

Antimicrobial polyethylene wax emulsion and its application on active paper-based packaging material

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ABSTRACT: Antimicrobial polyethylene wax (PEW) emulsions, prepared by emulsifying polyethylene wax grafted with polyhexamethylene guanidine hydrochloride (PEW-g-PHGH), were used as wet-end additives or coating materials for fabricating hydrophobic and anti-mold hand-sheets or paper. To obtain PEW-g-PHGH, maleic anhydride (MAH) was adopted as a bridging agent. The melt or solution grafting of MAH to PEW was performed to achieve the appropriate grafting degree and grafting efficiency. The resulting PEW-g-PHGH was emulsified using a homogenizer by means of surfactants, and the resulted emulsions were characterized in terms of particle size, zeta potential, charge density, minimal inhibitory concentration (MIC), and adsorption capacity. After that the hydrophobicity of emulsion treated hand-sheets was determined by measuring water contact angle (WCA). The morphology of the hand-sheets treated by the emulsion was revealed using scanning electron microscope (SEM) and atom force microscope (AFM). Finally, the antimicrobial properties of the emulsion treated hand-sheets were investigated by anti-mold tests against *Aspergillus niger* and *Chaetomium globosum*. Results indicated that the PEW-g-PHGH emulsions exhibited good stability, high fiber adsorption capacity, and antimicrobial activity. The WCAs of the treated hand-sheets reached 82° -140° with 80%~99.9% growth inhibition against fungi. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42214.

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INTRODUCTION

Active packaging has become one of the major areas of research in food packaging in the past several decades.^{1–5} The conception of active packaging, according to Vermeiren *et al.*,⁶ can be defined as a type of packaging to extend shelf-life or improve safety of sensory properties while maintaining the quality of the food. One of the typical approaches for creating active packaging is to incorporate antimicrobial substances by internal addition^{1,3,7} or surface coating,^{2,8} to control undesirable growth of microorganisms on the surface.

Among the food packaging materials, paper is considered as a kind of environment-friendly material. However, paper packaging easily absorbs water from environment or from the food and loses its barrier properties and mechanical strengths. In order to obtain good barrier properties, paper is often laminated with other materials, such as plastic materials,^{9,10} or treated by natural polymers.^{11–13}

Recently, active paper-based packaging materials attract much attention as the food safety level has never been as high as today. Majority of researches focused on either barrier properties or antimicrobial properties,^{14–18} while only a few literatures covered both aspects: Bordenave *et al.*¹⁶ reported the elaboration of water-resistant, antimicrobial, chitosan, and paper-based materials as environment-friendly food packaging materials. Results showed the paper coated with chitosan exhibits good barrier properties and over 98% inhibition on *Salmonella Typhimurium* and *Listeria monocytogenes*. Rodriguez-Lafuente *et al.*¹⁹ presented a new active paraffin coating for paper and evaluated the antimicrobial protection and decay retardation for cherry tomatoes. Almost total inhibition of the fungus was obtained when 6% of bark cinnamon essential oil was applied to the packaging material.

This work was aimed at developing water proof, antimicrobial paper-based packaging materials treated with the antimicrobial

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Figure 1. Preparation of PEW-g-MAH and PEW-g-PHGH.

PEW-g-PHGH emulsions. PEW is a kind of ultra-low molecular weight polyethylene with hydrophobic, chemical stable, and nontoxic properties. The oxidized PEW is permitted in the United States as a protective coating for fresh avocados, bananas, beets, coconuts, eggplants etc.²⁰ Polyhexamethylene guanidine hydrochloride (PHGH) possesses excellent antimicrobial properties.^{21–23} Combined two polymers, a type of antimicrobial emulsion based on PEW-g-PHGH was prepared and applied on hand-sheet by wet-end addition, dip coating, and roll coating methods. The surface hydrophobicity of hand-sheet was characterized by WCA. MICs of the emulsions against *Escherichia coli* were detected; and anti-mold tests for the treated hand-sheets were conducted against *Aspergillus niger* and *Chaetomium globosum*.

EXPERIMENTAL

Materials

Polyethylene wax MPP-611XF (melt point 109–111°C, mean particle size 5.0–6.0 microns) was provided by Micro Powders, USA. PHGH with molecular weight of 1000~3000, was synthesized as described in our previous work.²⁴ Benzoyl peroxide (\geq 97.0%, Fluca) was purified by dissolving in chloroform and then recrystallized in methanol. MAH, Span 60, Tween 80, cetyltriethylammonium bromide (CTAB) were purchased from Sigma–Aldrich (USA) and used without further purification. Xylene, acetone, and methanol were analytical grade, purchased from Sigma–Aldrich (USA).

Preparation of PEW-g-PHGH

The grafting of PHGH to PEW was prepared using MAH as a bridging agent, as shown in Figure 1.

PEW-g-MAH was prepared by melt or solution grafting approaches: (1) melt grafting: PEW and MAH at proper ratios were charged in a three-neck flask equipped with thermometer, magnetic stirrer, and nitrogen protection. After the mixture was melt at 120°C, BPO (10 wt % of MAH) was added into the flask to induce the reaction. One hour later, xylene was charged into the flask to dissolve the product, followed by precipitation in excess acetone. The precipitate was extracted with acetone for 48 h to remove low molecular weight compounds and unreacted MAH. The final grafted product was obtained after vacuum drying and marked as PEW-g-MAH. (2) Solution grafting: using the equipment mentioned above, PEW was dissolved in xylene at 100°C. Thereafter, MAH and BPO were put into the solution and stirred for 4 h. The collection of the product could be referred to the melt grafting.

About 20 g of PEW-g-MAH (prepared by melt grafting, G_d =2.45%) and 5 g of PHGH (\overline{M}_n =1000) were charged into a 50 mL of three-necked flask with magnetic stirrer and thermometer. The reaction was performed at 140°C for half-anhour. Thereafter, the product was dissolved in refluxing xylene followed by being precipitated in methanol. The precipitate was washed with methanol twice to remove unreacted PHGH, marked as PEW-g-PHGH.

Preparation of PEW-g-PHGH Emulsions

According to the ratios described in Table I, PEW-g-PHGH (or PEW), emulsifier, and water were placed into a 250 mL of beaker. Thereafter, the mixture was emulsified for 15 min, using a CAT X120 homogenizer (Ingenieurbüro M. Zipperer GmbH, Staufen, Germany) with the speed set at 20,000 rpm. When the emulsions were cooled down, charged them into sample bottles.

Preparation of Hand-sheets Treated with Emulsions

Wet-end addition: the kraft fiber suspension and the emulsion (fiber: PEW-g-PHGH=10:1, g/g) were charged in a tank and stirred for 10 min. Then the hand-sheets at 60 g·m⁻² and 120 g·m⁻² were fabricated using a hand-sheet former, respectively, followed by being dried at 130°C for 15 min. The hand-sheets (60 g·m⁻², 16 cm in diameter) without using emulsions as control samples were also produced.

Roll coating method: the native hand-sheets were coated with EI or EII using a bar coater (K303 multicoater) at the speed of 10 m·min⁻¹. Each hand-sheet was coated on both sides with coating rod (number 7) and the total coating weight was $10\sim20$ g·m⁻². The coated paper dried at 130° C for 15 min.

Dip coating method: the native hand-sheets were immersed into the EI or EII and taken out immediately. They were placed vertically by a clamp to dry naturally for 24 h, followed by being dried at 130° C for 15 min.

Determination of Grafting Degree and Grafting Efficiency

The grafting degree (G_d) and grafting efficiency (G_e) were determined by back titration: the purified PEW-g-MAH sample (0.5 g) was completely dissolved in 40 mL xylene under reflux. After the solution cooled to 90°C, 20 mL 0.05 mol·L⁻¹ NaOH-ethanol solution was slowly added with vigorous stirring. The titration was conducted using Metrohm 809 Titrando (Metrohm, Switzerland) with 0.1 mol·L⁻¹ HCl aqueous solution. A

Table I. Ingredients of Emulsions

Emulsion	PEW	PEW-g-PHGH	Emulsifier ^a	Water
EI	0	10	S60 0.25, T80 0.25	89.5
EII	0	10	CTAB 0.5	89.5
EIII	10	0	S60 0.25, T80 0.25	89.5
EIV	10	0	CTAB 0.5	89.5

^aS60 and T80 are non-ionic surfactants, span 60 and tween 80, respectively.

CTAB is a type of cationic surfactant, cetyltrimethyl ammonium bromide.



blank solution was also treated under the same conditions. The mass fraction of MAH, *MF* (wt %), was calculated by eq. (1):

$$MF = \frac{m_{gM}}{m_s} = \frac{C_{Naoh}V_{Naoh} - C_{HCI}V_{HCI}}{2m_s} \times M_{MAH}$$
(1)

where $m_{\rm gM}$ and $m_{\rm s}$ are the mass weight of grafted MAH and the sample (g), respectively. $c_{\rm NaOH}$ is the concentration of sodium ethoxide (mol·L⁻¹), which can be calculated from the blank sample. $v_{\rm NaOH}$ is the volume of NaOH-ethanol solution (L). $v_{\rm HCl}$ is the consumed volume of HCl solution at the end point of titration (L). $M_{\rm MAH}$ is the molecular weight of MAH (98.06 g·mol⁻¹). The titration was repeated three times for each sample. Then, $G_{\rm d}$ and $G_{\rm e}$ can be calculated by eqs. (2) and (3):

$$G_d = \frac{m_{\rm gM}}{m_{\rm p}} = \frac{MF}{1 - MF} \times 100\% \tag{2}$$

$$Ge = \frac{m_{\rm gM}}{m_{\rm M}} = \frac{m_{\rm p} \times G_{\rm d}}{m_{\rm M}} \times 100\% \tag{3}$$

where $m_{\rm M}$ and $m_{\rm P}$ are the feeding weight of MAH and PEW (g).

Characterizations of PEW-g-PHGH and Emulsions

The structures of PEW-g-MAH and PEW-g-PHGH were characterized using a FTIR spectrometer (Perkin Elmer spectrum 100). At least 64 scans were applied and data were collected between 450 and 4000 cm⁻¹.

The PEW-g-PHGH emulsions were characterized based on the particle size, zeta potential, MIC, absorption, and AFM observation. The emulsions were diluted to 0.1% to detect the particle size using 90Plus/BI-MAS (Brookhaven Instruments Corp., USA). The parameters were set as follows: temperature 25°C, angle 90°, wavelength 670 nm. Each sample was determined 10 times in parallel. BIC ZeraPLAS/Zeta Potential Analyzer (Brookhaven Instruments Corp., USA) was used to determine the average zeta potential. To a 50-mL beaker, 0.2 mL of the emulsion was added with 20 mL of 1 mmol·L⁻¹ KCl. The temperature inside the cell chamber was kept constant at 25°C. Each sample was run 10 times in parallel.

MIC against the gram-negative bacteria *Escherichia coli* (*E. coli, ATCC 11229*) was carried out using a serial dilution method to characterize the antimicrobial property of the emulsion. The emulsion was diluted to serial concentration from 1000 to 8 ppm with sterile lysogeny broth (LB). The bacterial cultures were added into the glass tubes containing LB broth of different concentration of tested samples and the final concentration of the cells (in the tubes) was adjusted to 10^6 CFU·mL⁻¹. After incubation for 24 h at 37° C, the tubes were visually examined for turbidity compared with control samples which has the same concentration of samples without bacterial.

AFM images of EI dried at room temperature and 130°C were obtained with a Nanoscope IIIa (Veeco Instruments) in contacting mode using a silicon probe (NP-S20, Veeco Instruments) with settings of 512 pixels/line and 1 Hz scan rate.

To determine the adsorption of the antimicrobial emulsions to fiber, the concentration variation of PEW-g-PHGH in the aqueous fibrous suspensions was detected by measuring the transmittance change:²⁵ A fibrous suspension of 500 mL with fiber consistency of 0.5% was stirred at 500 rpm for 10 min.



Figure 2. Effect of MAH addition on G_d and G_e in melt or solution grafting.

A 200-mesh screening chamber, which was used to filter out pulp fibers and extract the emulsion, was set inside the pulp slurry. The filtrate was transferred into a cuvette with a syringe and measured the transmittance at expected time. The control samples, including the pure fiber suspension and pure emulsion, were measured with same conditions and procedures.

Characterization of Antimicrobial Hand-sheets

WCAs of hand-sheet samples were measured with JC2000D contact angle measuring device (Shanghai Powereach, Shanghai, China). The anti-mold tests against *Aspergillus niger* and *Chaetomium globosum* were carried out according to TAPPI T 487 (USA), which was recommended for determining the resistance to fungal growth of paper and paperboard. Detailed procedures would refer to our previous work.²⁶ SEM analysis of hand-sheet samples were performed using a scanning electron microscope (SEM, JSM-6400, Jeol, Japan) at an accelerating voltage of 15 kV, where the samples were carbon-sputtered prior to observation.

RESULTS AND DISCUSSION

Effect of MAH Addition on G_d and G_e

Figure 2 presents the effect of MAH addition on G_d and G_e in melt or solution grafting. It can be seen that the melt grafting revealed conspicuous improvement in comparison to the solution grafting approach, on both G_d and G_e . The mechanism of grafting MAH to polyethylene (PE) had been elaborately investigated by Heinen et al.²⁷ As described in Figure 1, the free radicals generated from BPO transferred to PEW chains, followed by the attachment of MAH to the polymer chain as a single succinic anhydride unit or possibly even larger oligomers. Actually, the diffusion of free radicals played an important role to the grafting. Because of the low viscosity of melt PEW, the diffusion became much easier than in melt PE, possibly close to solution grafting. In addition, the diffusion of free radicals to solvents decreased the G_d and G_e for the solution grafting. In view of the efficiency and facility, the melt grafting was adopted to continue the following work.

In the melt grafting, the G_d increased with the ascending MAH addition. In particular, G_d reached 2.5% when MAH addition was 6 g per 100 g PEW, and the grafting efficiency exceeded





Figure 3. FTIR spectra of (A) PEW, (B) PEW-g-MAH, and (C) PEW-g-PHGH.

40%, suggesting a satisfied result compared with 1.59% for the melt ultrasound and solid co-irradiation method.²⁸ When increasing the MAH addition to 8 g, the G_d was up to 2.8%

while the $G_{\rm e}$ was down to 35%. This would account for the increasing of self-polymerization of MAH associated with the increasing concentration. When the MAH addition was up to 20%, the pronounced crosslinking appeared which was also reported by Gaylord *et al.*²⁹ By comprehensive consideration, PEW-g-MAH with $G_{\rm d}$ of 2.5% was used to prepare PEW-g-PHGH (see point A in Figure 2).

FTIR Analysis of Grafted PEW

Figure 3 presented the FTIR spectra of PEW, PEW-g-MAH, and PEW-g-PHGH. The absorption bands at 729 cm⁻¹, 1462 cm⁻¹, 2850 cm⁻¹, and 2921 cm⁻¹ were the characteristic absorptions of PEW. The spectrum of PEW-g-MAH [Figure 3(B)] showed new absorbance bands at 1860 cm⁻¹ and 1780 cm⁻¹ corresponding to symmetric and asymmetric stretching of the carbonyl group of MAH.³⁰ After the reaction with PHGH, those two bands disappeared and new absorption bands were observed at 1770 cm⁻¹, 1700 cm⁻¹, and 1550 cm⁻¹ which verified the generation of imide.^{29,31} Another bands around 1635 cm⁻¹ and 3400 cm⁻¹ were ascribed to -C=NH group of PHGH. Since all the specimens were carefully purified, the FTIR results suggested that the PEW-g-PHGH were successfully synthesized.

Table II. Characterizations of PEW-g-PHGH Emulsions

	рН	Particle size (nm)	Zeta potential (mV)	Charge density meq⋅g ^{−1}	MIC (µg⋅mL ⁻¹)
EI	7.2	544.5	+11.9	0.135	125
EII	7.3	251.2	+21.51	0.31	125
EIII	-	Not stable	-	-	-
EIV	-	Not stable	-	-	-



Figure 4. The schematic diagram of PEW and PEW-g-PHGH emulsion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]



Figure 5. Concentration calibration curves for (A) EI and (B) EII determined by UV at the wavelength of 500 nm.

Characterizations of Emulsions

Table II showed PEW and PEW-g-PHGH emulsions emulsified by Span-60/Tween-80 (S/T) and CTAB, respectively. Li et al.32 had reported the preparation of paraffin wax submicron emulsions using Span-80/Tween-80, and the stable emulsions had the droplet diameters about 700 nm. However, it was difficult to obtain stable PEW emulsions using the common surfactants, as illustrated in Figure 4. Due to the rigid quality and high melt point of PEW, it remained large-size particles despite of the vigorous homogenization. Therefore, the PEW emulsion performed demulsification after standing for 24 h. After modification, PEW-g-PHGH molecules, comprised of hydrophobic and hydrophilic chains, could be considered as large surfactants. Therefore, it was easy to break into smaller particles. On the one hand, those small particles revealed larger specific surface area, and absorbed more surfactants which increased the stability in water. On the other hand, the grafting of PHGH improved the hydrophilicity of PEW, which also played important role in the stable emulsions.

Table II also presented the pH, particle size, zeta potential, charge density, and MIC of EI and EII, respectively. Compared with two emulsions, EII (CTAB as an emulsifier) exhibited pH and MIC values similar to EI (S/T as an emulsifier), while the former had smaller particle size and higher zeta potential and charge density. With respect to EI, the slight electropositivity



Figure 6. Adsorption of PEW-g-PHGH on Kraft fiber (PEW-g-PHGH/ fiber=1/10, g/g).

definitely accounted for the grafted PHGH, as the emulsifiers were non-ionic surfactants. For EII, the excess electropositivity was derived from the cationic surfactant CTAB. The two types of emulsifiers were selected based on the following reasons: (1) the emulsions prepared by CTAB led to high electropositivity, which was beneficial for their adsorption on fiber at wet-end addition; (2) S/T surfactants are food additives, which can be used for fabricating food contact packaging materials.

Adsorption Capacity of PEW-g-PHGH Emulsions

As shown in Figure 5, in dilute solution (below $0.2 \text{ g} \cdot \text{L}^{-1}$) the concentration of PEW-g-PHGH revealed a linear relationship with log(1/T), where T was the transmittance determined by UV at the wavelength of 500 nm. By means of curve fitting, eqs. (4) and (5) with high accuracy (R²> 0.99) were obtained to calculate the unabsorbed PEW-g-PHGH in the fiber suspension for EI and EII, respectively.



Figure 7. Function process of PEW-g-PHGH in wet end addition and roll coating treatments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table	III.	WCAs	of	Emulsion	Treated	Paper	Samples	
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		Basis weigl	nt (g·m ^{−2})	
Treating method	Emulsion	Before treating	After treating	Contact angle (°)
Control		60	60	0
Wet-end	EI	60	63	82.3
		120	126	91.9
	EII	60	65	115.8
		120	130	111.4
Roll coating	El	60	82	139.5
	EII	60	83	127.2
Dip coating	EI	60	78	126.8
	EII	60	81	116.6

$$lg(1/T) = 4.53C + 0.02$$
(4)
$$lg(1/T) = 4.5C + 0.01$$
(5)

Figure 6 shows the adsorption curves of PEW-g-PHGH in 2% Kraft fiber suspension for EI and EII, respectively. Both adsorptions exhibited a rapid growth in the first 10 minutes. Thereafter, the growth was slowed down till the fibers achieved the saturated adsorptions eventually. Besides, fiber/EII was observed not only a faster but also a larger saturated adsorption in comparison to fiber/EI. The saturated absorption was 0.073g/g fiber for PEW-g-PHGH in EI/fiber system, and 0.088 g/g fiber for PEW-g-PHGH in EII/fiber system.

The surface of the fiber is negative-charged, which facilitates the adsorption of the positive-charged PEW-g-PHGH due to electrostatic association, as illustrated in Figure 7. EII had higher charge density, resulting in faster and larger saturated adsorption in comparison to EI.

Hydrophobicity of Hand-sheets Treated with Emulsions

Table III lists the WCAs of emulsion treated hand-sheets with wet-end addition, roll coating, and dip coating approaches. It can be seen that the emulsion treated hand-sheets revealed significant hydrophobicity in comparison to the native



Figure 8. SEM images of (S1) native hand-sheet sample, (S2) wet end addition sample, and (S3) roll coating sample.



Figure 9. AFM images of diluted EI before (A1) and after (A2) treated at 130°C for 10 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]





Figure 10. SEM images of dip coating sample treated at 130°C for 10 min (S4) or 30 min (S5).

hand-sheets. The WCA was up to 116°, 140°, and 127° for wetend addition, roll coating, and dip coating treatment, respectively. Figure 7 illustrates the function process of PEW-g-PHGH at wet-end addition and roll coating treatments. As for wet-end treatment, the emulsions were used as functional additives, similar to those used in the conventional papermaking process. The PEW-g-PHGH particles adsorbed on the fibers were distributed within fiber networks, and formed a hydrophobic layer covered on the fiber surface when the temperature exceeded the melt point of PEW (around 110°C). The adsorption amount of PEW-g-PHGH could be calculated from the change of paper basis weight, i.e. 0.05 g/g fiber and 0.083 g/g fiber for EI and EII, respectively. The results indicated EII treated hand-sheets had higher WCAs due to the higher adsorption amount of PEW-g-PHGH. Therefore, EII was more suitable for wet-end addition treatment than EI.

With respect to coating treatments, the treated hand-sheets revealed higher WCAs, clearly due to larger PEW-g-PHGH amounts; for example, 0.37 g/g fiber for EI in roll coating treatment. Besides, EI treated hand-sheets exhibited higher WCAs than EII treated, probably related to the hydrophobicity of the surfactants (S/T >CTAB).

To confirm the function process of the emulsions, surface topographies of the treated hand-sheets were observed by SEM, as shown in Figure 8. From the images of the native hand-sheet (S1), wet end treated (S2), and roll coated hand-sheet (S3), it can be seen that the fibers of native hand-sheet had neat surface and stacked at random, while fibers of wet-end treated hand-sheet covered by a thin "film" and began to joined together. The "film" was more conspicuous in S3, as the melt PEW was enriched between the fibers. Figure 9 provides the AFM images of the extremely diluted EI before and after treatment at 130°C. The round micro particles were PEW-g-PHGH clusters, which collapsed down after being treated that the PEW-g-PHGH improved hydrophobicity of hand-sheets by forming a hydrophobic layer on the fibers.

Figure 10 presents the SEM images of dip coating hand-sheets treated at 130°C for 10 min (S4) or 30 min (S5). It clearly demonstrated the formation of hydrophobic layer. As can be seen from S4, plenty of PEW-g-PHGH particles adsorbed on the fibers and began to melt. Additionally, the outlook of particles could be observed and the mean particle size could be estimated at approximately 500 nm, which was in accordance with the result in Table II. After treating for 30 min, the overwhelming majority of particles had been melt, forming a PEW-g-PHGH layer of film on the fibers (see S5).



(M1)



(M2)

Figure 11. Anti-mold results of the native hand-sheet, wet end addition treatment with EII, and coating treatment with EII against *Aspergillus niger* (M1) and *Chaetomium globosum* (M2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Anti-mold Properties of Emulsion Treated Paper

Figure 11 shows the growth of *Aspergillus niger* and *Chaetomium globosum* on the native hand-sheet and PEW-g-PHGH emulsions treated hand-sheets. The control hand-sheet presented tremendous growth after incubating for 14 days at 28°C, while the emulsion treated hand-sheets exhibited notable antimold activities, i.e. 80% and 99.9% inhibition against two fungi for-wet end and coating treatment, respectively. The results indicated that PEW-g-PHGH emulsions were high effective in fabricating anti-mold paper materials.

Besides fungi, PEW-g-PHGH emulsions revealed high inhibition to bacteria, for example *Escherichia coli*. Table II lists the MIC against *E. coli* was 125 μ g·mL⁻¹. Our previous work had ascertained that both modified PHGH^{21,24} and grafted PHGH^{22,33} showed excellent antimicrobial activities. The antimicrobial mechanism was to destruct cell membrane and cause leakage of intracellular components from bacteria. Since the PHGH was grafted to PEW, the antimicrobial effect would not be diminished with time prolonged. Moreover, the contamination issue caused by the leakage of antimicrobial agents could also be addressed.

CONCLUSIONS

The focus of this study was to fabricate hydrophobic and antimold hand-sheets, by virtue of PEW-g-PHGH emulsions. In conclusion, we can emphasize that: (1) PHGH was successfully grafted on PEW using MAH as a bridging agent, preferably using melt grafting approach; (2) PEW-g-PHGH not only combined the hydrophobicity of PEW and antimicrobial property of PHGH, but also possessed high adsorption capacity to fibers; (3) the PEW-g-PHGH emulsions are effective and promising as wet-end functional additives for rendering paper hydrophobic and antimicrobial; and (4) the hand-sheets coated by PEWg-PHGH emulsions exhibited excellent hydrophobicity and complete growth inhibition of fungi.

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