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Synthesis and Characteristics of *m*-TMXDI-based Waterborne Polyurethane Modified by Aqueous Chitosan

Hsien-Tang Chiu1*, Xiao-Yong Hsu1, Hui-Min Yang1 and Yu-Sian Ciou2

¹Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan ²Department of Testing and Certification, Taiwan Textile Research Institute, New Taipei City, Taiwan

Abstract

Environmental issues have received increasing attention recently. Compared to solvent borne polyurethane (PU), waterborne PU requires relatively little solvent dosage. Therefore, waterborne PU is used to replace traditional solvent borne PU to satisfy environmental and economic requirements. Chitosan is a material that has been discussed widely in recent years because of its exceptional antimicrobial performance, biocompatibility, bioactivity, and biodegradability.

This study primarily uses a prepolymer mixing process to synthesize m-TMXDI based waterborne PU with different ratios of aqueous chitosan and chain extenders (ethylenediamine; EDA). Modification reactions are conducted and waterborne PU modified by aqueous chitosan is synthesized. Through this experimental method, emulsions modified by different compositional proportions of aqueous chitosan to EDA were tested. For material determination, FTIR, NMR, and XPS were used to conduct chemical structure determination and GPC molecular weight tests. Regarding membrane properties, a contact angle meter analyzed the hydrophility of the membrane and the antimicrobial performance of the prepared waterborne PU membrane against *Staphylococcus aureus* and *Escherichia coli*. The test results showed the following characteristics: (1) The terminal NCO group of the waterborne PU (WPU) was bonded with the terminal amino group(-NH2) of chitosan, and (2) as the proportion of aqueous chitosan added increased, improvements were observed regarding molecular weight, hydrophility, and antimicrobial performance.

Keywords: Prepolymer; Emulsions; Antimicrobial; Adhesives; Aqueous; Waterborne

Introduction

Because of recent increasing environmental consciousness, waterborne polyurethane (WPU) has been widely accepted. This is because it can reduce solvent use and volatile organic compound (VOC) percentage, thereby preventing excessive solvents from evaporating into atmospheric layers and causing pollution [1]. It also contained the merits of being non-toxic, odorless, safe to use and present no harm to the environment have been developed and widely used in coatings, adhesives, surface finishing, paper and textile industries [2-5]. Consequently, WPU presents extraordinary environmental protection performance. WPU thin-films membranes with polyester glycol as the soft segment possess higher tensile strength and WPU with polyether glycol as the soft segment improves water vapor permeability [6].

On the other hand, some approaches were reported about grafting hydrophilic polymer, such as poly(ethylene glycol) (PEG) onto chitin and chitosan, to improve their affinity to water or organic solvent [7-10]. As reported in our previous article [11], m-TMXDI based anionic poly(urethane urea) dispersions were prepared by a prepolymer mixing process and WPU/AC hybrid emulsions were prepared by the emulsion polymerization of a mixture of AC monomers (styrene, methyl methacrylate and butyl acrylate) in the presence of WPU.

Chitosan possesses excellent biocompatibility (minimal toxicity and no antibody generation), bioactivity (it has the ability to lower cholesterol, blood lipids, and blood pressure and to improve immune function), film-forming properties, gel-forming properties, and positive electrical charges in acidic solutions (antimicrobial, adsorbing, and arresting hemorrhage). Therefore, Chitin and chitosan are widely applied in agriculture, medicine, food products, chemical engineering, and environmental protection fields. Chitosan has been a popular natural polymer material exploited in recent years.

This experiment investigated evaluation assessment technology for the proposed environmental protection WPU to develop properties for an environment-friendly, antimicrobial WPU biomedical material that fulfill evaluations.

Experiments

Materials

The materials used by this study were N-Methyl-2-pyrrolidone (NMP) from the Riedel-dehaën company, USA; Dimethylol propionic acid (DMPA) from the ACROS company, USA; Poly(tetramethylene ether) glycol (PTMEG-2000, Mn=2000), a polyhydric alcohol fabricated by Scientific Polymer Products (SP²) Inc., USA; 1,3-Bis(2-isocyanato-2-propyl) benzene (m-TMXDI of reagent grade), an isocyanate fabricated by Tokyo Kasei Kogyo Co. (TCI), Japan; Triethyl amine (TEA) and Ethylene diamine (EDA) from the TEDIA company, USA; 2-Amino-2-methyl-1-propanol (product number: AMP-95) fabricated by the ANGUS company, USA; and aqueous chitosan (product number: W031) fabricated by the CHARMING and BEAUTY Co. Ltd., Taiwan.

*Corresponding author: Hsien-Tang Chiu, Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, Tel: 00923339350722; E-mail: xyhsu.0879@ttri.org.tw

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Preparation of *m*-TMXDI-based WPU and WPU/aqueous chitosan

Preparation of *m*-TMXDI-based WPU prepolymer: *m*-TMXDIbased WPU prepolymer was prepared by the prepolymer mixing process [2]. The prepared WPU solid content for this experiment was controlled at 40% using an 8wt% of DMPA. A constant NCO/OH=1.8 was used to synthesize 1000 ml of WPU emulsion. The required content wt. % and NCO% theoretical values are shown in Table 1. First, we placed 2,2-Bis(hydroxyl-methyl) propionic acid (DMPA) containing a hydrophilic group into a four-mouthed reaction flask before adding an N-methyl -2-pyrrolidone (NMP) solvent. After sufficiently mixing the solution, we added polytetramethylene ether glycol with a molecular weight of 2000 (PTMEG 2000) into nitrogen gas and slowly increased the temperature to 70°C, stirring at a rotation speed of 300 rpm. After the solution in the four-mouthed reaction flask was completely dissolved, we gradually increased the temperature to 85°C and added precisely pre-weighted 1,3-Bis(2-isocyanato-2-propyl)benzene, also known as m-tetramethylene xylene diisocyanate (m-TMXDI), into the flask to initiate the WPU synthesis reaction. During the reaction process, NCO% must be measured continuously based on the ASTM D2572 method. Following approximately 1 h of heating and stirring reactions, the NCO% reached the expected value. When the NCO% achieved the theory value, we decreased the oil bath temperature to 60°C to prevent the subsequently added neutralizer triethylamine (TEA) from evaporating. Finally, the product in the four-mouthed reaction flask constituted WPU prepolymer.

Preparation of WPU emulsions: The synthesis reaction of the *m*-TMXDI-based WPU is shown in Figure 1. The addition or additive volume ratio in this stage is shown in Table 2. After the 60°C TEA neutralized WPU prepolymer was evenly stirred for 20 min, the prepolymer emulsion had an electrically charged ionic state, achieving the neutralizing effect. In this stage, because of the influence of the TEA addition and the time factors, the NCO% content decreased. Therefore, the NCO% content of the emulsion [13] was determined again and the subsequent required additive volume of the chain extenders was confirmed. Subsequently, the temperature of the WPU prepolymer was reduced to 35°C. An ice water bath was prepared for use to

initiate the water dispersible reaction. After the temperature decrease was completed, the WPU prepolymer in the four-mouthed reaction flask was slowly added to deionized (DI) water at a maintained water temperature of 15°C. Simultaneously, the water-diluted chain extender ethylenediamine anhydrous (EDA) solution was dripped slowly into the flask. Because EDA and WPU prepolymers have an extremely fast reaction speed, the stirrer must stir the solution at a high rotation speed of 1200 rpm to avoid phase separation. After the WPU prepolymer was completely added to the DI water and the titration with the EDA chain extender was finished, the high-speed stirring continued for 20 min before adding 0.25% pH conditioning agents and stirring for an additional 20 min to maintain a stable base state of pH = 8 to 8.5. Consequently, the storage stability of the emulsion was controlled. Through these steps, we obtained stable WPU emulsion or dispersion.

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Preparation of WPU emulsions modified by aqueous chitosan: The synthesis reaction of *m*-TMXDI-based WUP modified by aqueous chitosan are show in Figure 2. The additive volume ratio of this stage is shown in Tables 2 and 3. WPU prepolymer was added to the TEA neutralizer at 60°C and evenly stirred for 20 min. This enabled the prepolymer emulsion to be in an electrically charged ionic state, thereby attaining a neutralizing effect. In this stage, because of the influence of the TEA addition and time factors, the NCO% content decreased. Therefore, an additional determination regarding the NCO% content of the emulsion [14], and subsequent required additive volumes of chain extenders and aqueous chitosan, were conducted. Subsequently, the temperature of the PU prepolymer is reduced to 35°C. The water dispersible reaction was conducted using a prepared ice water bath. After the temperature was successfully decreased, the WPU prepolymer in the four-mouthed reaction flask was slowly added into the DI water at a temperature below 15°C. Additionally, the water-diluted chain extender EDA (TEDIA) and water-dissolved aqueous chitosan were separately loaded into the burette to slowly drip into the PU prepolymer. Stirring at a high rotation speed of 1200 rpm, the stirrer used high shear stress to enable the EDA and aqueous chitosan to rapidly react with the terminal NCO group of the PU to avoid entangling molecular chains. After the WPU prepolymer was completely added to the DI water and the titration with EDA chain

NCO/OH	<i>m-</i> TMXDI (wt%) ^a	PTMEG-2000 (wt%) ^a	DMPA (wt%) ^a	NMP (wt%) ^b	NCO% of prepolymer predicted ^c		
1.8	38.07	53.93	8	10	5.82		
a. NCO/OH= <u>equiv. of DMPA + equiv. of PTMEG2000</u>							
b. NMP (wt.%) content is the dosage or use percentage of the overall aqueous PU weight of the sample.							
c. NCO% = (equiv. of TMXDI – equiv. of DMPA – equiv. of PTMEG2000) weight of sample × 42.02 × 100%							

 Table 1: Primary compound proportions of the *m*-TMXDI-based WPU prepolymer.

Final NCO% of the prepolymer (measured value through experiment ^a)	TEA (wt%) ^b	EDA/H ₂ O (wt%)°	Chitosan/ H ₂ O	Pure water ^d (wt%)		
3.52	6.03	2.51/25	X ^e /25	200		
a. Synthesized PU prepolymer was measured using the ASTM D2572 method regarding the NCO% after neutralization to determine the dosage or use amount of the chain extender.						

b.TEA(wt%) = (equiv. of DMPA) × TEA M.w.

c.EDA(wt%) = (Final NCO% content × weight of sample× EDA M.w.) ÷ 42 ÷ 100%.

d. Using an overall configuration of 500 ml WPU as the base amount, the ratio equation was as follows: $\frac{200 \text{ (wt%)PU}}{200(\text{wt%)PU} + 50(\text{wt%}) + 250(\text{wt%})\text{PureWater}}$

e. X is the various weight ratios of the aqueous chitosan and EDA based on Table 3.

Table 2: Experimental ratio of the neutralizer, chain extender, aqueous chitosan, and pure water contents of the WPU.





extender and aqueous chitosan was completed, the high-speed stirring continued for 20 min. Finally, a 0.25%pH conditioning agent was added and stirred for 20 min to maintain a pH of 8 to 8.5, resulting in a stable base state. Consequently, the emulsion storage stability was controlled.

No	Sample code	EDA: chitosan Composition (g)	EDA: chitosan NH group molar ratio ²
01	WPU		
02	WPU-CH-O.2	1: 0.2	30: 1
03	WPU-CH-O.4	1: 0.4	30: 2
04	WPU-CH-O.6	1: 0.6	30: 3
05	WPU-CH-1	1: 1	30: 5

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Table 3: Sample Code Designations and Different Formulations of the WPUs.

Through these steps, a series of WPU dispersions were modified using stable aqueous chitosan Table 3.

Preparation of films

Using the perfusion membrane-forming method, we pour WPU emulsion into the membrane or film frame with a membrane thickness of 0.3 mm. Release paper is attached to the bottom of the membrane frame. After allowing the frame to stand at a temperature of 22 to 27°C for approximately 7 days, the primary curdling or congealing occurred in the membrane and on the surface. In addition, to prevent the production of porous membrane surfaces caused by the rapid evaporation of water vapors inside the membrane, we further processed the frame at mid-to-low temperatures (40 to 50°C) for approximately 14 days, and the membranes were dried at a high temperature (90°C) for approximately 30 min to form membranes.

Measurements

FTIR structural analysis

We used an attenuated total reflection (ATR) device method to test the various sample membranes using an FTIR spectrometer. The operational parameters were set as 20 scanning times, a resolution of 8 cm⁻¹, and a wavenumber scanning range from 700 to 4000 cm⁻¹. Using the T percentage value of the various samples, we observed the functional group variation of the sample being tested.

¹³C-NMR and ¹H-NMR spectral analysis

The dried sample was dissolved into either a d6-DMSO solvent with a concentration of 20 mg/ml. The chemical shifts used TMS as the internal standard and were tested using a Bruker Avance-500 MHz FTNMR.

XPS element bond energy analysis

The sample was placed into a load lock chamber and was extracted to less than 10-7 Torr. A high voltage generated high-speed electrons that attacked the aluminum and magnesium and discharged X-rays. When the X-rays struck the sample, the photoelectric current was examined and the electron beam binding energy was determined. Electron beam binding energy can be used to determine what element unknown elements belong to. This experiment used the differences in the element bond energies to assess the element bond structures.

GPC molecular weight test

We dissolved a 0.02 g dried membrane sample into 10 ml tetrahydrofuran. This solution was further filtered through a syringe filter (0.2 µm PVDF Membrane). The tetrahydrofuran was used as the mobile phase, and the flow speed was controlled at 1.0 ml/min with a pressure of 700 psi to determine the molecular weight.

Contact angle test

This test was conducted on a Model 100E machine produced by

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Sindatek Instruments Co., Ltd. The formed membrane samples were placed on a platform horizontally before drawing DI water with a pipette to drip on the material surface. The lower drop dosages had better results. The diameter was best within 0.5 mm. After placing a drop on the material surface, we calculated the contact angle through the extracted side image using video cameras. The measured value of each material was the mean of three measurements.

Antimicrobial efficacy

We used the JIS Z2801-2000 testing method, which is applicable to antimicrobial efficacy or strength tests for products with antimicrobial functions. The bacteria used in this study were *Staphylococcus aureus* ATCC 6538 and *Escherichia coli* ATCC 8739. The antimicrobial activity value = Log (bacterial counts of the control group after 24 h/bacterial counts of the sample group after 24 h. If the antimicrobial activity value was greater than 2, the sample was antimicrobial.

Results and Discussion

Material determination

FTIR: Figure 3a-e show the FTIR spectrum of each sample. We

observed that WPU, WPU-CH-0.2, WPU-CH-0.4, WPU-CH-0.6, and WPU-CH-1 all presented similar characteristic peaks. The broad absorption peak of the 3300-3500 cm⁻¹ soft segment polyol vanished in the WPU, whereas a narrow –NH characteristic peak formed at 3300 to 3400 cm⁻¹, which belongs to the amino group of urea and urethane groups separately. The peak at 1701 cm⁻¹ was the urethane >C=O carbonyl group and the peak at 1654 cm⁻¹ was the urea -COO⁻ group. Therefore, we inferred that the –OH and –NCO reacted to generate the -NHCOO- functional group. The -N=C=O functional group near 2270 cm⁻¹ vanished following reaction. In addition, the 1099 cm⁻¹ transmission peak band belonged to the C-O-C group of aliphatic compounds. In the range from 2950 to 2700 cm⁻¹, the peak belonged to symmetric and asymmetric stretching C-H bonds.

The WPU modified by aqueous chitosan is shown in Figure 3e (i.e., the WPU-CH-1 spectrum). The -NH characteristic peak formed between 3300 to 3400 cm⁻¹, which belongs to the amino group of the urea and urethane groups separately. The peak at 1703 cm⁻¹ was the urethane >C=O carbonyl group, and the peak at 1653 cm⁻¹ was the urea -COO⁻ group. Therefore, we inferred that the –OH and –NCO reacted to generate the -NHCOO- functional group. In addition, the 1071



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cm⁻¹ transmission peak band belongs to the C-O-C group of aliphatic compounds. In the range from 3055 to 2790 cm⁻¹, the peak belonged to the symmetric and asymmetric stretching C-H bonds.

Silva et al. [14] argued that the reactivity of the $-NH_2$ group of chitosan is higher than that of the -OH group. Therefore, the chitosan $-NH_2$ group reacted with the terminal NCO group of the WPU to form the urea group (-NHCONH-). Figure 3a-e show that the 1653 cm⁻¹ characteristic peak of the WPU-CH-1 spectrum was significantly higher in strength than the 1654 cm⁻¹ characteristic peak of the WPU spectrum. This characteristic peak represented the strengthening of the urea structure, indicating that the chitosan $-NH_2$ group reacted with the terminal NCO group of the WPU to generate the urea group; therefore, the urea group strength of the WPU-CH-1 was greater than that of the WPU. Furthermore, the WPU-CH-0.2, WPU-CH-0.4, and WPU-CH-0.6 possessed stronger characteristic peaks (approximately

1650 cm⁻¹), similar to WPU-CH-1.

¹³C-NMR and ¹H-NMR: The WPU analysis spectrum proposed by Chiu [11] was used to compare and analyze this experiment, as shown in Figure 4 (the WPU-CH-1¹³C-NMR spectrum). A number of common chemical shift characteristic peaks were observed: the chemical shifts of the soft segment locations C-1 and C-2 were, respectively, 26.07 ppm and 69.71 ppm. The chemical shift of location C-3 was 154.61 ppm. The characteristic peak strength of C-3 was weaker than that of C-4 in the WPU ¹³C-NMR spectrum proposed by Chiu [11], and the strengths of C-3 and C-4 were nearly identical in the WPU-CH-1¹³ C-NMR spectrum in this study. This indicates that the C-3 characteristic peak strength of the WPU-CH-1 was much stronger than that of the WPU. This proves that the chitosan amino group $(-NH_2)$ reacted with the terminal NCO group of the WPU to generate a more urea structures, thereby strengthening the C-3 strength.





The chemical shifts of the hard segments C-4, C-5, and C-6 were, respectively, 173.8 ppm, 48.48 ppm, and 17.21 ppm. Regarding the isocyanate, the chemical shifts of C-7, C-8, C-9, C-10, C-11, and C-12 were, respectively, 30.1 ppm, 54.21 ppm, 121.17 ppm, 122.23 ppm, and 127.26 ppm. Compared to the WPU analysis spectrum proposed by Chiu [12], the WPU-CH-1 had additional characteristic peaks, as follows: the chemical shift of C-3 and C-19 was 69.48 ppm; the chemical shift of C-16 and C-18 was 66.56 ppm; and the chemical shift of C-14 was 54.45 ppm. The strong characteristic peak of 39.5 ppm was the chemical shift of the d⁶-DMSO solvent.

Figure 5 shows the ¹H-NMR spectrum for WPU using d⁶-DMSO as the solvent. The significant chemical shift at 2.5 ppm was the characteristic peak of the solvent (d⁶-DMSO). The chemical shifts of soft segment locations H-1 and H-2 were, respectively, 3.3192 ppm and 1.5004 ppm. The chemical shifts of isocyanate hard segments H-3, H-4, H-5, H-6, and H-7 were, respectively, 7.4834 ppm, 1.1468 ppm, 7.1404 ppm, 7.3127 ppm, and 7.3652 ppm. The chemical shift for H-8 and H-9 of the hydrophilic ion center were, respectively, 3.3192 ppm and 1.3566 ppm. Because of the identical chemical environment of H-2 and H-8, their chemical shifts were the same: 3.3192 ppm. The H-1 had characteristic peak strength greater than that of H-2, and simultaneously corresponded to 3.3192 ppm and possessed more identical chemical environments; that is, H-1 and H-8 had the same chemical environment.

Figure 6 shows the ¹H-NMR spectrum of WPU-CH-1 using d⁶-DMSO as the solvent. The chemical shift of the d⁶-DMSO solvent was 2.5 ppm Figures 4-6.

As shown in the WPU ¹H-NMR spectrum, the chemical shifts of soft segment locations H-1 and H-2 were, respectively, 3.3514 ppm and 1.4985 ppm. The chemical shifts of the isocyanate hard segments H-3, H-4, H-5, H-6, and H-7 were, respectively, 7.4757 ppm, 1.1558 ppm, 7.1409 ppm, 7.3062 ppm, and 7.3492 ppm. The chemical shifts of the hydrophilic ion center H-8 and H-9 were, respectively, 3.3514 ppm and 1.366 ppm. The characteristic peak of the identical chemical shifts of H-1 and H-8 at 3.3192 ppm was higher than that of H-2 at 1.4985 ppm. The ¹H-NMR spectrum of the WPU-CH-1 had the following additional peaks compared to the ¹H-NMR spectrum of the WPU: H-10 and H-17 were 2.9052 ppm; H-11 was 7.4585 ppm; H-12 was 2.6928 ppm, H-13 and H-18 were 3.288 ppm; and H-14, H-15, and H-19 were 3.9856 ppm. These were novel chemical shift characteristic peaks produced by the modification of the chitosan.

XPS: Figure 7 shows that the bond energy of the WPU thin-film or membrane N^{1S} was 401.7 eV and the bond energy of the WPU-CH-1 was 389.85 eV. This was induced by the reaction of the amino group $(-NH_2)$ of chitosan with the terminal NCO group of WPU. Paik Sung [15] et al. indicated that element N has two energy states, which are -NHCONH- (first energy state) and -NHCOO- (second energy state). The first energy state of the N^{1S} bond energy was significantly lower than that of the second energy state. Although WPU and WPU-CH-1 both have -NHCONH- (first energy state) and -NHCOO- (second energy state) bonds, WPU-CH-1 possesses additional chitosan amino group (-NH₂) and WPU terminal NCO group reactions as compared to WPU. Therefore, the -NHCONH- (first energy state) possessed more bonds, resulting in the lower bond energy of the WPU-CH-1, that is, 11.85 eV lower than that of the WPU.

Figure 8 shows the C¹⁵ spectrum (C¹⁵ electron bond energy) of the WPU and WPU-CH-1 thin-films or membranes. The C¹⁵ spectrum of the WPU-CH-1 presented two peaks: The first peak of 284.4 eV was the bond energy of the C-C(C-H) bonds; the second peak of 288.5 eV was the bond energy of the combination of the -NHCONH- and -NHCOO-groups. For the WPU thin-films or membranes, the bond energies of the C¹⁵ spectrum were 284.4 eV and 288.7 eV. Aside from the ester carbonyl groups, the chitosan amino group (-NH₂) and WPU terminal NCO group bonds in the WPU-CH-1 generated more urea carbonyl groups than did the simple WPU. The ester carbonyl groups. Therefore, the WPU possessed higher bond energy than did the WPU-CH-1. This proved that there was a bond between the terminal NCO group of the WPU and the chitosan amino group (-NH₂).

GPC: The measured molecular weights of the WPU, WPU-CH-0.2, WPU-CH-0.4 WPU-CH-0.6, and WPU-CH-1 were, respectively, 12769, 16153, 16188, 16425, and 18582, and the polydispersity (PDI) was1.35, 1.30, 1.31, 1.33, and 1.40, respectively. Regarding the WPU modified by adding chitosan, when the proportion of chitosan content



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increased, the reaction possibility between the polymer chitosan and the terminal NCO of the WPU increased. Therefore, the chitosan amino group $(-NH_2)$ reacted with the terminal NCO group of the WPU to fabricate longer chain segments, resulting in increased molecular weights. The PDI values of the various samples were all between 1 and 1.4 and all extremely close to 1. This indicates that the molecular weight distribution range of the various samples is small. However, with increasing added proportions of the modification chitosan, the PDI value also increased, indicating an increased molecular weight distribution range.

Membrane performance analysis

Contact angle: A contact angle meter was used to determine whether the membrane surface was hydrophilic or hydrophobic. When a droplet contacted the substance surface, the measured angle was named the advancing angle when the droplet volume increased gradually during measurement. If the droplet volume decreased gradually during measurement, the measured angle was called the receding angle. The molecular chain arrangement and chemical properties of the polymer surfaces varied with different external environments. The variation speed caused differences between the advancing angle and receding angle, which is called hysteresis.

Because biomedical materials come into direct contact with human bodies, the quality of the surface properties have direct and significant influences on the human body. When the contact angle between the solid and liquid is 180° with strong surface tension, the material is hydrophobic. When the contact angle is 0° with small surface tension, the material is hydrophilic. As shown in Figure 9, the contact angle



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of the WPU thin-film or membrane modified by chitosan was smaller than that of the unmodified WPU thin-film or membrane. In other words, the WPU modified by chitosan was hydrophilic compared to the unmodified WPU. When the chitosan content proportion increased, the contact angle decreased and the material became increasingly hydrophilic. Because chitosan contains hydrophilic functional groups, such as -OH and -NH₂, that can form hydrogen bonds with water, chitosan has favorable hydrophilic qualities. Therefore, when the proportion of chitosan addition increased, the thin-film or membrane surface contained more chitosan; the contact angle thereby decreased and the hydrophility increased.

Antimicrobial property: Figure 10 shows the antimicrobial activity values of each sample. The initial concentration (immediate leaching) of Staphylococcus aureus was 2.5×105/ml, and 2.4×105/ml following 24 h of bacteria cultivation. The bacteria concentration of the WPU was 2.1×10^{5} /ml after 24 h of cultivation, less than the 3×10^{4} / ml of the blank control group after 24 h of cultivation. The bacterial inhibition of the WPU was 0.1. When chitosan was added to modify the WPU, the antimicrobial activity increased significantly. The bacteria concentration of WPU-CH-0.4 was 3.6×104 following 24 h of cultivation, and the antimicrobial activity value increased to 0.8. The bacteria concentration of the WPU-CH-1 was 5.2×103 following 24 h of cultivation, and the antimicrobial activity value increased to 1.7. Because the amino group (-NH₂) of the chitosan structure carried a positive charge before reacting with the terminal NCO group of the WPU and the bacteria carried a negative charge, the amino group (-NH₂) forcefully adsorbed the bacteria to destroy the bacteria and slow metabolism functions, killing the bacteria. The higher proportion of chitosan content increased the bacterial inhibition effect. Although the antimicrobial activity value of the WPU modified by chitosan did not reach the antimicrobial standard (antimicrobial activity value greater than 2) for the Staphylococcus aureus, the increased antimicrobial activity value indicated that the modified WPU had bacteria inhibiting effects on the Staphylococcus aureus.

The influence effects of antimicrobial properties regarding the *E. coli* were similar to that of the *Staphylococcus aureus*. The initial concentration (immediate leaching) of the *E. coli* was 2.3×10^5 / ml, and 1.8×10^7 /ml following 24 h of bacteria cultivation. The WPU bacteria concentration was 1.1×10^7 /ml following 24 h of cultivation, less than the 7×10^6 of the blank control group cultivated for 24 h. The bacterial inhibition of the WPU was 0.2. The antimicrobial activity significantly increased when chitosan was added to modify the WPU. The bacteria concentration of the WPU-CH-0.4 was 2.5×10^4 /ml

following cultivation for 24 h, and the antimicrobial activity value was increased to 2.9. The bacteria concentration of the WPU-CH-1 was 3.1×10^3 / ml following 24 h of cultivation, increasing the antimicrobial activity value to 3.8. Higher proportions of chitosan content increased the bacterial inhibition effect. The antimicrobial activity values of the WPU modified by chitosan were greater than 2 regarding *E. coli*. The antimicrobial effect was confirmed. Therefore, the unmodified WPU did not possess bacterial inhibition and antimicrobial effects regarding both of the bacteria types discussed. WPU modified by chitosan possessed bacterial inhibition, and especially possessed antibacterial properties for *E. coli*. When the chitosan additive volume increased, the antimicrobial activity values increased.

Conclusion

Material determination

The FTIR analysis result showed that the WPU and WPU modified by aqueous chitosan possessed similar characteristic peaks. Substantial C=O functional group characteristic absorption peaks and -NH functional group absorption peaks were observed at approximately 1700 to 1600 cm⁻¹ and 3400 cm⁻¹ to 3300 cm⁻¹, respectively. The original 2240 cm⁻¹ absorption peak of the added isocyanate *m*-TMXDI terminal NCO group disappeared following the synthesis of WPU, WPU-CH-0.2, WPU-CH-0.4, WPU-CH-0.6, and WPU-CH-1. This indicated that, during the synthesis process, the m-TMXDI underwent an addition reaction with the glycol for which the terminal functional group was -OH or the chain extender with the terminal -NH functional group to fabricate urethane (-NHCOO-) or urea (-NHCONH-) molecular structures. In addition, the absorption peak strengths of the urea (-NHCONH-) and urethane (-NHCOO-) structures of the WPU were identical. However, the absorption peak of the urea (-NHCONH-) structure of the WPU modified by aqueous chitosan was stronger than the absorption peak of the urethane (-NHCOO-) structure. This indicated that following modification by the aqueous chitosan, the chitosan -NH₂ group reacted with the terminal NCO group of the WPU to generate the urea functional group and to strengthen the absorption peak.

• Comparing the m-TMXDI based WPU ¹³C-NMR analysis spectrum proposed by Chiu [12] and the WPU-CH-1 ¹³C-NMR spectrum proposed by this experiment, as well as the ¹H-NMR spectrums of WPU and WPU-CH-1, we found that, in addition to characteristic peaks similar to that of WPU, the WPU-CH-1 possessed extra chitosan characteristic peaks.

The bond energy of aqueous chitosan can be observed using XPS. XPS was used to analyze the WPU and WPU-CH-1 thin-film or membrane N15 spectra (N15 electron bond energy). The N15 bond energy of the WPU (401.7 eV) was higher than that of the WPU-CH-1 (389.85 eV). Because, in the WPU-CH-1, the chitosan amino group (-NH₂) reacted with the terminal NCO group of the WPU to generate more-NHCONH- bonds, the bond energy of the WPU-CH-1 thin-film or membrane was 11.85 eV less than that of the WPU thin-films regarding bond energy. In addition, the bond energy of the WPU C1S spectrum was 284.4 eV and 288.7 eV. In addition to the ester carbonyl groups, the chitosan amino group (-NH₂) of the WPU-CH-1 bonded with the terminal NCO group of the WPU to fabricate additional urea carbonyl groups compared to WPU. Furthermore, because the ester carbonyl groups possessed higher bond energies than the urea carbonyl groups, the WPU possessed higher bond energy compared to the WPU-CH-1. This also demonstrates that bonds existed between the terminal NCO group of the WPU and the chitosan amino group (-NH₂).

• GPC was used to measure the molecular weight. Regardless of Mw. or Mn., WPU-CH-1 > WPU-CH-0.8 > WPU-CH-0.4 > WPU-CH-0.2 > WPU. PDI presented the same trends, which were close to 1. This represented a minimal distribution for the emulsion molecular weights. The previous four results confirm that in the *m*-TMXDI-based WPU modified by aqueous chitosan, chitosan reacted with the terminal NCO group of WPU to form a new polymer chain segment.

Membrane performance

• A contact angle meter was used to determine whether the thin-film or membrane surfaces were hydrophilic or hydrophobic. The contact angle of the WPU thin-film or membrane modified by chitosan was smaller than the unmodified WPU thin-films or membranes. In other words, WPU modified by chitosan was more hydrophilic compared to the unmodified WPU. With the increase of the chitosan content, the contact angle decreased and the material became more hydrophilic. The hydrophilic levels of the samples were WPU-CH-1 > WPU-CH-0.6 > WPU-CH-0.4 > WPU-CH-0.2 > WPU.

• The WPU unmodified by chitosan possessed no antimicrobial properties or bacteria inhibition regarding *Staphylococcus aureus* and *E. coli*. The WPU modified by chitosan possessed greater antimicrobial effects on *E. coli* than on *Staphylococcus aureus*. The antimicrobial activity values of the modified WPU were greater than 2 for *E. coli*, demonstrating its antimicrobial ability. Regarding the *Staphylococcus aureus*, the antimicrobial activity values of the modified WPU did not reach the antimicrobial standard of 2. However, the antimicrobial activity values were significantly higher than that of the pure WPU. This signifies the bacteria inhibition effect of the modified WPU on *Staphylococcus aureus*. As the proportion of chitosan increased, the bacterial inhibition and antimicrobial effects (or bacterial inhibition) were determined to be the following order: WPU-CH-1 > WPU-CH-0.6 > WPU-CH-0.4 > WPU-CH-0.2 > WPU.

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