Properties of Waterborne Polyurethane-Fluorinated Marine Coatings: The Effect of Different Types of Diisocyanates and Tetrafluorobutanediol Chain Extender Content

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ABSTRACT: Three series of waterborne polyurethane- (WBPU) fluorinated coatings were prepared with single aliphatic (4,4′-dicyclohexylmethane diisocyanate, H_{12}MDI), aromatic (4,4′-diphenylmethane, MDI) and a mixture of aliphatic and aromatic diisocyanates (1 : 1). Different contents of 2,2,3,3-tetrafluoro1,4-butanediol (TFBD) as a chain extender were used in the WBPU coatings. The fluoro-enriched surface of the WBPU coatings was obtained with a combination of a high TFBD content (8.77 mol %) as well as the aliphatic or mixed diisocyanates. The tensile strength, Young's modulus, elongation at break (%) and adhesive strength were characterized with respect to the TFBD contents. The mechanical strength and adhesive strength increased with increasing TFBD content in the three series. In artificial salt water, the maximum adhesive strength of WBPU was observed for this coating, which was achieved by TFBD bonded H_{12}MDI of mixed diisocyanates with a higher TFBD content (8.77 mol %). © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2013**, *000*, 39905.

INTRODUCTION

In the 21st century, the demand for environmentally safety materials has increased considerably. Moreover, the use of toxic materials and organic volatile solvents has been restricted. Therefore, there has been increasing need to replace solvent-borne techniques with environmentally friendly waterborne systems. In this respect, waterborne polyurethane (WBPU) is a good choice as an environmentally friendly technique. In addition, the available starting materials and good mechanical strength make it very attractive in the coating and adhesive industries. WBPU is used widely in the automotive, packaging, transportation, electronics, tape, paper, and textiles industries.[1–7]

Plenty of works have been published in the last two decades in WBPU dispersion synthesis.[3,7–10] Different methodologies such as crosslinking,[11–13] blending,[12] and curing at different stages[13] were considered. Recently, many hybrid polymers and nanocomposites[14,15] have been considered in WBPU dispersions and their films. WBPU dispersions can be prepared using polyols, diisocyanates, hydrophilic agents with a pendant acid group,

neutralizing agents and chain extenders.[2,5,7] The properties change with the different types and contents of the above monomers.[2,5] The diisocyanates used in polyurethane industry are divided into aromatic and aliphatic diisocyanates.[1,10] Aliphatic and aromatic diisocyanates have its unique properties and each diisocyanate has its own advantages and disadvantages. In taking the advantage of both diisocyanates the use of mixed diisocyanates (H_{12}MDI and MDI) in WBPU also used to improve the properties. Different chain extenders such as ethylene diamine (EDA), hydrazine, butanediol (BD) and ethylene glycol are reported in WBPU dispersions.[4] Both adhesive strength and mechanical strength varied with respect to CE and their contents. Rahman et al.[10] showed how the properties can be altered with excess of chain extender. Adhesive strength decreased about 30% with excess of EDA in WBPU adhesives.

One of the major advantages of WBPU is their ability to migrate some specific groups (siloxane and fluoro groups) with a lower free energy on the surface.[2,5,16] The migration of those groups also depends on the soft segments and their contents. A proper soft segment can cover the entire surface with siloxane and fluoro groups. The siloxane and fluoro-enriched surface has

superior advantages to protect the coating from fouling corrosion and water penetration.[16,17] Unfortunately, siloxane-based WBPU coatings have a tendency to sacrifice their adhesive strength after a certain siloxane content.[16] This limitation of siloxane WBPU has prompted interest in other alternatives, such as fluorinated WBPU. Fluorinated WBPU was reported to exhibit excellent adhesive strength, thermal stability, chemical resistance and weatherability.[8,9,17–19]

WBPU coatings have already been applied to painting. Previous studies showed that WBPU coatings can also be considered for marine applications.[16] One of the major challenges for WBPU coatings in a marine environment is the adhesive strength in salt water. Normally, the adhesive strength decreases in presence of water and deteriorates quite rapidly under a marine environment.[2] Therefore, the adhesive strength of these coatings in a marine environment needs to be increased to improve the anticorrosion and anti-fouling properties.

Fluorinated WBPU has attracted considerable research attention but the studies reported thus far focused mainly on improving the properties using fluorinated polyol and chain extenders[8,9,18,19] None of these studies considered different diisocyanates (aliphatic/aromatic/mixed of aliphatic and aromatic) and their bonding to TFBD or the resulting flexibility/rigidity to improve the adhesive strength under a marine environment. The aim of the present study was to improve the properties of WBPU coatings by introducing fluorinated groups, which can improve the adhesive strength under salt water. Single aliphatic (4,4′-dicyclohexylmethane diisocyanate ($H_{12}MDI$)) and aromatic diisocyanates (4,4′-diphenylmethane diisocyanate (MDI)) and their mixtures (1 : 1) were considered to increase the migration of the fluorinated group of TFBD on the surface. In this regard, different TFBD contents (4.81, 6.88, and 8.77 mol %) were used in the WBPU dispersions. The mixed diisocyanates at the same ratio (1 : 1) as WBPU showed excellent mechanical properties.[20] Poly(tetramethyleneoxideglycol) (PTMG), dimethylol propionic acid (DMPA), and triethylamine (TEA) were fixed for all coatings. Fourier transform infrared (FTIR) spectroscopy was utilized to identify the structure of the WBPU films. X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) techniques were used for surface analysis. The mechanical properties (tensile strength, Young's modulus and elongation at break), and adhesive strength (under water) were also evaluated.

EXPERIMENTAL

Materials
Poly(tetramethyleneoxideglycol) (PTMG, number-average molecular weight = 2000 g/mol; Sigma Aldrich) was vacuum dried at 90°C under a pressure of 1–2 mmHg for 3 h prior to use. Triethylamine (TEA; Junsei Chemical, Tokyo, Japan), N-methyl-2-pyrrolidone (NMP; Junsei Chemical), 4,4′-dicyclohexylmethane diisocyanate ($H_{12}MDI$, Sigma Aldrich) and 4,4′-diphenylmethane diisocyanate (MDI, Sigma Aldrich) were used after dehydration using 4 Å molecular sieves for 1 week. 2,2-Dimethylol propionic acid (DMPA, Sigma Aldrich) and dibutyltin dilaurate (Sigma Aldrich) were used as received.

Preparation of WBPU Dispersion
All WBPU dispersions were prepared using a prepolymer process (see Scheme 1) reported elsewhere.[10] NCO terminated prepolymer was prepared using PTMG, DMPA/NMP and diisocyanates. Methyl ethyl ketone (MEK, 20 wt %) was added to the NCO-terminated prepolymer mixture before neutralization. TEA was added to the reaction mixture to neutralize the carboxyl groups of the NCO-terminated PU prepolymer. After 30 min neutralization (confirmed by FTIR), distilled water (70 wt %) was added to the reaction mixture with vigorous stirring (1300–1500 rpm). The neutralized prepolymer was chain-extended by TFBD (mixed with water) at 40°C for 1 h, and the reaction was allowed to continue until the NCO peak (2000–2300 cm^{-1}) in the IR spectrum had disappeared. After evaporating the MEK (collected separately), the WBPU dispersion was obtained. For WBPU-10b, WBPU-11b, and WBPU-12b, the MDI was added first to react with PTMG and DMPA. $H_{12}MDI$ was then added to the reaction mixture. Similarly for WBPU-10a, WBPU-11a, and WBPU-12a, $H_{12}MDI$ was added first to react with PTMG and DMPA, and MDI was added to the reaction mixture.

Preparation of the WBPU Film
WBPU films were prepared by pouring aqueous dispersions (10 g) onto a Teflon disc (diameter, 7 cm) followed by drying under ambient conditions for 48 h. The films (typically ~0.5-mm thick) were also dried at 60°C for 6 h and vacuum dried at 80°C for 6 h. The vacuum dried films were stored in a desiccator at room temperature.

Mounting Coatings onto PVC Solid Supports
The WBPU was mounted onto flat PVC solid supports with an applicator. The coated samples (200 μm) were dried at ambient temperature, and immersed in artificial salt water (3 wt %) to evaluate the adhesive strength under this condition.

Characterization
FTIR spectroscopy (Impact 400D, Nicolet, Madison, WI) was used to identify the WBPU film structure. The dispersion was coated on a thalliumbromide/thalliumiodide crystal surface as a thin liquid film and dried for analysis. For each sample, 32 scans at a resolution of 4 cm^{-1} were collected in transmittance mode.

The polymer surface was analyzed by XPS (ESCA 250 XPS, UK) using A1Kα radiation (1486.6 eV). The AFM topography was measured by scanning probe microscopy (SPM, SPM-Solver P47, NT-MDT, Russia) in contact mode.

The tensile properties were measured at room temperature using a United Data Systems tension meter (SSTM-1 United Data Systems, Japan) according to the ASTM D 638 specifications. A crosshead speed of 50 mm/min was used throughout these studies to determine the ultimate tensile strength, Young's modulus and elongation at break (%) for all samples. The values quoted are the means of five measurements.

For swelling study, the WBPU films were immersed in water for 48 h at 30°C and the swelling (%) was determined from the weight increase as
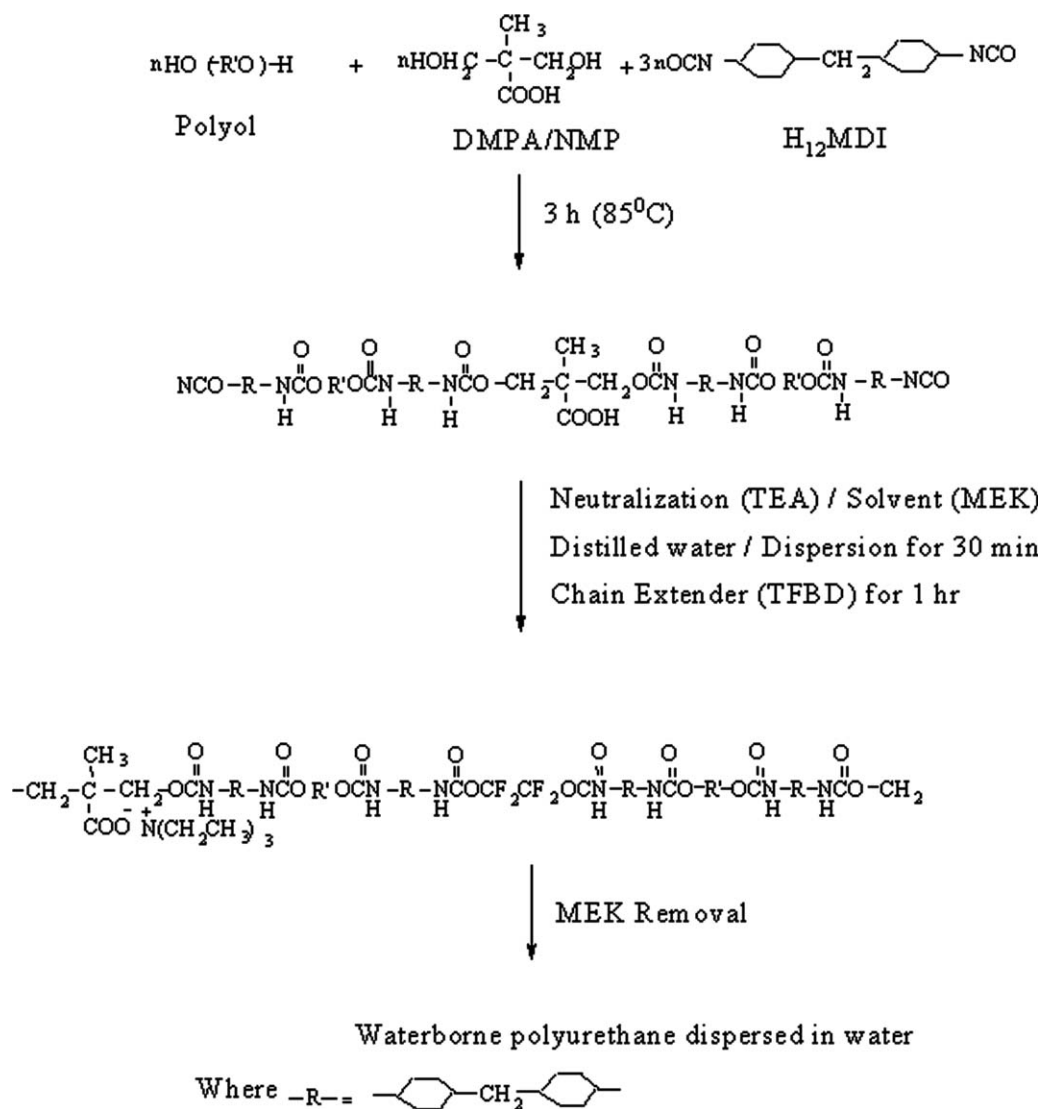
Scheme 1. Preparation of WBPU dispersion.

$$\text{Swelling (\%)} = \frac{W - W_0}{W_0} \times 100$$

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

The adhesive properties (peel resistance of the adhesive, i.e. T-peel strength) were measured using a universal testing machine according to ASTM D 1876-01. A peel rate of 100 mm/min was used. The values quoted are the means of five measurements.

RESULTS AND DISCUSSION

The WBPU dispersions were prepared using a prepolymer process. Table I lists the sample designations, compositions, molecular weight and surface fluorine (1 s) content (from XPS analysis) of WBPU dispersions and their respective films. The solid content was fixed to 30 wt %. Single diisocyanate-based WBPU dispersions (WBPU1–8) were prepared by the one-time addition of diisocyanate. For WBPU-9, both $H_{12}MDI$ and MDI were added at a time. $H_{12}MDI$ was added to the WBPU-10a,

WBPU-11a, and WBPU-12a dispersions to react with polyol and DMPA. Therefore, MDI reacted with TFBD at the chain extension step. For WBPU-10b, WBPU-11b, and WBPU-12b, $H_{12}MDI$ was added after a complete reaction of MDI. Therefore, TFBD can only react with $H_{12}MDI$. The WBPU films were identified by the characteristic IR peaks (Figures 1 and 2). The absence of a peak in the range of 2000–2300 cm^{-1} indicated that all of the isocyanate groups reacted.[7] The spectrum is mainly characterized by the bands at 3150–3600 cm^{-1}, 2800–3000 cm^{-1}, 2795 cm^{-1}, 1600–1760 cm^{-1}, and 1109 cm^{-1}, which correspond to NH, CH, O—CH$_2$, C=O, and C—O—C stretching and the ether group, respectively. The band at 1415 cm^{-1} is attributed to CH$_2$ scissoring and CH$_3$ deformation, while the absorbance between 1002 and 1012 cm^{-1} is attributed to stretching and rocking vibrations of the C—C and CH$_2$ groups, respectively. A very weak single band is observed at 833 cm^{-1} and is attributed to either the coupled vibrations of the C—O stretching or CH$_2$ rocking modes. A strong band assigned to the asymmetric stretching vibration of the C—N

Table I. Sample Designation and Composition of Waterborne Polyurethane (WBPU) Coatings

Sample designation	Composition (molar ratio)						TFBD	F1s (%)[a]	Molecular weight	Molecular weight distribution
	DMPA	PTMG	H_{12}MDI	MDI	TFBD	TEA				
WBPU-1	0.054	0.04	0.094	0	0	0.054	0	0	8000	2.0
WBPU-2	0.054	0.04	0.104	0	0.01	0.054	4.81	0	10,000	2.1
WBPU-3	0.054	0.04	0.109	0	0.015	0.054	6.88	0	14,000	2.2
WBPU-4	0.054	0.04	0.114	0	0.02	0.054	8.77	3.1	22,000	2.1
WBPU-5	0.054	0.04	0	0.094	0	0.054	0	0	9000	2.1
WBPU-6	0.054	0.04	0	0.104	0.01	0.054	4.81	0	12,000	2.2
WBPU-7	0.054	0.04	0	0.109	0.015	0.054	6.88	0	18,000	2.3
WBPU-8	0.054	0.04	0	0.114	0.02	0.054	8.77	0	21,000	2.9
WBPU-9	0.054	0.04	0.047	0.047	0	0.054	0	0	8000	2.0
WBPU-10-a[b]	0.054	0.04	0.052	0.052	0.01	0.054	4.81	0	9000	2.1
WBPU-10b[c]	0.054	0.04	0.052	0.052	0.01	0.054	4.81	0	10,000	2.1
WBPU-11-a[b]	0.054	0.04	0.0545	0.0545	0.015	0.054	6.88	0	14,000	2.2
WBPU-11-b[c]	0.054	0.04	0.0545	0.0545	0.015	0.054	6.88	0	16,000	2.2
WBPU-12-a[b]	0.054	0.04	0.057	0.057	0.02	0.054	8.77	1.3	20,000	1.9
WBPU-12-b[c]	0.054	0.04	0.057	0.057	0.02	0.054	8.77	2.6	23,000	1.9

[a] TFBD reacted with MDI.
[b] TFBD reacted with H12MDI.
[c] F1s (%) on surface from XPS analysis.

group is expected at 1040 cm^{-1}; however, this band overlaps with the very strong band at 1109 cm^{-1}, which corresponds to the C—O—C stretching vibration of the ether groups in the PU films. Using MDI, a new peak appeared at 1502 cm^{-1} (see Figure 2), which was assigned to the aromatic proton in WBPU5–12 films.

XPS was used to analyze the chemical compositions of the film surfaces. Several identical peaks for PU were evident in all samples: The peaks at 531, 285, and 400 eV were assigned to oxygen (1 s), carbon (1 s), and nitrogen (1 p), respectively (Figure 3). The peaks at 689 eV correspond to fluorine (1 s), which was observed only for the three samples, WBPU-4, WBPU-12a, and

WBPU-12b. This suggests that only these sample surfaces have a high concentration of fluorine groups. Although WBPU-8 has higher TFBD content (8.77 mol %), the rigid structure due to MDI might inhibit the migration of fluorine groups on the surface. A lower amount of TFBD might be the cause of a non-fluorine enriched surface for WBPU-2, WBPU-3, WBPU-6, WBPU-5, WBPU-9, WBPU-10a, WBPU-10b, WBPU-11a, and WBPU-11b samples. Therefore, XPS confirmed that there should be a sufficient amount of TFBD chain extender to migrate the fluorine group. In addition, the diisocyanates (aliphatic or aromatic) and their bonding with TFBD also can affect the migration of fluorine groups. The maximum fluorine-enriched surface is WBPU-4 (see Table I) that can be obtained using single H$_{12}$MDI. This might be due to presence of less
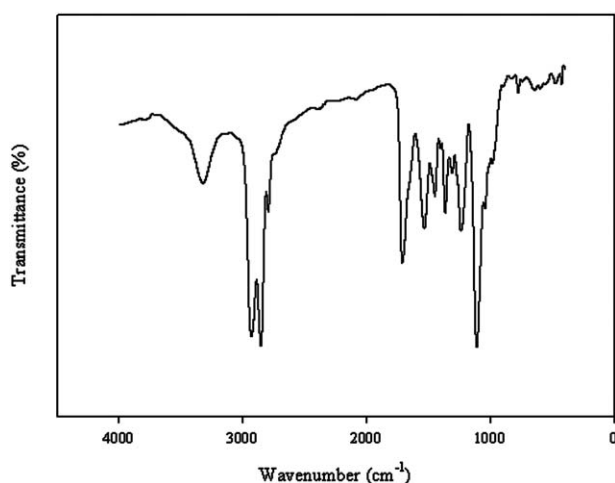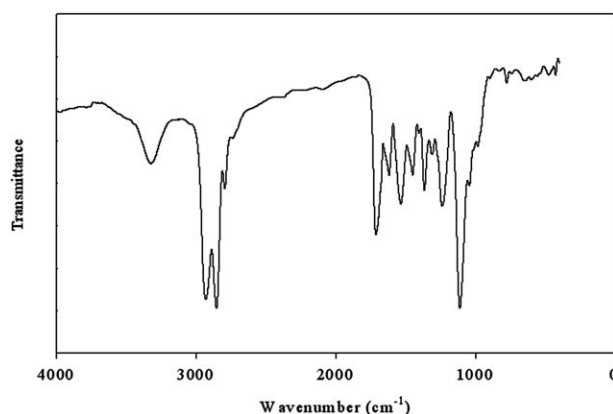

Figure 1. FTIR spectrum of WBPU-4.
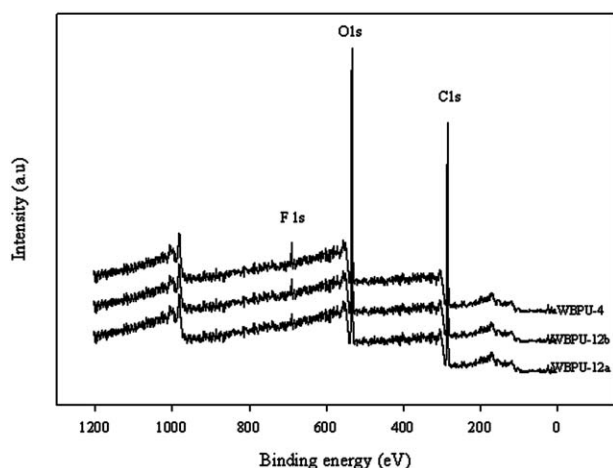

Figure 2. FTIR spectrum of WBPU-8.

Figure 3. Typical XPS spectra of WBPU films.

Table II. Mechanical Properties and RMS Values of WBPU Films

Sample designation	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Root mean square roughness (RMS) (nm)
WBPU-1	8	0.5	989	1.25
WBPU-2	29	3	973	1.33
WBPU-3	31	4	965	2.51
WBPU-4	35	7	950	7.75
WBPU-5	10	1	251	1
WBPU-6	69	43	238	1.03
WBPU-7	79	58	201	1.19
WBPU-8	94	74	143	1.45
WBPU-9	9	1	800	1.15
WBPU-10-a	51	15	781	1.04
WBPU-10-b	51	16	778	1.15
WBPU-11-a	59	22	750	1.21
WBPU-11-b	58	23	746	1.91
WBPU-12-a	67	30	720	2.21
WBPU-12-b	67	32	718	4.12

rigid diisocyanate which make it easy for fluorine groups to migrate over the surface.

AFM is a powerful technique for characterizing surfaces. Figure 4 shows typical AFM images of the samples. The Root mean square roughness (RMS) values are summarized in Table II. Usually the higher RMS value implies the surface changed from smooth to rough.[16] The RMS value increased with increasing TFBD content for all three series. The RMS value also increased when TFBD bonded to H_{12}MDI. The higher RMS values imply that the surface changed to a rough area with increasing TFBD content and bonding TFBD and H_{12}MDI, which was attributed to the increase in fluorine containing groups on the surface. The largest RMS values were found when higher TFBD content (8.77 mol %) was bonded to the H_{12}MDI. This suggests that those groups of TFBD can move more easily to the surface with comparatively flexible aliphatic hard segments.

The mechanical properties of the films were evaluated using a tensile test. Table II lists the corresponding tensile strength, Young's modulus, and elongation at break (%) of the films. The tensile strength and Young's modulus of the WBPU films increased with increasing TFBD content. This was attributed to the higher content of hard segment content and might reflect a higher tensile strength and Young's modulus.[2] With a fixed TFBD content, the tensile strength and Young's modulus values decreased in the order of MDI > mixed diisocyanates >

H_{12}MDI. The highest tensile strength and Young's modulus were found with MDI and a higher TFBD content. On the other hand, bonding between the diisocyanates and TFBD had an almost negligible effect on the mechanical properties.

The certain level of water resistance of coatings is prerequisite for commercial application. Usually, the water resistance of a coating is assessed by its water swelling (%).[7] Here, the water swelling (%) decreased with increasing TFBD content (Table III). This improvement in water resistance might be due to the presence of hydrophobic fluoro groups on the coating. The least water selling was observed for the coatings with TFBD of 8.77 mol % in each series. This might be due to enriched of larger content of hydrophobic fluoro groups in coatings. With an 8.77 mol % TFBD content, the water swelling decreased 6% of WBPU coatings.

Table III lists the adhesive strength of the coatings. Under the untreated conditions (before immersing the coatings in artificial salt water), the adhesive strength depends on the diisocyanate
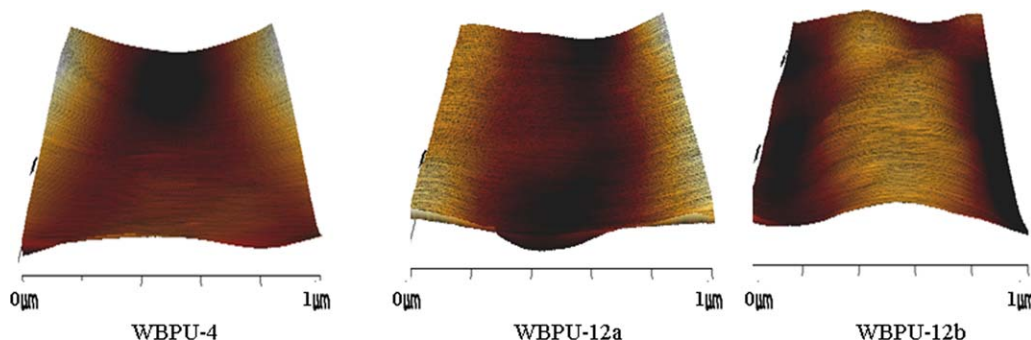

Figure 4. Typical AFM photograph of WBPU film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Adhesive Strength (kgf/cm) Before and After Immersing the Solid-Supported PVC-Coating in Artificial Salt Water

Sample designation	Water swelling (%)	Before immersion	Adhesive strength (kgf/cm)		
			After immersion		
			(1 month)	(2 month)	(3 month)
WBPU-1	20	0.3	–	–	–
WBPU −2	16	1.1	0.4	–	–
WBPU-3	11	1.9	0.5	0.1	–
WBPU-4	6	2.8	2.6	2.6	2.5
WBPU- 5	18	0.5	–	–	–
WBPU-6	13	2.6	1.4	0.5	0.1
WBPU-7	9	3.2	1.7	0.6	0.1
WBPU-8	8	3.9	2.2	0.8	0.2
WBPU-9	20	0.8	–	–	–
WBPU-10-a	16	3.5	1.9	0.9	0.3
WBPU-10-b	15	3.5	2	1	0.5
WBPU-11-a	13	3.9	2.1	1	0.5
WBPU-11-b	11	3.9	2.4	1.2.	0.6
WBPU-12-a	7	4.4	3.3	2.5	1.7
WBPU-12-b	4	4.5	4.4	4.4	4.4

and TFBD content. No significant changes in adhesive strength were observed with the bonding of different diisocyanates to TFBD. The adhesive strength increased with increasing TFBD content in all aspects. At a fixed TFBD content, the adhesive strength decreased in the following order: mixed diisocyanates > MDI > H_{12}MDI. The mixed diisocyanates with a higher TFBD content showed the maximum adhesive strength. All the coatings except for WBPU-4, WBPU-12a, and WBPU-12b showed highly deviated adhesive strength values under artificial salt water. WBPU-4 and WBPU-12b showed similar values to their untreated counterparts. This was attributed to the unaffected interlocking bonding between the coating and PVC. As these two coatings had sufficiently enriched fluorine surfaces, it might be difficult for water to penetrate through the coatings due to hydrophobic fluorine groups. This results in an almost unaffected adhesive strength in water. Other coatings might have absorbed water, which resulted in decreased mechanical interlocking of the coatings to PVC and a decrease in adhesive strength. The highest adhesive strength was observed for WBPU-12b due to a combination of mixed diisocyanates, higher TFBD content and TFBD-bonded H_{12}MDI. All these favored to make a highly protected coating for water and kept the adhesive strength almost 3 months.

CONCLUSIONS

WBPU coatings were prepared with different TFBD contents. The coating surface changed to a fluorine-enriched surface with a combination of aliphatic diisocyanate and a higher TFBD content. A higher tensile strength and Young's modulus were observed with MDI based WBPU films. A higher adhesive strength in artificial salt water was only observed when the WBPU coatings consisted of a higher TFBD content (8.77 mol %), mixed diisocyanates and TFBD bonded H_{12}MDI. Consider-

ing the good adhesive strength in artificial salt water, this type of WBPU coating can be considered an alternative to the current solvent-based marine coatings.

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