한국염색가공학회지

Research Paper

pISSN 1229-0033, eISSN 2234-036X

https://doi.org/10.5764/TCF.2018.30.1.9

Preparation and Properties of Bio-inspired Waterborne Polyurethanes Containing Different Amount of Paraffin Wax

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Received_January 31, 2018
Revised_March 22, 2018
Accepted_March 23, 2018

Abstract To prepare bio-inspired antifouling coating materials having similar structure with lotus, self-crosslinkable waterborne polyurethanes emulsions containing paraffin wax (CWPU/P0, 0.25, 0.5, 1.0, 1.5, 2.0, the number indicated the wt% of wax) were prepared by an emulsifier-free/solvent free prepolymer mixing process. The as-polymerized CWPU/P emulsions containing 0 - 1.00wt% of paraffin wax were found to be stable after 4 months, however, CWPU/P emulsions containing 1.50 and 2.00wt% of paraffin wax were unstable within 1 month storage. Considering the stability of emulsions, the optimum paraffin wax content was found to be about 1wt% to obtain stable antifouling coating emulsion material. The surface topology of CWPU/P film samples was characterized by atomic force microscopy (AFM). This study examined the effect of paraffin wax content on the surface roughness, water contact angle/surface energy, water swelling, light transmittance and tensile properties of CWPU/P film samples.

Textile Coloration and Finishing
TCF 30-1/2018-3/9-19

Keywords *bio-inspired, waterborne polyurethane, surface roughness, paraffin wax, antifouling coating*

1. Introduction

The objective of this research is the fabrication of antifouling coating materials having similar structure with lotus from waterborne polyurethanes (WPUs) emulsions containing different content of paraffin wax. The WPUs, which is environment friendly, have received considerable attention in the past few decades because of their applications in coatings and adhesives for various substrates[1,2]. The properties of WPUs dispersion materials are dependent on the chemical structure and compositional variation, the block length, and ionic group/hard segment content. Generally, the WPUs are linear thermoplastic polymers contained little gel which allows re-solubility in organic solvents. Therefore, crosslinking has been used in many coatings and adhesives to improve chemical resistance and thermal/mechanical properties of WPUs. Hydrophobic vinylalkoxysilanes are some of the functional groups that can introduce self-cross-linking structure during the film formation process[3-6]. In this study, vinyl triethoxysilane is used as a crosslinking agent for WPUs.

Paraffins are a class of aliphatic hydrocarbons (linear/branched low molecular polyethylenes (wax), molecular weight: 500-5000)[7]. Low toxicity, high water repellency, smooth texture, and low dielectric constant are paraffin wax nature. They are white, translucent, tasteless, and odorless solids consisting of a mixture of solid hydrocarbons of high molecular weight.

Sophisticated hierarchical structures (e.g. bone, beaks, nacre, wood) and fibers (e.g., spider silk, polar bear hair, mussel byssus) were developed to generate e.g., functional light-weight structures with outstanding mechanical properties[8]. Furthermore, a lot of functional surfaces were developed to address various problems like e.g., wettability (e.g., lotus leaf), friction and wear (e.g., pangolin skin), antifouling (e.g., shark skin), reflectivity (e.g. butterfly wings) and adhesion (e.g., gecko feet). Numerous plants (e.g., lotus leaf)[9] have developed superhydrophobic surfaces by combining hydrophobic materials (paraffin waxes) with surface profiles that are hierarchically structured by combining a waviness on the microscale with a roughness on the nanoscale. Bio-inspired principles have attracted increasing attention in materials science and engineering[8].

One of the major advantages of WPUs is their ability to migrate some specific groups (siloxane and fluoro groups)[5,6,10] and hydrophobic components (paraffin wax) with a lower surface free energy. It is well known that the siloxane and fluoro - enriched surface has surpassing advantages to protect the coating from fouling corrosion and water penetration[11]. However, researches on the influence of paraffin wax content in crosslinkable waterborne polyurethane/paraffin wax (CWPU/P) emulsions on the migration of paraffin wax component into surface, the surface morphology and properties of CWPU/P film have not been reported.

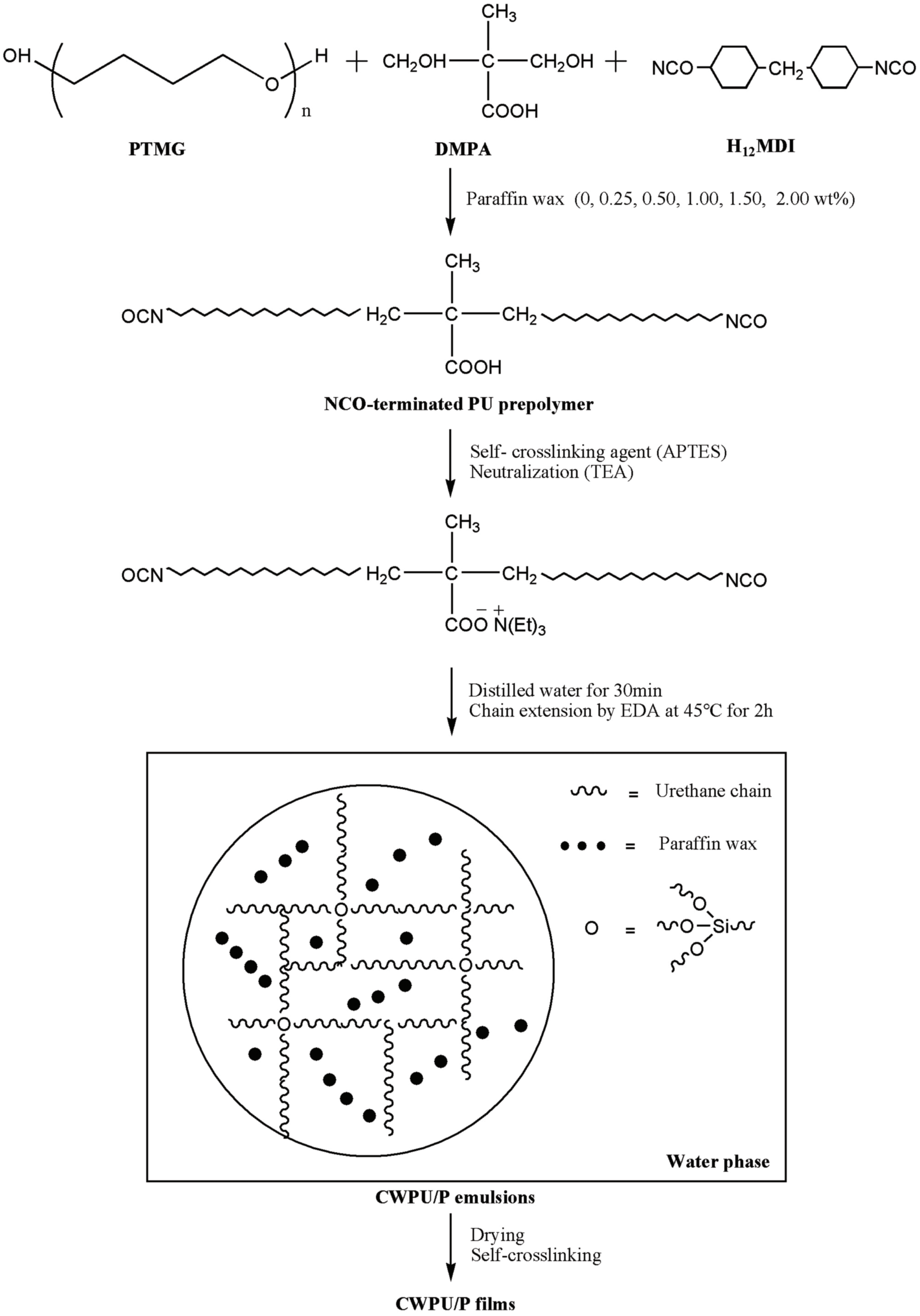
The cause of self-cleaning properties is the hydrophobic water-repellent double structure of the surface[12]. This structure enables the contact area and the adhesion force between polymer surface and water droplet to be significantly reduced resulting in a self-cleaning process[13-15]. This water-repellent double structure is formed out of a characteristic epidermis and the covering paraffin waxes. It is well known that the epidermis of the lotus possesses papillae with 10μm to 20μm in height and 10μm to 15μm in width on which the so-called epicuticular paraffin waxes are imposed.

In this study, to make WPUs with Lotus-like biomimetic hierarchical structure, crosslinkable waterborne polyurethane containing 0-2.0wt% of paraffin wax (CWPU/P) were prepared from 4,4′ dicyclohexylmethane diisocyanate ($H_{12}MDI$)/poly(tetramethylene oxide glycol) (PTMG)/dimethylol propionic acid (DMPA)/ethylene diamine (EDA)/self-crosslinkable 3-aminopropyl triethoxysilane (APTES)/trimethylamine (TEA)/paraffin wax. The final CWPU/P film samples having hierarchical roughness were obtained by the migration of paraffin wax component during drying condition. The resulting CWPU/P film samples were characterized using Fourier transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM), transmitted light optical microscopy, UV-visible spectra and contact angle measurement. This study focused on the effect of paraffin wax content (0, 0.25, 0.50, 1.00, 1.50, 2.00wt%) on the surface morphology, water swelling, water/ethylene glycol contact angle/surface tension and mechanical strength of CWPU/P films with a fix content of self-crosslinkable APTES and DMPA.

2. Experimental

2.1 Materials

Poly(tetramethylene oxide glycol) (PTMG, number-average molecular weight = 2000g/mol; Aldrich Chemical, Milwaukee, WI) was dried at 85℃ under 1-2m/108mmHg for several hours until no bubbling was observed. Dimethylol propionic acid (DMPA, Aldrich Chemical, Milwaukee, WI) was dried in a vacuum oven at 100°C for 5h. 4, 4′ -dicyclohexylmethane diisocyanate ($H_{12}MDI$, Aldrich Chemical, Milwaukee, WI) and triethylamine (TEA, Aldrich Chemical, Milwaukee, WI) were used after dehydration with 4-A molecular sieves for 1 week. 3-aminopropyl triethoxysilane (APTES, Aldrich Chemical, Milwaukee, WI), dibutyltin dilaurate (DBTDL, Aldrich Chemical, Milwaukee, WI),



Scheme 1. Preparation process of CWPU/P emulsions and films.

distillated deionized water, ethylene diamine (EDA, Aldrich Chemical, Milwaukee, WI) and paraffin wax (P, Aldrich Chemical, Milwaukee, WI) were used without further purification.

2.2 Preparation of crosslinkable waterborne polyurethane/paraffin wax (CWPU/P) emulsions

Crosslinkable waterborne polyurethane/paraffin wax blends was synthesized by the prepolymer mixing process (Scheme 1). PTMG and DMPA were placed in a four-neck, round-bottom flask equipped with a thermometer, mechanical stirrer, condenser with a drying tube, an inlet for dry nitrogen and a heat jacket, and was degassed in a vacuum at 85°C for 2h. The mixture was allowed to cool to 45°C with moderating stirring (175-200rpm). H_{12}MDI was then slowly dropped into the flask, and the reaction mixture was allowed to react at 85°C under stirring (125-150rpm) until the theoretical NCO content was reached. The change in the NCO value during the reaction was determined with the standard dibutylamine back-titration method (ASTM D 1638). The obtained NCO-terminated urethane prepolymer was cooled to 45°C, and 3-aminopropyl triethoxysilane (APTES) was added to the flask and reacted at 45°C for 30min. TEA was added to the reaction mixture to neutralize the carboxyl group of the NCO-terminated prepolymer. After 1h of neutralization, the reaction mixture was cooled to 45°C, and distilled water was added to the reaction mixture with vigorous stirring (1000-1500rpm) to obtain stable dispersions. The neutralized NCO-terminated prepolymer was chain extended by dropping EDA/water (1/16 w/w) at 45°C for 1h, and the chain extension reaction continued until the NCO peak (2270cm^{-1}) in the IR spectra had completely disappeared. The solid content of crosslinkable waterborne polyurethane paraffin wax blends (CWPU/P0, 0.25, 0.5, 1.0, 1.5, 2.0, the number indicated the wt% of paraffin wax) was fixed at 30wt%. The composition of crosslinkable waterborne polyurethane/paraffin wax emulsions is given in Table 1.

2.3 Preparation of CWPU/P films

CWPU/P films were prepared by pouring the dispersion into a glass disc and dried under ambient conditions for 24h. The films were then peeling off from the glass disc. The films were vacuum dried at 60°C for 24h under 20mmHg to remove the moisture and unreacted monomer. The vacuum dried films (thickness: 0.32-0.38mm) were stored in a desiccators at room temperature.

2.4 Characterization

Laser-diffraction particle size analyzer (LS 13 320, Beckman coulter, USA) was used to measure the mean particle size at 25˚C.

Table 1. Sample designation, composition, viscosity, mean particle size and shelf stability of crosslinkable waterborne polyurethane/paraffin wax (CWPU/P)

Sample designation	Composition of CWPU/P (molar ratio)						Paraffin wax(wt%)	Viscosity (cP/25℃)	Mean particle size (nm)	Shelf stability*
	H_{12}MDI	PTMG	DMPA	TEA	EDA	APTES				
CWPU/P0	1.4	0.4	0.48	0.48	0.32	0.37 (6wt%)	0	41	136	Stable
CWPU/P0.25	1.4	0.4	0.48	0.48	0.32	0.37 (6wt%)	0.25	39	138	Stable
CWPU/P0.50	1.4	0.4	0.48	0.48	0.32	0.37 (6wt%)	0.50	38	145	Stable
CWPU/P1.00	1.4	0.4	0.48	0.48	0.32	0.37 (6wt%)	1.00	37	150	Stable
CWPU/P1.50	1.4	0.4	0.48	0.48	0.32	0.37 (6wt%)	1.50	36	160	Unstable
CWPU/P2.00	1.4	0.4	0.48	0.48	0.32	0.37 (6wt%)	2.00	35	179	Unstable

* The shelf stability after 4 months.

Brook field digital viscometer (Brookfield LVDV Ⅱ+, USA) was used to measure the viscosity of the CWPU/P emulsions at 25˚C. The measurements were performed at 100rpm using a spindle RV-3.

FTIR spectroscopy was used to confirm the chemical components of the CWPU/P samples by NICOLET iS5 Fourier transform infrared spectrometer (Thermo scientific, USA). For each samples, 32 scans at 4cm^{-1} resolution were collected in the transmittance mode and recorded in the range of 4000-650cm^{-1}. The dispersion was coated on the KRS-5 disc (25/4mm) surface as a thin liquid film and drying them using hair drier.

Water and ethylene glycol contact angles were measured at 25˚C using a G-1 contact angle goniometer (Erma Contact Angle Meter, Japan). The results reported are the mean of five values. The contact angle, which is a measure of the surface wettability, was used to determine the hydrophobicity and hydrophilicity. The surface energy of the solid film can be determined using the following equation:

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad \cdots\cdots (1)$$

$$\gamma_L(1+\cos\theta_L) = 2(\gamma_L^d\,\gamma_S^d)^{1/2} + 2(\gamma_L^p\ \ \gamma_s^p)^{1/2} \quad \cdots\cdots (2)$$

where γ is the surface energy of solid film, γ_s^d is the dispersion force, and γ_s^p is the polarity force. The testing liquids used were water (L1) and ethylene glycol (L2), and their γ_{L1}^d, γ_{L1}^p, γ_{L2}^d, and γ_{L2}^p were 21.8, 51.0, 29.27 and 19.0 mN/m, respectively$^{16)}$.

For water swelling study, all films were immersed in water for 48h at 25℃. The water swelling (%) of the films was determined from weight increase as:

$$Swelling(\%) = 100(W - W_0)/W_0 \quad \cdots\cdots (3)$$

where W_0 is the weight of the dried film and W is the weight of the film at equilibrium swelling.

Universal testing machine (UTM, WL2100, WITHLAB, USA) was used to measure the tensile properties at room temperature. A cross-head speed of 1mm/min was used to determine the ultimate tensile strength and modulus as well as the elongation at break. The values quoted are the average of three measurements.

The UV-visible spectra were measured using a UV-visible spectrophotometer (T70+UV/VIS Spectrometer, PG Instruments, England).

The surface morphology of the samples was examined using a transmitted light optical microscopy (Leica ICC50 HD, Germany). The AFM topography was measured by atomic force microscopy (AFM, BRUKER, Icon-PT-PLUS, USA) in tapping mode.

The hardness was measured using a Shore A type durometer (Kobunshi Keiki, Japan) according to the ASTM D 2240. The values quoted are the average of five measurements.

3. Results and discussion

3.1 Preparation and stability of CWPU/P emulsions

The sample designation, composition, mean particle size, viscosity and stability of crosslinkable CWPU/P emulsions are given in Table 1. In this study, the emulsions of CWPU/P (solid content: 30wt%) were successfully obtained without external diluent solvent/emulsifier. The mole percentage of DMPA containing ionic groups was fixed at approximately 17mol%. Also, self-crosslinkable APTES content was fixed at approximately 19mol%. The self-crosslinking was formed by the condensation reaction (dehydration reaction) of the hydroxy group formed after the hydrolysis reaction of the three alkoxy groups of APTES.

To attain the intimate molecular mixing between WPU and paraffin wax, paraffin wax were homogeneously mixed with urethane prepolymer. The final emulsions of CWPU/P containing in the range of 0 - 1.00wt% of paraffin wax were stable over 4 months, however, the final emulsions of CWPU/P containing

1.50 and 2.00wt% of paraffin wax were found to be unstable after 1 month. Considering the stability of emulsions, the optimum paraffin wax content was found to be about 1.00wt% to obtain stable antifouling coating emulsion material.

3.2 Mean particle size and viscosity of CWPU/P emulsions

The mean particle size and viscosity of CWPU/P emulsion samples are shown in Table 1. It was found that the mean particle size of CWPU/P emulsions was in the range of 136-179nm. As the paraffin wax content increased from 0 to 1.50wt%, the mean particle size increased from 136nm to 160nm, but the viscosity decreased from 41 to 36cPs at 25℃. Higher particles and smaller viscosities resulted, with increased paraffin wax content in CWPU/P emulsions. This phenomenon was due to the increase of the hydrophobic component in CWPU/P particles through the addition of more hydrophobic paraffin wax.

3.3 Identification of functional groups

Figure 1 shows the FTIR spectra of (a) NCO-terminated PU prepolymer, (b) CWPU/P0 film, (C) CWPU/P1.00 film. The NCO terminated prepolymer has the NCO peak at 2270cm^{-1}, however, no peak of NCO group in crosslinked CWPU/P0 and CWPU/P1 film samples was observed, indicating the complete reaction of NCO groups in crosslinked film samples. The characteristic bands at approximately 1724cm^{-1}, 1082-1085cm^{-1}, 1110cm^{-1} and 3300-3360cm^{-1} confirm the carbonyl group of urethane, ether (C-O-C) of the ester group, ether group (C-O-C) of PTMG and amide group in samples, respectively. The characteristic peak of Si-O-Si at near 476cm^{-1} and 1065cm^{-1} were detected in crosslinked film samples. The carbon-hydrogen stretching absorption and bending band at 2955-2855cm^{-1} and 1470cm^{-1}, respectively, and the symmetric carbon-hydrogen bending band of the CH_3 group at 1380cm^{-1} and the CH_2 rocking absorption at 725cm^{-1} confirm the linear saturated aliphatic structure of the impossible to identify quantitatively the paraffin wax[17,18]. On the other hand, many peaks of the urethane CH_2, CH_3/paraffin wax CH_2, CH_3 groups overlapped each other. This makes it content of paraffin wax in the range of 0-2.00wt%.

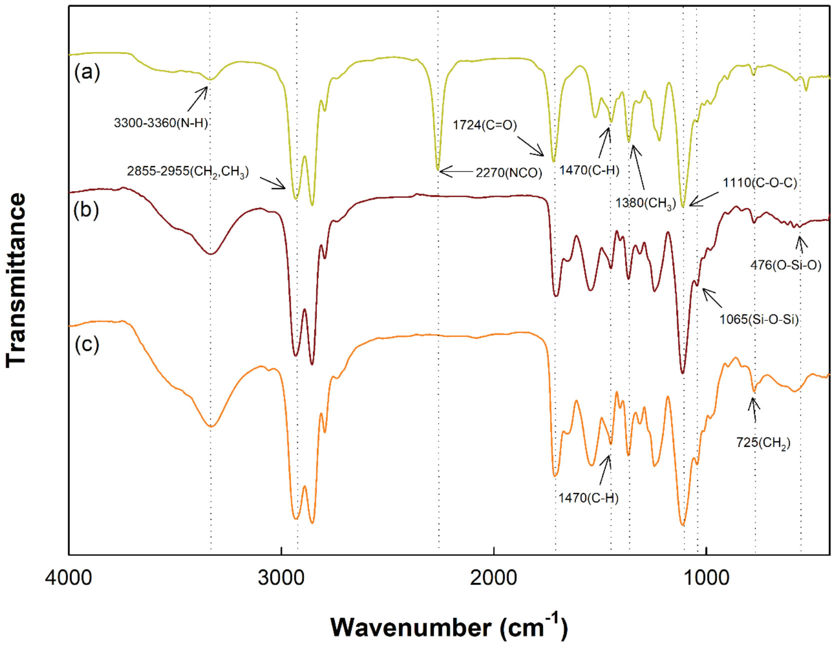


Figure 1. FTIR spectra of (a) isocyanate terminated PU prepolymer, (b) CWPU/P0 film and (c) CWPU/P1.00 film.

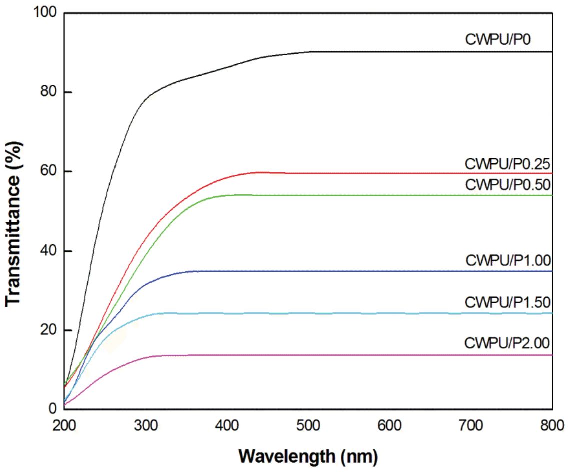


Figure 2. UV–visible spectra of CWPU/P film samples.

3.4 The transmittance % of CWPU/P films

Figure 2 shows the UV-visible spectra of the film samples (CWPU/P0, CWPU/P0.25, CWPU/P0.50, CWPU/P1.00, CWPU/P1.50 and CWPU/P2.00). The CWPU/P0 film showed a high transmittance % of near 90% in the visible range. The transmittance % of the CWPU/P film samples decreased from about 90% to 15% with increasing paraffin wax content from 0 to 2.00wt%. This should be due to higher scattering of visible light which arose from the higher content of dispersed paraffin wax in polyurethane matrix.

3.5 Transmitted light optical microscope and AFM images of CWPU/P film samples

Figure 3 shows transmitted light optical microscopy images of CWPU/P film samples. The number of bright-field particle increased with increasing paraffin wax content from 0wt% to 2.00wt%. The bright-field particle (paraffin wax particle) was distributed uniformly throughout the region when the paraffin wax content increased up to 1.00wt%. However, the connecting of particle increased when the paraffin wax contents were above 1.00wt% (1.50 and 2.00wt%).

Figure 4 shows typical AFM images of the CWPU/P films. The root mean square roughness (RMS) values are summarized in Table 2. Usually the higher RMS value implies the surface changed from smooth to rough[19]. The RMS value and the protuberance in AFM images increased with increasing paraffin wax content, indicating the roughness of CWPU/P film surface increased with increasing paraffin wax content. However, the connecting of the particle increased markedly when the paraffin wax content was above 1.00wt% (1.50 and 2.00wt%). The 3D surface topology of the typical films was characterized by AFM at low tapping forces. The paraffin wax content in the CWPU/P films had the decisive influence on the sur-

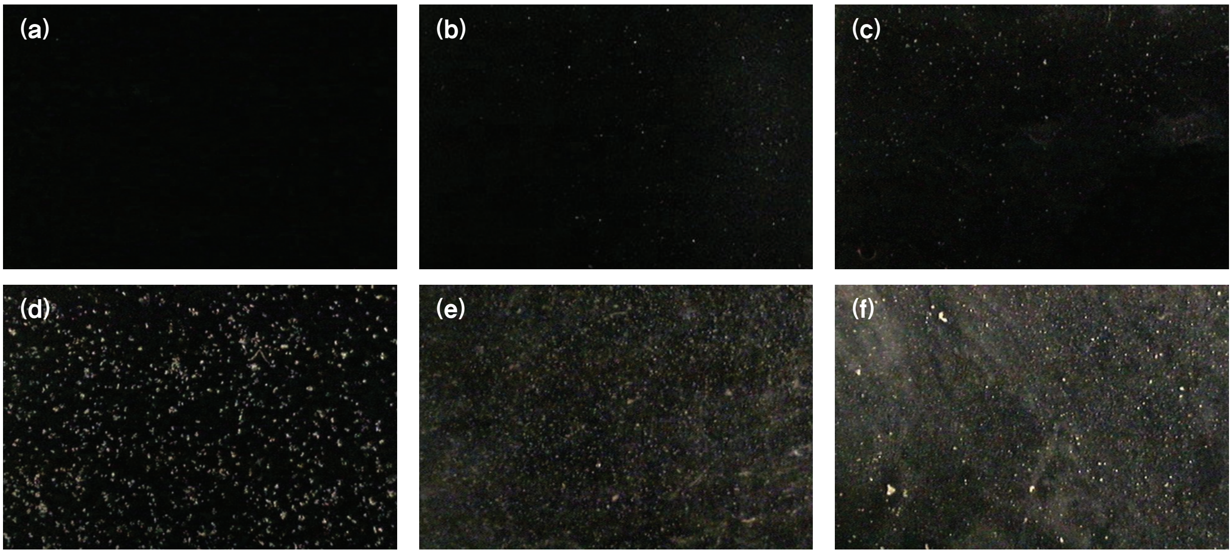


Figure 3. Transmitted light optical microscopy of film samples. (a) CWPU/P0, (b) CWPU/P0.25, (c) CWPU/P0.50, (d) CWPU/P1.00, (e) CWPU/P1.50, (f) CWPU/P2.00.

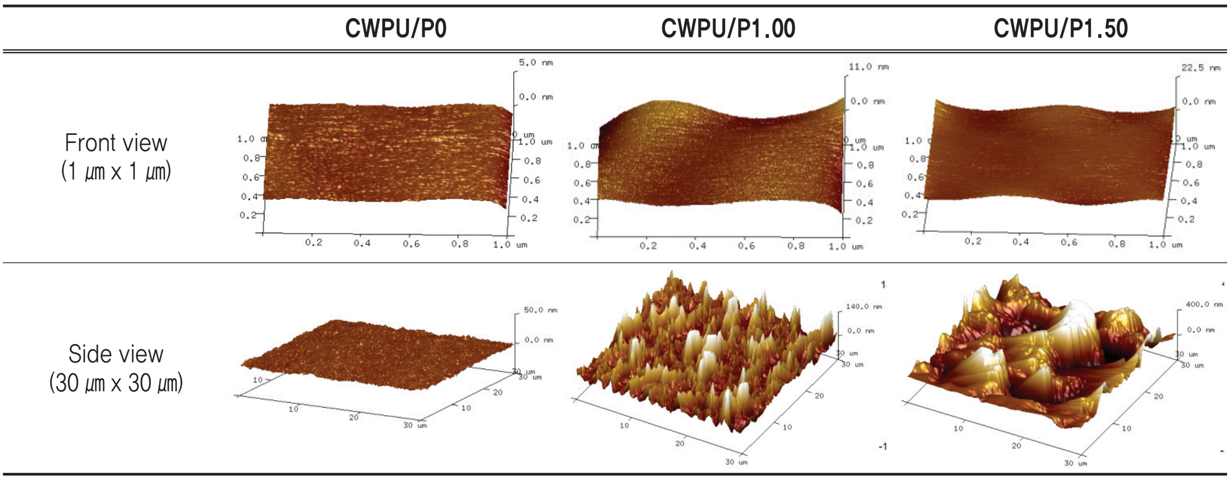


Figure 4. AFM images of CWPU/P0, CWPU/P1.00 and CWPU/P1.50 film samples.

face morphology. As shown in Figure 4, the increment in paraffin wax content had an obviously influence on the surface roughness of films, resulting in a somewhat consequent increase to make the processed surface much more rough. The mean roughness parameters ranged between 1.40nm and 31.10nm increased with increasing paraffin wax content. These results might be due to the migration of hydrophobic paraffin wax into the surface during drying process. Especially, higher migration resulted, with increased paraffin wax content after 1.00wt%. This indicated that the higher nucleation and migration of paraffin wax particles was occurred when the paraffin wax content was above 1.00wt%.

3.6 Surface properties and water swelling of CWPU/P film samples

Figure 5 and Table 2 show the water/ethylene glycol contact angles and surface tension of the CWPU/P film samples. Generally, the contact angle/low surface tension was used as the criteria of water repellent/antifouling property. The contact angles increased/the surface tension decreased with increasing paraffin wax. In addition, as paraffin wax content was increased from 0 to 2.00wt%, the water and ethylene glycol contact angles of the film samples increased from 102.01 to 120.32° and from 71.58 to 93.40°, respectively, while the surface tension decreased from 30.82 to 21.13mN/m. The lower surface energies of

Table 2. Water/ethylene glycol contact angles, surface tension, mechanical properties, hardness and root mean square roughness of CWPU/P films

Sample designation	Contact angle (˚)		Surface tension (mN/m)	Mechanical properties			Hardness (Shore A)	Root mean square roughness (RMS, nm)
	Water	Ethylene glycol		Tensile strength (MPa)	Elongation at break (%)	Modulus at 5% strain (MPa)		
CWPU/P0	102.01	71.58	30.82	38.71	661.33	21.40	84	1.40
CWPU/P0.25	108.73	78.91	28.65	30.20	763.27	16.18	76	12.96
CWPU/P0.50	114.84	84.90	27.62	28.44	784.49	14.72	71	17.66
CWPU/P1.00	116.13	88.70	22.99	27.36	799.38	12.81	68	27.60
CWPU/P1.50	118.69	91.64	21.75	31.25	746.15	18.26	78	29.42
CWPU/P2.00	120.32	93.40	21.13	36.87	683.67	20.43	80	31.10

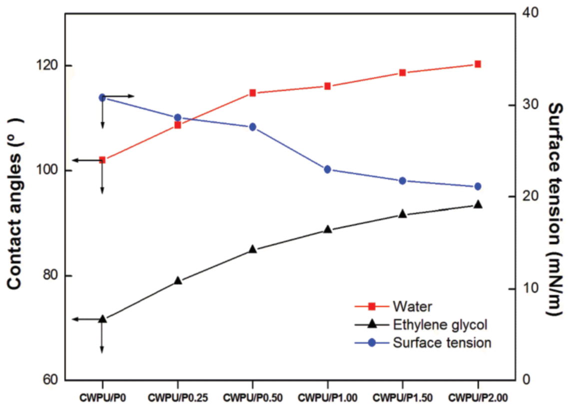


Figure 5. Water/ethylene glycol contact angles and surface tension of CWPU/P film samples.

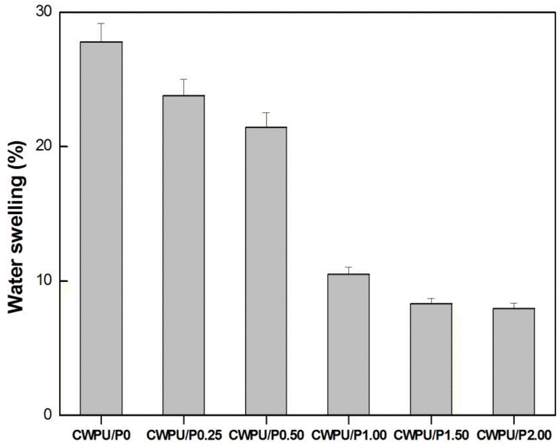


Figure 6. Water swelling % of CWPU/P film samples.

CWPU containing paraffin wax can be explained by the orientation of paraffin wax component to the outmost layer of polymer-air interface. This indicated that the dispersed paraffin wax component in the polyurethane matrix migrated to the surface layer during the formation of CWPU/P film. This would contribute to enhancing the water repellency of antifouling coating materials having similar structure with lotus.

Figure 6 shows the water swelling% of the CWPU/P film samples. The water swelling% of film surface decreased markedly with increasing paraffin wax content. The decrease of water swelling % also should be attributed to both the migration of hydrophobic paraffin wax content on the surface and the increase of surface roughness.

3.7 Tensile properties and hardness of the CWPU/P films

Figure 7 shows the stress-strain curves of the CWPU/P film samples. The tensile strength/modulus, elongation at break, and hardness of the CWPU/P film samples are shown in Table 2. There is close correlation between mechanical properties and remained paraffin wax content in CWPU/P blends. The tensile strength/modulus of the film samples decreased markedly from 38.71/21.40 to 27.36/12.81MPa with increasing paraffin wax content up to 1.00wt%, and then increased significantly, while the elongation at break increased from 661.33 to 799.38%, and then decreased. The tensile modulus and hardness (Shore A) of the film samples decreased with increasing paraffin wax content up to 1.00wt%, and then increased significantly. From these results, we can assume that the content of remained paraffin wax in polyurethane matrix increased with increasing paraffin wax content up to 1.00wt%, and then decreased significantly. Generally, in a blend of incompatible components, a small amount of the dispersed phase component is dispersed to some extent in the continuous phase. The mechanical properties of the incompatible blend material decrease as the content of the dispersed phase component increases. This indicates that the mechanical properties of the CWPU/P film is dependent on the amount of dispersed wax remaining in the film, The tensile strength of CWPU/P film samples prepared in this study was found to decrease with increasing the dispersed component paraffin wax content up to 1wt%. However, AFM studies showed that the excessive wax content (1.50-2.00wt%) caused the large amount of wax to migrate to the film surface. This indicated that the content of wax component remaining in the film sharply decreased when more than 1 wt% of wax were used, For this reason, film samples with 1.50-2.00wt% paraffin wax should be resulted in higher tensile strength than film sam-

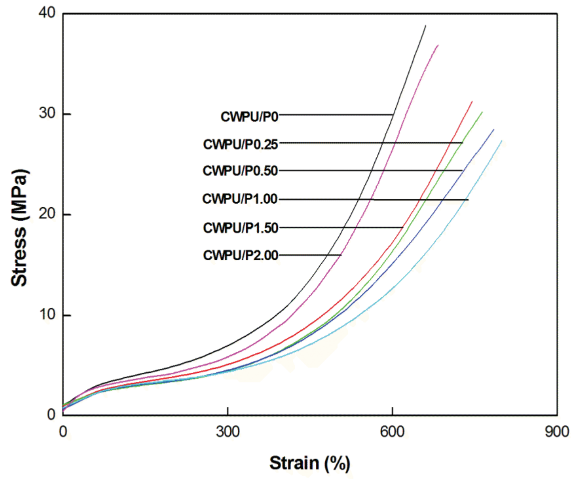


Figure 7. Stress-strain curves of CWPU/P film samples.

ples containing wax less than 1 wt%.

4. Conclusions

To obtain bio-inspired antifouling coating materials having similar structure with lotus, self-crosslinkable waterborne polyurethanes emulsions with various content of paraffin wax (CWPU/P0, 0.25, 0.50, 1.00, 1.50, 2.00, the number indicated the wt% of wax) were prepared by an emulsifier-free/solvent free prepolymer mixing process. The as-polymerized CWPU/P emulsions containing 0-1.00wt% of paraffin wax were found to be stable after 4 months, however, CWPU/P emulsions containing 1.50 and 2.00wt% of paraffin wax were unstable within 1 month storage. The surface topology of CWPU/P film samples were characterized using atomic force microscopy (AFM). The CWPU/P coating films have developed hydrophobic surfaces by combining hydrophobic materials (waxes) with surface profiles that are hierarchically structured. The surface roughness of CWPU/P increased with increasing wax content. As wax content increased, the contact angle of CWPU/P film surface increased, however, the surface energy, light transmittance and water swelling of CWPU/P film surface decreased significantly. The tensile strength of CWPU/P film decreased with increasing wax content up to 1.00wt%, and then increased significantly. The optimum wax content was found to be about 1.00wt% to obtain stable antifouling coating material.

Acknowledgement

This work was supported by a 2-Year Research Grant of Pusan National University.

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