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Anti-algal Performance and Strength of Wood Poly(vinyl chloride) Composites with Different Wood Types

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ABSTRACT

Anti-algal performance and mechanical properties of wood/poly(vinyl chloride) composites (WPVC) filled with commercial algaecides were studied. Three types of wood flour used; namely: *Xylia Kerrii* Craib & Hutch (XK), *Hevea Brasiliensis* Muell (HB) and *Mangifera Indica* Linn (MI), were considered based on their constituents and physical characteristics of wood particles. Commercial algaecides, namely Isoproturon (3-(4-isopropylphenyl)-1,1-dimethylurea) and Terbutryn (N2-tert-butyl-N4-ethyl-6-methylthio-1,3,5-triazine-2,4-diamine) with concentration range from 0 to 1,500 ppm were doped in PVC and WPVC composites. Clear zone test using Chlorella vulgaris as testing algae was used for evaluating the anti-algal performance and the adhesion of algal cell on the surface of PVC and WPVC specimens were observed via optical (OM) and scanning electron microscope (SEM). Flexural strength, flexural modulus and surface roughness of specimens were also examined. The results revealed that the Terbutryn samples clearly performed a great anti-algal performance while the Isoproturon samples did not. Regarding the effect of wood types, the WPVC with XK wood had the most satisfactory anti-algal performance. The recommended dosage of Terbutryn for WPVC with XK was 500-1,000 ppm. The increases in algaecide content in PVC and WPVC composites were not found to correlate with the changes in flexural properties and surface roughness of materials. The SEM results indicated that the specimens treated with the algaecides did not show the adhesion of algal cell and bio-film formation.

Keywords: *wood powder, polymer composite, biocide, anti-microbial test*

INTRODUCTION

It is generally agreed that in high humidity surroundings and aquatic environment, algae is a primary organism to form a biofilm on materials surfaces, and then increase the attachment of other microorganism to form macro-fouling attachment [1-4]. Wood polyvinyl chloride composite (WPVC) is one of the most common wood polymer composites in which they have become increasingly used for outdoor applications, particularly in tropical climate countries due to endurability for sunlight exposure, high service temperature, biological and solvent attacks, and low moisture absorption of polyvinyl chloride itself [5]. Nevertheless, many research evidences

have been reported on biodeteriaration by microorganisms on both of PVC and WPVC composites [6-9]. Possible explanations for microbial susceptibility of WPVC mainly involve high surface energy of PVC and moisture induction of wood. Any substances with high polarity, such as proteins, spore, germ and microorganism cells, could attach on the WPVC surface [10-11]. To prevent further deterioration by microorganisms and biological attacks, biocides are usually considered to introduce into the WPVC.

In this current study, the anti-algal performance of WPVC were studied in terms of the effects of type and content of algaecides, and type of wood flour used using clear zone method and Chlorella vulgaris as testing algae. Two commercial algaecides used were Isoproturon, as a group of phenylurea herbicides, and Terbutryn, as a group of methylthiotriazine herbicides. The wood flours used in this study were available in tropical climate region and categorized by differences in chemical constituents, physical and mechanical properties. The types of wood used included *Xylia Kerrii* Craib & Hutch (XK), *Hevea Brasiliensis* Muell (HB) and *Mangifera* Indica Linn (MI). Flexural properties and surface roughness of the composites were examined in accordance with ASTM D790 and roughness profilometer. Optical microscope and scanning electron microscope were used for investigating the adhesion of algal cell on the PVC and WPVC surfaces.

EXPERMENTAL

Raw materials and chemicals

Suspension PVC powder, having a K value of 58, and necessary additives were supplied by V.P. Wood Co. Ltd. (Bangkok, Thailand) and the formulation of PVC compound was the same as used in our previous work [12]. Three types of wood flour; namely: *Xylia Kerrii* Craib & Hutch (XK), *Hevea Brasiliensis* Muell (HB) and *Mangifera Indica* Linn (MI) used had an average particle size of less than 250 μm (60 mesh size) and were supplied by Phongsiri Ltd., Part. (Ratchaburi, Thailand). All woods were chemically-surface treated by a silane coupling agent (N-2(aminoethyl)-(3-aminopropyl)trimethoxysilane) before incorporating in PVC. Isoproturon (3-(4-Isopropylphenyl)-1,1 dimethylurea), and Terbutryn (N^2-*tert*-butyl-N^4-ethyl-6-methylthio-1,3,5-triazine-2,4-diamine) were provided by Troy Asia Co. Ltd. (Bangkok, Thailand). *Chlorella vulgaris* (*C. vulgaris*), TISTR 8580 was purchased from the Thailand Institute of Scientific and Technological Research (Pathum Thani, Thailand).

Specimen preparations

A compression molding technique was used for preparing the test specimen. The procedure was commenced by direct mixing PVC compound and wood particles using high speed mixer at a fixed wood concentration of 100 pph by weight to obtain WPVC composites. The WPVC composites were dried at 80^{o}C for 24 h in a hot air oven in order to eliminate residual humidity and then filled in the mold cavity with dimensions of 200×200×1 mm^3. The processing temperature used was 190^{o}C under a pressure of 150 kg·cm^{-2}, for 5 min, to obtain WPVC composite sheet. For anti-algal test, the sheet was made in square pieces of 10×10 mm^2 while made in a rectangular form of 12.7×60 mm^2 and 25×50 mm^2 for mechanical properties and algal adhesion observation, respectively.

Materials characterizations

Physical and mechanical characteristics of PVC and WPVC doped with algaecides were performed by surface roughness (Ra) property, using a SV-3000 profilometer (Mitutoyo,

Kawasaki, Japan) and flexural properties, followed by ASTM D790-03, using universal testing machine, respectively. In addition, surface area of wood particles was analyzed using gas adsorption technique by Brunauer, Emmett, Teller (BET) method (BELSORP-max 00092, Bel Japan Inc., Japan)

Anti-algal evaluation

Clear zone testing method was used to evaluate the anti-algal properties of the PVC and WPVC samples. The procedure was commenced by preparing culture media of *C. vulgaris* cell at a concentration of 10^7 cells·ml^{-1} in mineral soft agar. A test piece was then gently laid down at the center of the culture media in Petri dish (9 cm in diameter). The incubation condition for this test was carried out under a temperature of 25^{o}C for 4 weeks in dark and light cycles of 12 h and 12 h under 2,000 lux of fluorescence light. After that, the killing area (clear zone) around test piece was calculated in term of "Inhibition area of algal growth" in mm^2. In addition, adhesion of algal cell on the specimens was performed by immersion of the specimens into algal cell suspension media and placing two pieces of samples, having dimensions of 2.5×5.0 cm^2 for each, in 250 ml Erlenmeyer flask containing 100 ml of algal suspension media at approximate 10^7 cell·ml^{-1}. The prepared flask was stirred using an orbital shaker machine at 150 rpm for 4 weeks under the same conditions for the clear zone test. At the end, the test pieces were rinsed by distilled water to remove any organic matters. The algal cell adhesion was then examined through OM and SEM.

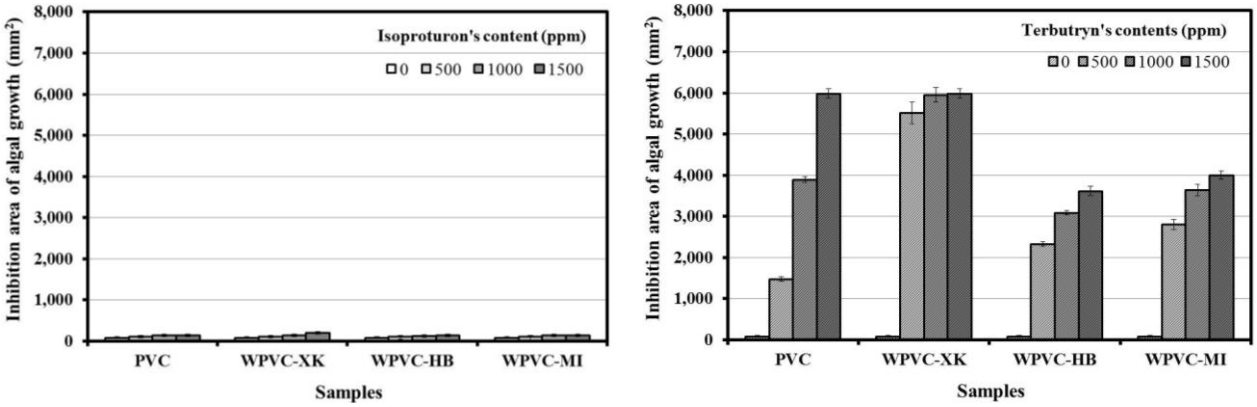
RESULTS AND DISCUSSION

Table 1: Flexural properties and roughness value *(Standard deviation value in parentheses)*

Sample	Content of algaecide [ppm]	Flexural modulus [MPa]		Flexural strength [Mpa]		Roughness, Ra [Micron]	
		Isoproturon	Terbutryn	Isoproturon	Terbutryn	Isoproturon	Terbutryn
PVC	0	1,830.6 *(192.2)*	1,830.6 *(192.2)*	37.6 *(3.5)*	37.6 *(3.5)*	1.03 *(0.56)*	1.03 *(0.56)*
	500	1,728.4 *(116.4)*	2,056.9 *(307.9)*	35.9 *(2.0)*	42.2 *(3.1)*	1.87 *(1.09)*	1.77 *(0.98)*
	1000	1,608.3 *(516.4)*	1,832.9 *(362.2)*	29.2 *(8.0)*	42.6 *(4.4)*	1.18 *(0.27)*	0.98 *(0.27)*
	1500	1,641.8 *(375.4)*	1,594.3 *(318.1)*	30.0 *(7.2)*	26.6 *(4.9)*	1.33 *(0.20)*	1.44 *(0.11)*
WPVC-XK	0	2,799.5 *(145.0)*	2,799.5 *(145.0)*	34.2 *(3.0)*	34.2 *(3.0)*	7.36 *(1.79)*	7.36 *(1.79)*
	500	3,201.1 *(321.5)*	2,980.3 *(139.8)*	38.4 *(1.4)*	38.0 *(2.4)*	7.16 *(2.41)*	6.53 *(2.24)*
	1000	3,157.2 *(191.1)*	3,033.8 *(310.2)*	34.2 *(1.5)*	37.7 *(6.0)*	8.24 *(2.54)*	6.20 *(1.99)*
	1500	3,421.5 *(680.8)*	3,078.5 *(116.1)*	43.6 *(4.2)*	41.5 *(3.1)*	8.50 *(2.04)*	7.59 *(1.82)*
WPVC-HB	0	3,181.0 *(275.7)*	3,181.0 *(275.7)*	40.9 *(1.3)*	40.9 *(1.3)*	7.16 *(2.03)*	7.16 *(2.03)*
	500	3,629.9 *(323.6)*	3,243.9 *(37.2)*	41.8 *(4.7)*	36.4 *(4.0)*	5.94 *(2.34)*	6.27 *(1.90)*
	1000	3,436.6 *(155.5)*	3,028.3 *(532.4)*	42.7 *(1.3)*	34.7 *(4.5)*	5.75 *(1.72)*	5.37 *(0.93)*
	1500	3,597.4 *(123.4)*	3,267.7 *(307.9)*	47.9 *(2.9)*	34.9 *(3.3)*	6.26 *(1.89)*	6.97 *(1.27)*
WPVC-MI	0	3,138.0 *(218.2)*	3,138.0 *(218.2)*	41.4 *(1.6)*	41.4 *(1.6)*	6.58 *(2.01)*	6.58 *(2.01)*
	500	3,348.1 *(259.1)*	3,180.4 *(273.8)*	39.9 *(3.5)*	38.3 *(0.8)*	5.64 *(1.32)*	6.63 *(0.92)*
	1000	2,982.5 *(242.5)*	3,361.4 *(122.0)*	35.3 *(2.8)*	40.6 *(4.1)*	4.97 *(0.85)*	4.55 *(1.20)*
	1500	3,576.9 *(486.6)*	2,427.1 *(290.1)*	46.7 *(4.8)*	41.5 *(0.9)*	5.42 *(2.30)*	5.01 *(1.91)*

Table 1 shows the flexural modulus, flexural strength and surface roughness of PVC and WPVC for various types and contents of algaecides. It was found that the WPVC samples showed higher flexural properties and surface roughness than the PVC samples. This was because of the reinforcing effect by wood particles and the emerging of wood particles on the specimen surfaces

[13-14]. The addition of algaecides in this study did not affect the flexural properties and surface roughness. This may be a small amount of the algaecides used. Regarding the effect of wood, it was found that the mechanical properties of PVC with different types of wood were not much different although the previous study by Jeamtrakul *et al* [12] reported that the flexural properties of WPVC with XK, HB or MI for concentrations of 20-60 pph were dependent on the wood constituents, physical and mechanical properties of wood particles. The differences in these two works may be because the wood concentration used in this work was relatively high (100 pph) and this generated excessive interfacial defects within the WPVC composites which overruled the effect of wood type.



(a) (b)

Figure 1: Inhibition area of algal growth for PVC and WPVC at diferent wood types where (a) Isoproturon sample and (b) Terbutryn samples

Table 2: Porous surface area of wood particles by BET analysis

Content of analysis	Type of wood flour		
	XK	**HB**	**MI**
Surface area (a_s) $\times 10^{-1}$ ($m^2 \cdot g^{-1}$)	1.14	1.22	1.29
$V_m \times 10^{-2}$ ($cm^3(STP) \cdot g^{-1}$)	2.62	2.80	2.95

Where, V_m: The largest pore volume

Figure 1 shows the inhibition area of *C. vulgaris* for PVC and WPVC specimens at different types of wood and algaecides. It was found that the anti-algal performance of Terbutryn samples was much greater than that of Isoproturon samples. The explanation for this result was a better diffusibility of Terbutryn in PVC matrix. Since the molecular structure of Terbutryn is large and complex by heterocyclic ring of triazine with hindrance groups of alkyl amine and methylthio, as well as low polarity, when compared with those of Isoproturon. This would cause Terbutryn to have lower interaction with PVC molecules and thus, more likely to diffuse away from PVC matrix than Isoproturon. It could also be explained by the half of maximal effective concentration (EC50) value, work by Rioboo et al [15] showed that terbutryn had a greater inhibition on the growth of *Chlorella vulgaris* than Isoproturon due to the fact that the EC50 value of Terbutryn (EC50 of Terbutryn = 0.097 μM) for algal growth was twice lower than that of Isoproturon (EC50 of Isoproturon = 0.199 μM). For the effect of wood types, WPVC with XK performs exhibited the greatest anti-algal effectiveness, and the optimal concentration of Terbutryn used in WPVC with XK was in the range of 500 – 1,000 ppm. The BET results given

in Table 2 could be utilized to explain this. It was found that surface area and the pore volume of wood particles were found to decrease in order of MI, HB and XK. Therefore, it would be possible that the XK wood had lower interfacial area and molecular interaction with the algaecide and the PVC. If this was the case, Terbutryn substance in XK/PVC composites would be free to diffuse and spread out from the composites to kill the algae as compared with Terbutryn substance in HB/PVC and MI/PVC composites.

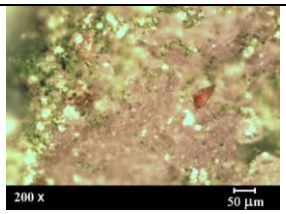
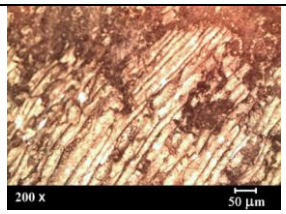
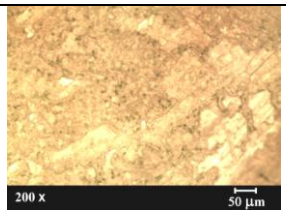
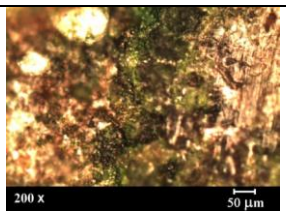
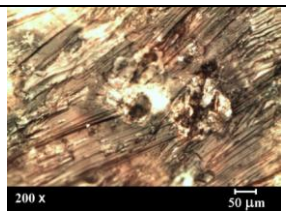
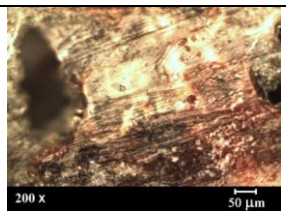
Sample	Algaecide (at fixed concentration of 1,500 ppm)		
	None	Isoproturon	Terbutryn
PVC			
WPVC-XK			

Figure 2: Surface of specimens with different types of algaecide after immersion in algal cell suspension for 4 weeks by optical microscope (OM)

Figure 2 shows the OM results of the specimen surfaces of PVC and WPVC with XK wood, with and without algaecide after immersion in algal cell suspension for 4 weeks. It can be observed that all specimens with algaecides, both Isoproturon and Terbutryn, did not show the adhesion of algal cell on the specimen surfaces. This may be surprising since the results in Figure 1 indicated that Isoproturon did not show the clear zone. This suggested that Isoproturon may have an ability to kill the algae, but the algaecide itself could not diffuse.

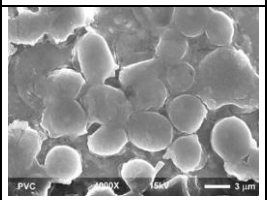
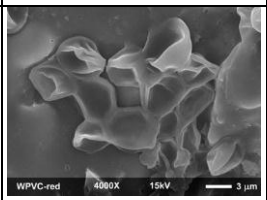
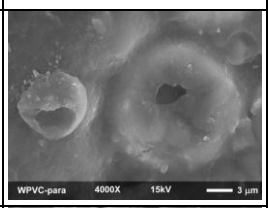
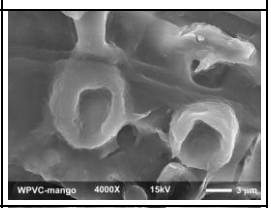
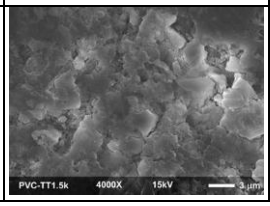
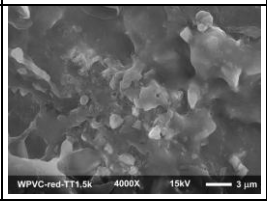
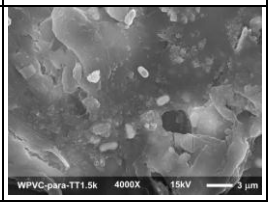
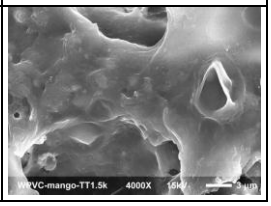
Algaecide	PVC	WPVC-XK	WPVC-HB	WPVC-MI
None				
Terbutryn (1,500 ppm)				

Figure 3: Surface morphology of specimens after immersion in algal cell suspension for 4 weeks by scanning electron microscope (SEM)

The SEM results in Figure 3 clearly indicated that all specimens (PVC and WPVC with XK, HB and MI) with Terbutryn at 1,500 ppm did not have any adhesions by algal cell on the

specimen surfaces. However, adhesions of algal cell in different patterns were found on the non-sterilized specimens (without algaecide).

CONCLUSION

In this study, increasing Terbutryn or Isoproturon algaecides in PVC and WPVC did not result in the changes of the mechanical properties and surface roughness. The anti-algal performance of composites with Terbutryn samples was much greater than those with Isoproturon. For the effect of wood type, the WPVC composites with XK exhibited the greatest anti-algal effectiveness and the optimal concentration of Terbutryn was between 500 – 1,000 ppm. The results from optical and scanning electron microscope showed that there were no algal adhesions on the WPVC composite specimens added with algaecide.

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