Wood-Fiber/High-Density-Polyethylene Composites: Coupling Agent Performance

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ABSTRACT: The coupling efficiency of seven coupling agents in wood–polymer composites (WPC) was investigated in this study. The improvement on the interfacial bonding strength, flexural modulus, and other mechanical properties of the resultant wood fiber/high-density polyethylene (HDPE) composites was mainly related to the coupling agent type, function groups, molecular weight, concentration, and chain structure. As a coupling agent, maleated polyethylene (MAPE) had a better performance in WPC than oxidized polyethylene (OPE) and pure polyethylene (PPE) because of its stronger interfacial bonding. A combination of the acid number, molecular weight, and concentration of coupling agents had a significant effect on the interfacial bonding in WPC. The coupling agents with a high molecular weight, moderate acid number, and low concentration level were preferred to improve interfacial adhesion in WPC. The backbone structure of coupling agents also affected the interfacial bonding strength. Compared with the untreated composites, modified composites improved the interfacial bonding strength by 140% on maximum and the flexural storage modulus by 29%. According to the statistical analysis, 226D and 100D were the best of the seven coupling agents. The coupling agent performance was illustrated with the brush, switch, and amorphous structures. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 93–102, 2005

Key words: composites; coupling efficiency; fibers; thermoplastics; wood–HDPE interfaces

INTRODUCTION

Polyethylene (PE) is one of four most popular thermoplastics in the world. PE is generally divided into high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE). It is reported that HDPE accounts for about 47% of the total PE products in 2000 in the United States.[1] HDPE is usually produced as bottles, containers, film or sheet, inject molding, pipe, conduit, and other products. Over 50% of HDPE products are manufactured with blow and injection molding.[2] Since the 1970s, significant effort has been made to recycle the out-of-service thermoplastic products and plastic wastes in the world.[3] Like other thermoplastic olefins, virgin and recycled PE polymers have been extensively used in wood–polymer composites (WPC).[4]

In the last two decades, much effort has been made to improve the interfacial bonding strength between the polar wood fiber and nonpolar thermoplastic matrix.[5,6] Kokta and coworkers[7] investigated the influence of four different isocyanate coupling agents on the mechanical properties of wood fiber–polystyrene composites. They reported that the chemical structure and molecular weight of coupling agents had an important impact on the mechanical properties of the resultant composites. With the longer molecular chains and more function groups per mole, poly-[methylene(polyphenol isocyanate)] (PMPPIC) had a better coupling effectiveness than other isocyanate coupling agents.

More recently, Snijder and Bos[8] investigated the coupling efficiency of nine different maleated polypropylene (MAPP) copolymers in agrofiber–polypropylene (PP) composites by injection molding. It was found that the molecular weight of MAPP was a more important parameter than maleic anhydride (MA) content in MAPP for coupling efficiency. The backbone structure of MAPP influenced the interfacial adhesion in the resultant composites because of miscibility in the PP matrix. In another paper,[9] they reported that the mechanical properties of the resultant composites increased with the amount of MAPP, but the effect leveled off or decreased at high MAPP concentration levels.

The most effective coupling forms at the interface in WPC are usually created through the interfacial similarity rule.[10] Coupling agents (such as maleic anhydride and dichlorotriazine) create a crosslinking structure on the wood surface. Simultaneously, some of the polymer matrix is grafted onto wood by the coupling

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TABLE I
Properties of Coupling Agents Used

Coupling agent	Molecular weight[a] (g/mol)		Backbone structure	Density (kg/m^3)	Acid number (mg KOH/g)	Amount of function groups (wt %)[b]	Viscosity (Pa s)
	$\bar{M}_w$	$\bar{M}_n$					
E17	4200	1050	LDPE	908	25.0	5.50	0.55 (at 125°C)
E20	7500	1600	HDPE	960	17.0	3.74	0.80 (at 150°C)
C10	35000	7700	LDPE	906	<0.05	<0.01	7.80 (at 190°C)
C16	26000	5600	LDPE	908	5.0	0.50	8.50 (at 190°C)
226D	67600	21700	LLDPE	930	4.7	0.47	—
100D	59700	19500	HDPE	960	6.0	0.61	—
E-43	9100	3900	PP	930	47	4.74	0.40 (at 190°C)

[a] $\bar{M}_w$ and $\bar{M}_n$ are the weight and number average molar masses, respectively.
[b] wt % is the weight percentage of the backbone polymer.

agents. Thus, modified wood has a surface similar to the matrix. Alternately, the coupling agents with a structure similar to the matrix are grafted onto wood, which is helpful to improve interfacial adhesion. The wood fiber–MAPP–PP structure belongs to the latter coupling form. A similar coupling structure at the interface may exist in wood fiber–PE composites. Maleated polyethylene (MAPE) or maleic anhydride-grafted–polyethylene (PE-*g*-MA) has been extensively used as a compatibilizer in HDPE/LDPE–starch composites.[11,12] However, there have been few reports on using MAPE as a coupling agent in WPC.[13] Therefore, it is necessary to investigate whether MAPE is effective in improving the interfacial bonding strength in WPC.

The objectives of this study were 1) to examine the interfacial similarity rule with the wood fiber–MAPE–HDPE structure, 2) to investigate the effects of coupling agent type and structure on the mechanical properties of the resultant composites, 3) to evaluate the coupling efficiency of the coupling agents at the interface, and 4) to search for the best coupling agents for the wood fiber–HDPE interface in the terms of coupling agent performance.

EXPERIMENTAL PROCEDURES

Materials

Mixed thermomechanical pulp (TMP) fiber was obtained from Temple-Inland Company (Diboll, TX). Before the compounding process, the TMP fiber was dried in an oven at 100°C for 24 h. Moisture content of the dried TMP fiber was between 2 and 3% during blending.

HDPE pellets (PE10462N, Dow Chemical, Midland, MI) were purchased commercially. The density of HDPE is 962.5 kg/m³. Its melting temperature and melt index are 134°C and 10 g/10 min, respectively. The tensile strength and modulus of PE10462N are 12 MPa and 0.75 GPa, respectively.

In this study, the coupling agents included MAPE copolymers, oxidized polyethylene (OPE), and pure polyethylene (PPE). Two MAPEs (100D and 226D) were obtained from Dupont Canada Inc. (Ontario, Canada). Another MAPE (Epolene C16) was supplied by Eastman Chemical Company (Longview, TX). Epolene E-43 (a product of MAPP, Eastman Chemical Company) was used as a reference for MAPEs. The unmaleated polymers included Epolenes E17, E20, and C10, which were obtained from Eastman Chemical Company. E17 and E20 are oxidized LDPE and HDPE polymers, respectively, whereas C10 is a pure LDPE. These three coupling agents have different amounts of monocarboxylic groups on their molecular chains. The basic properties of all the coupling agents are listed in Table I. The concentration levels of coupling agents used were 0, 1, 3, 5, and 10% based on the weight of the oven-dried wood fiber.

Dicumyl peroxide (DCP; Aldrich, St. Louis, MO) was used as an initiator. The amount of DCP was controlled to be 1% coupling agent by weight.

Manufacture of wood fiber–HDPE composites

The melt-molding process used for manufacturing wood fiber–HDPE composites followed a one-step process reported in the literature.[14] The wood fiber, thermoplastics, coupling agent, and initiator were sequentially fed into a Haake rotor mixer (Model Rheomix 600; Dreieich, Germany). For the untreated wood fiber–HDPE composites, the weight ratios of oven-dried wood fiber and HDPE were 10/90, 30/70, 50/50, and 70/30 w/w. The weight percentage of the oven-dried wood fiber to HDPE was 50 wt % for all the modified composites.

The compounding process was conducted at a temperature of 165°C and a mixing time of 10 min with a rotation speed of 90 rpm. After the compounding, the melts were removed from the blender and cooled to room temperature. The melts were ground into 20-mesh powder with a Thomas-Wiley miller (Model 3383L10; Swedesboro, NJ).

The ground powder with a required weight was placed into a two-piece aluminum molding set. The mold was pressed with a miniature hot press at 168°C for 3 min and then cooled to room temperature under pressure for 1 min. The pressure for heating and cooling was controlled to be 0.16 MPa. All the specimens were made with the molding set for tensile testing and dynamic mechanical analysis (DMA). The density of all the specimens was controlled to be 1,000 ± 50 kg/m^3.

Mechanical property measurement

The dynamic mechanical properties (i.e., storage modulus E', loss modulus E'', and phase angle δ) of the resultant composites were analyzed with a Seiko DMS 110 DMA system (Chiba, Japan). Each specimen was measured with a three-point bending mode at a frequency of 1 Hz and a temperature range between 25 and 27°C. After the DMA analysis, all the tensile specimens were made as a dog-bone shape according to the ASTM standard ASTM D 638. The tensile strength of each specimen was tested with an INSTRON machine (Model 1125, Boston, MA).

Data analysis

A 7 × 5 completely randomized design factorial experiment was conducted to investigate the influence of coupling agent type (seven coupling agents) and concentration (0, 1, 3, 5, and 10 wt %) on the mechanical properties of the resultant composites. Based on the factorial experiment, a two-way analysis of variance (ANOVA) was conducted to determine the main and interaction effects. The coupling effectiveness of maleated copolymers was compared with a Tukey's studentized range test.

RESULTS AND DISCUSSION

Mechanical properties of the resultant composites

Figure 1 shows the measured tensile strength and flexural storage modulus of the untreated wood–HDPE composites as a function of the wood fiber weight percentage. The tensile strength of the resultant composites increased slightly at the low weight percentage (< 15 wt %) and reached its maximum at 15 wt % wood fiber and decreased with an increase in the wood fiber content (> 20 wt %). The flexural storage modulus of the untreated composites increased with an increase in the wood fiber content at the low weight percentage (Fig. 1). The storage modulus reached its maximum value at 35 wt % wood fiber and gradually decreased with a further increase in the wood fiber content (> 40 wt %). The results agreed with those reported by Kishi et al.[15]
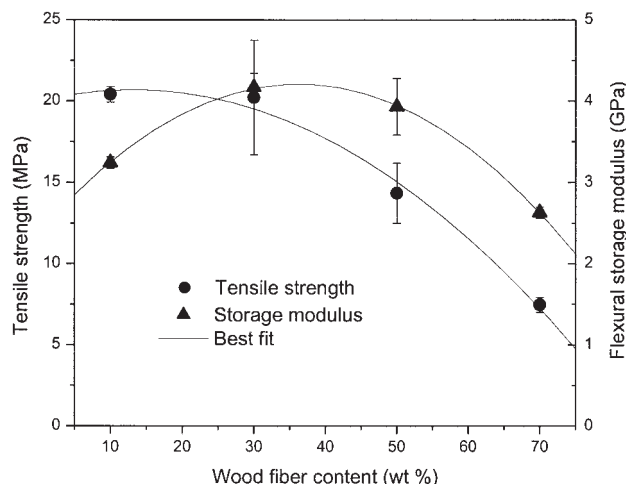

Figure 1 Influence of the wood fiber weight percentage on the mechanical properties of wood fiber–HDPE composites.

All the modified composites had better mechanical properties than the untreated composites (control). Compared with the control, the modified composites improved the interfacial bonding strength by 140% on maximum and flexural modulus by 29% (Table II). As shown in Figure 2, 226D had the best performance among the seven coupling agents. The tensile strength of 226D-treated composites was 25.33 MPa at the 3 wt % concentration level. For 100D-treated composites, the tensile strength increased with an increase in the coupling agent concentration. The strength reached the maximum value of 24.41 MPa at the 10 wt % level. C16 also had a better performance. C16-treated composites had a trend similar to 226D-treated composites. C16-treated composites had the maximum tensile strength (23.97 MPa) at the 3 wt % concentration level. However, they had a low tensile strength at the high concentration levels (> 5 wt %) (Table II).

For E17-, E20-, E43-, and C10-treated composites, the tensile strength increased at the low concentration levels, but it decreased at the high concentration levels (Fig. 2). At the 1 wt % concentration level, the tensile strength of E20- and E17-treated composites was around 20 MPa and close to that of 100D- and 226D-treated composites at the same concentration. At the low concentration levels (< 3 wt %), C10, E20, and E17 were competitive with 226D, 100D, and C16 in the terms of tensile strength (Fig. 2). However, C10-, E20-, and E17-treated composites had a lower tensile strength at the high concentration levels (> 5 wt %). Compared with other coupling agents, E43 had the lowest tensile strength of 16.1 MPa at the 1 wt % concentration level. Its performance at high concentration was similar to that of E17 and E20.

Based on the storage modulus E', all the coupling agents were divided into the following two groups. The first group included MAPEs such as 226D, 100D, and C16, whereas the second group consisted of the

TABLE II
Mechanical Properties of Modified Wood Fiber–HDPE Composites

Coupling agent	Concentration of coupling agent (%)	Density (kg/m³)	Tensile strength (MPa)	Flexural modulus at 1 Hz and 27°C (GPa)			tan δ at 1 Hz and 27°C (×10⁻²)
				E'	E''	E^*	
Control	0	1069	10.53 (0.67)	3.54 (0.15)	0.245 (0.009)	3.55 (0.15)	6.91 (0.07)
E17	1	998	19.35 (1.18)	3.64 (0.49)	0.230 (0.027)	3.64 (0.50)	6.33 (0.10)
	3	1014	18.55 (2.57)	3.32 (0.31)	0.220 (0.031)	3.33 (0.48)	6.61 (0.13)
	5	992	17.35 (0.72)	3.13 (0.19)	0.209 (0.013)	3.14 (0.19)	6.68 (0.11)
	10	998	17.54 (1.83)	3.04 (0.27)	0.215 (0.017)	3.05 (0.27)	7.05 (0.11)
E20	1	1011	22.11 (2.74)	3.61 (0.39)	0.228 (0.005)	3.61 (0.40)	6.32 (0.10)
	3	1027	20.34 (0.52)	3.38 (0.12)	0.222 (0.008)	3.34 (0.12)	6.56 (0.05)
	5	1041	19.40 (0.99)	3.36 (0.24)	0.225 (0.016)	3.37 (0.24)	6.71 (0.04)
	10	1021	16.00 (1.17)	3.21 (0.45)	0.217 (0.006)	3.22 (0.44)	6.75 (0.10)
C10	1	1030	20.13 (0.90)	3.47 (0.25)	0.220 (0.014)	3.48 (0.26)	6.35 (0.11)
	3	1034	22.84 (1.88)	3.50 (0.38)	0.225 (0.024)	3.51 (0.39)	6.41 (0.07)
	5	1025	19.26 (1.56)	3.15 (0.34)	0.207 (0.022)	3.16 (0.34)	6.57 (0.10)
	10	1006	20.36 (3.28)	2.99 (0.30)	0.196 (0.020)	3.00 (0.30)	6.56 (0.09)
C16	1	1017	20.39 (2.98)	4.22 (0.37)	0.268 (0.023)	4.22 (0.37)	6.37 (0.12)
	3	1021	23.97 (0.49)	4.42 (0.35)	0.277 (0.018)	4.43 (0.35)	6.28 (0.13)
	5	975	21.83 (2.33)	4.11 (0.14)	0.268 (0.009)	4.12 (0.15)	6.51 (0.04)
	10	1008	19.24 (3.14)	3.89 (0.42)	0.253 (0.003)	3.90 (0.42)	6.51 (0.05)
100D	1	1039	21.17 (1.03)	4.51 (0.39)	0.277 (0.024)	4.52 (0.39)	6.14 (0.09)
	3	1063	22.29 (0.83)	4.11 (0.47)	0.249 (0.030)	4.11 (0.47)	6.06 (0.15)
	5	1045	22.34 (0.18)	3.66 (0.31)	0.225 (0.018)	3.66 (0.32)	6.14 (0.06)
	10	1056	24.41 (3.30)	4.05 (0.29)	0.253 (0.019)	4.06 (0.29)	6.25 (0.07)
226D	1	1050	22.82 (2.57)	3.89 (0.49)	0.243 (0.031)	3.90 (0.49)	6.23 (0.05)
	3	1038	25.33 (3.32)	3.97 (0.29)	0.240 (0.015)	3.98 (0.29)	6.06 (0.17)
	5	1047	23.33 (0.42)	4.04 (0.17)	0.251 (0.010)	4.05 (0.17)	6.21 (0.04)
	10	1068	23.30 (3.54)	4.56 (0.45)	0.285 (0.026)	4.57 (0.45)	6.24 (0.07)
E43	1	1033	16.06 (0.76)	3.64 (0.09)	0.231 (0.004)	3.64 (0.09)	6.35 (0.09)
	3	1019	18.85 (1.02)	3.39 (0.33)	0.217 (0.021)	3.39 (0.33)	6.39 (0.11)
	5	1018	15.15 (1.23)	3.40 (0.14)	0.222 (0.009)	3.40 (0.14)	6.53 (0.06)
	10	1025	18.87 (4.10)	3.59 (0.26)	0.233 (0.017)	3.60 (0.26)	6.49 (0.08)

The weight ratio of oven-dried wood fiber and HDPE was 50 : 50. The values in parentheses are the standard deviations.

unmaleated PE polymers (e.g., C10, E17, and E20) and E43. Within each group, the coupling agents had a similar performance. In the first group, E' of 226D-treated composites increased with an increase in the coupling agent concentration. For 100D-treated composites, a larger E' appeared at the low concentration levels (< 3 wt %), but E' decreased or leveled off at the high concentration levels (> 5 wt %). C16-treated com-
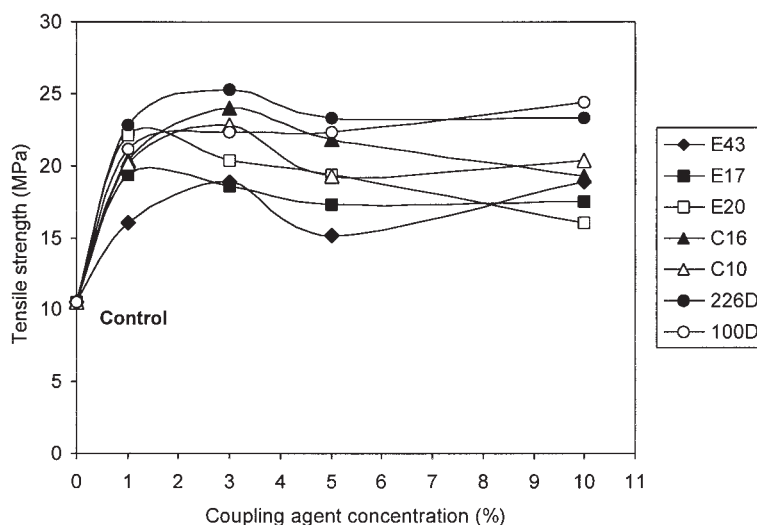

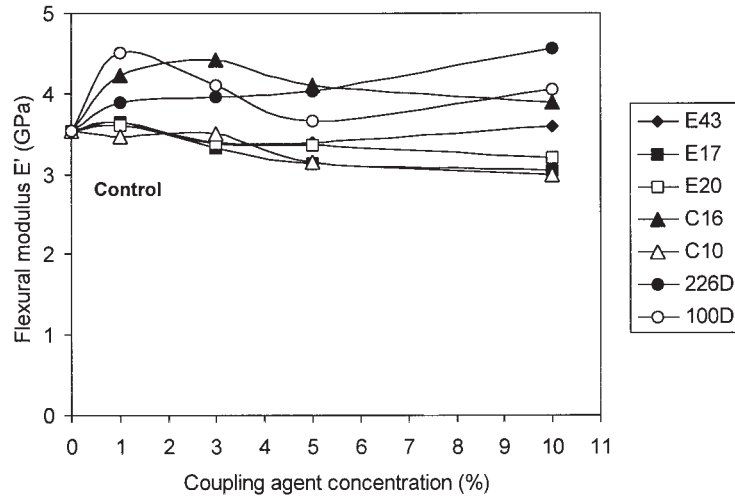Figure 2 Influence of the coupling agent concentration on the tensile strength of wood fiber–HDPE composites.

Figure 3 Influence of the coupling agent concentration on the flexural storage modulus of wood fiber–HDPE composites.

posites had a trend similar to 100D-treated composites (Fig. 3). For the second group, the coupling agents did not significantly influence the E' of the resultant composites. The coupling agent C10 had a large molecular weight, but it did not have a significant influence on E'. For the four coupling agents in the second group, E' decreased with an increase in the coupling agent concentration (Fig. 3).

The loss modulus (E'') varied with the coupling agent type and concentration. Compared with the untreated composites, 226D-, 100D-, and C16-treated composites had a higher E'' (Table II). For 100D- and C16-treated composites, E'' decreased at high concentration. However, E'' of 226D-treated increased with an increase in the coupling agent concentration. E17-, E20-, E43-, and C10-treated composites had a lower E'' than the untreated and maleated composites (Table II). For these four agents, E'' decreased with an increase in the coupling agent concentration.

The phase angle δ of the resultant composites was also influenced by the coupling agent concentration. Since tan δ is equal to the ratio of E'' and E', it is an inverse

function of E'. The phase angle of the resultant composites increased with an increase in the coupling agent concentration (Table II). E17- and E20-treated composites had the highest tan δ values at the 10 wt % concentration level. However, 100D- and 226D-treated composites had lower tan δ values than other coupling agent-treated composites, which were almost independent of the concentration levels. Hence, MAPEs increased the stiffness of the resultant composite because of the crosslinking structure at the interface. However, high concentration increased the brittleness of the maleated composites. Although E17, E20, and C10 did not significantly improve the interfacial adhesion, they enhanced the damping property of the resultant composites by decreasing the E'' values (Table II).

According to the two-way ANOVA on the interfacial bonding strength, the main effect of the coupling agent type and the interaction effect between the coupling agent type and concentration were significant (Table III). However, the main effect of the coupling agent concentration on the interfacial bonding strength was not significant. For the storage modulus, the main effects of the

TABLE III
Statistical Analysis for the Tensile Strength of Wood Fiber–HDPE Composites

Source	DF	Type III sum of squares	Mean square	F value	Pr>F
Model	28	845.483	30.196	6.23	<0.0001
CA	7	468.693	66.956	13.81	<0.0001
CAconcen	3	24.640	8.213	1.69	0.1784
CA*CAconcen	18	352.150	19.564	4.03	<0.0001
Error	58	281.304	4.850		

Tukey's grouping[a]	226D	100D	C16	C10	E43	E20	E17	Control
	A				B			C

CA, coupling agent type; CAconcen, coupling agent concentration; DF, degrees of freedom; F value (or F), the value of F test; Pr, P value, i.e., the power of F test.
[a] Coupling agents with the same letter are not significantly different.

TABLE IV
Statistical Analysis for the Storage Modulus of Wood Fiber–HDPE Composites

Source	DF	Type III sum of squares		Mean square		F value		Pr>F
Model	28	28.890		1.032		9.35		<0.0001
CA	7	20.787		2.970		26.89		<0.0001
CAconcen	3	2.592		0.864		7.82		<0.0001
CA*CAconcen	18	5.520		0.307		2.78		0.0005
Error	147	13.140		0.110				
Tukey's grouping[a]	226D	100D	C16	C10	E43	E20	E17	Control
		A				B		

CA, coupling agent type; CAconcen, coupling agent concentration; DF, degrees of freedom; *F* value (or F), the value of *F* test; *Pr*, *P* value, i.e., the power of *F* test.

[a] Coupling agents with the same letter are not significantly different.

coupling agent type and concentration and their interaction effect were significant (Table IV).

Coupling models

Based on the mechanical properties of wood fiber–HDPE composites treated with different coupling agents, three models were proposed to illustrate the coupling agent performance at the interface (Fig. 4). The wood fiber–polymer interactions at the interface may include the brush [Fig. 4(a)],[16] switch [Fig. 4(b)],[17] and amorphous [Fig. 4(c)] structures with the primary interphases of the wood fiber (**1**, boxes), the coupling agent or polymer (**2**, solid or dashed scribbles), and the polymer matrix (**3**, bold scribbles). In the interfacial region between **1**

Figure 4 Schematic of the wood fiber–polymer interactions between the wood fiber and thermoplastic matrix.

and **3**, the dashed curves present the free chains of the polymer or ungrafted coupling agent. The coupling agent grafted on the wood (with solid ends) may be crosslinked with the polymer matrix (with nodes). The coupling agent or polymer may be fixed on the wood by mechanical interblocking (with dashed ends). Also, the coupling agent may be grafted on the polymer molecular chains (with nodes). The free ends of the coupling agent and polymer may be linked together through molecular chain entanglement.

In general, coupling agents with a high acid number and low molecular weight easily resulted in a brush structure at the interface.[16] Since E43 had a high acid number of 47 mg KOH/g, but a low molecular weight of 9100 g/mol, it easily generated a brush structure at the interface. Similar to E43, E20 and E17 had a high acid number but low molecular weight. A brush structure was also built up for these OPE coupling agents at the interface. For these three coupling agents, however, their molecular chains were so short that they were not so effective for strengthening the interfacial bonding.[10]

With a moderate acid number and high molecular weight, 100D and 226D were preferred to the switch structure. Both 100D and 226D greatly improved the interfacial bonding strength with respect to the untreated and unmaleated composites (Fig. 2). C16 had a close acid number but a low molecular weight with respect to 226D and 100D. It also had a better performance because of the switch structure.

Without effective graft copolymerization, C10 formed the amorphous structure at the interface. It strengthened the interface through the molecular chain entanglement and mechanical interblocking. C10 had no chance to react with the wood fiber and thermoplastic matrix because it had few function groups on the molecular chains.

Coupling efficiency

Unlike the continuous interface of wood veneer–polymer laminate composites,[17] the wood fiber was ran-
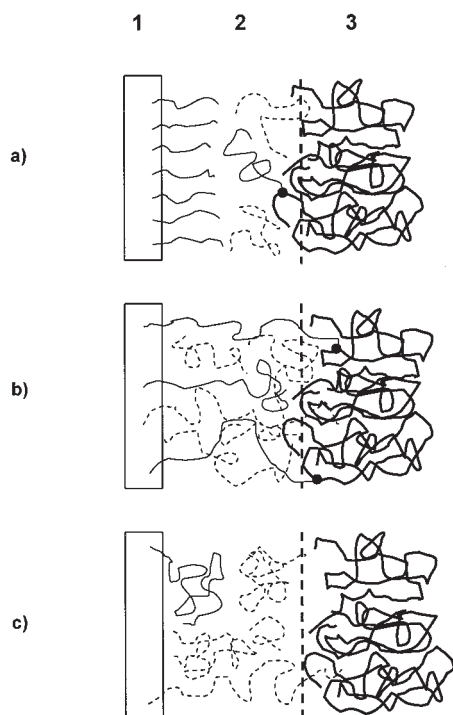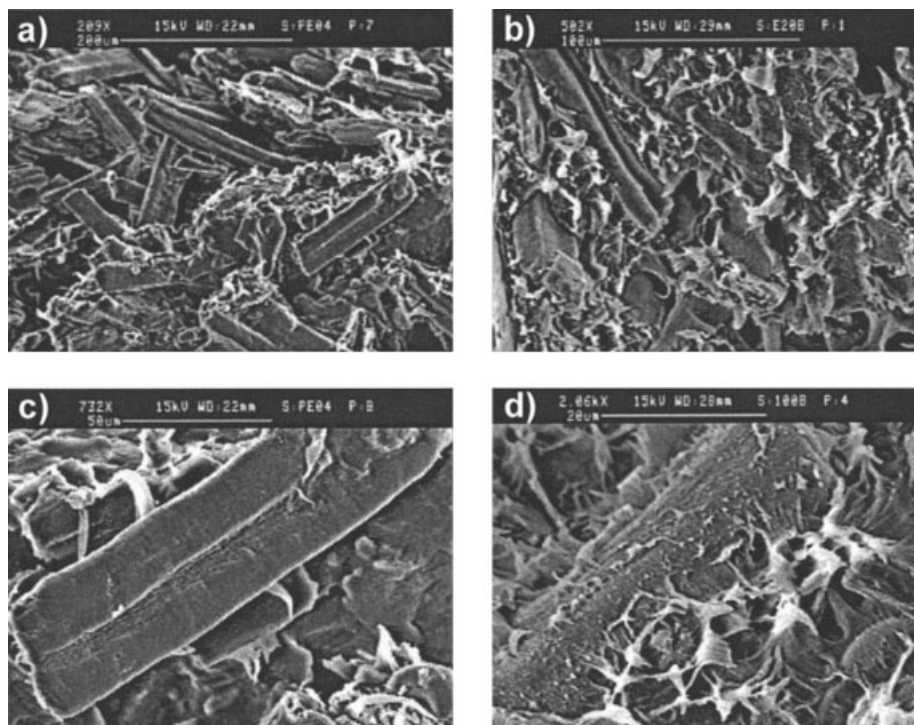
Figure 5 SEM micrographs of the tensile fracture surface of wood fiber–HDPE composites: (a) untreated composites (×209), (b) composites with 3 wt % E20 (×502), (c) untreated composites (×732), and (d) composites with 3% 100D (×2,060).

domly distributed and separated in a continuous thermoplastic matrix in WPC. It was encapsulated or enveloped by the thermoplastic matrix mainly with a mechanical connection. Without coupling treatment, the interfacial region was weakly linked. Under loading, the resultant composites were mainly damaged along the loose and weak interfacial connections between the wood fiber and thermoplastic matrix [Fig. 5(a)] and the fracture structure followed a cohesive mode.

For most of the modified composites, the wood fiber was combined with the thermoplastic matrix through the covalent bonding or strong interfacial bonding. The interface was strengthened with the coupling agents, thus resulting in a stronger interfacial structure [Fig. 5(b)]. For this coupling structure, the interfacial fracture usually accompanied with a cross section damage of the wood fiber. After the tensile failure, the fiber surface in the untreated composites was smooth [Fig. 5(c)], whereas the wood fiber in the maleated composites had a rough surface and it was embedded in the matrix with a chemical link [Fig. 5(d)]. Consequently, this adhesion mode effectively improved the mechanical properties of WPC (Table II).

The coupling agent type had an important impact on interfacial adhesion. As shown in Table II and Figure 2, the maleated coupling agents had a better performance than the unmaleated coupling agents. The maleic anhydride groups of MAPE were easily hydrolyzed into double carboxylic groups. These dou-

ble carboxylic groups were more reactive for esterification under an initiator than the monocarboxylic groups of OPE and PPE. Moreover, the succinic structure of maleic anhydride groups on the MAPE molecular chains were preferred to form a stable ester bridge between the wood fiber and thermoplastics.[15,17] Hence, MAPE was more effective in improving interfacial adhesion than OPE and PPE.

The interfacial bonding strength was related to the coupling agent concentration. Among the seven coupling agents, the coupling agent performance was usually improved at low concentration (≤ 3 wt %). However, the coupling effectiveness was poor at high concentration (> 5 wt %) (Figs. 2 and 3). This was due to the fact that an excess of coupling agents generated many byproducts and interfered with the coupling reaction, and thus resulting in a low bonding strength at the interface.[18,19] On the other hand, the existence of excessive coupling agents might enlarge the gap between the wood fiber and thermoplastic matrix and weaken the interface.

The molecular weight of coupling agents had a profound effect on interfacial adhesion in WPC. As shown in Figure 6, the interfacial bonding strength and storage modulus were proportional to the molecular weight. The interfacial bonding strength had a large increase at a molecular weight less than 10,000. However, it had a small increase when the molecular weight ($\overline{M}_w$) was larger than 30,000. Hence, the effect of the molecular weight on the interfacial bonding strength was not significant at the high molecular
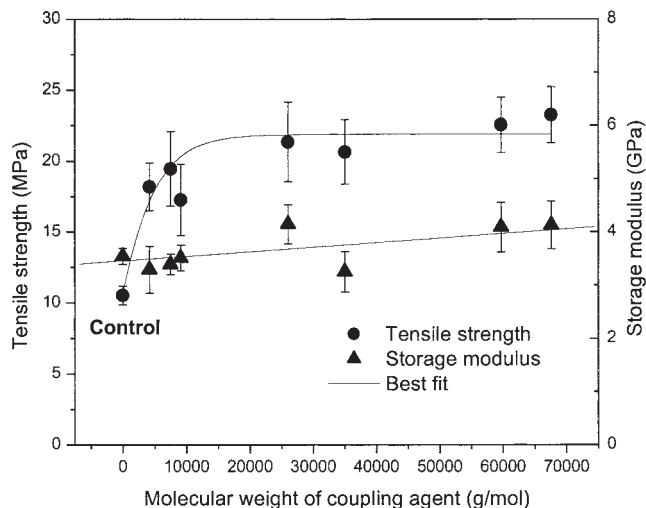
Figure 6 Relationship of the coupling agent molecular weight and storage modulus with the interfacial bonding strength of wood fiber–HDPE composites.

weight. It is also shown that the storage modulus was proportional to the molecular weight (Fig. 6).

The acid number significantly influenced the coupling agent performance at the interface. For the unmaleated coupling agents (e.g., E17, E20, and C10), E20 and E17 had a low molecular weight but high acid number with respect to C10. E20- and E17-treated composites competed against C10-treated composites in the terms of the tensile strength and storage modulus (Table II and Fig. 6). This was due to the fact that E20 and E17 improved the interface with an ester link instead of a mechanical connection. As shown in Figure 6, all the maleated composites had the higher storage modulus and interfacial bonding strength than the untreated and unmaleated composites. C16 and C10 both had a close molecular weight, but C16 had a higher acid number than C10 (Table I). Although C16 had a low molecular weight with respect to C10, it had a better performance at the interface. Among MAPEs, 226D, 100D, and C16 had a close acid number, but they were different in the molecular

weight. 226D and 100D had a better performance than C16 because of their longer molecular chains.

The backbone structure of coupling agents also affected the interfacial bonding strength of the resultant composites. E43 had the lowest tensile strength among the maleated copolymers, although it had a high coupling performance coefficient. E43 performed similarly to E17, E20, and C10 but poorer than 226D, 100D, and C16 (Figs. 2 and 3). This was attributed to the fact that PP and PE were immiscible due to their large difference in melting and glass transition temperatures during and after compounding, notable phase separation in the resultant blends, and poor stress transfer at the interface.[20–22] E43 may crosslink with some of the PE matrix through the carbon–carbon bonding. However, its PP tail is not compatible with the PE matrix. Therefore, E43 had a poor performance at the interface than MAPEs because of its incompatibility with the PE matrix. As a result, the wood fiber–HDPE interface was preferred for the MAPE coupling agents.

Although E20 and E17 have a different backbone structure (Table II), there was no significant difference between E20 and E17 in coupling effectiveness because they had a close coefficient value (Table V). The maleated LLDPE copolymers were better than the maleated HDPE or LDPE copolymers at low concentration (Table II). Since LLDPE is composed of copolymers of ethylene with modest amounts of butene, hexene, or octene linear α–olefins,[23] a MAPE molecule with these linear olefin structures easily formed the graft copolymerization with the polymeric matrix or other MAPE molecules to strengthen the interface through the carbon–carbon bonding. On the other hand, coupling agents with a LLDPE backbone also improved interfacial adhesion by the molecular chain entanglement.

In this study, an estimating method is proposed to evaluate the coupling efficiency of different coupling agents. This system is based on the reactiveness and molecular chain structure of coupling agents. The reactiveness is mainly related to the amount of function

TABLE V
Coupling Performance Coefficient of Different Coupling Agents

Coupling agent	$\bar{M}_w$ (g/mol)	Acid number (mg KOH/g)	Coupling performance coefficient	Tensile strength (MPa)	Storage modulus E' (GPa)
E17	4200	25.0	1.16	18.20 (1.69)	3.29 (0.44)
E20	7500	17.0	1.36	19.46 (2.63)	3.39 (0.19)
C10	35000	<0.05	1.82	20.65 (2.26)	3.25 (0.38)
C16	26000	5.0	2.09	21.36 (2.80)	4.15 (0.37)
100D	59700	6.0	2.82	22.55 (1.95)	4.09 (0.470
226D	67600	4.7	2.86	23.25 (1.97)	4.13 (0.45)
E43	9100	47.0	1.87	17.27 (2.52)	3.51 (0.24)

The values in the last two columns are the average tensile strength and storage modulus for each coupling agent, respectively. The values in parentheses are the standard deviations.

groups and graft rate of coupling agents, which determine the graft copolymerization structure at the interface. The latter factor is determined by the molecular structure and morphology of coupling agents (e.g., the coupling agent type and molecular weight). This factor usually enhances the macromolecular chain entanglement and mechanical blocking at the interface. Since E43 has a low molecular weight but a high acid number, it can be used as an evaluating reference for other copolymers. For a coupling agent, its coupling efficiency can be evaluated with the coupling performance coefficient (η) as follows:

$$\eta = \left(\frac{N_x}{N_{E43}}\right)^{1/3}\left(1 + \sqrt{\frac{n_x}{n_{E43}}}\right)^{\xi} \qquad (1)$$

where, N_x and n_x are the degree of polymerization and acid number of the coupling agent, respectively; N_{E43} and n_{E43} are the degree of polymerization and acid number of E43, respectively; and ξ is the graft rate of the coupling agent on the wood fiber.

According to Lu et al.,[17] the graft rates on the wood were 0 and 90% for the unmodified and maleated polypropylene (or polyethylene), respectively. The graft rates of the OPE coupling agents were estimated to be 50%.

The coupling performance coefficient of PPE was proportional to the molecular weight. For MAPEs and OPEs, however, the coefficient was related to the acid number and molecular weight (Fig. 6). 226D had the highest coupling performance coefficient, whereas E17 had the lowest. Hence, the coupling performance coefficients of other coupling agents were between those of E17 and 226D. In this study, all the MAPE copolymers had a higher coupling performance coefficient than the OPE and PPE copolymers (Table V).

As shown in Table V, the coupling performance coefficient matched well with the interfacial bonding strength and flexural storage modulus of the resultant composites. Except for E43-treated composites, composites treated with other coupling agents plus the control followed a polynomial relationship with the interfacial bonding strength (Fig. 7). E43-treated composites were beyond the curve as an outlier because E43 was incompatible to the PE matrix at the interface. Therefore, this system was feasible to evaluate the coupling agent performance.

According to the Tukey's studentized range test, MAPE-treated composites were significantly different from the untreated composites (Tables III and IV). For the interfacial bonding strength, 226D and 100D were the best of the seven coupling agents (Tables II and III). Although it was difficult to separate C16 from C10, E20, and E17, C16 was better than these OPE and PPE coupling agents. E43-treated composites had a performance similar to C10-, E20-, E17-treated composites (Table III). For the storage modulus, 226D,
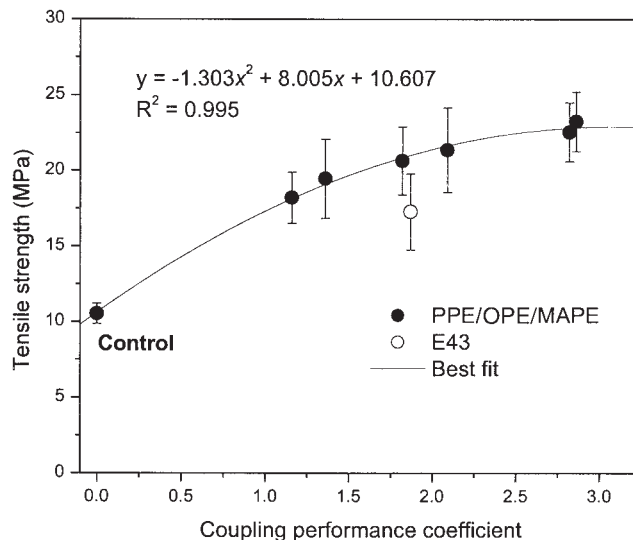

Figure 7 Relationship between the coupling performance coefficients of various coupling agents and interfacial bonding strength of the resultant composites.

100D, and C16 were significantly different from other coupling agents (Table IV). However, E43, E20, E17, and C10 were not significantly different from the untreated composites. Based on the aforementioned statistical analysis, the coupling efficiency for these agents was ranked as follows: 226D > 100D > C16 > C10 > E43 > E20 > E17.

CONCLUSION

For the modified composites, the improvement on the interfacial bonding strength, flexural modulus, and other mechanical properties was mainly related to the coupling agent type, function groups, molecular weight, concentration, and chain structure. The maximum value of interfacial adhesion was achieved at the 3 wt % concentration level for most maleated composites. Compared with the untreated composites, the modified composites improved the interfacial bonding strength by 140% on maximum and the flexural storage modulus by 29%. MAPE coupling agents were more effective in improving interfacial adhesion in wood fiber–HDPE composites with respect to OPE and PPE coupling agents.

The acid number, molecular weight, and concentration of coupling agents were the three important parameters for interfacial adhesion in WPC. The mechanical properties of the resultant composites were influenced by the interactions among these three indexes. Usually, a high concentration level had a negative effect on the interface bonding strength. However, the molecular weight had a positive effect on interfacial adhesion. The interfacial bonding strength was proportional to the molecular weight. Therefore, a combination of the acid number, molecular weight,

and concentration had a significant impact on coupling efficiency. The coupling agents with a high molecular weight, moderate acid number, and low concentration level were preferred to improve interfacial adhesion in the resultant composites.

The backbone structure of coupling agents also affected the interfacial bonding strength. At the same or close acid number and molecular weight, there was no significant difference between MAPEs with a LDPE backbone and those with a HDPE backbone. However, MAPEs with a LLDPE backbone were better than those with a HDPE or LDPE backbone, because the linear α-olefin structure of LLDPE improved interfacial adhesion. Based on the statistical analysis, 226D and 100D were the best coupling agents for the resultant wood fiber–HDPE composites.

References

1. Anonymous. Chemical & Engineering News 2002, 80, 42.
2. Chenier, P. J Survey of Industrial Chemistry; Wiley-VCH: New York, 1992; 2nd ed.
3. Anonymous. Environmental Packaging: U. S. Guide to Green Labeling, Packaging, and Recycling; Thompson Publishing Group: Washington, DC, 2001.
4. Chtourou, H.; Riedl, B.; Ait-Kadi, A. J Reinf Plast Comp 1992, 11, 372.
5. Xanthos, M. Plast Rubber Process Appl 1983, 3, 223.
6. Woodhams, R. T.; Thomas, G.; Rodgers, D. K. Polym Eng Sci 1984, 24, 1166.
7. Kokta, B. V.; Maldas, D.; Daneault, C.; Beland, P. Polym–Plast Technol Eng 1990, 29, 87.
8. Snijder, M. H. B.; Bos, H. L. Comp Interfaces 2000, 7, 69.
9. Snijder, M. H. B.; Wissing, E.; Modder, J. F. In Proceedings of 4th International Conference on Woodfiber–Plastic Composites; Forest Products Society, Madison, WI, 1997; pp 181–191.
10. Lu, J. Z.; Wu, Q.; McNabb, H. S. Wood Fiber Sci 2000, 32, 88.
11. Bikiaris, D.; Panayiotou, C. J Appl Polym Sci 1997, 70, 1503.
12. Sailaja, R. R. N.; Chanda, M. J Appl Polym Sci 2001, 80, 863.
13. Sanadi, A. R.; Rowell, R. M.; Young, R. A. In Materials Interactions Relevant to Recycling of Wood-based Materials; Rowell, R. M.; Laufenberg, T. L.; Rowell, J. K., Eds.; Materials Research Society: Pittsburgh, PA, 1992; Vol. 266, pp 81–92.
14. Lu, J. Z.; Wu, Q.; Negulescu, I. I. J Appl Polym Sci 2004, 93, 2570.
15. Kishi, H.; Yoshioka, M.; Yamanoi, A.; Shiraishi, N. Mokuzai Gakkaishi 1988, 34, 133.
16. Gatenholm, P.; Felix, J. M. In New Advances in Polyolefins; Chung, T. C., Ed.; Plenum Press: New York, 1993; pp 237–244.
17. Lu, J. Z.; Wu, Q.; Negulescu, I. I. Wood Fiber Sci 2002, 34, 434.
18. John, W. E. J Adhes 1982, 15, 59.
19. Beshay, A. D.; Kokta, B. V.; Daneault, C. Polym Comp 1985, 6, 261.
20. Wenig, W.; Scholler, Th. Prog Col Polym Sci 1985, 71, 113.
21. Teh, J. W; Rudin, A. Adv Polym Technol 1994, 13, 1.
22. Li, J.; Shanks, R. A., Long, Y. J Appl Polym Sci 2000, 76, 1151.
23. Delassus, P. T.; Whiteman, F. In Polymer Handbook; Brandrup, J.; Immergut, E. H.; Grulke, E. A.; Abe, A.; Bloch, D. R., Eds.; Wiley: New York, 1999; pp V159–V169.