). Consequently, an excess of a coupling agent is detrimental to the coupling reaction and may act as an inhibitor rather than a promoter of adhesion.

TABLE 2. Optimum ratios of coupling agent, polymer and wood fiber in WFPC.^a

Polymer	Wood fiber	Coupling agent ^b	Coating and mixing temperature ^c	Fabrication method	Reference
PP 70%	WF 30%	MAPP 6%	—	injection molding	Dalvåg et al. 1985
PS685D 70%	CTMP (aspen) 30%	A-172, A-174 4%	145–225°C (70–75°C)	Carver press	Maldas et al. 1989a
PP 50%	WF 50%	MAPP (E-43) 5%	215°C (200°C)	injection molding	Myers et al. 1991, 1993
PP 12–15% or 27–30%	CTMP (hemlock) 70% or 85%	MAPP (E-43) 1–4%	RT	air-forming, hot press	Krzysik et al. 1990; Krzysik and Youngquist 1991
PP 50%	RGP (radiata pine) 50%	MAPP 5%	170°C (200°C)	hot press	Takase and Shiraishi 1989
PS201 70–80%	CTMP (75% black spruce + 20% balsam + 5% aspen) 20–30%	PMPPIC 8%	175°C (175°C)	Carver press	Maldas et al. 1989b
PS201 65%	CTMP (aspen) 35%	PHA 10%	175°C	molding	Maldas and Kokta 1989, 1990c
PVC 70–80%	CTMP (aspen) 20–30%	PMPPIC 1–5%	145–150°C	Carver press	Kokta et al. 1990a
PS685D 75%	TMP (aspen) 25%	PMAA 4%	180–200°C	transfer molding	Liang et al. 1994
HDPE 70%	CTMP (aspen) 30%	PMPPIC 7%	130–160°C (RT)	Carver press	Raj et al. 1989

^a RT—room temperature, PP—polypropylene, PS—polystyrene, PVC—polyvinyl chloride, HDPE—high density polypropylene, WF—wood flour, TMP—thermomechanical pulp, CTMP—chemithermomechanical pulp, RGP—refiner ground pulp, A-172—vinyltri(2-methoxyethoxy) silane, A-174— γ -methacryloxy propyltrimethoxy silane, MAPP—maleated polypropylene, PHA—phthalic anhydride, PMAA—polymethacrylic acid, and PMPPIC—poly[methylene(polyphenyl isocyanate)].

^b By weight of wood fiber.

^c Values in the parentheses are coating temperature.

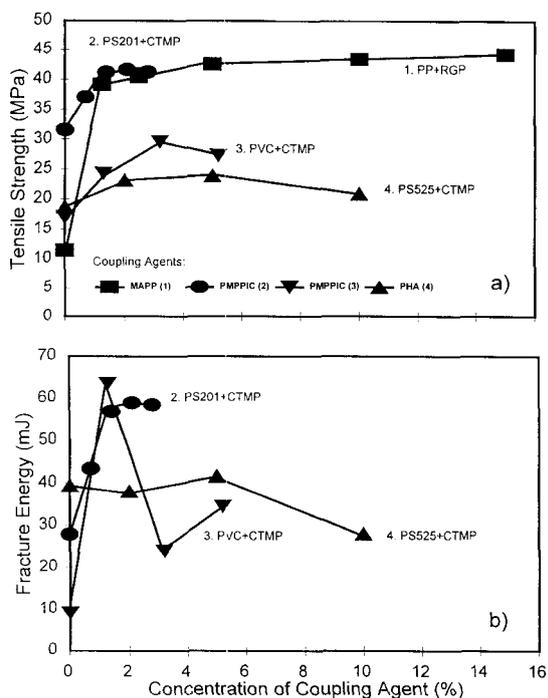


FIG. 3. Influence of concentration of coupling agents on the mechanical properties of WFPC: (a) tensile strength and (b) fracture energy (plots made with test data published by Han et al. 1989; Maldas et al. 1989a; Maldas and Kokta 1990c; Kokta et al. 1990a). Concentration of coupling agents was based on weight of the composite. Concentration of MA was 1.85 weight percent of MAPP. Composite type: 1. PP:RGP (radiata) = 50%:50%, 2. PS201: CTMP (aspen) = 70%:30%, 3. PVC:CTMP (aspen) = 70%:30%, and 4. PS525:CTMP (aspen) = 65%:35%.

Additives

Initiators are usually required with coupling agents during the coupling treatment, especially in graft copolymerization. The most widely used initiators are organic peroxides, including dicumyl peroxide (DCP), benzoyl peroxide (BPO), lauroyl peroxide (LPO), *tert*-butyl peroxy benzonate (TBPB), and di-*tert*-butyl peroxide (DTBPO) (Table 1). DCP is usually used with BMI, MAPP, PMPPIC, and silanes; and BPO with MA, SA, silane A-1100, and chlorotriazines. TBPB is used as a free radical initiator of MA and acrylates. LPO and DTBPO can be used in the silane coupling agents. In graft reactions, the concentration of

peroxide is usually between 0.5–1% by weight. Excess peroxide may adversely affect the mechanical properties of the composite because molecular chain scission of the polymer and cellulose occurs when peroxide is too abundant (Maldas and Kokta 1991a). DCP has also been found to be a better initiator for MA compared with BPO because the free radicals of DCP have superior thermal stability that leads to better graft performance (Maldas and Kokta 1991c). The free-radical initiator, 2,2'-azobisisobutyronitrile (also called Vazo), is usually combined with gamma radiation for graft reaction of styrene and vinyl monomers (Meyer 1981).

Organic solvents may be required with certain coupling agents. For example, carbon tetrachloride (CCl_4) is used in silanes A-172 and A-174 (Maldas et al. 1989a; Maldas and Kokta 1990c), while methylene dichloride (CH_2Cl_2) is a solvent of titanate coupling agents such as KR 138S (Dalvåg et al. 1985). Other solvents include xylene, pyridine, methanol, and ethanol (Xanthos 1983; Hau et al. 1987; Han et al. 1989; Myers et al. 1990, 1991; Gatenholm et al. 1993; Simonsen and Rials 1996).

During the coupling treatment, antioxidants, stabilizers, plasticizers, and other processing aids are also added to the blends to improve the physical and mechanical properties of a composite. For example, alumina trihydrate [$\text{Al}(\text{OH})_3$], magnesium oxide (MgO), boric acid (H_3BO_3), or borax ($\text{Na}_2\text{B}_4\text{O}_7$) provides flame retardation to the composite (Kishi et al. 1988; Han et al. 1989; Maldas and Kokta 1991a; Sain et al. 1993). The addition of magnesium oxide and boron compounds can protect wood fiber from thermal decomposition and degradation during high-temperature composite processing (Han et al. 1989; Sain et al. 1993). In addition, adding a moderate amount of MgO can improve the performance of MA because MgO reacts with water and the acid group to yield carboxylate ions ($-\text{COO}^-$). Concurrently, Mg^{2+} interacts with two carboxylate ions as a crosslinking agent and yields ionomer systems (Han et al. 1989). Organic additives

primarily used in coupling treatments are dioctyl phthalate (DOP), barium acetate (BaAc), Irganox-1010, Ionol, mono- and diglycerides of fatty acids (GMS), and distearyl thiodipropionate (DSTP) (Han et al. 1989; Krzysik et al. 1990; Myers et al. 1991).

Mixing conditions

Mixing conditions, i.e. temperature, time, and rotation speed, directly influence the coating quality and coupling agent performance (Takase and Shiraishi 1989; Maldas and Kokta 1990d; Chen et al. 1995). Usually, mixing temperature is controlled at less than 200°C for most coupling treatments to avoid decomposition and degradation of wood fibers and some thermoplastic matrices (Woodhams et al. 1984; Maldas et al. 1989a; Takase and Shiraishi 1989; Myers et al. 1993). For refiner ground pulp (RGP) and PP composites, the optimum mixing conditions are 10 minutes under a mixing temperature of 180°C and a rotation speed of 50 rpm (Takase and Shiraishi 1989). Maldas and Kokta (1990d) reported that the maximum improvement in mechanical properties of chemithermomechanical pulp (CTMP) and PS composites was achieved when the mixing time was 15 min at 175°C. For melt-blended composites, the blends are required to re-mix 5–10 times (about 6–8 min) during compounding to achieve a better distribution of coupling agents at the interface, when directly mixing coupling agents with polymer and wood fiber (Maldas et al. 1989a; Maldas and Kokta 1990a, b, c). Rotation speed has similar influence on the coupling effectiveness as does mixing time. It was reported that moderate mixing speeds were preferred for better fiber length distribution and coupling effectiveness (Takase and Shiraishi 1989).

CONCLUSIONS

Coupling agents in WFPC play a very important role in improving compatibility and adhesion between polar wood fibers and non-polar polymer matrices. So far, more than for-

ty coupling agents have been used in production and research. Organic coupling agents are better than inorganic coupling agents, because stronger adhesion is produced at the interface. Although a number of coupling agents are used or have been tested in production and research, the most popular are isocyanates, anhydrides, silanes, and anhydride-modified copolymers, such as PMPPIC and MAPP.

Coupling agents are usually coated on the surface of wood fiber, polymer or both by compounding, blending, soaking, spraying, or other coating methods. There are three basic mixing processes in production and research. Coupling agents can be directly mixed with wood fiber and polymer in the melt-blending formation, such as injection molding, extrusion, and transfer molding. They can also be coated or grafted on the surface of wood fiber, polymer or both. Then the pretreated and untreated wood fiber and polymer are kneaded. Usually, pretreatment of wood fiber and polymer by coating or grafting helps enhance the mechanical properties of WFPC.

Some of the important considerations in choosing coupling treatments are concentration and chemical structure of coupling agents, choice of wood fiber and matrix (e.g., shape, size, and species), ratio of wood fiber to total matrix weight, formation methods, and end-use requirements of the finished product. Future publications in this series will discuss the adhesion mechanism and coupling performance of different coupling agents.

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NOMENCLATURE

AA	acetic anhydride
AACA	2-diallylamino 4,6-dichloro-s-triazine
ABAC	abietic acid
AN	acrylonitrile
ASA	alkyl succinic anhydride
BA	butyl acrylate
BaAc	barium acetate
BMI (or PDM)	N,N'- <i>m</i> -phenylene bismaleicimide
BO	butylene oxide
BPO	benzoyl peroxide
BPP	N,N'- <i>m</i> -phenylene bismaleicimide modified polypropylene
⁶⁰ Co	Colbat-60 gamma radiation
CTMP	chemithermomechanical pulp
DCP	dicumyl peroxide
DMM	mono- and dimethylolmelamine resin
DOP	dioctyl phthalate
DSTP	distearyl thiodipropionate
DTBPO	di- <i>tert</i> -butyl peroxide
EIC	ethyl isocyanate
EPMA	epoxypropyl methacrylate
Epolene E-43 (or 47L)	maleated polypropylene with low-molecular weight ($M_w = 10,000$)
E/VAC	ethyl/vinyl acetate
GMA	glycidyl methacrylate
GMS	mono- and diglycerides of fatty acids
13H	maleated polypropylene with high-molecular weight ($M_w = 31,900$)
63H	maleated polypropylene with high-molecular weight ($M_w = 40,000$)
HDPE	high-density polyethylene
HEMA	hydroxyethyl methacrylate
Hercoprime G	maleated polypropylene with high-molecular weight ($M_w = 39,000$)
HMDIC	hexamethylene diisocyanate
Ionol	a butylated hydroxy toluene
Irganox-1010	a tertiary butyl hydroxyhydrocinnamate
KR 138S	titanium di(dioctylpyrophosphates)oxyacetate
15L	maleated polypropylene with low-molecular weight ($M_w = 14,600$)
47L	maleated polypropylene with low-molecular weight ($M_w = 10,000$)
LAC	linoleic acid
LPO	lauroyl peroxide
MA	maleic anhydride
MAA	methacrylic acid
MAA-CAAPE	methacrylic acid, 3-((4,6-dichloro-s-triazine-2-yl)amino)propyl ester
MAPE	maleated polyethylene (or maleic anhydride-modified-polyethylene)

MAPP	maleated polypropylene (or maleic anhydride-modified-polypropylene)
MMA	methyl methacrylate
M_w	average molecular weight (or average molar mass)
OACA	2-octylamino 4,6-dichloro- <i>s</i> -triazine
PDM	see BMI
PE	polyethylene
PEPPIC	poly[ethylene(polyphenyl isocyanate)]
PF	phenol-formaldehyde resin
PHA	phthalic anhydride
PMAA	polymethacrylic acid
PMPPIC	poly[methylene(polyphenyl isocyanate)]
PO	propylene oxide
PP	polypropylene
PS	polystyrene
PS201	high-heat crystal polystyrene
PS525	high-impact polystyrene
PS685D	general-purpose and high-heat polystyrene
PS-PMAA	polystyrene/polymethacrylic acid
PVAC	polyvinyl acetate
PVC	polyvinyl chloride
RGP	refiner ground pulp
RT	room temperature
SA	succinic anhydride
SEBS	styrene-ethylene-butylene-styrene copolymer
SEBS-MA	styrene-ethylene-butylene-styrene/maleic anhydride
Silane A-172	vinyltri(2-methoxyethoxy) silane
Silane A-174	γ -methacryloxypropyltrimethoxy silane
Silane A-186	β -(3,4-epoxy cyclohexyl)ethyltrimethoxy silane
Silane A-187	γ -glycidoxy propyltrimethoxy silane
Silane A-1100	γ -aminopropyltrimethoxy silane
SMA	styrene/maleic anhydride
TBPP	<i>tert</i> -butyl peroxy benzoate
TDIC	toluene 2,4-diisocyanate
TMP	thermomechanical pulp
Vazo	2,2'-azobisisobutyronitrile
WF	wood flour
WFPC	wood fiber and polymer composites
WPC	wood plastic composites