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Influence of Impact Modifier–Coupling agent Combination on Mechanical Properties of Wood Flour–Reinforced Polypropylene Composit

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The tensile properties and impact strength of wood flour–polypropylene composite with or without impact modifier and coupling agent have been investigated. The addition of maleic anhydride and dicumyl peroxide improved the tensile properties and impact strength. With increasing ethylene–propylene rubber (EPR) and maleic anhydride (MAH)–modified ethylene–propylene rubber (MEPR), impact strength were increased, whereas tensile strength and Young's modulus were decreased. At the same EPR or MEPR content, the higher filler loadings resulted in higher Young's modulus and lower impact strength. Tensile properties and impact strength were greatly improved by adding EPR combined with maleic anhydride–grafted polypropylene (MAPP) and dihydroquinoline.

Key words: wood flour, polypropylene, composite, coupling agent, impact modifier

INTRODUCTION

In general, wood–plastic composites (WPC) is manufactured by dispersing wood flour (WF) or fibers into molten plastic with or without the addition of coupling agent or additives using various process techniques such as extrusion, compression and injection moldings. The term of WPC covers an extremely wide range of matrix polymers such as polypropylene (PP), polyethylene (PE), and poly(vinyl chloride) (PVA) and fillers such as WF and agriculture fibers. Compared with thermoplastics, the main purpose of adding WF to thermoplastics is to reduce the cost per unit volume due to low price WF, to improve stiffness, and to lower density. Thus, WPC have many advantages such as high specific strength and modulus, low cost, low density, and low friction. One of the most attractive features in WPC is that it can help recycle thermoplastic and wood wastes (Febrianto *et al.*, 2006a).

However, there is poor interfacial adhesion between hydrophilic filler and hydrophobic matrix polymer, resulting in the decrease in mechanical properties (Klason and Kubat 1986; Han *et al.* 1989; Bakar and Hasan 2003; Febrianto *et al.*, 2005). It was reported in the number of literatures that the addition of coupling agent can greatly improve the mechanical properties (Kishi *et al.*, 1988; Han *et al.*, 1989; Oksman and Clemons 1998; Febrianto *et al.*, 1999, 2006a, 2006b).

However, there are some different opinions on the effect of MAPP on impact strength of WF–PP composite. Some researchers reported that the addition of MAPP as coupling agent improved the impact strength (Dalväg *et al.* 1985; Felix and Gatenholm 1991; Gatenholm *et al.*, 1992), but Myers *et al.* (1991a, 1991b) reported negative effect on the impact strength.

Toughness of the composites can be improved in several ways: 1) to increase the matrix toughness; 2) to optimize the interface (or interphase) between the filler and the matrix using coupling agents, compatibilizers, and sizing agents; 3) to optimize the filler–related properties such as filler content, particle size, and dispersion. The aspect ratio and orientation distributions also play a role to improve the toughness of the composites with more fiberous materials (Oksman and Clemons, 1998).

Elastomers such as trans–1.4–isoprene rubber and cis–1,4–isoprene rubber have been used as an excellent matrix resin for WF–elastomer composites (Febrianto *et al.*, 1999, 2001, 2014). Oksman and Clemons (1998) tested several elastomers, i.e., ethylene propylene diene monomer (EPDM), maleated EPDM (EPDM–MA) and maleated styrene ethylene butylene styrene (MA–SEBS) as an impact modifier for WF–PP composites. The results showed that MA–SEBS can be an effective impact modifier in the WF–PP composite. Moreover, the addition of maleic anhydride–grafted PP (MAPP) as a coupling agent has a positive effect on the stiffness, tensile strength, and impact strength of the composite. This study investigated the combined effect of elastomer–compatibilizer on the mechanical properties of WF–PP composite.

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MATERIALS AND METHODS

Materials

WF that passed through a 200 mesh sieve was used as filler. PP (PN 260, MFR 25, Tokuyama Co., Japan) was used as matrix resin. Ethylene–propylene rubber (EPR; EP912SP, propylene 22 wt%, MFR = 8.6, Asahi Chemical Industry Co., LTD, Japan) and maleic anhydride (MAH) modified ethylene–propylene rubber (MEPR/T7711SP, Mw = 160.000, MFR = 2.5, Asahi Chemical Industry Co., LTD, Japan) were used as an impact modifier. MAPP (MPP06, MI =60~70; MAH content 0.4%, Tokuyama Co., Japan) was used as a coupling agent. MAH and dicumyl peroxide (DCP) were used as modifier and initiator, respectively. A mixture of pentacrythritol tetrakis (3–3',5',–di–tert–butyl–4',–hydroxyphenyl) propionate, 3,3',–thiodipropionic acid di–n–octadecyl ester and 2,6–di–tert–butyl–p–cresol (BHT) was used as antioxidant (AO). N,N'–1,3–phenylene–di–maleimide and dihydroquinoline (PM) was used as rubber cross–linking agent.

Methods

Four experimental sets were designed to prepare WF–PP composites and are summarized in Table 1. Compounding WF–PP composites with or without the impact modifier and coupling agent under various WF loadings in the presence of several additives were carried out using a kneader (Labo Plastomil, Toyo Seiki, Tokyo, Japan).

Experiment set 1

The ratio of PP and WF was set to be 50:50. The amount of MAH, DCP and AO was set to be 1.5, 0.5 and 0.75% in the basis of PP amount, respectively. Prescribed amount of PP was kneaded at 180°C, 30 rpm for 2 min,

Table 1. Composition of WF–PP composites at each experimental set

Experimental set	WF (%)	PP (%)	EPR (%)	MEPR (%)	MAH (%)	DCP (%)	MAPP (%)	AO (%)	PM (%)	Total (%)
1	50	50	–	–	–	–	–	–	–	100
	50	48.66	–	–	0.73 [1.5]	0.24 [0.5]	–	0.36 [0.75]	–	100
2	50	48.08	1.92 [4]	–	–	–	–	–	–	100
			–	1.92 [4]	–	–	–	–	–	100
	50	44.64	5.36 [12]	–	–	–	–	–	–	100
			–	5.36 [12]	–	–	–	–	–	100
	50	41.67	8.33 [20]	–	–	–	–	–	–	100
			–	8.33 [20]	–	–	–	–	–	100
3	50	47.17	1.89 [4]	–	0.71 [1.5]	0.23 [0.5]	–	–	–	100
	50	47.39	–	1.89 [4]			–	–	–	100
	50	43.86	5.26 [12]	–	0.66 [1.5]	0.22 [0.5]	–	–	–	100
	50	44.05	–	5.26 [12]			–	–	–	100
	50	40.98	8.20 [20]	–	0.61 [1.5]	0.20 [0.5]	–	–	–	100
	50	41.15	–	8.20 [20]			–	–	–	100
	60	37.91	1.52 [4]	–	0.57 [1.5	0.18 [0.5]	–	–	–	100
	60	37.91	–	1.52 [4]			–	–	–	100
	60	35.06	4.21 [12]	–	0.53 [1.5]	0.18 [0.5]	–	–	–	100
	60	35.24	–	4.21 [12]			–	–	–	100
	60	32.78	6.56 [20]	–	0.49 [1.5]	0.16 [0.5]	–	–	–	100
	60	32.92	–	6.56 [20]			–	–	–	100
	70	28.30	1.13 [4]	–	0.43 [1.5]	0.14 [0.5]	–	–	–	100
	70	28.44	–	1.13 [4]			–	–	–	100
	70	26.32	3.16 [12]	–	0.40 [1.5]	0.13 [0.5]	–	–	–	100
	70	26.43	–	3.16 [12]			–	–	–	100
	70	24.59	4.92 [20]	–	0.37 [1.5]	0.12 [0.5]	–	–	–	100
	70	24.64	–	4.92 [20]			–	–	–	100
4	50	46.66	2.00 [4.3]	–	–	–	1.25 [2.5]	–	0.10 [0.2]	100
	60	37.33	1.60 [4.3]	–	–	–	1.00 [2.5]	–	0.08 [0.2]	100
	70	27.99	1.20 [4.3]	–	–	–	0.75 [2.5]	–	0.06 [0.2]	100

Note: [ ] value means the percentage of the additives in the basis of PP amount

Table 2. Effect of the addition of MAH, DCP and AO on the tensile properties and impact strength of WF–PP composite

MAH, DCP and AO	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Impact strength (kJ/m^2)
Without addition	14.9 ± 0.5	1,808 ± 124	2.2 ± 0.1	6.1 ± 0.3
With addition	30.8 ± 1.5	2,235 ± 186	2.3 ± 0.1	7.4 ± 0.3

then MAH, DCP and AO were added within 1 min and further reacted for 1 min. WF was added subsequently within 3 min and rotation speed was increased to 50 rpm and kneading was conducted for 10 min.

Experiment set 2

The ratio of PP and WF was the same as the Experimental set 1. The addition amount of EPR and MEPR were 4, 12, and 20%. PP with EPR or MEPR was kneaded at 180°C, 30 rpm for 2 min. Then, WF was subsequently added within 3 min and further kneaded at the same temperature and at 50 rpm for 10 min.

Experiment set 3

The amount of WF addition against PP was changed from 50 to 70%. The amount of EPR and MEPR addition was the same as the Experimental set 2. The amounts of MAH and DCP were 1.5% and 0.5%, respectively. Prescribed amount of PP, EPR, MAH and DCP were kneaded at 180°C, 30 rpm for 1 min. After further reaction for 1 min, the WF was added subsequently in 3 min and kneaded at 50 rpm for 10 min.

Experiment set 4

WF addition amount was same with Experimental set 3. PM as rubber cross–linking agent of 0.2% was added. The amount of EPR and MAPP was set to be 4.3 and 2.5 wt%, respectively. PP, EPR, MPP and PM were kneaded at 180°C, 30 rpm for 1 min. After further reaction for 1 min, the WF was added subsequently within 3 min. The rate of rotation increased at 50 rpm and the kneading was continued for 10 min.

Preparation of composites sheet

The compounded samples were compression–molded into sheet by hot press (Toyo Seiki, Tokyo, Japan) at 190 °C and 0–50 kgf cm^{-2} and 100 kgf cm^{-2} pressures for 5 min and 30 sec., respectively, and followed by cold pressed at the same pressure for 30 sec.

Tensile and impact tests

Strip samples with a dimension of 80.0 × 5.0 × 0.3 mm were prepared for tensile test. The measurements were conducted using tensile tester (DCS–R–500, Shimadzu Autograph, Kyoto, Japan) with a span length of 40 mm and cross head speed of 5 mm/min at 20°C and 60 R.H. Ten samples were measured. For impact strength, specimen preparation and test procedure were followed by ASTM D256 and the measurement was conducted using Yasuda Impact Tester (Osaka, Japan).

RESULTS AND DISCUSSION

In Experimental set 1, the effect of the addition of MAH, DCP and AO on the tensile strength, elongation at break, Young's modulus and impact strength of WF–PP composites were evaluated. The obtained results are

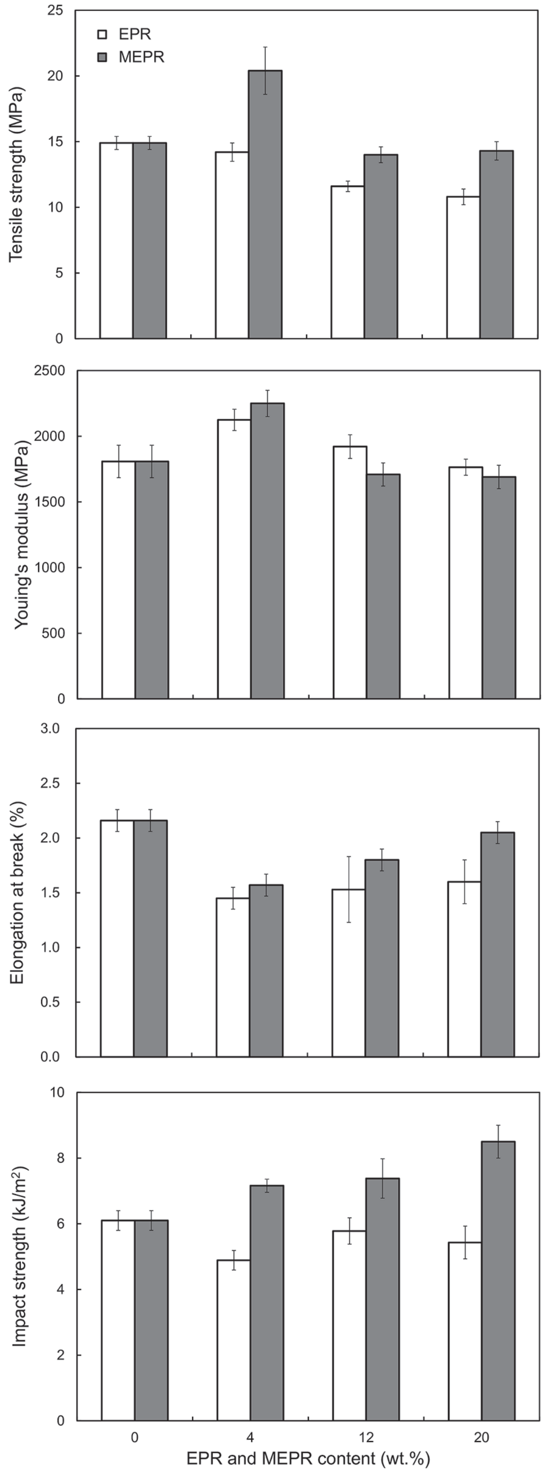

Fig. 1. Effects of the rubber type and content on the tensile properties and impact strength of WF–PP composites. (Note: WF content; 50 wt%).

summarized in Table 2. It is clear that the addition of MAH, DCP and AO on the WF–PP composite greatly improved tensile strength and Young's modulus. On the other hand, the elongation at break showed similar value. The impact strength was also slightly improved with the addition of MAH, DCP and AO. The MAH and DCP addition can form MAPP, which can act as a compatibilizer in the WF–PP composites (Kishi *et al.*, 1988; Han *et al.*, 1989; Oksman and Clemons, 1998; Sombatsompop *et al.*, 2005; Febrianto *et al.*, 2005, 2006a, 2006b). These improvements would be due to a better homogenous dispersion of the filler and the enhanced interfacial adhe-

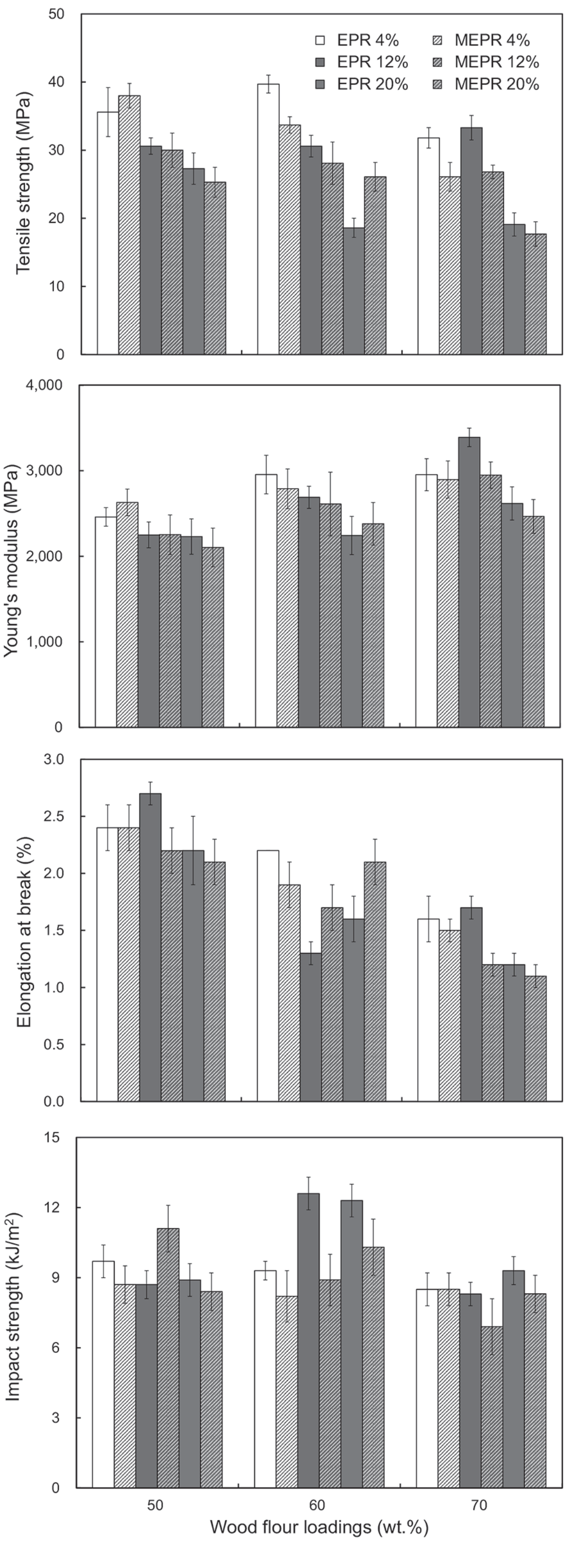

Fig. 2. Effect of the impact modifier addition in the presence of MAH and DCP on the tensile properties and impact strength of WF–PP composites with various WF loading. (Note: MAH and DOP content; 1.5 and 0.5 wt%).

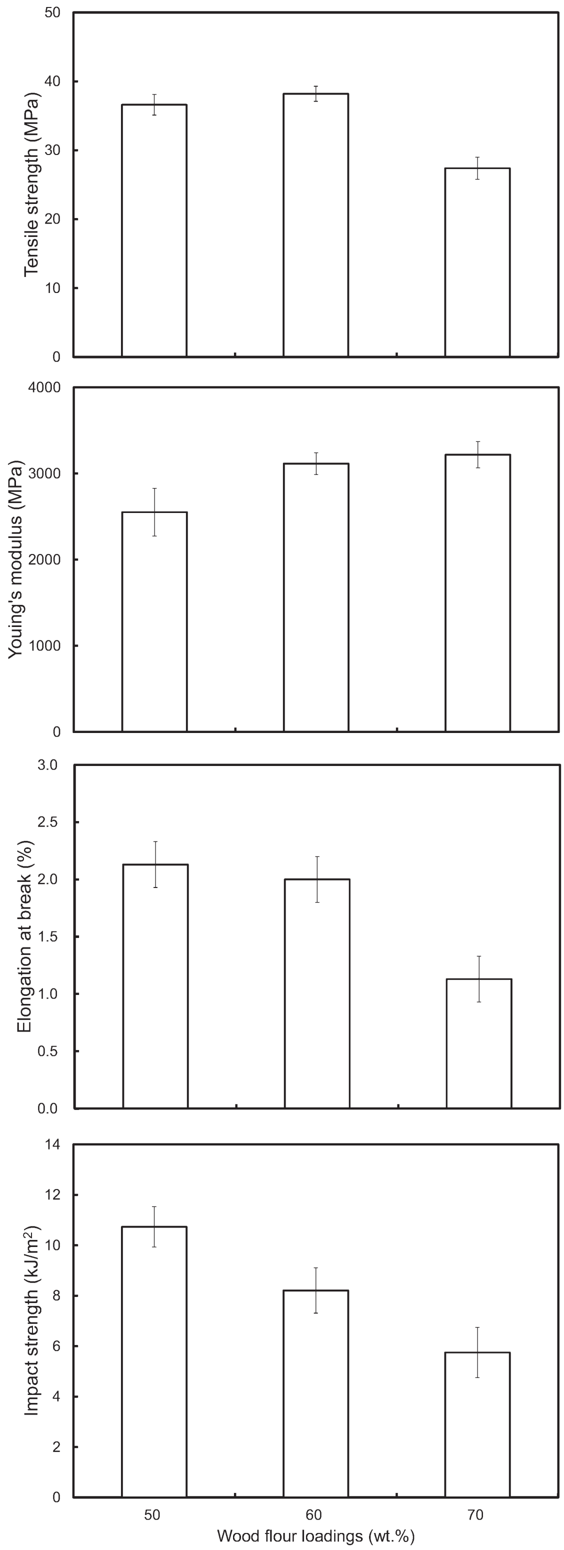

Fig. 3. Effect of the addition of EPR, MAPP, and PM on the tensile properties and impact strength of WF–PP composites with different WF loadings. (Note: EPR, MAPP, and PM content; 4.3, 2.5, and 0.2 wt%).

sion between filler and matrix polymer by the formation of MAPP. Similar results have been published by other researchers (Dalväg *et al.*, 1985; Felix and Gatenholm, 1991; Gatenholm *et al.*, 1992; Kord, 2011; Tabari *et al.*, 2011).

In Experimental set 2, the effect of the addition of EPR and MEPR as an impact modifier on the tensile properties and impact strength of WF–PP composites were evaluated and thus–obtained results are summarized in Fig. 1. The content of impact modifier was set to be 4, 12, and 20% in the basis of PP matrix weight. With increasing EPR and MEPR, tensile strength and Young's modulus were decreased, whereas elongation at break and impact strength were increased. That is, both impact modifier improved impact strength of the composite, but showed a negative effect on tensile strength and Young's modulus. And the improvement was higher in the composite with MEPR than those with EPR. Compared to the properties of the composite without impact modifier, the MEPR addition of 4 wt% resulted in improvement of tensile strength and Young's modulus. Further, all composites with MEPR showed higher impact strength than that of the composite without MEPR. Oksman and Clemons (1998) tested three elastomer additives (i.e., EPDM, EPDM–MA, and SEBS–MA) for WF–PP composites. Their results showed that maleated elastomers were effective as impact modifiers for the PP–WF composite and the addition of MAPP showed a positive effect on the stiffness, tensile strength, and impact strength.

In Experimental set 3, the effect of the impact modifier addition in the presence of MAH and DCP of 1.5 and 0.5 wt% in the basis of PP content, respectively, on the tensile properties and impact strength of WF–PP composites with different WF loading were evaluated. Fig. 2 summarizes the results. In all composites with 50–70 wt% WF loading, tensile properties showed the decreasing tendency with increasing EPR and MEPR content. However, impact strength was not significantly changed. Compared to the results in the absence of MAH and DCP as shown in Fig. 1, the presence of MAH and DCP remarkably enhanced tensile strength, Young's modulus and impact strength. Furthermore, a degree of the increase was larger in the composite with EPR than those of with MEPR. At the same EPR or MEPR content, the higher filler loadings resulted in higher Young's modulus and lower impact strength. The highest properties was found in the WF–PP composite with 60 wt% WF.

In Experimental set 4, the effect of the addition of EPR, MAPP, and PM on the tensile properties and impact strength of WF–PP composites with different WF loadings was investigated and the obtained results are summarized in Fig. 3. MAPP and PM are expected to play a role of coupling–linking agent between PP and WF and between EPR and EPR, respectively. Tensile strength, Young's modulus, and impact strength were greatly improved by adding EPR combined with MAPP and PM, compared to those of the composite without additives (shown in Fig. 2). This improvement may be due to the cross–linking of EPR itself and the presence of MAPP at the interface between PP and WF phases. Tensile strength was increased with increasing WF content to 60 wt% and decreased at the composite with 70 wt% WF. With an increase in the WF content, Young's modulus was improved, whereas elongation at break and impact strength decreased.

CONCLUSION

The addition of MAH, DCP and AO for the production of MAPP improved the tensile strength and Young's modulus of the WF–PP composites but did not significantly affect the elongation at break and impact strength. The impact strength was improved by the addition of EPR and MEPR as an impact modifier, and tensile properties and impact strength were further improved by adding MAH and DCP in the presence of EPR and MEPR. In the presence of MAH and DCP, tensile properties showed the decreasing tendency with increasing EPR and MEPR content, but impact strength was not significantly changed. The addition of PM in the presence of EPR greatly improved tensile strength, Young's modulus, and impact strength, compared to those of the composite without additives.

AUTHOR CONTRIBUTIONS

Yoshikuni Teramoto, Tetsuo Kondo, and Nam–Hun Kim designed the study and partly analysed the data. Fauzi Febrianto carried out the entire experiments and wrote the paper. Wahyu Hidayat, I Nyoman Jaya Wistara, Se Hwi Park, Jae–Hyuk Jahn, Seung–Hwan Lee partly performed and assisted partly the experiments, in particular the analyses parts. All authors assisted in editing of the manuscript and approved the final version.

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