

## Research Article

# Synthesis of Cationic Waterborne Polyurethanes from Waste Frying Oil as Antibacterial Film Coatings

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Cationic waterborne polyurethane (CWPU) was synthesized from waste frying oil and utilized as antibacterial film coatings. Waste oil-based monoglyceride was synthesized by the alcoholysis reaction of waste oil with glycerol, while CWPU were prepared by esterification with methylenediphenyl 4,4'-diisocyanate (MDI) and bis(2-hydroxyethyl)dimethyl ammonium chloride (BHMAC) as an internal emulsifier. The effect of internal emulsifier contents on the chemical structures and properties of the obtained polyurethanes was studied. Bactericidal activity of the obtained polyurethanes toward *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) was investigated using the time kill assay. CWPU were successfully synthesized as confirmed by proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR) and Fourier transform infrared spectroscopy (FT-IR). Effects of the internal emulsifier on particle size of CWPU and mechanical properties of the resulting polyurethane films were investigated and measured by transmission electron microscopy (TEM). Particle size diameter of CWPU ranged from 13.38 to 28.75 nm. The resulting polyurethane films were very pliable, with moderate adhesion and hardness. All films showed good resistance to water and diluted acid but poor resistance to dilute alkali. Obtained CWPU provided excellent antibacterial activity, with efficiency increasing with increasing amount of BHMAC. Interestingly, antibacterial ability against *S. aureus* was more rapid than that against *E. coli* under similar conditions. Results offered an alternative utilization of waste frying oil as a sustainable raw material for the preparation of value-added polymers in the chemical industry.

## 1. Introduction

Various agricultural products have recently received increasing attention as sustainable raw materials because of environmental concerns and diminishing petroleum resources [1]. In particular, plant-based oils are widely studied as alternative feedstocks for polymeric materials due to their inherent biodegradability, low toxicity, and natural abundance [2]. Much effort has been expended to develop many innovative technologies to transform these natural resources into novel monomers and polymers. Some technologies have already generated competitive industrial products with properties comparable to conventional petrochemical polymers [3]. However, a major obstacle for industrial utilization of plant-based oils as sustainable feedstocks is competition with demand for human consumption.

The annual amount of waste frying oil produced globally from households and food industries is huge. This waste oil is usually composed of many harmful decomposition products resulting from oxidation, hydrolysis, and polymerization [4–6]. Management of this waste is a significant challenge because unrestricted disposal contaminates water and land resources. Therefore, waste frying oil must be disposed of safely or utilized in an efficient way. Waste oil is cheaper than pure vegetable oil and shows promise as a raw material for the polymer industry. Utilization of waste frying oil is forecast to have the potential to enhance the economy and also reduce the number of waste products which negatively impact on the environment.

Polyurethanes are extremely versatile polymers that are widely used in many industries because of their excellent mechanical properties and flexible processing methods [7].

However, conventional polyurethane products, like coatings and adhesives, usually contain significant amounts of organic solvents [8]. Due to the increase in environmental regulations regarding volatile organic compounds (VOCs) and hazardous air pollutants (HAPs), conventional polyurethanes are now being replaced by waterborne polyurethanes as binary colloidal systems where the polyurethane particles are dispersed in a continuous aqueous media [9–13]. Recently, anionic waterborne polyurethanes have become more widespread both in research and in industry. However, cationic waterborne polyurethanes are seldom used commercially although they exhibit excellent adhesion properties to various anionic substrates and provide antimicrobial properties through interaction with bacterial cell membranes [12, 14–16]. Many studies have synthesized cationic waterborne polyurethanes by incorporating various internal emulsifiers into the polymer structures such as N-methyl diethanolamine [14–18] and quaternary ammonium groups [19–21] to increase the stability of hydrophobic polyurethane in the aqueous phase.

However, despite extensive studies focusing on using plant-based oils to manufacture waterborne polyurethanes [14–17, 19–21], lack of data exists in using waste oil as feedstock. Here, environmentally friendly cationic waterborne polyurethanes (CWPU)s were synthesized from waste frying oil, and the effect of an internal emulsifier on the properties of the obtained polyurethanes was studied. Potential use of CWPU)s as antibacterial film coatings was evaluated using Gram-positive bacteria *Staphylococcus aureus* (*S. aureus*) and Gram-negative bacteria *Escherichia coli* (*E. coli*), and bacterial reduction was analyzed.

## 2. Materials and Methods

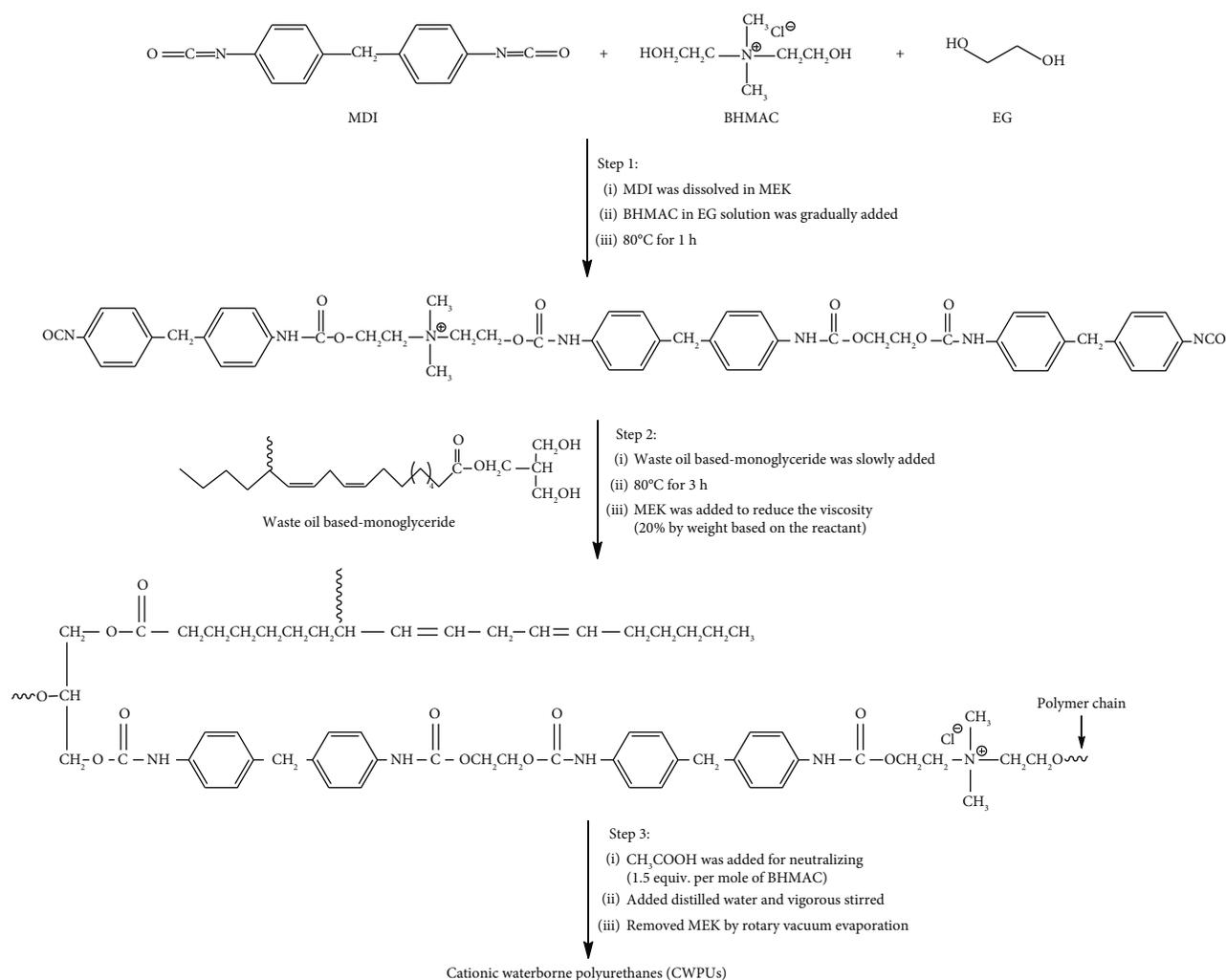
**2.1. Materials.** Waste frying oil was collected from small shops after being used several times for frying purposes. Activated bleaching clay (Wonder Earth NK 309) was a gift from Bornnet Corporation Co. Ltd., Bangkok, Thailand. Ethylene glycol (EG; 99.8%) and sodium chloride (NaCl; 99.9%) were purchased from Univar-Ajax Finechem, Australia. Calcium oxide (CaO; 99.9%) was purchased from Fluka, Switzerland. Glacial acetic acid ( $\text{CH}_3\text{COOH}$ ; 99.7%), methanol (99.8%), ethanol (99.8%), and methyl ethyl ketone (MEK; 99.5%) were purchased from Labscan, Asia. Methylenediphenyl 4,4'-diisocyanate (MDI; 97%) and bis(2-hydroxyethyl)dimethylammonium chloride (BHMACHL; 99.99%) were purchased from Tokyo Chemical Industry, Japan. Peptone and culture growth media and its components were purchased from HiMedia Laboratories, India. All other chemicals were used directly without further purification.

**2.2. Synthesis of Waste Oil-Based Monoglyceride.** Prior to synthesis, waste frying oil was filtered to eliminate any residues and then decolorized according to previous procedures [22]. Briefly, the filtrated oil was gently stirred for 2 h in the presence of 5% *w/w* of activated bleaching clay at 80°C under a nitrogen atmosphere. After that, the mixture was centrifuged and filtered to remove the bleaching clay. Waste oil-based monoglyceride was synthesized by alcoholysis with

glycerol according to the modified conditions previously described [23]. First, 100 g of waste oil and 20 g of glycerol were added to the glass reaction vessel. The mixture was stirred at 500 rpm and heated to 210°C under a nitrogen atmosphere, followed by addition of 0.05 g of CaO as the catalyst. The temperature was then raised to 230°C, and the mixture was maintained at this temperature for 2 h until the reaction mixture (1 part) was soluble in ethanol (2 parts), indicating complete alcoholysis reaction. Finally, the mixture was cooled to room temperature and stored in an airtight container.

**2.3. Synthesis of Cationic Waterborne Polyurethanes (CWPU)s.** The preparation approach for CWPU)s is shown as Scheme 1. Briefly, MDI was dissolved in MEK (50% by weight based on the reactant) in a four-necked round bottom flask equipped with a condenser and stirred at 80°C until completely dissolved under a nitrogen atmosphere. Then, a solution of internal emulsifier (BHMACHL in EG) was gradually added and vigorously stirred for 1 h, after which time the as-prepared monoglyceride was slowly added into the mixture. The reaction was continuously carried out at 80°C for 3 h, and MEK (20% by weight based on the reactant) was added to reduce the viscosity of the system. Finally, the reaction was cooled to room temperature and then neutralized by the addition of acetic acid (1.5 equivalents of BHMACHL). Distilled water was added to the mixture with agitation at high shearing rates (1500 rpm) to emulsify the solution. CWPU)s with a solid content of ~40 wt% were obtained after the removal of MEK from the emulsion at 50°C by rotary vacuum evaporation under reduced pressure. The isocyanate to hydroxyl (NCO/OH) molar ratios were fixed at 0.7/1.0 while amounts of BHMACHL were varied. The molar ratios of NCO were kept lower than that of OH in order to avoid reaction of isocyanate end groups of the obtained CWPU)s with water. Formulations used for the synthesis in this step are given in Table 1.

**2.4. Characterization.** Physical properties of waste oil, as well as the as-prepared monoglyceride, were examined with regard to iodine value (IV), acid value (AV), hydroxyl value (OH), and molecular weight ( $M_w$ ). Iodine value was determined following the modified method based on ASTM D1959. Acid value was calculated based on ASTM D1980. Hydroxyl value was determined based on ASTM D 2849 (Method C). Molecular weight was determined using a GPC system (Shimadzu Class-VP, Shimadzu Scientific Instruments, Columbia, MD, USA). Chemical structures were characterized using a Nicolet FT-IR spectrophotometer (Model Thermo Nicolet Nexus 670, Nicolet Instruments Inc., Madison, WI, USA) and  $^1\text{H-NMR}$  spectroscopy (Varian Unity Inova 500 MHz NMR, Georgia, USA). Differential scanning calorimetry (DSC) measurement of the CWPU) films was carried out on a DSC200 PC apparatus (Netzsch Co., Germany) with a cooler system of liquid nitrogen. Each sample was heated from -80°C to 250°C at a heating rate of 10°C/min. Crystallinity of the CWPU) films was verified by X-ray diffraction (XRD; RINT Ultima III, Rigaku Corporation, Japan). The data collection was recorded in the range of  $2\theta = 5\text{--}60^\circ$ .



SCHEME 1: Synthesis of cationic waterborne polyurethanes (CWPU).

TABLE 1: Chemical composition of CWPU with various internal emulsifier contents.

Formula	Mole ratios				SC <sup>a</sup> (wt%)	BHMAC <sup>b</sup> (wt%)
	NCO MDI	Monoglyceride	OH BHMAC	EG		
CWPU-1	0.84	1.0	0.1	0.1	61.37	2.80
CWPU-2	0.91	1.0	0.2	0.1	58.06	5.32
CWPU-3	0.98	1.0	0.3	0.1	55.08	7.56

<sup>a</sup>Soft segment content: mass of monoglyceride/mass of (monoglyceride+MDI+EG+BHMAC). <sup>b</sup>BHMAC content: mass of BHMAC/mass of (monoglyceride+MDI+EG+BHMAC).

A commercial peak fitting module (PFM) inbuilt in Microcal Origin 7.5 software<sup>16</sup> was used for decomposition of single peak data from CWPU sample peak clusters. The PFM was operated through a wizard interface, and a Gaussian function was used as a fitting function for symmetrical peaks. The determination of the amorphous to crystalline percentage was obtained from peak area ratios. Morphology of the cationic waterborne polyurethane was observed using a Philips TECNAI 20 transmission electron microscope (TEM). Dis-

persions were prepared and diluted with distilled water to about 0.1 wt%. One drop of the diluted dispersion was placed on the coated side of a 200-mesh nickel grid. After drying, the polymer thin layer was stained by OsO<sub>4</sub> before observation.

To evaluate the coating properties, films were formed by applying the obtained CWPU on tin plates using a film applicator. Thickness of each film was fixed at approximately 30 μm. Samples were then tested for hardness based on ASTM D3363 using a mechanical scratch test apparatus

TABLE 2: Properties of waste oil and the as-prepared monoglyceride.

Sample	IV (g I <sub>2</sub> /100 g)	AV (mg KOH/g)	OH (mg KOH/g)	Viscosity (cP)	M <sub>w</sub> (g/mol)
Waste oil	91	0.48	1.8	95	1,041
Monoglyceride	42	0.50	125.0	140	1,280

(Sheen Instruments Ltd., Santa Fe Springs, CA, USA); for flexibility based on ASTM D522 using a conical mandrel test apparatus (Sheen Instruments Ltd., Santa Fe Springs, CA, USA); and adhesion using a crosscut tape method based on ASTM D3359 Method B. Water and alkali resistances were analyzed based on ASTM D1647.

**2.5. Antibacterial Activity.** Antibacterial activities of the CWPU films were studied against both Gram-positive *Staphylococcus aureus* ATCC 6538P (*S. aureus*) and Gram-negative *Escherichia coli* ATCC 8739 (*E. coli*) as model bacteria, carried out according to the shaking flask method. Each model bacteria was cultured in tryptone soy broth (TSB) at 37°C for 18 h and then diluted with normal saline solution (NSS; 0.85% NaCl) to prepare a 10<sup>8</sup> CFU/ml inoculum. Then, the bacterial solutions were further diluted into 10<sup>5</sup> CFU/ml in peptone solution. Each sample of film (~200 mg) was suspended in 3 ml of inoculum diluted to 10<sup>5</sup> CFU/ml and incubated in a rotary shaker at 37°C for 0, 3, 6, and 24 h, respectively. After each time period, each sample was removed and 20 μl of solution was withdrawn and diluted by continuous 380 μl dilution with PBS. Afterward, 100 μl of each serial dilution was withdrawn and discharged into a sterile dish. After overnight incubation at 37°C, colony-forming units on the Petri dish were counted. Viability of bacteria cultured with a polyurethane sample without BHMACH and grown under the same conditions was used as a control. Values were reported as the means of three replicates. Bacterial reduction (%) was calculated according to the following equation:

$$\% \text{Bacterial reduction} = \frac{N_0 - N}{N_0} \times 100, \quad (1)$$

where  $N_0$  is the number of counted colonies in the control group (CFU/ml) and  $N$  is the number of counted colonies (CFU/ml) in the test group at the specified times.

**2.6. Statistical Analysis.** Data were presented as means ± standard errors of the means ( $n = 3$ ). A 1-way ANOVA was used to compare the means of different data sets, and statistical significance was accepted at the 0.05 confidence level ( $p < 0.05$ ).

### 3. Results and Discussion

**3.1. Properties of Waste Frying Oil and the As-Prepared Monoglyceride.** Normally, properties of the raw materials strongly affected the reaction as well as properties of the obtained products. Waste oil must first be characterized and its properties are illustrated in Table 2. The IV value which measures the degree of unsaturation was 91 g I<sub>2</sub>/100 g

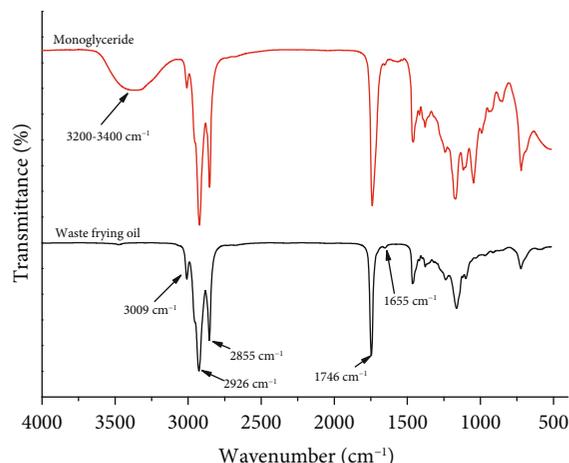


FIGURE 1: FT-IR spectra of waste frying oil and the as-prepared monoglyceride.

of sample. The AV value which represents the amount of free fatty acid occurring from hydrolysis of triglycerides was 0.48 mg KOH/g of sample. The OH value which measures the number of hydroxyl groups was 1.8 mg KOH/g of sample. In addition, the molecular weight ( $M_w$ ) and viscosity of waste oil were 1,041 g/mol and 95 cP, respectively. For the as-prepared monoglyceride, the IV value decreased to 42 g I<sub>2</sub>/100 g of sample and the OH value increased to 125.0 mg KOH/g of sample. These results indicated that alcoholysis reaction took place whereby the ester moieties of oil were partially replaced with hydroxyl groups of glycerol to form monoglycerides. The existence of monoglyceride was also confirmed by complete solubility in ethanol. In addition, the molecular weight and oil viscosity also increased to 1,280 g/mol and 140 cP, respectively. Gradual increase in molecular weight contributed to the observed increase in oil viscosity and was explained by further dimerization or polymerization through peroxide products presenting in waste oil [22].

To verify the chemical structure of waste oil and the as-prepared monoglyceride, FT-IR was performed. Figure 1 illustrates the FT-IR spectrum of waste oil with characteristic absorption peaks coinciding with the general evidence of triglyceride structure [24], including absorption intensity at 3009 cm<sup>-1</sup> (C=C-H stretching of aliphatic fatty acid), 2926 and 2855 cm<sup>-1</sup> (C-C-H stretching), 1746 cm<sup>-1</sup> (C=O stretching of ester linkages), and 1655 cm<sup>-1</sup> (C=C stretching of aliphatic fatty acid). For the as-prepared monoglyceride, the FT-IR spectrum displayed characteristic absorption similar to the spectrum of waste oil, except for a broad characteristic absorption peak in the range of 3200-3400 cm<sup>-1</sup> attributed to the presence of hydroxyl groups.

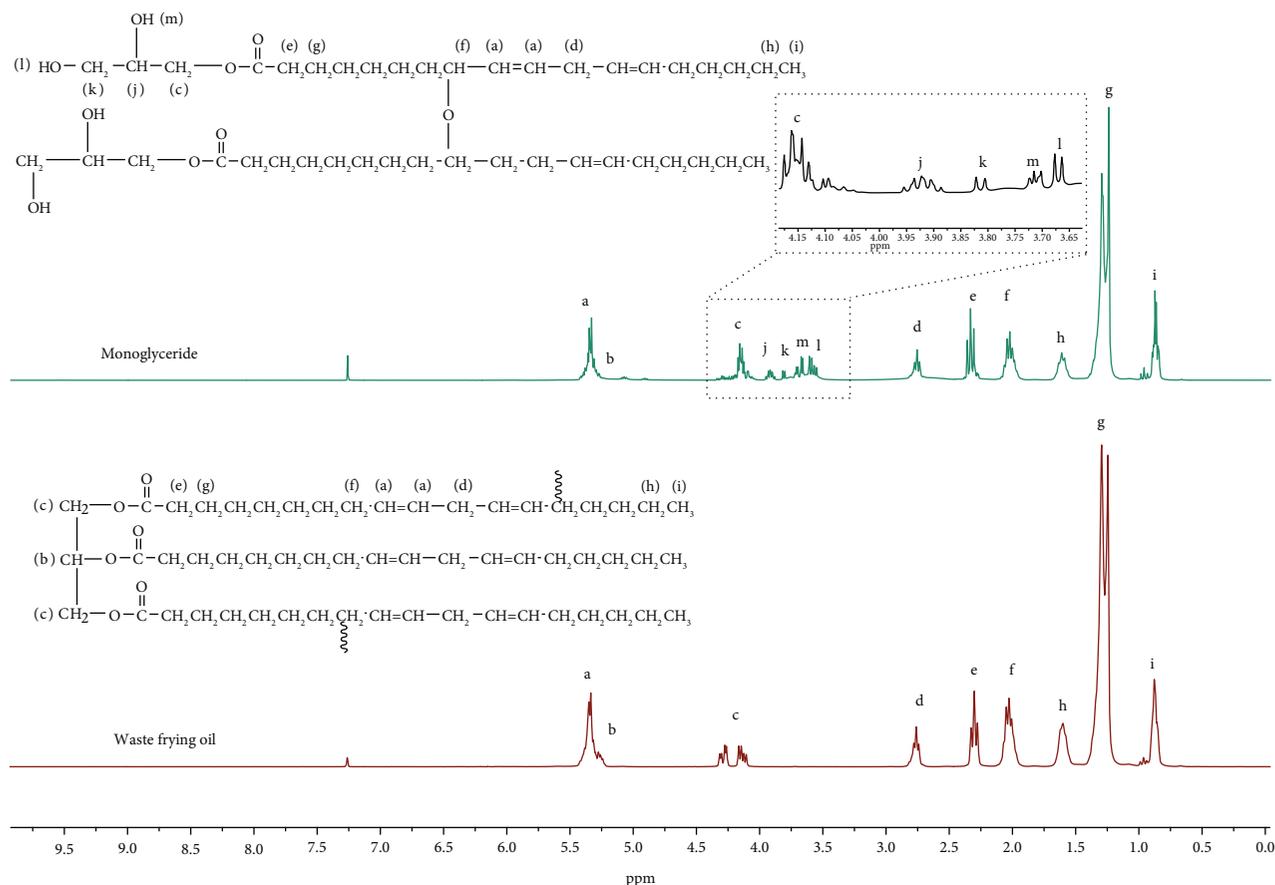


FIGURE 2:  $^1\text{H-NMR}$  spectra of waste frying oil and the as-prepared monoglyceride.

To confirm the alteration of chemical structure,  $^1\text{H-NMR}$  was performed. Figure 2 illustrates the  $^1\text{H-NMR}$  spectrum of waste oil which also showed relatively well-defined characteristics of triglyceride structures. Characteristic peaks at 0.87-0.91 ppm corresponded to protons of the terminal methyl group ( $-\text{CH}_3$ ). Peaks at 1.26-1.40 ppm were identified as protons of all the internal methylene groups ( $-\text{CH}_2-$ ) presenting in the fatty acid chains. Peaks at 1.55-1.65 ppm represented protons of the methylene group ( $-\text{CH}_2$ ) attached next to and above the terminal methyl group. Peaks at 2.0-2.1 ppm corresponded to allylic protons ( $=\text{C}-\text{C}-\text{H}$ ), at 2.25-2.35 ppm for protons of ester groups and at 2.70-2.80 ppm for  $\text{CH}_2$  of double allylic protons ( $=\text{C}-\text{CH}_2-\text{C}=\text{C}$ ). Characteristic peaks at 4.10-4.30 ppm indicated protons of glyceride moiety, while peaks of vinylic protons ( $=\text{C}-\text{H}$ ) moiety appeared at 5.30-5.40 ppm. For the as-prepared monoglyceride, new signal intensities of methylinic proton ( $-\text{CH}-\text{OH}$ ) of glycerol moiety appeared in the region of 3.8-4.0 ppm and protons associated with the hydroxyl groups in the region of 3.5-3.8 ppm.

**3.2. Characterization of Cationic Waterborne Polyurethanes (CWPU)s.** Chemical structures of CWPU)s were investigated by FTIR and  $^1\text{H-NMR}$  spectroscopy. As shown in Figure 3, characteristic absorption peaks of polyurethane

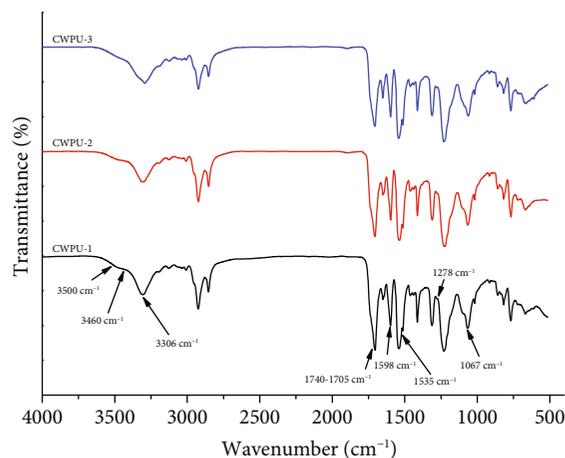


FIGURE 3: FT-IR spectra of cationic waterborne polyurethanes (CWPU)s with various internal emulsifier contents.

were observed at 3460  $\text{cm}^{-1}$  and 3306  $\text{cm}^{-1}$  assigned to  $-\text{N}-\text{H}$  stretching, 1740-1705  $\text{cm}^{-1}$  assigned to carbonyl stretching ( $\text{C}=\text{O}$ ), and 1535  $\text{cm}^{-1}$  assigned to  $-\text{N}-\text{H}$  bending. An intensive absorption peak due to ring stretching of MDI was also observed at 1598  $\text{cm}^{-1}$ . In addition, peaks at 1278  $\text{cm}^{-1}$  and 1067  $\text{cm}^{-1}$  were assigned to the stretching vibration of  $\text{N}^+-\text{C}$  bonds of quaternary ammonium

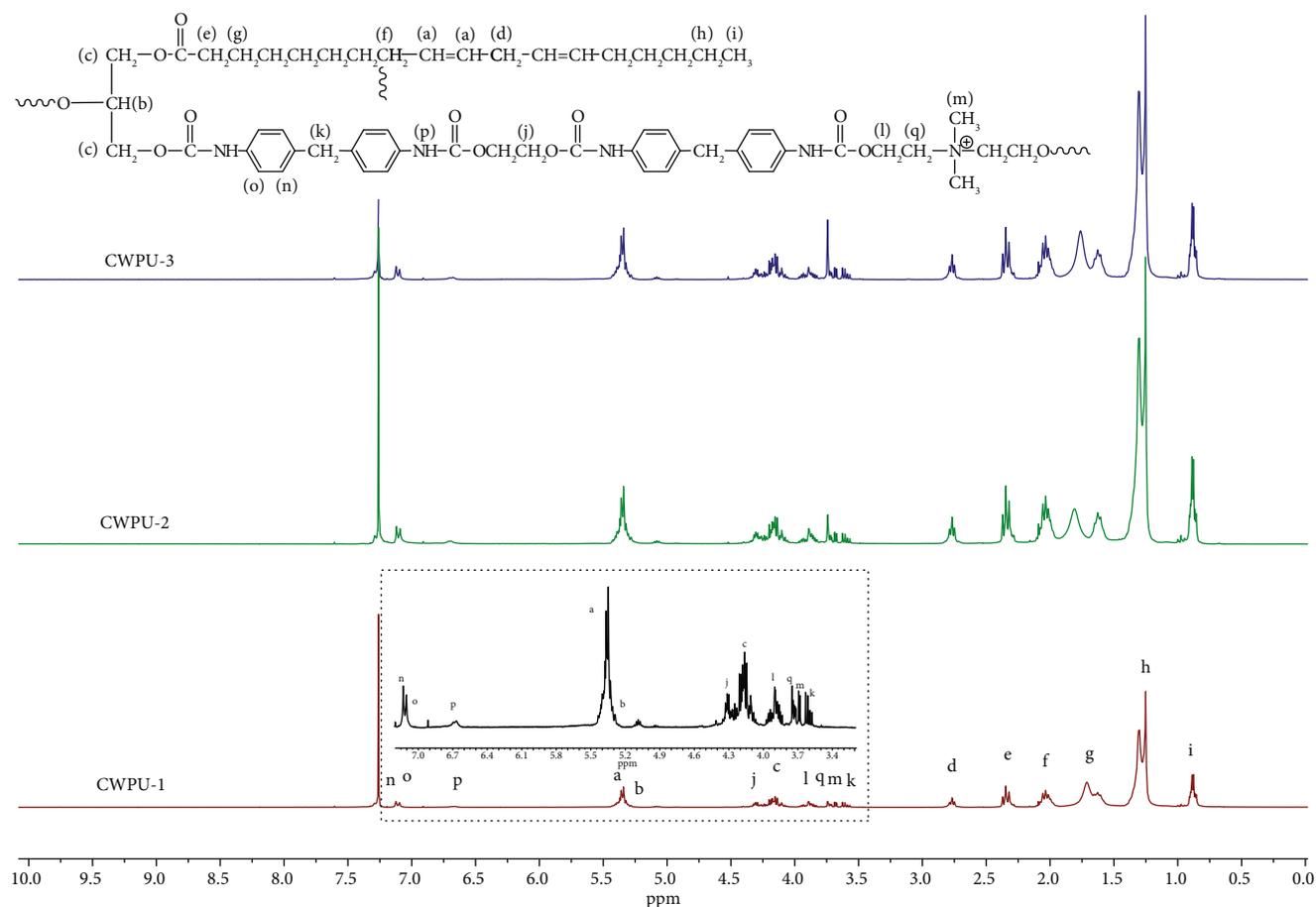


FIGURE 4:  $^1\text{H}$ -NMR spectra of cationic waterborne polyurethanes (CWPU) with various internal emulsifier contents.

moieties. This result indicated the success of incorporating BHMACH into the polyurethane structures. There was no peak at  $2270\text{ cm}^{-1}$ , indicating that the isocyanate groups of the MDI had completely reacted. However, characteristic absorption peaks of hydroxyl groups at  $3500\text{ cm}^{-1}$  were observed because of the excess hydroxyl groups in the formulae.

To confirm the chemical structure,  $^1\text{H}$ -NMR spectra were performed as illustrated in Figure 4. Corresponding to the FT-IR results, the  $^1\text{H}$ -NMR spectra of CWPU also showed relatively well-defined characteristics corresponding to the presence of triglyceride structures. Signals corresponding to the aromatic protons of MDI appeared between 7.18 and 7.35 ppm, and methylene protons ( $-\text{CH}_2-$ ) of MDI appeared at 3.78 ppm. Presence of the urethane bond was confirmed by signals at 6.56–6.70 ppm. In addition, presence of BHMACH in CWPU was confirmed by methylene protons of quaternary ammonium ( $\text{N}^+-\text{CH}_3$ ) at 3.53 ppm.

Hydrogen bonding is an important characteristic which has a significant effect on the properties of polyurethanes [17]. Hydrogen bonds involve the N–H bonds of the amide group as the donor and the urethane carbonyl or carbonyl group in the triglycerides as acceptor [25]. Thus, FT-IR spectra were used to investigate the phase structures of CWPU. As shown in Figure 5, a stretching band was observed

at  $\sim 3306\text{ cm}^{-1}$ , corresponding to the hydrogen-bonded N–H stretching vibration. A small shoulder peak at  $3460\text{ cm}^{-1}$  was attributed to nonhydrogen-bonded N–H stretching, indicating that most of the amide groups in the polyurethane films were involved in hydrogen bonding. The peak of the C=O stretching region appeared to be composed of three overlapping bands at around 1740, 1729, and  $1705\text{ cm}^{-1}$ . The peak at  $1740\text{ cm}^{-1}$  was assigned to free C=O stretching, whereas the peaks at  $1729\text{ cm}^{-1}$  and  $1705\text{ cm}^{-1}$  were due to hydrogen-bonded C=O stretching in disordered and crystalline regions, respectively [26, 27]. An ordered hydrogen-bonded carbonyl band was observed here, indicating the semicrystalline nature of CWPU. Crystallinity in polyurethane is commonly considered as an ordered structure of chain segments owing to hydrogen bond interactions between the soft and hard phases occurring in polyurethanes [28]. However, characteristic absorption peaks of the ordered structures decreased as the amount of BHMACH increased. This evidence was explained by the steric effect of methyl groups on BHMACH structure that hindered the close packing ability to form an ordered structure.

The semicrystalline nature of CWPU was confirmed by X-ray diffraction (XRD) analysis. As evidenced in Figure 6, the diffraction patterns exhibited broad peaks at  $2\theta$  angles around 6.3, 15.4, 17.6, 18.4, 19.7, 20.9, 23.1, 26.2, and  $41.6^\circ$ .

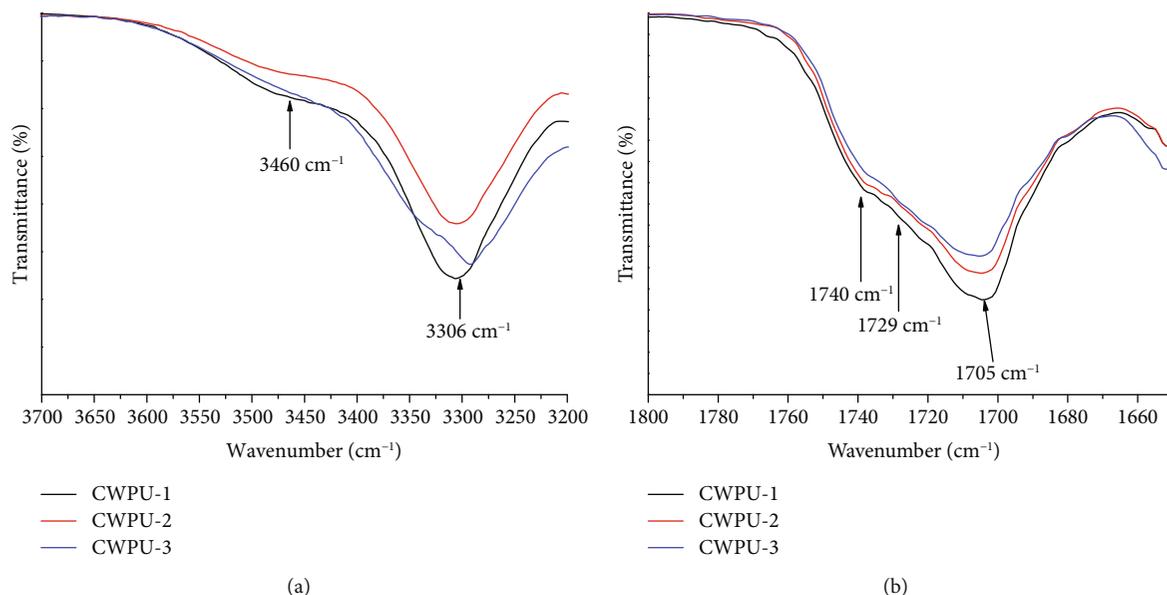


FIGURE 5: FT-IR spectra of cationic waterborne polyurethanes (CWPU) with various internal emulsifier contents in (a) N-H stretching region and (b) C=O stretching region.

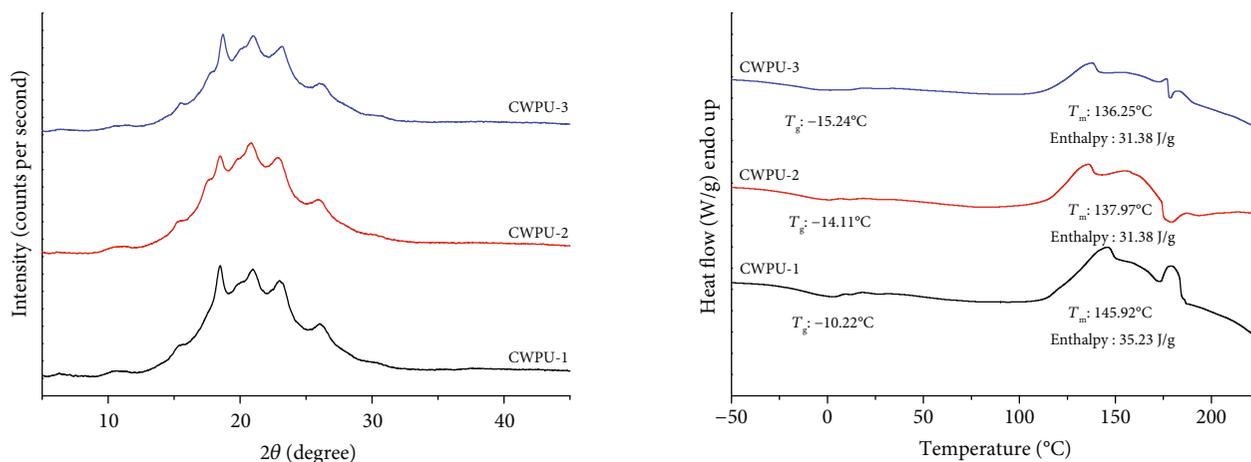


FIGURE 6: XRD patterns of cationic waterborne polyurethanes (CWPU) with various internal emulsifier contents.

FIGURE 7: DSC thermograms of cationic waterborne polyurethanes (CWPU) with various internal emulsifier contents.

TABLE 3: Degree of crystallinity of cationic waterborne polyurethanes (CWPU) with various internal emulsifier contents.

Formula	Degree of crystallinity (%)
CWPU-1	60.3
CWPU-2	48.3
CWPU-3	47.6

indicating some degree of crystallinity in hard segments that might be occurred from the reaction of MDI and EG. However, diffraction peaks of CWPU became weaker as the amount of BHMAC increased. This observation corresponded to reduction in the degree of crystallinity as shown in Table 3. CWPU-1 had 60.3% crystallinity, whereas

CWPU-2 and CWPU-3 were less crystalline at 48.3% and 47.6%, respectively. This implied that the orientation of polymer chains was significantly disturbed through the steric effect of methyl groups on BHMAC structure that hindered the close packing ability to form crystalline.

The effect of BHMAC contents on the degree of crystallinity was also confirmed by using DSC. As shown in Figure 7, all of CWPU provided endothermic peaks of glass transition temperature ( $T_g$ ) and crystalline melting temperature ( $T_m$ ) which their values were depended on the amount of internal emulsifier. The results showed that the intensity of melting endothermic peaks decreased as the amount of BHMAC increased, which suggests that the crystallization of the obtained CWPU was inhibited by the BHMAC.

TABLE 4: Selected TEM images of cationic waterborne polyurethanes (CWPU) with various internal emulsifier contents.

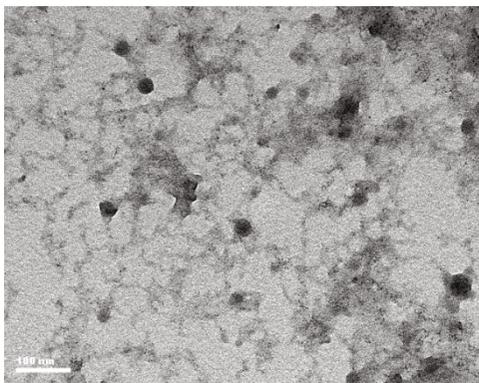
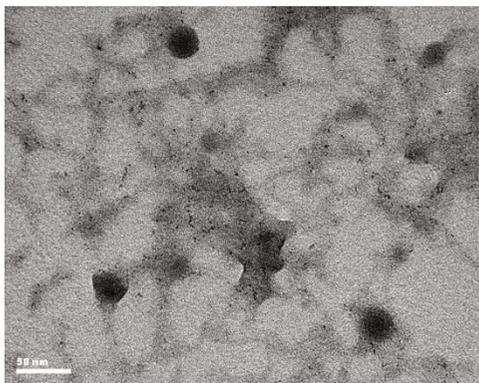
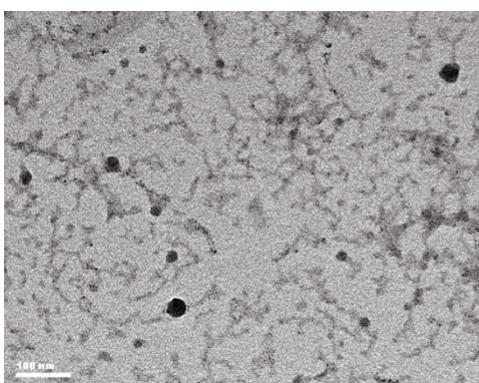
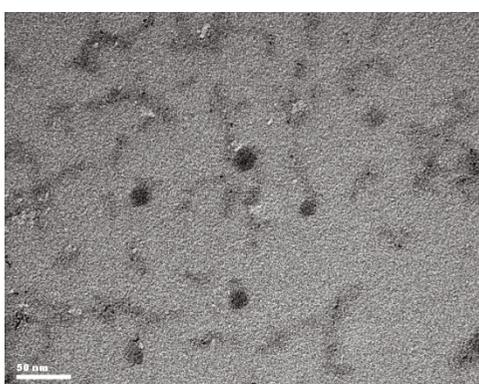
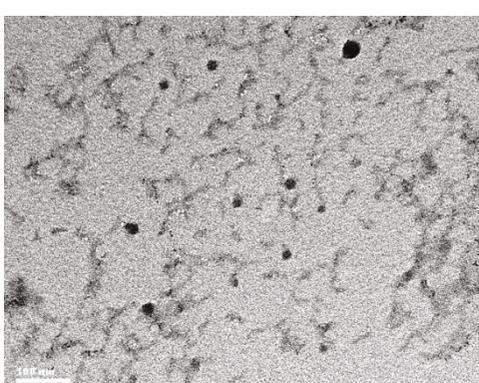
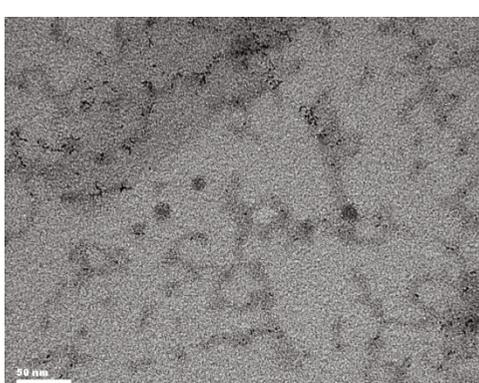
Formula	Scale bar = 100 nm	Scale bar = 50 nm
CWPU-1		 Particle size: $28.75 \pm 4.05$ nm
CWPU-2		 Particle size: $21.25 \pm 3.88$ nm
CWPU-3		 Particle size: $13.38 \pm 2.56$ nm

Table 4 shows selected TEM images of CWPU particles prepared from various BHMAL contents. TEM images showed regular shapes of nanoparticles with a uniform particle size distribution. A particle size of about  $28.75 \pm 4.05$  nm diameter was obtained from CWPU-1, and the particle size gradually decreased to  $21.25 \pm 3.88$  nm for CWPU-2 and  $13.38 \pm 2.56$  nm for CWPU-3. Decrease in average particle size with increasing concentrations of internal emulsifier was reported by several studies [15, 29, 30]. Many factors play key roles in the particle size of waterborne polyurethanes including hydrophilicity, prepolymer viscosity, chain rigidity, chemical structure of the soft segment, and

cross-linking [29, 30]. In this case, particle size of CWPU might be controlled by the amount of internal emulsifier. Higher amounts of BHMAL facilitate dispersion of the urethane prepolymers, resulting in smaller particle size for the corresponding CWPU particles.

**3.3. Properties of Cationic Waterborne Polyurethane Films.** Film formation of waterborne polyurethanes is extremely complex due to the heterogeneous composition along with simultaneous progression of several physicochemical processes, including water evaporation, molecular interdiffusion, phase separation, and droplet coalescence [31–33].

TABLE 5: Mechanical properties of cationic waterborne polyurethane (CWPU) films with various internal emulsifier contents.

Formula	Hardness <sup>a</sup> (g)	Flexibility <sup>b</sup> (Ø, mm)	Adhesion <sup>c</sup>
CWPU-1	200	3	3B
CWPU-2	300	3	3B
CWPU-3	300	3	3B

<sup>a</sup>Maximum criterion of hardness was 1000 g and minimum was 50 g.

<sup>b</sup>Maximum criterion of flexibility was 3 and minimum was 20. <sup>c</sup>Maximum criterion of adhesion was 5B and minimum was 0B.

TABLE 6: Water, acid, and alkaline resistance of cationic waterborne polyurethane (CWPU) films with various internal emulsifier contents.

Formula	Water	Acid	Alkaline <sup>b</sup>
CWPU-1	Excellent <sup>a</sup>	Excellent <sup>a</sup>	3 : 15
CWPU-2	Excellent <sup>a</sup>	Excellent <sup>a</sup>	3 : 28
CWPU-3	Excellent <sup>a</sup>	Excellent <sup>a</sup>	3 : 35

<sup>a</sup>Films did not change after immersion in distilled water or 5% v/v H<sub>2</sub>SO<sub>4</sub> for 24 h at room temperature. <sup>b</sup>Time (h : min) detected when films exhibited blistering after immersion in 5% (w/v) NaOH at room temperature.

The interdiffusion of polymer chains from one particle into another to create cohesive strength strongly depends on their chain mobility and plays a major role in the final properties of the obtained films. From the literature, waterborne polyurethane films synthesized from asymmetrical monomer structures provided an amorphous nature that enhanced molecular interdiffusion between particles, resulting in better mechanical properties than a crystalline nature [32].

Table 5 illustrates the coating properties of CWPU films. A slight difference in coating properties was observed as the amount of BHMACH increased. All coated films had smooth and bubble-free surfaces. Hardness of all coated films on the tin plate was in the range of 200-300 g, giving a moderate hardness for all films. Additionally, CWPU-2 and CWPU-3 had higher hardness than CWPU-1 because they had lower degree of crystallinity resulting in higher cohesive strength between the particles than CWPU-1. Crosscut adhesion on each coated film was performed to investigate its adhesion. Results indicated that about 10% of the coated films were removed for each coated film that was classified as 3B in the adhesion test. The inferior mechanical properties might be due to the crystalline nature of the obtained CWPU which hindered chain mobility to form molecular interdiffusion, resulting in poor cohesive strength between the particles. However, films showed no breaks or cracks and provided excellent flexibility. This might be due to the lower cohesive strength between particles that enhanced structural flexibility. Acid resistance, alkali resistance, and water resistance of the coated films are shown in Table 6. No change was observed for all films during acid resistance

and water resistance tests; however, all films exhibited poor alkali resistance because of the presence of ester groups that are hydrolyzed under alkaline conditions [34].

**3.4. Antibacterial Activity of Cationic Waterborne Polyurethane Films.** From the literature, polymers containing quaternary ammonium groups are known to be effective against a large spectrum of microorganisms [35, 36]. Bactericidal mechanism activity of quaternary ammonium moieties is not entirely clear; however, it is anticipated to result from direct electrostatic adsorption between positive charges of the polymer surface and the negatively charged bacterial cell wall. This can be explained by the diffusion of quaternary ammonium moieties into the bacterial cell wall and binding to the cytoplasmic membrane, disruption of the membrane by alkyl groups, and release of cytoplasmic constituents (K<sup>+</sup> ions) which finally cause cell death [35, 36]. In this research, the bactericidal activity of CWPU films toward Gram-positive *S. aureus* and Gram-negative *E. coli*, a major cause of various human and animal infections, was further investigated in terms of the time kill assay by observing the viability of the model pathogen cultured with these polyurethanes for 0, 3, 6, and 24 h. For comparison, bactericidal activity of a control polyurethane sample without BHMACH was also prepared.

Results obtained from the shaking flask test are given in Table 7. Viability of the bacteria decreased as culturing time increased, except for control polyurethane that showed no antibacterial activity. For 3 h of incubation, reductions in *E. coli* bacterial growth of 94.07% (CWPU-1), 96.30% (CWPU-2), and 97.59% (CWPU-3) were obtained and reductions increased to more than 99% after 6 h of incubation for all samples. However, reductions in *S. aureus* bacterial growth of all samples were greater than 99% after 3 h of incubation. At a given culturing time, efficiency of bacterial reduction also increased as the amount of BHMACH further increased. Thus, CWPU-3 provided the highest antibacterial activity because of greater quaternary ammonium content incorporated in the polymer chains. As expected, *S. aureus* was more susceptible to the obtained CWPU than the other pathogen. This observed difference was attributed to the cell membrane structure of Gram-negative bacteria which served as an additional permeability barrier to resist bactericidal moieties [35].

## 4. Conclusions

Cationic waterborne polyurethanes (CWPU) incorporated with an antibacterial moiety as BHMACH were successfully synthesized using monoglyceride derived from waste frying oil as the starting raw material for antibacterial film coatings. The BHMACH contents played an important role in controlling particle size of the obtained polyurethanes as well as mechanical properties of the corresponding CWPU films which were very pliable, with moderate adhesion and hardness. All films exhibited excellent resistance to water and dilute acid but poor resistance to dilute alkali. Bactericidal activity of the cationic waterborne polyurethane films toward the model Gram-positive

TABLE 7: Bacterial reduction of Gram-positive bacteria *S. aureus* and Gram-negative bacteria *E. coli* after incubation with cationic waterborne polyurethane (CWPU) films for 0, 3, 6, and 24 h evaluated by the shaking flask method.

Sample	Bacterial reduction (%)							
	0 h	Gram-positive bacteria <i>S. aureus</i>			Gram-negative bacteria <i>E. coli</i>			
		3 h	6 h	24 h	0 h	3 h	6 h	24 h
CWPU-1	0	99.7 ± 0.6	99.8 ± 0.5	99.9 ± 0.2	0	94.7 ± 0.2*	99.5 ± 0.1*	99.9 ± 0.5*
CWPU-2	0	99.9 ± 0.1	99.9 ± 0.5	99.9 ± 0.4	0	96.3 ± 0.5 <sup>#</sup>	99.9 ± 0.4 <sup>#</sup>	99.8 ± 0.5 <sup>#</sup>
CWPU-3	0	99.9 ± 0.1	99.9 ± 0.2	100.0 ± 0.1	0	97.6 ± 0.9 <sup>†</sup>	99.9 ± 0.6 <sup>†</sup>	100.0 ± 0.1 <sup>†</sup>
Control <sup>a</sup>	0	0.0	0.0	0.0	0	0.0	0.0	0.0

<sup>a</sup>Polyurethane sample without BHMAL. \*,<sup>#</sup>,<sup>†</sup> indicates significant difference at the 0.05 level ( $p < 0.05$ ).

bacteria *S. aureus* and model Gram-negative bacteria *E. coli* increased with increasing amounts of BHMAL. Results offer an alternative utilization of waste frying oil as a sustainable feedstock for the polymer industry.

### Data Availability

Any additional data is available upon request from the corresponding author.

### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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