อิทธิพลของสภาวะบ่มเร่งและสภาวะการใช้งานจริงที่มีต่อประสิทธิภาพการยับยั้งเชื้อรา ของวัสดุเชิงประกอบพอลิไวนิลคลอไรด์ผสมผงขี้เลื่อยไม้ที่ผสมสารยับยั้งจุลินทรีย์ชนิดเอชพีคิวเอ็ม

Effects of QUV-Accelerated Weathering Aging and Natural Weathering Conditions on Anti-fungal Efficacies of Wood/PVC Composites Doped with HPQM Anti-microbial Agent

ภาณุพงศ์ ศรีมาลานนท์[1,*], แววบุญ แย้มแสงสังข์[2] อภิสิทธิ์ โฆษิตชัยยงค์[1] และ ณรงค์ฤทธิ์ สมบัติสมภพ[1]
Panupong Srimalanon[1,*], Weawboon Yamsaengsung[2] Apisit Kositchaiyong[1] and Narongrit Sombatsompop[1]

[1]กลุ่มวิจัยการผลิตและขึ้นรูปพอลิเมอร์ สายวิชาเทคโนโลยีวัสดุ คณะพลังงานสิ่งแวดล้อมและวัสดุ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี 126 ถนนประชาอุทิศ แขวงบางมด เขตทุ่งครุ กรุงเทพมหานคร 10140
[2]สาขาวิชาวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยสุโขทัยธรรมาธิราช 9/9 หมู่ 9 ตำบลบางพูด อำเภอปากเกร็ด จังหวัดนนทบุรี 11120
[1]Polymer PROcessing and Flow (P-PROF) Research Group, Division of Materials Technology, School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi (KMUTT), 126 Prachautid Road, Bangmod, Thungkru, Bangkok, 10140, Thailand
[2]School of Science and Technology, Sukhothai Thammathirat Open University, 9/9 Mu 9, Bangpood, Pakkret, Nonthaburi, 11120, Thailand
*ผู้ติดต่อ: E-mail: panupong_sri@yahoo.com, เบอร์โทรศัพท์: 02-470-8647, เบอร์โทรสาร: 02-470-8647

บทคัดย่อ

งานวิจัยนี้ศึกษาประสิทธิภาพการยับยั้งเชื้อราของพอลิไวนิลคลอไรด์ และวัสดุเชิงประกอบพอลิไวนิลคลอไรด์ผสมผงขี้เลื่อยไม้ที่เติมสารยับยั้งจุลินทรีย์ชนิดเอชพีคิวเอ็ม และศึกษาอิทธิพลของสภาวะการบ่มเร่งและสภาวะการใช้งานจริง โดยปรับเปลี่ยนปริมาณสารเอชพีคิวเอ็มที่ 0 ถึง 50000 ส่วนในล้านส่วน และผงขี้เลื่อยไม้ที่ 0 50 และ 100 ส่วนในร้อยส่วน การทดสอบประสิทธิภาพการยับยั้งเชื้อรา ประกอบด้วยเทคนิคการทดสอบการยับยั้งการเจริญของเชื้อรา โดยเชื้อราที่ใช้ในการทดสอบ คือ *Aspergillus niger* ผลการศึกษา พบว่า วัสดุเชิงประกอบพอลิไวนิลคลอไรด์ผสมผงขี้เลื่อยไม้ปริมาณ 100 ส่วนในร้อยส่วน แสดงประสิทธิภาพการยับยั้งเชื้อราสูงกว่า วัสดุเชิงประกอบที่ผสมผงขี้เลื่อยไม้ปริมาณ 50 ส่วนในร้อยส่วน และพอลิไวนิลคลอไรด์ ตามลำดับ ดังนั้น การผสมผงขี้เลื่อยไม้ในพอลิไวนิลคลอไรด์ ทำหน้าที่เป็นวัสดุส่งเสริมการยับยั้งเชื้อรา โดยปริมาณสารเอชพีคิวเอ็มที่เหมาะสมในการยับยั้งเชื้อราของพอลิไวนิลคลอไรด์ วัสดุเชิงประกอบพอลิไวนิลคลอไรด์ผสมผงขี้เลื่อยไม้ปริมาณ 50 และ 100 ส่วนในร้อยส่วน เท่ากับ 50000 15000 และ 10000 ส่วนในล้านส่วน ตามลำดับ สำหรับการศึกษาอิทธิพลของสภาวะการบ่มเร่ง และสภาวะการใช้งานจริง พบว่า วัสดุที่ผสมสารเอชพีคิวเอ็มปริมาณน้อยกว่า 20000 ส่วนในล้านส่วน มีการเปลี่ยนแปลงประสิทธิภาพการยับยั้งเชื้อราที่ชัดเจนมากกว่าวัสดุที่ผสมสารเอชพีคิวเอ็มปริมาณ 50000 ส่วนในล้านส่วน

คำหลัก: การทดสอบสภาวะกลางแจ้ง/การบ่มเร่ง/ประสิทธิภาพการยับยั้งจุลินทรีย์/วัสดุเชิงประกอบพอลิเมอร์และไม้/เอชพีคิวเอ็ม

Abstract

This work aimed to study anti-fungal efficacies of polyvinylchloride (PVC) and polyvinylchloride/wood flour composites (WPVC) containing HPQM as anti-microbial agent as well as QUV-accelerated weathering aging and natural weathering conditions. HPQM with content ranging from 0 to 50000 ppm was doped in PVC and WPVC and wood flour at 0, 50, and 100 ppm was added. Fungal growth inhibition test was used for anti-fungal effective evaluation. Here, *Aspergillus niger* was used as a testing fungus. The results show that indicate that adding HPQM to WPVC-100 leads to the most effective anti-fungal, as compared to WPVC-50 and PVC, respectively. Therefore, this study suggests that wood flour are an anti-fungal promoter of the WPVC composites. The recommended dosages for killing fungal for HPQM in PVC, WPVC-50, and WPVC-100 were 50000, 15000, and 10000 ppm, respectively. The effects of QUV-accelerated weathering aging and natural weathering conditions result in anti-microbial evaluation indicates that the sample doped with HPQM below 20000 ppm has changes in the anti-fungal rather than the one doped with HPQM at 50000 ppm.

Keywords: Accelerated aging/Anti-microbial efficacies/HPQM/Natural weathering/Wood polymer composites

1. Introduction

Wood/polyvinylchloride composites (WPVC) can be converted into numerous products for specific applications, like buildings, construction industries, and automotive and infrastructure products, due to their desirable properties including cost effectiveness and easy customization [1]. For outdoor applications, various additives, such as stabilizers, reinforcing filler, and biocides, are needed to be doped in WPVC in order to prevent the degradation of the composites [2]. Naumann et al. [3] reported occurrences of surface micro- and macro-cracks of wood composite materials due to the accelerated-weathering aging effect. The results suggest that the accelerated weathering aging effect under UV radiation, water spray, and repeated freeze-thaw cycles causes enhancement of moisture sorption and microbial attacks. According to studies on biological attack on materials, colonization by a variety of fungal species has been mostly found on the surfaces of materials [4]. 2-Hydroxypropyl-3-piperazinyl-quinoline carboxylic acid methacrylate (HPQM) is a new commercial antibacterial agent and claimed as an environmental friendly organic biocide with broad range of the antimicrobial spectrum, low toxicity, light elution, and excellent color stability under UV light and pyrolysis conditions. Thus, the objective of this work is to study anti-fungal efficacies of PVC and WPVC containing HPQM as well as QUV-accelerated weathering aging and natural weathering conditions.

2. Experimental

2.1 Materials and chemicals

Suspension PVC SIAMVIC-258RB (K value of 58), necessary additives and wood flour (V.P. Wood Co., Ltd., Thailand) were used in this work. The PVC and necessary additives were manufactured from the formulations, as given by our previous study [5]. Wood flour was chemically treated with N-2(aminoethyl)-3-aminopropyl trimethoxysilane (KBM 603) (Shin-Etsu Chemical Co. Ltd., Japan), as a coupling agent. HPQM was used as an anti-fungal agent (Koventure Co., Ltd., Thailand) with the chemical formulation of 2-Hydroxypropyl-3-Piperazinyl-Quinoline carboxylic acid Methacrylate Thiazole. *Aspergillus niger* (*A. niger*, TISTR 3245) was used as a testing fungus (Thailand Institute of Scientific and Technological Research, Thailand).

2.2 Specimen preparation

The wood flour was chemically surface-treated by KBM 603 at 1.0 %wt. The PVC compound was dry-blended with treated wood flour and HPQM using a high speed mixer at 1000 rpm for 5 min. HPQM with content at 0 to 50000 ppm of PVC compound were doped in PVC and WPVC and treated wood flour at 0, 50, and 100 pph of PVC compound. All compositions were melt-blended using a counter-rotating twin screw extruder (CTW 1000C, Hakke Rheomex, Germany) at 140, 150, 160 and 160 °C for feed zone to die, respectively, and screw speed at 40 rpm. The produced pellets were dried in hot-air oven at 80^{o}C for 24 h to remove moisture. Then, pellets were test specimen prepared using a compression molding machine (LP-20M, Labtech Engineering, Thailand) at 170 ^{o}C under a pressure of 150 kg/cm^2 for 8 min.

2.2. Characterization

Fungal growth inhibition testing; Fungal growth inhibition test [6] against *A. niger*, as a testing fungus, was used for anti-fungal evaluation of specimens. The procedure was commenced by preparing initial fungal spore suspension containing 10^4 spores/mL in 100 ml of 1:1 [potatoes dextrose broth (PDB): potatoes dextrose agar (PDA)]. One piece of specimen (30 x 30 cm^2) was put on the PDA in a Petri dish. Then, prepared fungal spores were poured onto specimen in the dish and then incubated under a temperature 25 ^{o}C for 7 days. The results were reported as a percent of fungal growth inhibition.

Surface contact angle measurement; Surface contact angle value was followed by ASTM D7334 (2008) using contact angle goniometer (100-00; Ramé-hart Instrument Co., Succasunna, NJ, USA). The results were averaged from at least five independent of droplets at 100 μL/time of dropped volume size in advancing stage.

QUV-accelerated weathering aging testing; The testing was performed following ASTM G154 (2012) cycle I using a QUV-accelerated weathering tester (Q-UV test LU-0819, Q-panel lab products, USA). The condition of QUV- accelerated weathering aging testing includes UVA radiation wave length of 340 nm and intensity of 0.77 W/m^2 at 60 ^{o}C for 8 h and water-condensation at 50 ^{o}C for 4 h. The aging times were varied at 0, 4, 8, 16, and 32 days.

Natural weathering testing; The testing was performed in accordance with ASTM D1435 (2005). The specimens were exposed on the racks at a 45 angle in a south direction at a roof deck of School of Energy, Environment, and Materials building at King Mongkut's University of Technology Thonburi, Bangkok, Thailand from March to April 2014 for 52 days. The condition of natural weathering testing includes UVA intensity at 340 nm, temperature, rainfall, and relative humidity of 0.67 W/m^2, 26.7 to 36.9 ^{o}C, 23.7 ml/day, and 72.5 %, respectively. The climate data were provided by the Thai Metrological Department and National Institute of Metrology of Thailand. The natural weathering times were varied at 0, 14, 28, 42, and 56 days.

Surface Morphology; The morphology properties of WPVC were photographed using a scanning electron microscope (JSM-6301F; JEOL, Tokyo, Japan) under 15kV of accelerating voltage and backscattering detection mode. The aim of the tests were to study fracture surface of specimens before and after weathering testing.

3. Results and discussion

3.1 Effects of HPQM and wood flour contents

The results of the fungal growth inhibition test against *A. niger* for PVC and WPVC at different wood flour and HPQM contents are shown in Figure 1. The minimum HPQM contents to attain 100% fungal growth inhibitions for PVC, WPVC-50 (50 pph of wood flour), and WPVC-100 (100 pph of wood flour) were 50000, 15000, and 10000 ppm, respectively. It was found that the anti-fungal efficacies of PVC increased when increasing the HPQM contents and wood flour. This suggests that the wood flour allow more HPQM to migrate onto the WPVC composite surfaces. An explanation for this case is that introducing the wood flour, which are highly hydrophilic in nature into the WPVC makes the PVC become more hydrophilic. As a consequence, more water molecules can be absorbed into/onto the HPQM/wood/PVC surfaces [7]. According to this, wood flour act as an anti-fungal promoter of the WPVC.

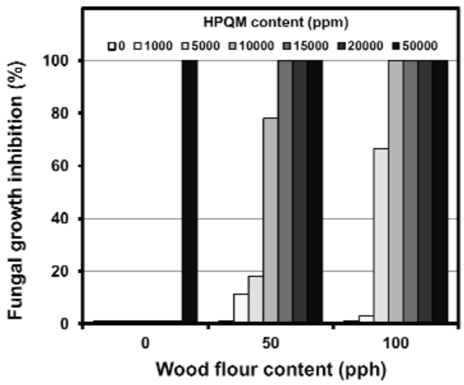

Fig. 1. Fungal growth inhibition value of PVC and WPVC with HPQM content and different wood flour content

Table 1 shows the surface contact angle values of PVC and WPVC with different HPQM and wood flour contents. It was observed that adding HPQM tended to lower the surface contact angle values of PVC and WPVC materials. This implies greater hydrophilicity of the PVC and WPVC when introducing HPQM into the composites. In the present work, the greater hydrophilicity of the PVC and WPVC was due to the high polarity and hydrophobicity of HPQM, which probably migrated onto PVC and WPVC surfaces. This indicates that the more wood flour, the lower the surface contact angle values. This would be associated with the presence of the wood flour in WPVC composites which is hydrophilicity, high water absorption and polar. For neat PVC, the addition of wood flour had significant effects on its hydrophilicity. This indicates that the WPVC became more hydrophilic due to the presence of wood flour. The changes in the hydrophilicity of WPVC by adding wood flour are related to the increase of the number of hydroxyl groups in the wood fiber structure.

Table 1 Contact angle of PVC and WPVC with HPQM content and different wood flour contents.

Wood flour content (pph)	HPQM content (ppm)						
	0	1000	5000	10000	15000	20000	50000
PVC	90.9°(±0.7)	88.3°(±0.3)	88.5°(±0.9)	86.8°(±0.5)	84.9°(±1.0)	80.8°(1.2±)	72.9° (±2.2)
WPVC-50	81.6° (±2.1)	80.6° (±1.6)	80.1° (±1.8)	79.2° (±1.5)	77.9° (±1.0)	75.3° (±0.5)	70.5° (±1.8)
WPVC-100	78.2° (±1.0)	77.8° (±1.1)	77.3° (±2.0)	74.1°(±0.2)	73.6° (±0.3)	73.4° (±0.2)	66.7° (±0.1)

3.2 Effects of QUV-accelerated weathering aging and natural weathering conditions

Figure 2 shows the fungal growth inhibition for WPVC-50 under the effect of QUV–accelerated weathering, by varying HPQM contents. From day 0 to day 8, it was observed that the degree of fungal growth inhibition for the WPVC-50 sample increased with increasing QUV–accelerated weathering time. Then, after day 8 the degree of fungal growth inhibition for the WPVC-50 sample decreased with increasing QUV–accelerated weathering time. In the first period of the aging process, lower anti-fungal potentials of WPVC-50 may be caused by the trapped of HPQM by PVC matrix. In this case, HPQM doped with wood flour was almost covered by PVC matrix, and then limited the diffusion rate of HPQM in the composites. After day 8 the degree of fungal growth inhibition for the WPVC-50 sample decreased with increasing QUV–accelerated weathering time. This is because the water condensation process accompanying the degradation of the WPVC-50 during UV aging initiated some cracks on the WPVC-50 composites, thereby increasing the diffusion rate of HPQM through the cracks. The numbers of crack increased for WPVC-50 when increasing aging time shown in Figure 3. The results correspond well with [8].

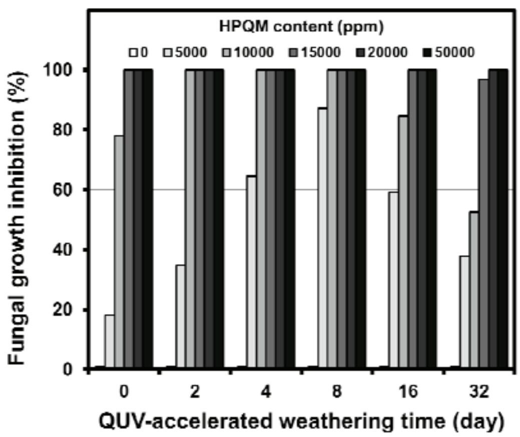

Fig. 2. Fungal growth inhibition value of WPVC-50 at different HPQM contents after QUV-accelerated weathering aging.

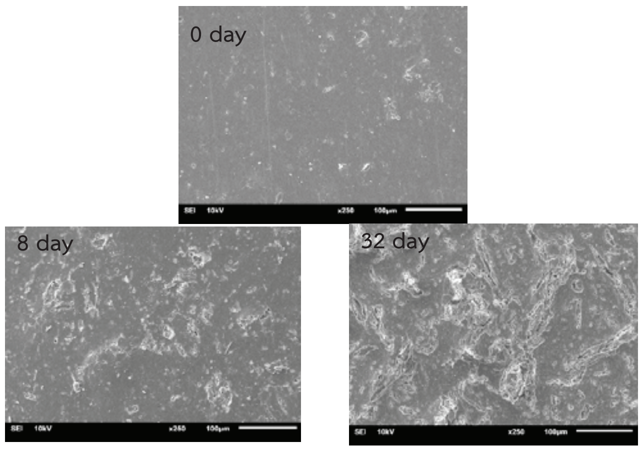

Fig. 3. SEM showing surface morphology of WPVC-50 doped with HPQM 5000 ppm after QUV-accelerated weathering aging.

Figure 4 shows the effects of natural weathering conditions on the anti-fungal inhibition of WPVC-50 varying HPQM contents. After natural weathering, the anti-fungal inhibition of WPVC-50 were found to decrease with increasing natural weathering time. This can be explained by the water condensation process accompanying the degradation of the neat PVC as mentioned previously. Until day 56, the anti-fungal inhibition of WPVC-50 increased. In this case, when the WPVC-50 samples encountered UV light, some cracks would occur due to WPVC-50 degradation (Figure 5). Then, the HPQM was able to migrate more easily (or be released through the cracks) and to increase the anti-fungal inhibition of WPVC-50.

0 day

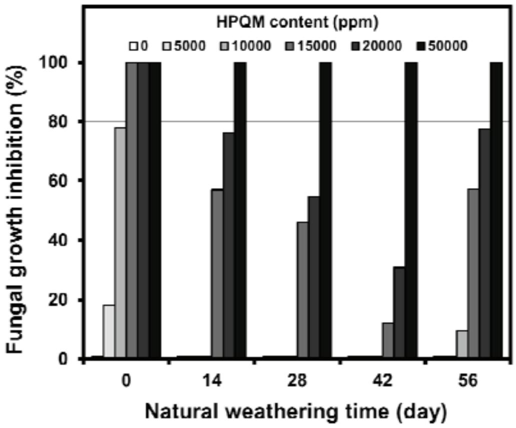

Fig. 4. Fungal growth inhibition value of WPVC-50 at different HPQM contents after natural weathering.

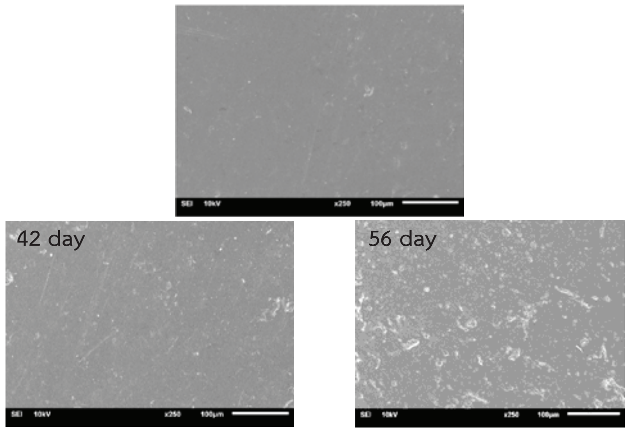

Fig. 5. SEM showing surface morphology of WPVC-50 doped with HPQM 15000 ppm after natural weathering.

3.3 The releasing behaviors model of the HPQM substance in WPVC matrix

Figure 6 shows the releasing behaviors model of the HPQM substance in WPVC matrix when exposed under QUV-accelerated weathering aging and natural weathering. Figure 6 (a) shows the stage I in WPVC matrix without applying weathering aging. This stage shows 3 types of HPQM on the WPVC composites: 1) forming H-bonding with a silane coupling agent, 2) forming dipol-dipol interaction with the carbon atom of PVC matrices, and 3) releasing HPQM species on the WPVC surface. Figure 6 (b) shows the stage II, water-discharging stage. In this stage, the degree of fungal growth inhibition for the WPVC decreased with increasing weathering time. Because only the free HPQM on the top surface were leached by water and trapped by the PVC matrix. Figure 6 (c) shows the stage III, surface crack. In this stage, the degree of fungal growth inhibition for the WPVC increased with increasing weathering time. This is because the water condensation process accompanying the degradation of the WPVC generated some cracks due to PVC degradation. Then, the HPQM was able to migrate more easily, or be released through the cracks, and was eventually washed away in the water condensation process during the UV radiation process. In general, HPQM species is replaced by water molecule and form H-bonding with OH group of the wood flour. Figure 6 (d) shows the stage IV, more surface crack. In this stage, the degree of fungal growth inhibition for the WPVC decreased with increasing weathering time. This is because less HPQM species left in the WPVC, according to the previous surface crack stage. For natural weathering, there are 3 stages that were discovered: stage I, II, and III. However, for QUV-accelerated weathering aging, there are 4 stages: stage I, II, III, and IV. It can be seen that the behavior in the first period of the natural weathering happened in the first period of the QUV-accelerated weathering aging. This is because the QUV-accelerated weathering aging has more extreme effect than the natural weathering.

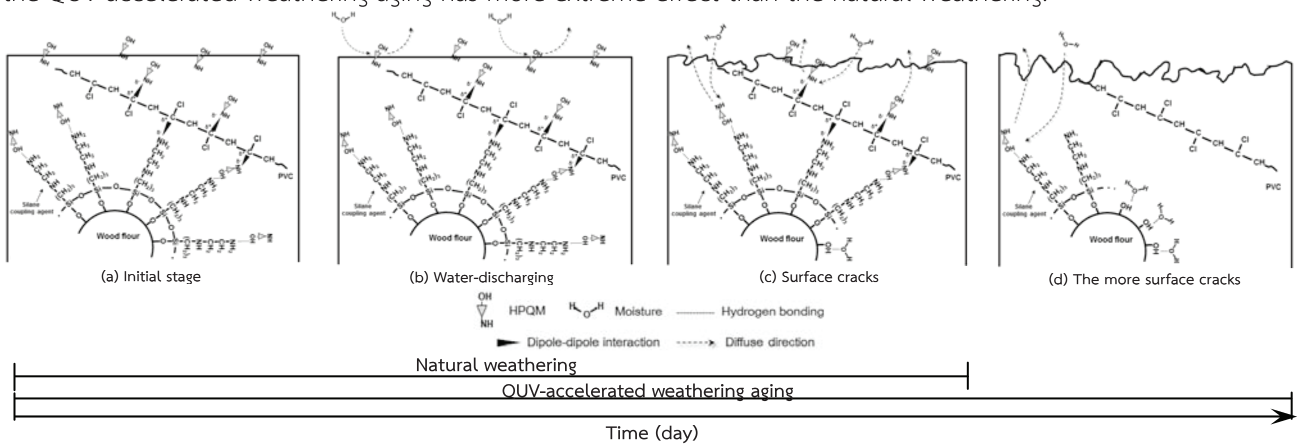

Fig. 6. Releasing behaviors of HPQM substance in WPVC matrix when exposed under QUV and natural weathering.

4. Conclusions

Adding wood flour into PVC matrix could improve the anti-fungal performances of the composites. It was suggested that wood flour is an anti-microbial promoter for the WPVC composites. The recommended dosages for killing fungal for HPQM in PVC, WPVC-50, and WPVC-100 were 50000, 15000, and 10000 ppm, respectively. The effects of QUV-accelerated weathering aging and natural weathering condition resulted anti-microbial evaluation indicated that sample doped with HPQM lower than 20000 ppm have changes in the anti-fungal efficacies rather than sample doped with HPQM 50000 ppm. The releasing behavior of the HPQM substance in WPVC matrix in the first period of the natural weathering happened in the first period of the QUV-accelerated weathering aging.

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