Research paper

Effects of Phosphoryl Triamide Treatment on the Strength and Dimensional Properties of Woodflour-Polypropylene Composites

Chin-Yin Hwang,[1,4]   Wen-Jun Ku,[2]   Hong-Lin Lee[3]

【Summary】

The purpose of this study was to investigate the effects of phosphoryl triamide treatment on the flexural properties, internal bond strength, and dimensional stability of woodflour-polypropylene composites. Factors investigated included 3 woodflour loading levels and 7 fire-retardant treatments. Results showed that fire-retardant treatments adversely affected the flexural strength, internal bond strength, and dimensional stability of composite panels at a 100% woodflour loading; however, all of the measured properties improved at higher polypropylene contents, except for the flexural stiffness which was unaffected by either factor. Woodflour loading and fire-retardant treatments collectively and interactively affected the performance of woodflour-polypropylene composites, with the woodflour content a more-important factor than the fire-retardant type.

Key words: woodflour-plastic composite, fire retardant, phosphoryl triamide, tripropyl phosphoramide, triphenyl phosphoramide.

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研究報告

磷醯三胺處理對木粉/聚丙烯複合材強度
及尺寸安定性質之影響

黃清吟[1,4]　　顧文君[2]　　李鴻麟[3]

摘　　要

本研究旨在探討木粉含量(WFL)及阻燃劑處理(FRT)對磷醯三胺處理木粉/聚丙烯複合材強度性質及尺寸安定性之影響。試驗結果顯示：各處理平均MOR在6.8~7.1 MPa間，MOE介於1160~1810 MPa間，未浸水(IB0)及浸水24小時之內聚力(IB24)分別在0.17~0.75和0.02~0.60 MPa範圍內，至於浸水2及24小時後之重量增加率(WA)及厚度膨脹率(TS)則分別為6.3~98.0% (WA2)和27.5~113.4% (WA24)，以及4.6~50.7% (TS2)和8.4~60.0% (TS24)。變方分析結果得知WFL與FRT共同影響木粉/聚丙烯複合材之性能，除MOR僅受WFL影響、MOE不受WFL及FRT影響外，其餘各項性質均受WFL與FRT的交感效應影響，而以WFL為主要影響因子。一般而言，除MOE外木粉/聚丙烯複合材WFL在100%，處理材較未處理材性能為差，而WFL在60%時複合材性能整體提升，FRT之負面影響也趨降低。

關鍵詞：木粉/塑膠複合材、阻燃劑、磷醯三胺、磷醯三丙基胺、磷醯三苯胺。

INTRODUCTION

Wood-plastic composites (WPCs) have received considerable attention from industry because of their desirable features such as ease of processing, light weight, dimensional stability, decay resistance, etc. A wide range of properties can be achieved to meet consumer demands by manipulating component formulations and processing factors. Applications of WPCs include decking, fencing, industrial flooring, landscape timbers, railings, moldings, and automobile parts (Clemons 2002, Smith and Wolcott 2006). However, the fire performance of WPCs has been a critical issue, since both components are thermally degradable and combustible polymer materials.

Macroscopically, combustion of polymer materials is characterized by a complex coupling between the condensed phase and the gas phase. Each phase involves a combination of chemical reactions with heat and mass transfer processes (Kashiwagi 1994). The combustion behaviors of the 2 components somewhat differ. As the temperature rises, the molecules in a thermoplastic solid become increasingly mobile, imparting viscous properties of a fluid to the material. The subsequent chemical bond breakage leads to a reduction in the average molecular weight and the formation of polymer fragments that constitute gas molecules. When the temperature reaches a certain level, reactions such as pyrolysis, thermal oxidation, thermal degradation, dehydration, condensation, cyclization, and carbonization are initiated, generating combustible and noncombustible gases, and char layers. For some polymers, the behavior of the condensed phase involves swelling, bub-

bling, melting, sputtering, and multi-stage combustion (Yang et al. 2000).

Wood is a composite of cellulose, hemicellulose, lignin, extractives, and trace minerals. The complex combustion behavior of wood reflects mixture of its principal components which exhibit dehydration, pyrolysis, thermal oxidation, and thermal degradation at various temperature regimes. Among the 3 major components, hemicellulose is the least, cellulose the intermediate, and lignin the most thermally resistant (Ramiah 1970, Yang et al. 2006, 2007). Cellulose contributes mostly to flaming combustion at a lower temperature range while lignin contributes to the subsequent glowing at a higher temperature range (Browne 1958).

When subjected to fire, both wood and plastics may undergo rapid failure, leading to a decrease in the product service life and an increase in environmental hazards. Many chemical modifications have been applied to improve the thermal performance of wood and thermoplastics. Among these, the most commonly used fire retardants (FRs) are inorganic salts which promote the formation of charcoal and serve as a thermal insulation layer (Browne 1958). Phosphate fire-retardant treatments (FRTs) are extensively used in wood and plastic products; one major drawback when applying this type of FR is that the strength of the treated wood decreases over time (LeVan and Winandy 1990, LeVan et al. 1990).

Phosphoramides, on the other hand, show improved reactivity over analogous phosphates because they possess phosphorus-nitrogen bonds (Langley et al. 1980). They also increase the char yield after pyrolysis of treated wood without a significant strength decrease (Hendrix et al. 1972, Pandya and Bhagwat 1981). Previous studies (Lee et al. 1999, 2001, 2004) also showed that phos-phoryl triamide treatment improves the fire-retardancy, and decay and termite resistance of treated wood. However, little was found in the literature regarding mechanical properties of phosphoramide-treated wood and wood composites. The purpose of this study was to gain a better understanding of the effects of phosphoryl triamide treatment on the mechanical properties, internal bond (IB) strength, and dimensional stability of wood-flour-polypropylene (WF-PP) composites.

MATERIALS AND METHODS

Materials

Major components used for WF-PP composite fabrication were China-fir (*Cunninghamia lanceolata* Lamb.) woodflour, and polypropylene (PP; Pro-fax 6331, USI Corp., Kaohsiung, Taiwan) powder (40 mesh). Air-dried China-fir waste wood strips were hammer-milled and screen-sieved to a size of 20~40 mesh, followed by 2 d of oven-drying at $60\pm3°C$ and storage in desiccators before further treatment. Three types of FRs, including 2 synthesized in the laboratory and 1 commercially acquired, were used for wood modification. The phosphoryl triamides were synthesized by reacting phosphorus oxychloride with each of the 2 amines, including 1 alkyl (propylamine) and 1 phenyl (aniline) amine, in a chloroform solution according to the procedures described in a previous paper (Lee et al. 2001). The resulting chemical compounds were tripropyl phosphoramide (P) and triphenyl phosphoramide (A), respectively. Dricon® (D; Kopper-Hickson Timber Protection Sdn. Bhd.) was selected as the representative commercial FR. A low-formaldehyde-emission urea-formaldehyde resin (UF), used as binder, was supplied by a local provider (SU501, Shiny Chemical Industrial, Kaohsiung, Taiwan).

WF-PP composites fabrication

Chemical modification: China-fir wood-flour was reacted with P and A by a reflux heating method for 3 h, and with D by impregnation for 24 h. After the chemicals were removed, the treated woodflours were oven-dried at $60 \pm 3 ℃$ for 2 d and stored in desiccators before panel fabrication.

Furnish preparation: WF-PP composites were prepared with 3 levels of compositions, i.e., WF: PP (w) = 100: 0, 80: 20, and 60: 40. For panels containing PP powder, woodflours were first manually premixed with PP powder. The mixture was then blended with UF resin at 8% by weight in a rotating drum mixer fitted with a compressed air spray gun.

Compression and setting: The furnish was then hand-felt into a 35×35-cm deckle box, and the mat was prepressed at room temperature under 0.98 MPa for 30 s before subjecting it to compression and setting. The mat was hot-pressed under 2.94 MPa until the plate temperature reached $190℃$, and this was maintained for 6 min in a hot press equipped with a cooling system. Subsequently, a cold-setting procedure was performed, while the mat was still compressed, until the temperature decreased to $80℃$.

Treatment combination: In total, 105 panels were made with 5 replicates for each of the 21 treatment combinations, including 3 woodflour loadings (WFLs, 100, 80, and 60%) and 7 FRTs, including an untreated (control, CTL), 2 concentration levels each of Dricon® (1%, D1; 2%, D2), tripropyl phosphoramide (1%, P1; 2%, P2), and triphenyl phosphoramide (1%, A1; 2%, A2).

Evaluation of properties

After conditioning at 65% relative humidity (RH) and $25℃$ for 2 wk, the WF-PP composite panels were subjected to edge trimming, surface sanding, and specimen extrac-tion of various dimensions in accordance with ASTM standards D 1037-99 (ASTM 1999). The following properties were investigated.

Flexural strength: Specimens for flexural test were $5 \times 20 \times 1$ cm. The three-point flexural tests were performed on a Computer-servo Material Testing Machine (Hung Ta, HT-9102, Taichung, Taiwan) at a load cell speed of 5 mm min^{-1} and a span-to-depth ratio of 16: 1. The flexural modulus of rupture (MOR) and modulus of elasticity (MOE) were obtained from the tests.

IB strength: Specimens for the IB test were $5 \times 5 \times 1$ cm. IB tests were performed on the same Material Testing Machine at a load cell speed of 5 mm min^{-1} using internal bond fixtures. IBs were measured both without (IB0) and with 24 h of water soaking (IB24).

Dimensional stability: The dimensional stability measurements included water absorption (WA) and thickness swelling (TS). The sample size was $5 \times 5 \times 1$ cm for both WA and TS. There were 2 water soaking durations of 2 (WA2 and TS2) and 24 h (WA24 and TS24).

Statistical analysis

All investigated data were analyzed using Statistics Analysis System ver. 9.1 (SAS Institute, Cary, NC, USA). A two-way analysis of variance (ANOVA) was performed to determine the statistical significance of the main effects of WFL and FRT, and the interaction between the 2 main effects.

RESULTS AND DISCUSSION

Flexural properties

Table 1 presents the flexural properties and IB strength of the FR-treated WF-PP composites. The average flexural MORs of all treatment combinations ranged 6.8~17.1

Table 1. Flexural properties and internal bond strength of fire-retardant-treated woodflour-polypropylene composites[1]

Fire retardant type[2]	Wood flour loading (%)	MOR	MOE	IB0	IB24
		------------------------------ MPa ------------------------------			
CTL	60	15.6 (2.0)[3]	1600 (200)	0.41 (0.10)	0.16 (0.05)
CTL	80	12.2 (2.1)	1580 (230)	0.24 (0.07)	0.10 (0.04)
CTL	100	10.6 (2.7)	1540 (340)	0.42 (0.08)	0.26 (0.06)
A1	60	16.4 (1.3)	1670 (90)	0.29 (0.07)	0.13 (0.06)
A1	80	9.7 (2.1)	1560 (290)	0.38 (0.04)	0.24 (0.02)
A1	100	9.5 (1.5)	1430 (230)	0.52 (0.14)	0.40 (0.21)
A2	60	15.2 (1.8)	1610 (140)	0.34 (0.12)	0.13 (0.07)
A2	80	11.2 (2.0)	1420 (240)	0.22 (0.04)	0.08 (0.05)
A2	100	8.9 (2.5)	1530 (320)	0.58 (0.13)	0.52 (0.21)
D1	60	15.6 (0.4)	1550 (60)	0.29 (0.09)	0.10 (0.02)
D1	80	9.6 (1.9)	1410 (330)	0.42 (0.10)	0.10 (0.08)
D1	100	7.9 (1.9)	1400 (390)	0.62 (0.10)	0.55 (0.12)
D2	60	15.2 (1.1)	1590 (110)	0.17 (0.06)	0.02 (0.01)
D2	80	9.9 (2.1)	1400 (300)	0.24 (0.10)	0.03 (0.01)
D2	100	6.8(1.1)	1160 (280)	0.61 (0.05)	0.60 (0.11)
P1	60	17.1 (0.5)	1400 (440)	0.41 (0.16)	0.07 (0.04)
P1	80	9.9 (2.1)	1430 (220)	0.57 (0.06)	0.24 (0.03)
P1	100	10.4 (2.6)	1810 (310)	0.75 (0.04)	0.43 (0.14)
P2	60	16.5 (0.8)	1660 (140)	0.42 (0.17)	0.11 (0.05)
P2	80	9.7 (1.9)	1540 (230)	0.44 (0.14)	0.15 (0.05)
P2	100	9.6 (2.0)	1470 (200)	0.62 (0.16)	0.44 (0.19)

[1] MOR, flexural strength; MOE, flexural stiffness; IB0, original internal bond strength; IB24, internal bond strength after 24 h of water soaking.

[2] CTL, untreated; A1 and A2, treated with 1 and 2% triphenyl phosphoramide; D1 and D2, treated with 1 and 2% Dricon®; P1 and P2, treated with 1 and 2% tripropyl phosphoramide.

[3] Numbers in parentheses represent standard deviations.

MPa. The overall average MOR of the WF-PP composites with a WFL of 60% in this study was 16.0 MPa, which is smaller than values reported in studies with the same composition (Karnani et al. 1997, Rowell 2007, Xue et al. 2007, San et al. 2008). The overall average MOR of the panels with a WFL of 100% in this study, which were literally conventional particleboards, was 9.1 MPa. This result was somewhat smaller than those reported in studies investigating the effects of FRTs on the mechanical properties of wood composites (Ayrilmis and Winandy 2007, Wang et al. 2008, Izran et al. 2009).

This difference is probably due to the larger woodflour particles and compression molding process used in this study, since the discrepancy in the mechanical properties of WPCs can be explained by differences in the target density, filler size, filler species, volume fraction of biomass in the composites, additives, pretreatment, processing technique,

and the type of thermoplastic used (Bledzki and and Gassan 1999, Rowell 2007). For FR treated composite panels, the wood species, the adhesives used, the types of FRs, the processing conditions, etc., play important roles in the properties of the panels.

Table 1 shows that FRT adversely affected the flexural MORs of the WF-PP composites at the 2 higher levels of WFL; whereas the adverse effects of FRT were unnoticeable at a WFL of 60%. The addition of PP profoundly enhanced the flexural MORs of the composite panels, with or without treatment. WF-PP composites with a 40% PP content exhibited the highest flexural MORs among all PP levels. However, ANOVA on MORs of all treatment combinations showed a highly significant WFL main effect ($p < 0.01$), a marginally significant FRT main effect ($p < 0.05$), and an insignificant WFL × FRT interaction (Table 2). A post-hoc Tukey's test was then performed, and results showed that average MORs of the 3 WFL levels were in the order of 60% (16.0 MPa) > 80% (10.3 MPa) > 100% (9.1 MPa), whereas no significant differences were detected among the 7 FRT types. These statistical analysis results suggest that FRT has an insignificant effect while WFL has a negative effect on the flexural strength of WF-PP composites, which goes against the conventional wisdom that FRTs generally have detrimental effects on the mechanical properties of wood. The

reason for this discrepancy, besides the more conservative characteristics of the Tukey's test, is probably due to FRT's effect tending to be overwhelmed by the increasing PP content which is reflected in WFL's effect.

The mechanisms that contribute to the strength reduction of wood are physical changes due to introduction of hydrated salt molecules into the wood cell walls, and chemical changes due to thermal degradation reactions catalyzed by the fire retardants (Berndt et al. 1990). The extent that FR chemicals adversely affect the strength properties of wood is largely dependent on the type of chemical and the exposure temperature, and is closely related to the degradation of hemicelluloses (Winandy and Richards 2003).

The average flexural MOEs of the FR-treated WF-PP composites in this study ranged 1160~1810 MPa (Table 1). The overall average MOE of panel composites with a WFL of 60% in this study was 1580 MPa. This value is somewhat smaller than the reported MOE values from other wood-PP composites studies with an equivalent composition (Karnani et al. 1997, Rowell 2007, Xue et al. 2007, San et al. 2008). Results of ANOVA on MOEs of all treatment combinations revealed neither significant main effects nor an interaction ($p > 0.05$, Table 2), indicating that the flexural stiffness of the WF-PP composites was unaffected by the WFL and FRT in this study.

Table 2. Results of ANOVA as expressed by _p_ values of the flexural properties and internal bond strengths of fire-retardant-treated woodflour-polypropylene composites[1]

Effect	MOR	MOE	IB0	IB24
Fire retardant type (FRT)[2]	0.0425*	0.3927	< 0.0001**	0.2612
Woodflour loading (WFL)	< 0.0001**	0.1796	< 0.0001**	< 0.0001**
WFL × FRT	0.3713	0.2112	0.0017**	< 0.0001**

[1] MOR, flexural strength; MOE, flexural stiffness; IB0, original internal bond strength; IB24, internal bond strength after 24 h of water soaking.
[2] ** Highly significant (Pr > F of < 0.01); * significant (Pr > F of < 0.05).

The MOR for WPCs is more sensitive to treatment effects than is the MOE (Winandy and Richards 2003, Winandy et al. 2008). This phenomenon can be further explained by the flexural property retention rate, which was calculated by dividing the FR treated values by the corresponding untreated (CTL) value and multiplying that by 100% (Fig. 1).

The MOR retention rates at a WFL of 100% for treatments A1, A2, D1, D2, P1, and P2 were 89.4, 84.2, 74.5, 63.9, 97.9, and 90.5% respectively, while the corresponding MOE retention rate were 92.7, 99.3, 91.0, 75.1, 117.5, and 95.7%, respectively. Treatment D exhibited the largest while treatment P exhibited the smallest difference with the untreated
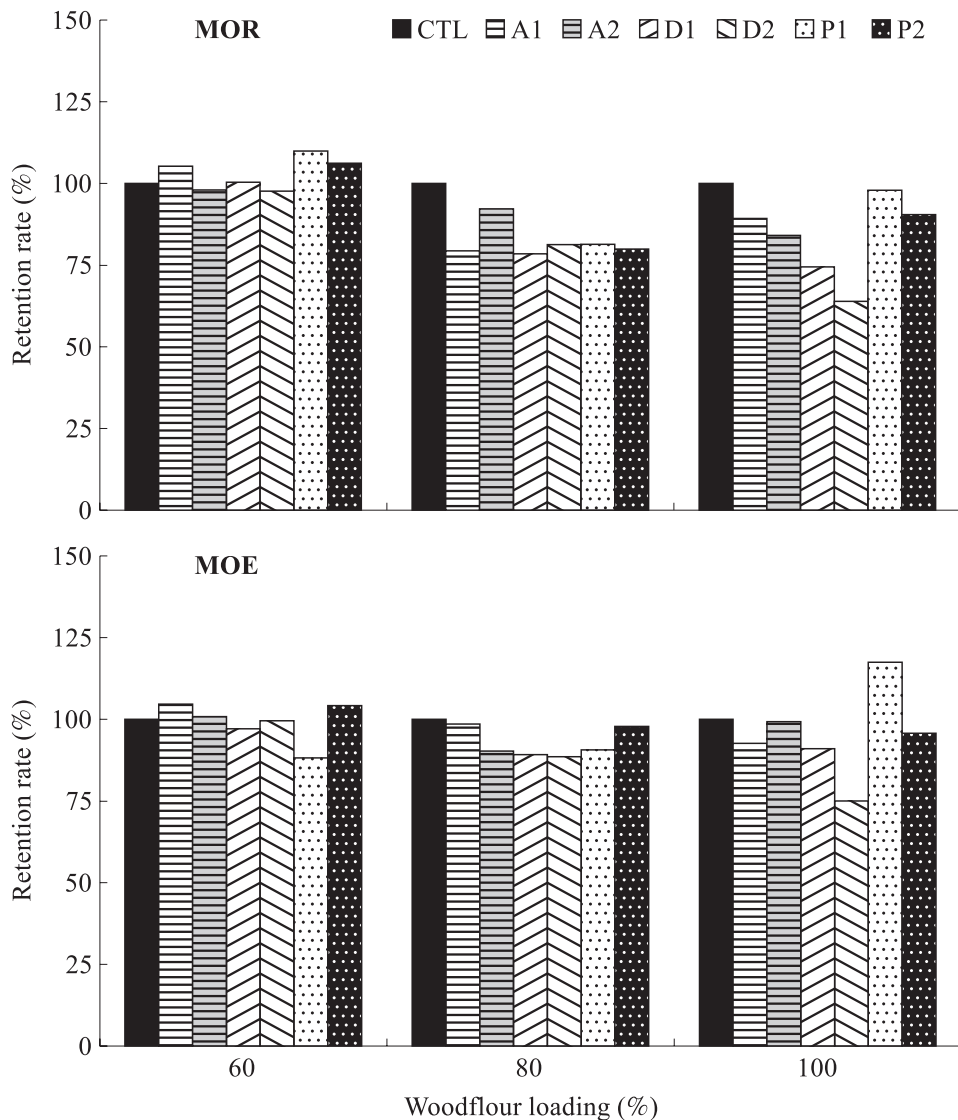

Fig. 1. Flexural retention rate of fire-retardant-treated and untreated woodflour-polypropylene composites at various woodflour loadings. [modulus of rupture (MOR): upper, modulus of elasticity (MOE): lower].

counterpart for both MOR and MOE. The difference was, however, more pronounced for the MOR than for the MOE, indicating that the MOE of WF-PP composite was less affected by the FRT, as also reported by Winandy et al. (2008).

IB strength

Average IB0 and IB24 values of all treatment combinations were between 0.17~0.75 and 0.02~0.60 MPa, respectively (Table 1). The average IB0s for treatments CTL, A1, A2, D1, D2, P1, and P2 at a WFL of 100% were 0.41, 0.29, 0.34, 0.29, 0.17, 0.41, and 0.42, respectively; these figures are similar to data reported by Wang et al. (2008) and Izran et al. (2009), but somewhat smaller than data reported by Semple and Smith (2006) and Ayrilmis (2007). The IB0 retention rate, as calculated by dividing IB0s of the FR treated WF-PP composites by the corresponding IB0 of CTL, were 71.3, 83.2, 69.8, 40.5, 99.1, and 102.4% for treatments A1, A2, D1, D2, P1, and P2, respectively, indicating that P1 and P2 had the highest while D1 and D2 showed lowest IB0 retention rates.

The 2 main effects and the WFL×FRT interaction were highly significant at $p < 0.01$ for IB0s (Table 2). The significant WFL× FRT interaction suggests that IB0s of the 7 FRT types responded differently as the WFL level changed (Fig. 2). As shown in Fig. 2, average IB0s of the 7 FRT types could be grouped into 3 clusters at a WFL of 100%, with treatments CTL, P1, and P2 the highest, A1 and A2 the medium, and D1 and D2 the lowest. Conversely, the FR treated WF-PP composites showed higher IB0s over the CTL composite panels at the 2 lower WFL levels. WF-PP composites with 60% WFL exhibited the highest IB0s among all WFL levels.

After 24 h of water immersion, IBs of the WF-PP composites had dropped consider-

ably. The average IB reduction rate caused by 24 h of water soaking was calculated as (IB0 - IB24)/IB0×100. Considering the WFL effect, IB reductions caused by water soaking were 22.4, 63.8, and 70.2%, for WFLs of 60, 80, and 100%, implying that the higher the WFL level, the more adverse was the effect of water immersion on IB24, and the addition of PP might preserve the integrity of the composites. Results of ANOVA on IB24s showed a highly significant WFL main effect and WFL×FRT interaction at $p < 0.01$ (Table 2). The significant WFL×FRT interaction suggests that, like those of IB0s, IB24s of the 7 FRT types responded differently as the WFL level changed (Fig. 2).

For wood composites, IB is a measure of the overall panel integrity that depicts how well the particles/fibers are bonded together. One of the major problems that are encountered with FRT of wood composites is the interference of chemicals with resin curing and bond development (Winandy et al. 2008). However, some reported that IBs were increased with FRTs tested either in dry or wet conditions (Winandy et al. 2008), while another report stated that IBs were lower than the untreated counterpart and decreased with increasing FR concentrations (Ayrilmis 2007). This ambiguity may be attributed to the complexity of material properties, chemical types and compositions, treatments and processing methods, and above all, the interactions between some or all of the variables.

Since plastic is hydrophobic and wood is hygroscopic, the wood content is responsible for the water absorption of WPCs. With the compression molding used in this study, the molten PP flour is prone to interpenetrate into the wood particle network and serves as a mechanical bonding agent of the composite once it hardens. The interfaces within such composite are postulated to be wood-adhesive-
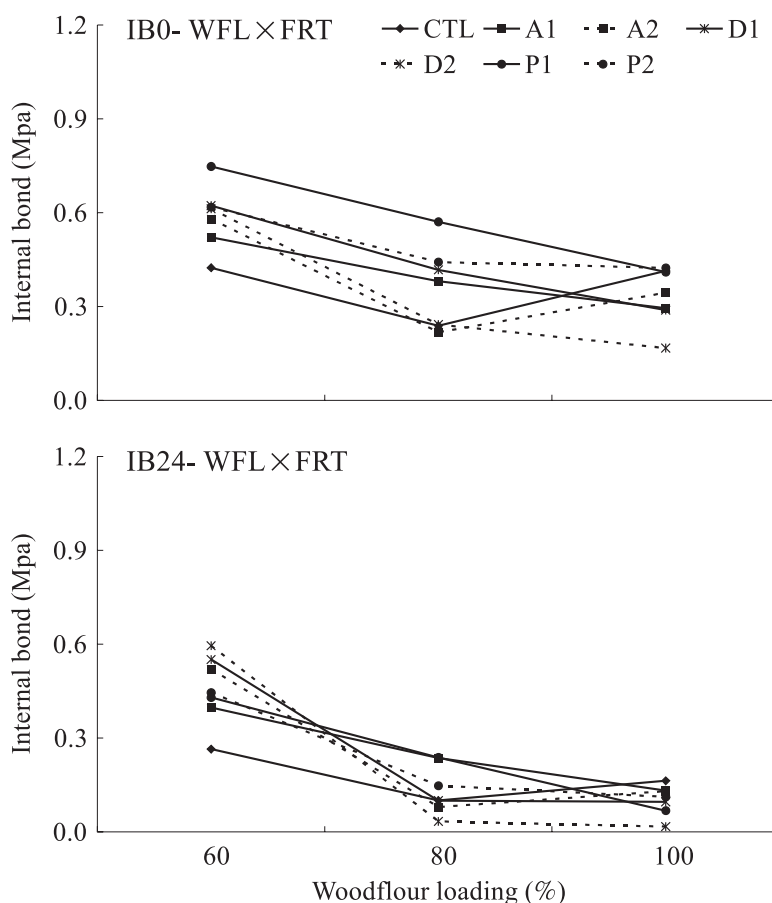
Fig. 2. Interaction between the woodflour loading and fire-retardant type on the internal bond strength of woodflour-polypropylene composites before (upper) and after 24 h of water soaking (lower).

wood, wood-adhesive-plastic, and plastic-plastic, when the wood particles are properly coated with adhesive. However, if wood particles break down to smaller particles during the processing procedures and reveal inner surfaces of the particles which are not coated with adhesive, the network may also include wood-wood and wood-plastic interfaces. The more the unencapsulated wood-adhesive-wood and wood-wood interfaces are exposed to moisture/water, the greater is the possibility that the integrity of the composites will be reduced. Furthermore, when wood particles absorb moisture and swell, it creates stress in

the matrix and leads to the formation of microcracks. These interfacial gaps will contribute to penetration of water into the composite with later exposure (Stark and Gardner 2008). This may explain the phenomenon that the IB reduction rate increases with an increasing WFL level. In conclusion, IB0 and IB24 of the FR treated WF-PP composites were collectively affected by the interaction of WFL and FRT.

WA

The average WA2 and WA24 for all treatment combinations ranged from 6.5

to 98.0% for WA2, and 26.7 to 113.4% for WA24, indicating that the WA of WF-PP composites increased with immersion time (Table 3). Among the 7 FRT types, A1 and A2 seemed to have dramatically lower initial water uptake rates than other treatments at all WFL levels; the difference, however, was less pronounced than in WA24. The overall average WAs for WFLs of 100, 80, and 60% were 65.9, 46.0, 15.7% for WA2, and 92.1, 65.5, 31.1% for WA24, respectively, while

the difference between the maximum and the minimum WAs for the 3 WFL levels were 74.2, 46.1, 20.3% for WA2, and 36.1, 21.3, 12.3% for WA24, indicating that after a longer immersion in water, differences in the water uptake rates for the 7 FRT types tended to converge.

ANOVA of WA2 and WA24 revealed highly significant FRT and WFL main effects and the WFL×FRT interaction ($p < 0.01$, Table 4), indicating that WFL and FRT collec-

Table 3. Dimensional stability of fire-retardant-treated woodflour-polypropylene composites[1]

Fire retardant type[2]	Wood flour loading (%)	WA2	WA24	TS2	TS24
		------------------------------- % -------------------------------			
CTL	60	22.3 (2.6)[3]	39.0 (3.0)	9.3 (2.3)	12.7 (2.3)
CTL	80	54.5 (14.7)	67.7 (12.2)	20.3 (7.0)	24.4 (8.0)
CTL	100	63.5 (4.8)	80.2 (8.0)	23.5 (3.5)	29.8 (4.1)
A1	60	7.1 (2.1)	26.7 (6.1)	6.4 (2.6)	11.0 (3.7)
A1	80	17.7 (9.1)	53.6 (8.5)	11.9 (2.5)	19.6 (2.3)
A1	100	30.5 (4.5)	79.8 (6.0)	21.6 (2.8)	35.1 (5.1)
A2	60	6.5 (1.0)	28.3 (2.8)	4.7 (0.5)	8.4 (0.5)
A2	80	26.4 (8.9)	69.6 (13.6)	19.0 (5.9)	28.3 (9.3)
A2	100	23.8 (7.5)	77.3 (8.7)	19.9 (4.2)	34.2 (6.2)
D1	60	12.4 (4.3)	28.0 (4.6)	5.9 (0.9)	9.3 (1.0)
D1	80	53.6 (4.7)	66.8 (6.1)	21.5 (5.1)	26.2 (6.3)
D1	100	81.3 (10.4)	95.8 (9.6)	33.2 (6.2)	42.5 (6.4)
D2	60	11.9 (3.9)	27.1 (5.4)	5.7 (1.2)	8.9 (1.0)
D2	80	63.7 (14.6)	74.9 (15.7)	25.1 (9.0)	32.2 (13.3)
D2	100	98.0 (15.4)	113.4 (15.6)	50.7 (11.8)	59.9 (13.6)
P1	60	22.7 (5.1)	33.3 (2.7)	8.2 (1.6)	9.8 (1.4)
P1	80	49.6 (2.7)	58.9 (2.7)	15.8 (0.7)	18.1 (0.7)
P1	100	86.9 (16.7)	102.5 (15.5)	42.8 (8.0)	50.7 (9.4)
P2	60	26.9 (4.8)	35.6 (3.2)	8.3 (1.7)	9.7 (1.5)
P2	80	56.5 (8.9)	67.1 (8.4)	21.4 (3.8)	23.8 (4.4)
P2	100	77.6 (7.8)	95.9 (7.0)	39.6 (5.8)	46.3 (6.3)

[1] WA2 and WA24, weight gained after 2 and 24 h of water soaking; TS2 and TS24, thickness swelling after 2 and 24 h of water soaking.
[2] CTL, untreated; A1 and A2, treated with 1 and 2% triphenyl phosphoramide; D1 and D2, treated with 1 and 2% Dricon®; P1 and P2, treated with 1 and 2% tripropyl phosphoramide.
[3] Numbers in parentheses represent standard deviations.

tively affected the WAs of the FR treated WF-PP composites, and the 7 FRT types reacted differently to the changing WFL level. Figures 3 clearly shows that WA2s of treatments A1 and A2 were lower than those of the CTL at all WFL levels; WA2s of treatments D1 and D2 were higher than the CTL at a WFL of 100% and were slightly lower than the CTL at a WFL of 60%; while treatments P1 and P2 showed higher WA2s than the CTL at WFLs

Table 4. Results of ANOVA as expressed by *p* values of the dimensional stability of fire-retardant-treated woodflour-polypropylene composites[1]

Effect	WA2	WA24	TS2	TS24
Fire retardant type (FRT)[2]	< 0.0001**	< 0.0001**	< 0.0001**	0.0002**
Woodflour loading (WFL)	< 0.0001**	< 0.0001**	< 0.0001**	< 0.0001**
WFL×FRT	< 0.0001**	< 0.0001**	< 0.0001**	< 0.0001**

[1] WA2 and WA24, weight gained after 2 and 24 h of water soaking; TS2 and TS24, thickness swelling after 2 and 24 h of water soaking.

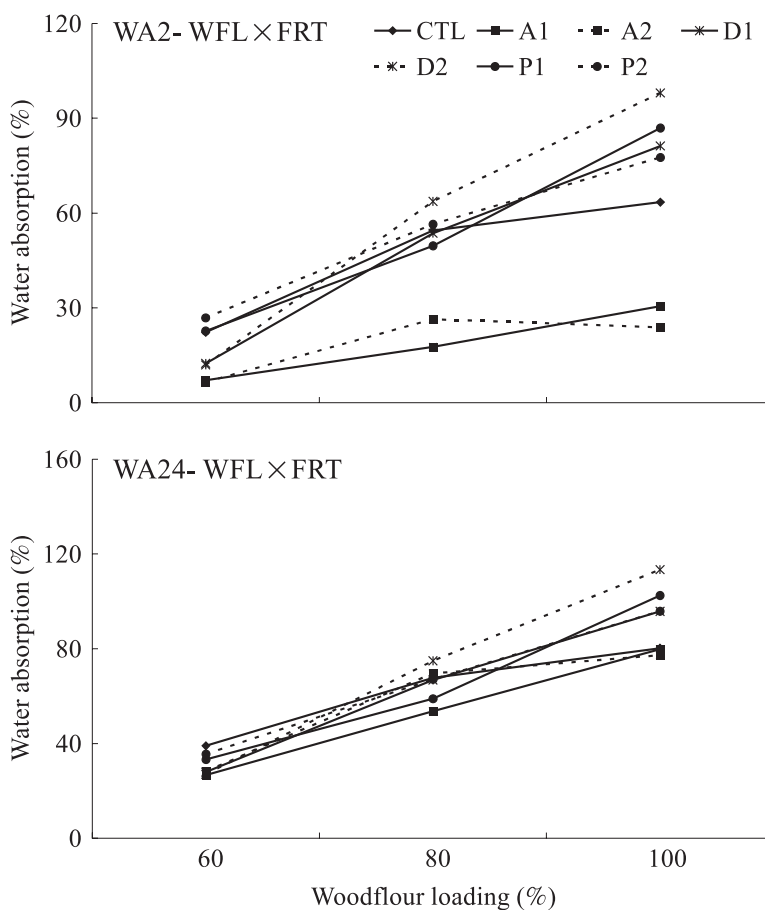[2] ** Highly significant (Pr > F of < 0.01).

Fig. 3. Interaction between woodflour loading and fire-retardant type with 2 (upper) and 24 hr (lower) of water absorption of woodflour-polypropylene composites.

of both 100 and 60%. As the immersion duration increased, treatments A1 and A2 were lower than those of the CTL at all WFL levels, except for A2 at a WFL of 80%. Similar to WA2, treatments D1, D2, P1, and P2 presented higher WA24 values than the CTL at a WFL of 100%; however, contrary to WA2, all treatments exhibited lower WA24 values than that of the CTL at a WFL of 60%.

Typically, the WAs of WPCs are < 2%, if they are made in a way that the wood component is fully encapsulated by the plastic matrix (English and Falk 1996, Klyosov 2007). An increase in the wood fraction to thermoplastic matrix will lead to increasing moisture uptake of the final products (Wolcott and Englund 1999). PP is a hydrophobic polymer with low moisture sorption, while wood is extremely hygroscopic because the 3 major components of wood contain abundant amounts of hydroxyl groups and oxygen-containing groups which can easily attract water molecules via hydrogen bonding (Gauthier et al. 1998, Steckel et al. 2007, Stark and Gardner 2008, Chang et al. 2009). Besides the intrinsic difference in material hygroscopicity, other factors such as compositional parameters and processing methods also affect the water uptake of WPCs (Huang et al. 2006, Steckel et al. 2007). For instance, WAs of WPCs are affected by processing methods, and the WA rate is in an order of extrusion molding > compression molding > injection molding (Clemons and Ibach 2004). Water uptake varies with wood species (Kim et al. 2008), and the moisture uptake is unevenly distributed across the board thickness, with the highest in the outer layer and progressively decreases into the bulk of the matrix. (Wang and Morrell 2004, Gnatowski 2005, Klyosov 2007). The initial moisture content of the formulation may produce volatile organic compounds (VOCs) during the process-

ing procedures, and the increased porosity of WPCs may enhance WA (Klyosov 2007). All in all, WPCs with a lower fiber/flour loading, smaller particle sizes, a lower void content, a polymer-rich surface layer, modified with coupling agents, and processed with injection molding method are expected to have lower moisture uptake rates (Steckel et al. 2007). However, the effects of these factors often interact with each other and make the WA behavior extremely complex.

Thickness swelling (TS)

Table 3 shows that the average TSs of all treatment combinations were 4.7~50.7% for TS2; and 8.4~59.9% for TS24. Like WA, the TSs of WPCs increased with the immersion time; however, the amounts that increased from TS2 to TS24 for all treatment combinations were less than those from WA2 to WA24. The overall average TSs for WFL of 100, 80, and 60% were 33.0, 19.3, 6.9% for TS2, and 42.7, 24.6, 10.1% for TS24, respectively. The difference between the maximum and the minimum TSs for the 3 WFL levels were 30.8, 13.3, 4.6% for TS2, and 30.1, 14.1, 4.2% for TS24. Moreover, if we take WA24 and TS24 as unity and calculate the proportions of WA2 and TS2 with the equations WA2/WA24×100% and TS2/TS24× 100%, respectively, the resulting numbers are 69.3, 69.3, 48.5% for WA, and 75.9, 78.4, 68.7% for TS, in the order of 100, 80, and 60% WFL. This result strongly suggests that TS responds more promptly to water immersion than does WA.

The 33.0 and 42.7% overall average TS2 and TS24 values of a WFL of 100% in this study are higher than those reported by other studies (Hashim et al. 1997, Winandy et al. 2008, Izran et al. 2009). The 6.9 and 10.8% overall average TS2 and TS24 values of a WFL of 60% are, however, difficult to com-

pare with other studies, since there are huge gaps between material parameters, WPC compositions, and processing conditions. As mentioned by Wang and Morrell (2004), the rate of moisture sorption depends on the wood particle size and geometry, the wood/polymer ratio, and the presence of other compounds that may repel water. In this research, before water immersion, the test specimens were subjected to sanding and the outmost layers were removed, which led to the exposure of "unprotected" wood-adhesive-wood and wood-wood interfaces allowing them to swell more freely. Moreover, the smaller specimen

dimensions also made them susceptible to reaching a near-equilibrium condition.

Results of ANOVA of TS2 and TS24 were similar to those of WA2 and WA24 (Table 4), exhibiting the highly significant main effects and the 2-way interaction at $p < 0.01$. It can be seen in Fig. 4 that, like the pattern in WA2, TS2 values of treatments A1 and A2 were lower than those of the CTL at all WFL levels, while TS2 values of treatments D1, D2, P1, and P2 were higher than the CTL at a WFL of 100%, and were slightly lower than the CTL at a WFL of 60%. Interestingly, in the case of TS24, all FR-treated WF-PP
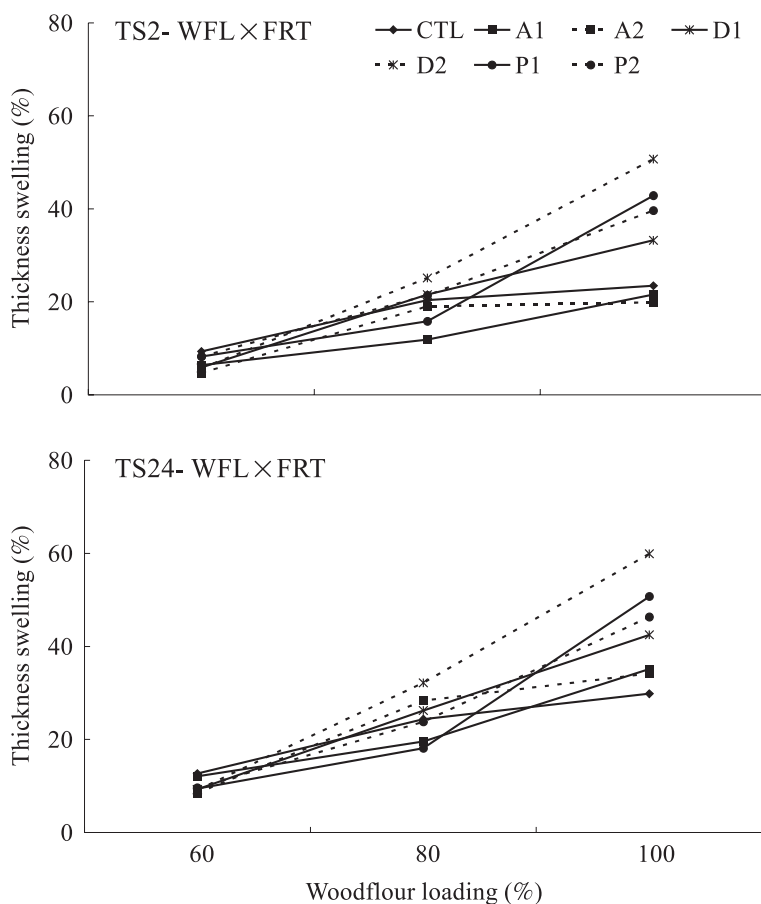

Fig. 4. Interaction between woodflour loading and fire-retardant type with 2 (upper) and 24 hr (lower) thickness swelling of woodflour-polypropylene composites.

composites were higher than those of the CTL at a WFL of 100% and lower than the CTL at a WFL of 60%.

Water absorption causes the swelling of the wood components in WPCs, which in turn affects the microstructure of the composites, expanding cracks, debonding wood-plastic interfaces, and creating more pathways for water penetration (Steckel et al. 2007, Kim et al. 2008, Stark and Gardner 2008).

The results from this experiment show that although after 24 h of water immersion the FR treated composite panels with 100% WFL revealed higher WA24 and TS24 values over the untreated CTL, and the trend was reversed when WFL was 60%, implying the dominant effect of WFL over FRT.

CONCLUSIONS

The performance of phosphoryl triamide-treated woodflour-polypropylene (PP) composites made with 3 levels of woodflour loading (WFL) and 7 fire-retardant treatments (FRTs) was investigated. Results showed that flexural strengths (MORs) of all the treatment combinations were strongly affected by the WFL: the lower the WFL, i.e., the higher the PP, the higher the MOR. The FRT factor only affected the MOR at the higher WFL levels. Conversely, the flexural stiffness (MOE) was unaffected by either factor. The internal bond strengths without (IB0) and with 24 h of water soaking (IB24) were collectively affected by the interaction of FRTs and WFLs. The dimensional stability of the composites, as measured by water absorption (WA) and thickness swelling (TS) at 2 water-immersion durations, were also interactively affected by the FRTs and WFLs. The 7 FRT types responded differently to the WFL level; however, all the WAs and TSs displayed lower values as the WFL decreased, indicating that the dimensional stability was improved by the higher PP content.

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