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Inhibition of Fungal Growth and Material Characteristics of PVC and Wood/PVC composites doped with Fungicides

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Abstract. Two commercial fungicides, namely, 3-Iodopropinyl-N-butylcarbamate (IPBC) and Methylbenzimidazole-2-ylcarbamate (Carbendazim) were used to improve anti-fungal properties of poly(vinyl chloride) (PVC) and wood/PVC composite (WPVC) materials. Disk diffusion test and dry weight technique, using *Aspergillus niger* as a testing fungi, were employed for the anti-fungal assessments. The effects of type and content of fungicides on anti-fungal performances were discussed in association with material properties. For material property characterizations, flexural properties, surface contact angle and surface color changes were observed. The results from anti-fungal test by disk diffusion test revealed that addition of IPBC in PVC or WPVC showed much greater anti-fungal performance than that of Carbendazim in PVC or WPVC. The WPVC samples exhibited better anti-fungal performances than the PVC samples. It can be concluded that wood particles could promote the fungicidal effect of the WPVC composites. It was found that type and content of fungicides used did not significantly alter the flexural properties of the materials whereas the presence of wood resulted in an increase of flexural modulus with a decrease in flexural strength. The surface contact and color changes of PVC and WPVC were observed with addition of IPBC, but not found with Carbendazim.

Introduction

Wood plastic composite (WPC) products are for wood-like products for both interior and exterior applications. Polyvinylchloride (PVC) and wood/polyvinyl chloride composite (WPVC) are semi-natural composite materials that have been well known for many years and still increasingly used in many applications [1-2]. However, one of the problems for utilization of the PVC-based wooden plastics is microbial contamination as well as degradation by biological agents, such as, decay mold or fungi, bacteria, and insects (e.g. termites, carpenter ants, post-powder beetles) [3-4]. Apart from material degradations and taken as sources of pathogen, those effects can also result in losses of economics and health problems of human. Many research evidences have been reported on microbial colonization on PVC and WPVC materials by micromycetes or fungi in both natural and artificial environments [3-5].

To prevent fungal colonization during a life span of materials, commercial fungicides were introduced into PVC and WPVC formulations and the fungicidal effects accompanying with material properties were studied. The commercial fungicides used were Carbendazim (Methylbenzimidazole-2-ylcarbamate) and IPBC (3-Iodopropinyl-N-butylcarbamate) whose technical data were supplied by the Troy Asia Co. Ltd., (Bangkok, Thailand). The effect of type and content of fungicides used was of our main interests for anti-fungal evaluations and material characterizations.

Experimental

Materials and chemicals: The formulations for PVC and WPVC specimens were used as the same as described by our previous work [2]. The wood flour used was *Xylia kerri* Craib & Hutch (designated as XK), supplied by Phongsiri Ltd. Part, R atchaburi, Thailand) and the concentration of wood in the composites was fixed at 100 pph. Commercial biocides, namely Carbendazim (Methylbenzimidazole-2-ylcarbamate) and IPBC (3-Iodopropinyl-N-butylcarbamate) were supplied by Troy Asia Co. Ltd. (Bangkok, Thailand).

Specimen preparations: All raw materials of PVC or WPVC recipes were mixed together using dry- and melt-blending methods. The mixtures were then put into the cavity of hydraulic press for producing the test-pieces having 1 mm thick. The processing temperature and pressure were 160^{o}C and 150 kg·cm^{-2}, respectively, with molding time of 5 min. Before anti-fungal test and material property characterizations, the molded test-pieces were cut into the standard test pieces given by the testing methods, which will be described later.

Anti-fungal test: Disk diffusion test and dry weight technique, using *Aspergillus niger* (TISTR 3245, Pathumthani, Thailand) as a testing fungus, were used for anti-fungal assessments in this study. The testing procedures of both techniques were obtained elsewhere [6]. The results from these tests were quantitatively described in terms of "Relative diameter of fungal growth" and "Dry weight of fungi (mg/L)" for "the disk diffusion test" and "dry weight techniques", respectively.

Material characterizations:

Mechanical property: Flexural properties were measured in terms of flexural modulus and strength. The testing method followed the ASTM D790 (1990). The measurements were carried out by averaging five independent determinations.

Surface contact angle: Measurement of surface contact angle of materials was conducted for investigating the surface chemistry changes of materials. The measurement was carried out by a drop method using standard goniometer (model 100-00-220; Ramé-Hart Instrument Company, Succasunna NJ, USA). The results were obtained from an average value of at least five independent droplets of 100 μL/time of dropped volume size in advancing stage.

Color change test: The surface color changes in term of the total color difference (ΔE*) were studied by accounting the lightness and chromatic coordinate values (L*, a* and b* values) under the CIE-LAB color system, using the UV-Vis spectrophotometer (Model UV-3100, Shimadzu, Kyoto, Japan). The measurement and calculation were based on a D65 light source.

Results and discussion

The flexural properties of PVC and WPVC materials by the effect of fungicide additions are given in Table 1. It was found that the flexural properties considerably improved by addition of Carbendazim or IPBC, except for the flexural strength of WPVC. The decrease in the flexural strength of WPVC implied that addition of fungicide did not give any reinforcing effect to the composites. This may be because the fungicide may introduce moisture and thus poorer interaction between wood and PVC matrix. For the effect of wood, the results suggested that the WPVC samples had higher flexural modulus, but lower flexural strength than the neat PVC samples. The decreases in flexural strength of the composites would be a result of imperfection dispersion of wood particles as well as the generation of a great number of defects and moisture in the composites.

The experimental results from Fig. 1 and Table 2 demonstrate the total colour changes and the surface contact angle values of the materials, respectively. It was observed that the surface colour different value (*ΔE**) and the surface contact angle did not change significantly when introducing the Carbendazim in the PVC or WPVC materials while those with IPBC changed significantly, except for the *ΔE** value of the wood composites. The explanations for the results would be associated with the physical and chemical properties of the fungicides used. Because of greater thermal stability (T_d > 300°C) and lower water-stability of Carbendazim substance as compared with IPBC substance, the Carbendazim samples would have difficulty in diffusing onto the material surfaces. In addition, IPBC substance, which has the thermal stability close to the processing temperature (T_d ~ 170.7°C), tended to degrade and subsequently yield the iodine substance, showing the dark colorant, [7] within the PVC matrix. As a result, the surface of PVC became more discoloured when introducing with IPBC. It should also be noted that the surface colour change of WPVC composites was difficult by the effect of IPBC degradation because of darkening effect by lignin substance in wood particle of the composites.

Table 1 Flexural properties of PVC and WPVC filled fungicides *(Standard deviation value in parentheses)*

Sample	Content of fungicide (ppm)	Flexural modulus (MPa)		Flexural strength (MPa)	
		Carbendazim	IPBC	Carbendazim	IPBC
PVC	**0**	2590.4 (±*351.2*)	2590.4 (±*351.2*)	63.9 (±*2.2*)	63.9 (±*2.2*)
	10000	2891.0 (±*77.2*)	2646.9 (±*364.4*)	56.1 (±*5.1*)	68.4 (±*1.8*)
	30000	2935.7 (±*231.9*)	2993.6 (±*139.5*)	64.3 (±*2.3*)	70.5 (±*1.7*)
	50000	2956.9 (±*196.4*)	2854.6 (±*241.7*)	67.0 (±*1.1*)	67.4 (±*1.8*)
WPVC-XK	**0**	4482.7 (±*159.3*)	4482.7 (±*159.3*)	53.2 (±*6.4*)	53.2 (±*6.4*)
	10000	4401.0 (±*214.4*)	4036.7 (±*184.7*)	43.3 (±*1.8*)	42.5 (±*1.7*)
	30000	4231.9 (±*477.3*)	4219.0 (±*565.2*)	41.4 (±*2.0*)	49.7 (±*4.8*)
	50000	4238.8 (±*446.2*)	3887.0 (±*365.1*)	38.1 (±*2.5*)	47.4 (±*3.3*)

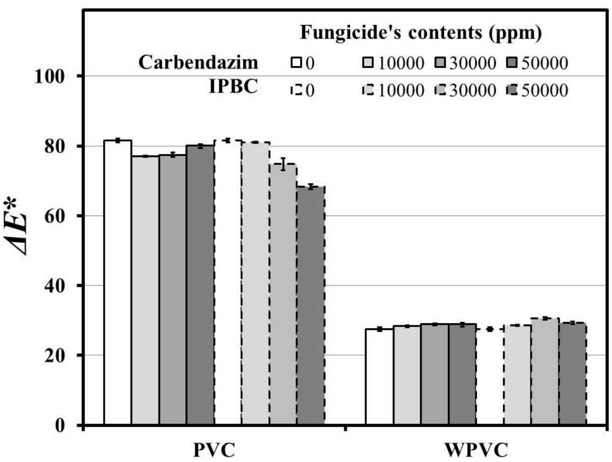

Figure 1 Surface colour difference (ΔE*) of PVC and WPVC specimens

Table 2 Surface contact angle of PVC and WPVC specimens *(Standard deviation value in parentheses)*

Fungicide concentration (ppm)		Sample PVC	WPVC
-	0	90.2 *(±5.5)*	73.3 *(±1.6)*
Carbendazim	10,000	91.1 *(±3.8)*	72.5 *(±6.7)*
	50,000	90.1 *(±1.0)*	73.0 *(±2.6)*
IPBC	10,000	93.3 *(±4.0)*	77.6 *(±1.0)*
	50,000	97.6 *(±4.4)*	82.5 *(±0.3)*

Fig. 2 and 3 show the anti-fungal assessment results by disk diffusion and dry weight techniques, respectively. It should be noted that smaller relative diameter of fungal growth and dry weight of fungi values indicate greater anti-fungal performance. It was found that the IPBC samples exhibited much higher anti-fungal performance than the Carbendazim samples. The explanation for these results involved the higher anti-fungal efficacy and more diffusion effect of IPBC substance as compared with Carbendazim substance as mentioned earlier. The anti-fungal properties of Carbendazim samples could be performed when using dry weight technique, this being a result of the dynamic testing mode. The WPVC samples exhibited much more effective anti-fungal performance than the PVC samples. This would be the result of the defects and imperfection textures and humidity occurred by wood particles, which could encorage diffusivity of fungicides to kill the fungi on the specimen surfaces.

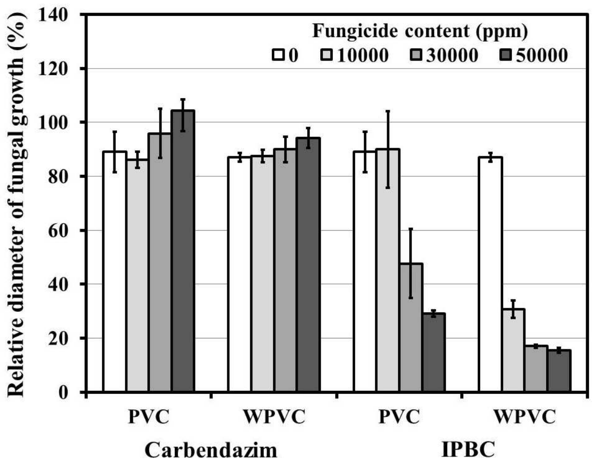

Figure 2 Anti-fungal performances by disk diffusion test

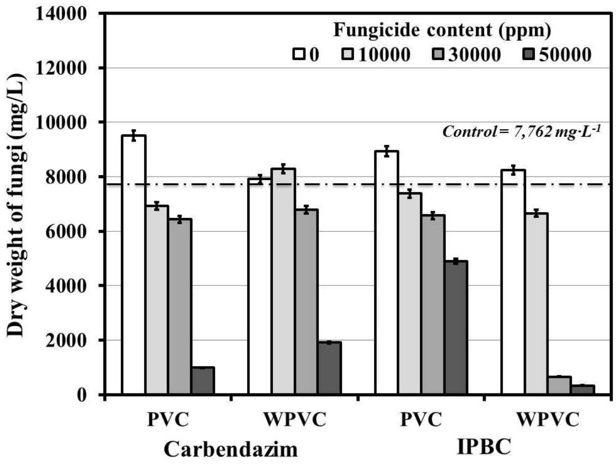

Figure 3 Anti-fungal performances by dry weight technique

Summary

The findings suggested that IPBC performed much more effective anti-fungal agent than Carbendazim in PVC and WPVC materials. The anti-fungal performance for WPVC specimens was more pronounced than that for neat PVC specimens. The anti-fungal performances of the materials were found to be dependent on loading content of fungicides as well as the testing method used. The flexural properties were found to improve with fungicide loadings, except for the flexural strength of WPVC. The physical appearance and surface chemistry, observed by the *ΔE** and contact angle values, respectively, were found to change only with IPBC addition.

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