

Mechanical and Surface Properties and Hydrolytic Stability of Cycloaliphatic Polyester-Based Waterborne Polyurethanes Modified with Fluoro Oligomer

Sang Hong Park,¹ Su Kyoung Lee,¹ Hee Young Choi,¹ Eon Mi Lee,¹ Eun Young Kim,² Chung Hwan Lim,³ Dong Woon Lee,³ Byung Kyu Kim¹

¹Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea

²Institution of Industrial Science and Technology, Pukyong National University, Busan 609-737, Korea

³Plastic Coating R&D Team, KCC Co., Yongin 446-912, Korea

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ABSTRACT: Polyurethane dispersions (PUDs) have been designed and synthesized based on different types of soft segments, namely, poly(2,4-diethyl-1,5-pentamethylene adipate) glycol (PDPAD; $\overline{M}_n = 1000$) and poly(2,4-diethyl-1,5-pentamethylene-1,4-cyclohexane dicarboxylate) glycol (PDPCD; $\overline{M}_n = 1000$), and were subsequently modified with fluoro oligomer (BA-N fluoroalcohol). It was found that the PDPCD segments improved the hydrolytic stability, whereas the contact angle with water drop was signifi-

cantly increased with the addition and increasing amount of Zonyl for PDPAD-based PU and it was marginally increased with PDPCD-based PU. In addition, the PDPCD provided PUD with enhanced mechanical properties compared with the PDPAD. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1828–1834, 2009

Key words: PDPCD; cycloaliphatic structure; fluoro oligomer; hydrolytic resistance

INTRODUCTION

Waterborne polyurethane (PU) can be formulated with little or no solvent, and, hence, they are non-toxic, nonflammable, and do not pollute the air. Such environmental advantages coupled with increasing solvent price have steadily expanded their usages in a number of applications in surface coatings, fiber sizing, and adhesives of many polymeric and glassy surfaces.^{1,2}

Depending on the field of application, polyester polyols (PEPOs) have often been chosen as the soft segment.^{3,4} A most important aspect of PEPO in coatings is the hydrolytic stability that can promote main chain scission. To improve lifetime deficiencies of PEPO, model compound studies have been performed based on steric, anchimeric, hydrophobic, inductive, and resonance effects coupled with the ester moiety. This has provided insight into approximate lifetime prediction.^{5–8}

With regard to the surface property of coated films, hydrophilic segments of aqueous PU adversely affect water and oil repellency because of the relatively high surface free energy. One method to rectify such a flaw is to introduce fluorinated poly-

mers on the surface.^{9,10} This gives enhanced chemical, thermal, hydrolytic, and oxidative stability together with increased oxygen permeability.¹¹

In this article, PEPO was prepared using 1,4-cyclohexanedimethanol and the effects of cycloaliphatic acid-based PEPO in PU dispersions have been studied in term of mechanical property and hydrolytic stability. And polyurethane dispersions (PUDs) were modified with fluoro material (BA-N fluoroalcohol). Surfaces were subsequently examined by static contact angle measurements, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Raw materials

Poly(2,4-diethyl-1,5-pentamethylene adipate) glycol (PDPAD; $\overline{M}_n = 1000$), 1,4-cyclohexanedicarboxylic acid (1,4-CHDA; Aldrich, St. Louis, MO), 2,4-diethyl-1,5-pentanediol (DEPD, TCI, Tokyo, Japan), and 1,4-butanediol (1,4-BD; Junsei Chemicals, Tokyo, Japan) were dried and degassed at 80°C, 1–2 mmHg, for 3 h before use. Dimethylol butanoic acid (DMBA; Aldrich) and adipic acid (Junsei Chemicals) was dried at 50°C for 48 h *in vacuo*. 1,6-Hexamethylene diisocyanate (HDI; Aldrich), cyclohexylmethane diisocyanate (H₁₂MDI; Aldrich), and dibutyltin dilaurate (Aldrich) were used as received. Triethylamine

Correspondence to: B. K. Kim (bkkim@pnu.edu).

TABLE I
Formulations to Prepare PUDs

Designation	Soft segment				Hard segment						Prepolymer molecular weight	Solid content (%)
	PDPAD 1000 (mol)	PDPCD 1000 (mol)	HDI (mol)	DMBA (wt %/mol)	H ₁₂ MDI (mol)	1,4-BD (mol)	HSC (wt %)	Zonyl (mol)	TETA (mol)	TEA (mol)		
A30Z0	5.28	–	7.30	3.5/2.38	8.90	6.87	30	–	0.50	2.38	10,000	40
A30Z25	5.28	–	7.30	3.5/2.38	8.68	6.75	30	0.64	0.32	2.38	10,000	40
A30Z50	5.28	–	7.30	3.5/2.38	8.54	6.65	30	0.95	0.24	2.38	10,000	40
C30Z0	–	5.28	7.30	3.5/2.38	8.90	6.87	30	–	0.50	2.38	10,000	40
C30Z25	–	5.28	7.30	3.5/2.38	8.68	6.75	30	0.64	0.32	2.38	10,000	40
C30Z50	–	5.28	7.30	3.5/2.38	8.54	6.65	30	0.95	0.24	2.38	10,000	40

(TEA; Aldrich) and triethylene tetramine (TETA; Aldrich) were dried over 4-Å molecular sieves before use. Zonyl BA-N (Zonyl; $\overline{M}_n = 538$; DuPont, Wilmington, DE) as a fluoroalkyl alcohol was used as received, while tetrahydrofuran (THF; Aldrich) was dried over 4-Å molecular sieve before use.

Synthesis of poly(2,4-diethyl-1,5-pentamethylene-1,4-cyclohexane dicarboxylate) glycol

Poly(2,4-diethyl-1,5-pentamethylene-1,4-cyclohexane dicarboxylate) glycol (PDPCD) was prepared from 1,4-CHDA and DEPD by direct esterification method, and the detailed procedures are available elsewhere.¹² The number average molecular weight (\overline{M}_n) of PDPCD calculated by using the measured hydroxy value (OHV) (114) according to the following equation was ~ 984 (g/mol).

$$\overline{M}_n = \frac{56,100 \times \text{Functionality}}{\text{OHV}}$$

Preparation of waterborne PUs

The formulation and preparation procedure are given in Table I and Scheme 1, respectively. A 500-mL round-bottomed, four-necked separable flask with a mechanical stirrer, thermometer, and condenser with drying tube and N₂ inlet was used as reactor. The reaction was carried out in a constant temperature oil bath. HDI and DMBA were charged into the dried flask. While stirring, the mixture was maintained at 70°C for about 4 h to obtain NCO-terminated prepolymer. DMBA is indispensable for ionic dispersion but deteriorates drying and hydrolytic stability. So, it is a basic policy to minimize the content of DMBA as far as the dispersion is stable. According to our earlier work,¹³ ionic centers located in soft segments (SSs) rather than the ones located in hard segments (HSs) gave much finer dispersion. In this regard, DMBA was first reacted with an excess amount of HDI which has linear and flexible struc-

ture to obtain NCO terminations which were subsequently reacted with PDPCD and PDPAD to obtain OH terminated SS. This SS was reacted with H₁₂MDI and chain extended with 1,4-BD to build up HS. The NCO-terminated prepolymer was reacted with Zonyl BA-N to obtain fluoro-modified prepolymer. Then the prepolymers were cooled to 60°C, and a neutralizing agent, i.e., TEA was added and stirred for 3 h while maintaining the temperature at 60°C. An aqueous dispersion of PUs was obtained by adding water (35°C) to the mixture (60°C) using a tubing pump, followed by chain extension with TETA. The resulting product was a stable PUD with a solid content of about 40%.

Characterizations

Films were prepared by casting the dispersion onto Teflon plate, followed by drying at 40°C for 12 h. The resulting films were then heated overnight in an oven at 60°C under 2–3 mmHg. Microtensile test specimens were prepared according to ASTM D 1822.

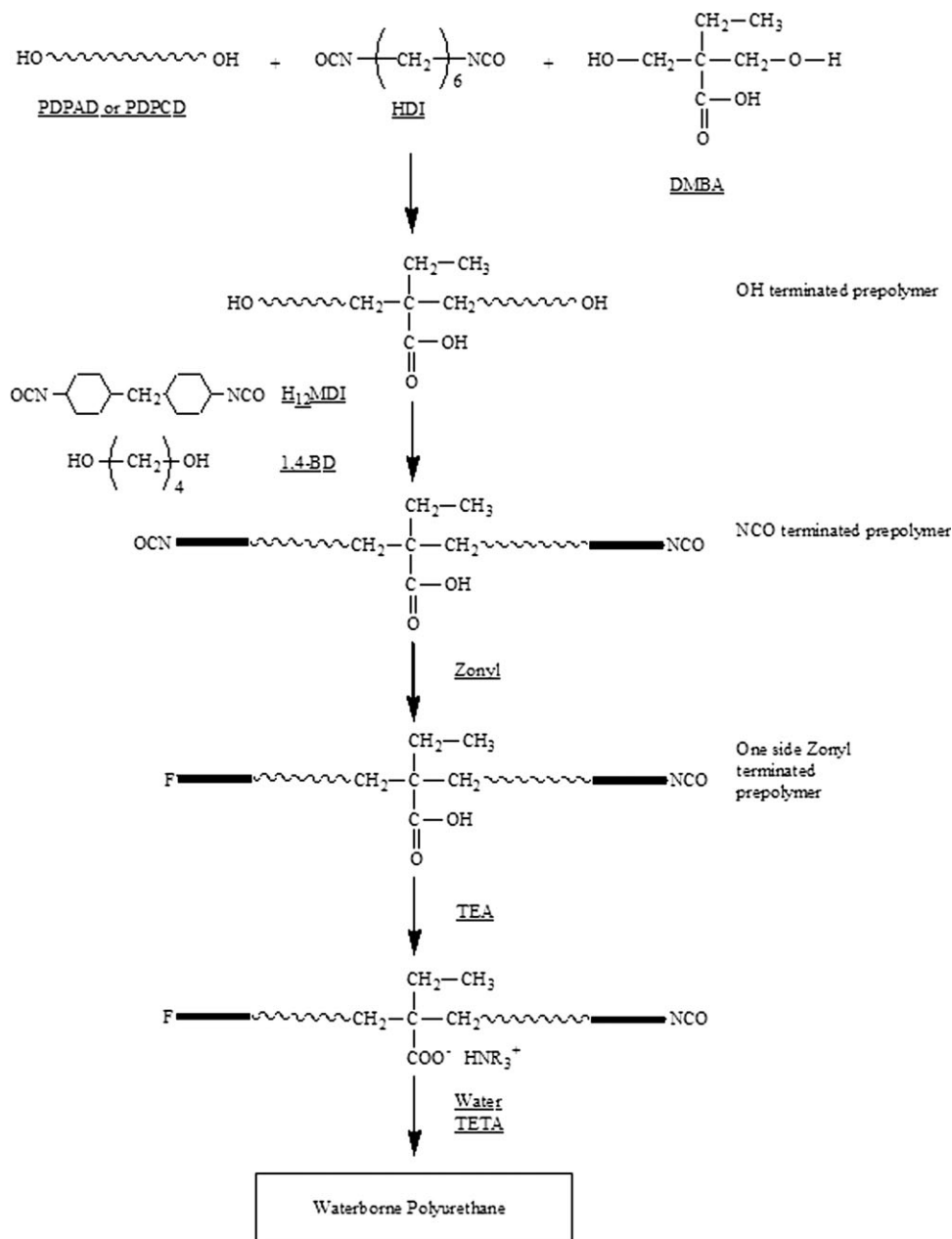
Tensile properties of PUD cast films were measured using a Tinius Olsen tensile tester at a cross-head speed of 500 mm/min, and an average of at least five measurements were taken.

Dynamic mechanical tests were performed with a dynamic mechanical thermal analyzer (DMTA MK-IV; Rheometric Scientific). Experiments were carried out at a frequency of 10 Hz, heating rates of 4°C/min, and 0.02% strain over a temperature range from –100 to 150°C.

Shore a hardness was measured using an indentation hardness tester according to ASTM D 2240-75.

A contact angle analysis was performed at five points for each specimen. Distilled-deionized water was used to obtain advancing and receding water contact angles with conventional contact angle goniometer (G-1; Erma).

Hydrolytic stabilities of the PUs were tested by a thermohumidistat (DW-TH-1510) at 60°C and 98% relative humidity for a duration of 3 weeks. After



Scheme 1 Reaction scheme to prepare PUD.

hydrolysis, dynamic mechanical properties of the test specimens were measured using the DMTA. The % hydrolysis as a function of hydrolysis time was calculated by the following equation:

$$\% \text{ Hydrolysis} = \frac{E}{E_0}$$

where E_0 is the modulus of original film and E is the one after hydrolysis.

Film surface has been characterized by AFM using a Nanoscope III equipped with 1553D scanner (Digital Instruments), following a height mode in air. The XPS study was performed with a VG-Scientific

ESCALAB 250 spectrometer with monochromatized Al K α X-ray source. Survey and high-resolution spectra were collected using 160 and 20 eV pass energies, respectively.

RESULTS AND DISCUSSION

Mechanical properties

Figure 1 shows the stress-strain curves of PDPCD- and PDPAD-based PUD cast films. Stress-strain behavior of PDPCD-based ones shows much higher modulus and strength, whereas that of PDPAD-

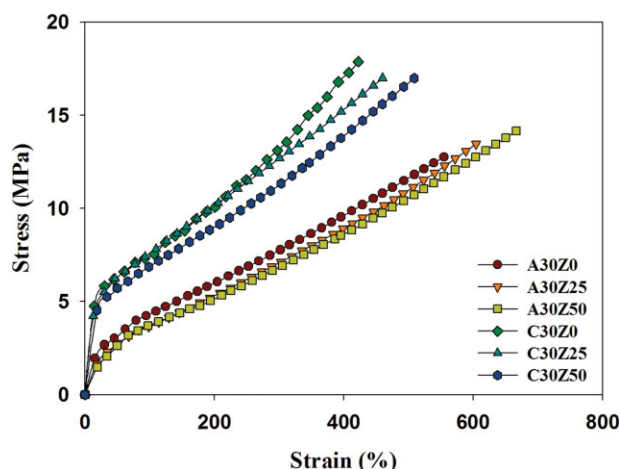


Figure 1 Tensile behavior of PUDs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

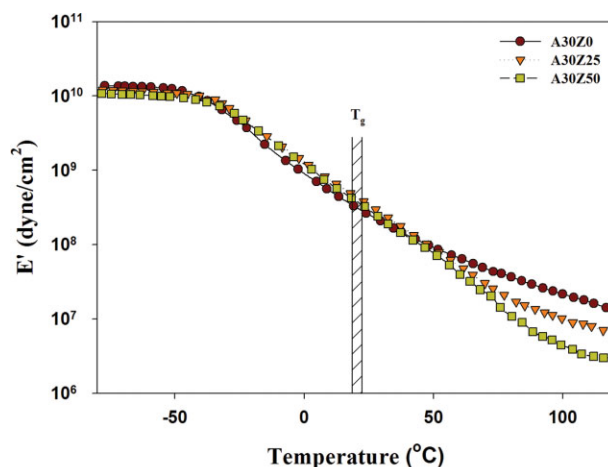
based one shows high elongation at break. These results show that the cycloaliphatic structure of PDPCD gives higher stiffness than the linear one. Generally, the cycloaliphatic structure gives intermediate physical properties between aromatic and linear aliphatic polyesters except yellowing resistance which correlates better with linear diacids.¹⁴ For both types of PU, initial modulus decreases and elongation at break increases smoothly with the addition and increasing amount of Zonyl because of the decreased crosslinking density. On the other hand, tensile strength increases with Zonyl content for PDPAD and decreases for PDPCD series.

Dynamic mechanical measurements (Fig. 2) show that the glass transition temperature (T_g) based on the point of inflection of storage modulus (E') curve is higher for PDPCD than for PDPAD series by about 25°C. This gives higher room temperature modulus for PDPCD than for PDPAD series. The linear structure of diacids in the PEPO should provide PU with lower T_g than the cycloaliphatic diacids. It is also noted that the rubbery modulus (E_N°) decreases with increasing Zonyl content because of decreased crosslinking density given by the ideal rubber theory:

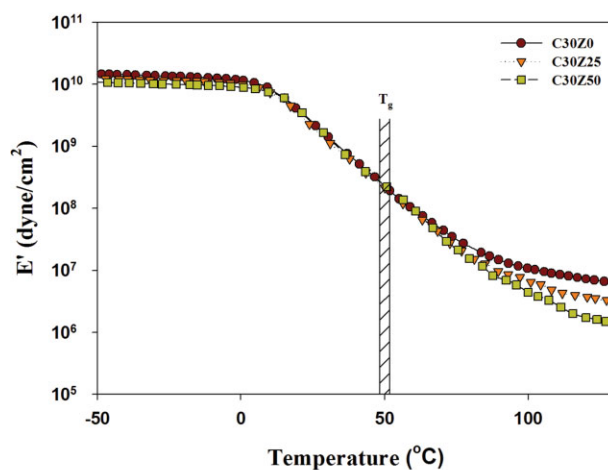
$$E_N^\circ = \frac{3\rho RT}{M_c}$$

where ρ is the density of the film, R is the gas constant, T is the absolute temperature, and M_c is the molecular weight between crosslinks. With the addition and increasing amount of Zonyl, M_c increased to give lower rubbery state modulus.

Table II shows that the hardness of PDPAD series is higher than that of PDPAD series. It was noted earlier that the modulus of cycloaliphatic polyester was higher than that of linear aliphatic polyester at



(a)



(b)

Figure 2 Dynamic mechanical properties of PUDs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

room temperature. With the addition and increasing amount of Zonyl, the hardness decreased like modulus because of decreased crosslink density.

Surface and hydrolytic properties

Hydrolytic stability of the PUD cast films is shown in Figure 3 and the results are summarized in Table III.

TABLE II
Hardness and Contact Angle of PUD Cast Films

Zonyl contents (%)	Hardness (shore A)		Contact angle (°)	
	PDPCD	PDPAD	PDPCD	PDPAD
0	91.6	83.2	77	72
25	90.5	80.2	80	92
50	87.3	80.0	83	103

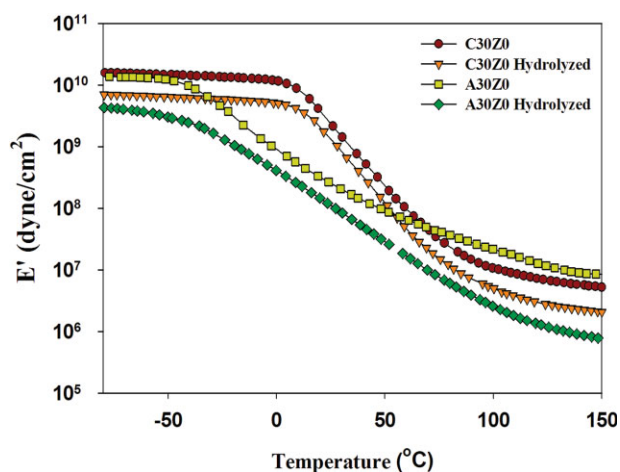


Figure 3 Hydrolytic stability of PUD cast films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PDPCD-based PU gave higher hydrolytic stability than PDPAD series because of the greater hydrolytic stability of carbonyl groups of cyclic structure. This implies that the cycloaliphatic structures have greater ability to physically impede the nucleophilic attack of water molecule because of interconversion of chair and boat conformations.⁵ Linear aliphatic acid-based PEPO has intramolecular catalysis effect, known as the anchimeric effect which is the ability of an attached hetero atom or group to participate in the hydrolysis of an ester.

Table II shows the contact angle of the dispersion cast film with water drops. Contact angle of PDPCD-based PU is greater than that of the PDPAD-based one because of the hydrophobic nature of PDPCD. However, contact angle is significantly increased with the addition and increasing amount of Zonyl for PDPAD series, but it is marginally increased with the PDPCD ones. As a result, contact angles for PDPAD series are much greater than those of PDPCD series. This implies that the fluoro alkyl segments preferably migrates toward the surface and the process is more pronounced in the rubbery state than in the glassy state.¹⁵ In this regard, we noted that the PDPCD-based PU is in its glassy state, whereas the PDPAD-based PU is in its rubbery state at room temperature (Fig. 2).

TABLE III
Hydrolysis Resistance of PUD Cast Films

	Hydrolysis resistance			
	25°C	50°C	100°C	150°C
A30Z0	62	48	32	29
C30Z0	78	61	49	40

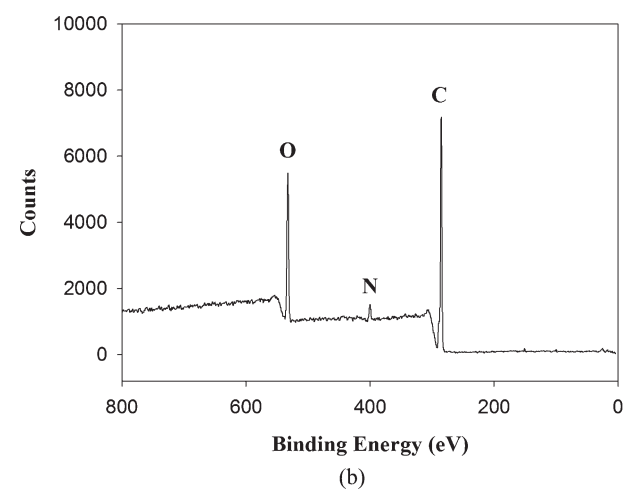
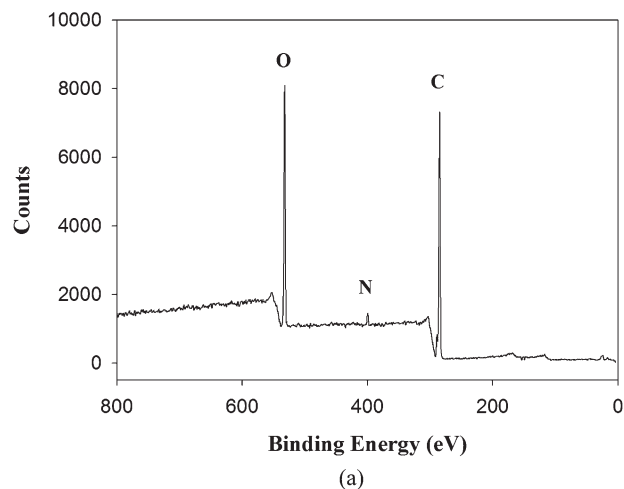
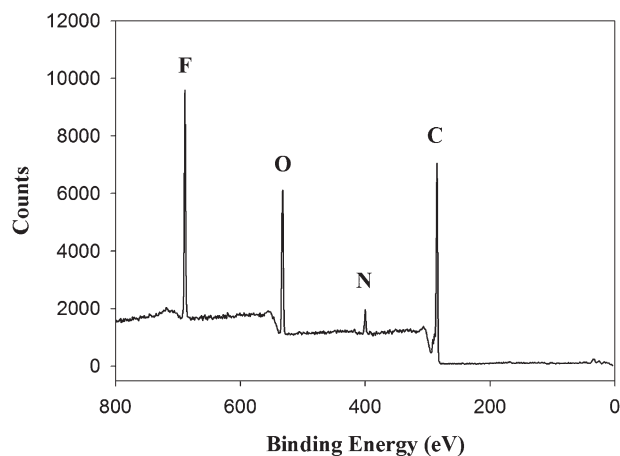


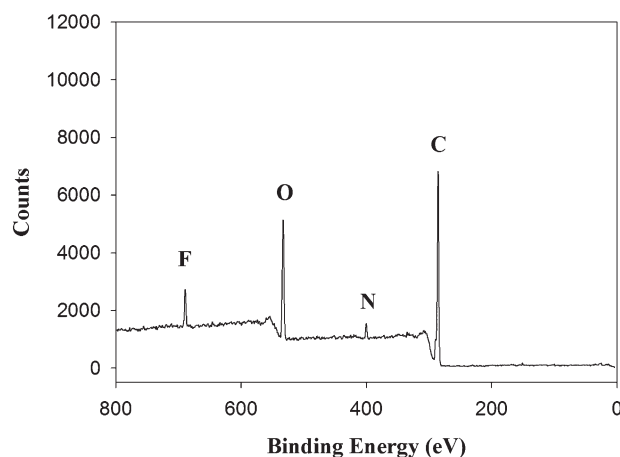
Figure 4 XPS survey spectra of A30Z0 (a) and C30Z0 (b).

Figures 4 and 5 show the XPS survey spectra of base PUD and surface-modified PUD cast films. Peaks corresponding to carbon (C 1s), nitrogen (N 1s), oxygen (O 1s), and fluorine (F 1s) are seen. Naturally, fluorine is not seen with the base PU at all. Table IV shows the experimental atomic compositions calculated from the XPS intensities of the films. The composition of F atom for A30Z50 (13.25% Zonyl) is much higher than that of C30Z50 (3.19% Zonyl) near the surface, and the results agreed with the contact angle measurements. This implies that the migration of fluorine end groups toward the surfaces is much easier for PDPAD than for PDPCD series because of the higher mobility of the PDPAD series that are in rubbery state.

The three-dimensional AFM pictures of the films are presented in Figure 6. The RMS roughness of A30Z50 (18.743 nm) is much higher than that of C30Z50 (5.819 nm). These results well agreed with the XPS survey spectra. The effect of fluorine modification is much greater with PDPAD than with PDPCD series because of the easier migration of fluorine segments toward the surfaces. The



(a)



(b)

Figure 5 XPS survey spectra of A30Z50 (a) and C30Z50 (b).

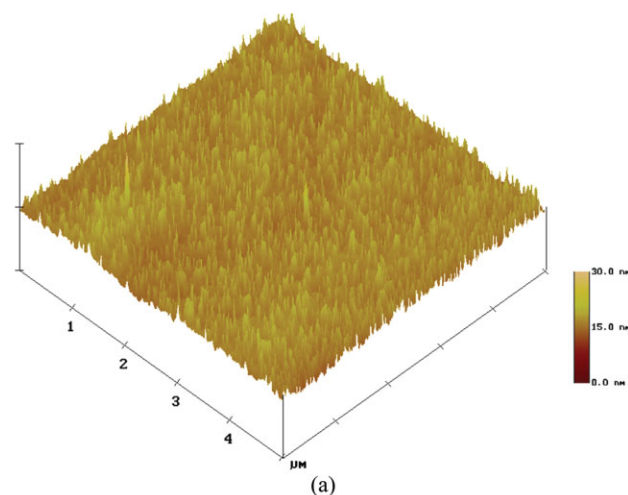
cycloaliphatic structure of 1,4-CHDA-based PDPCD enhanced the mechanical strength and hydrolytic resistance but decreased the chain flexibility. RMS roughness would be an indirect measure of surface free energy, i.e., lower surface free energy creates more surfaces which can take the form of spikes as shown in our AFM images of the PDPAD series.

CONCLUSIONS

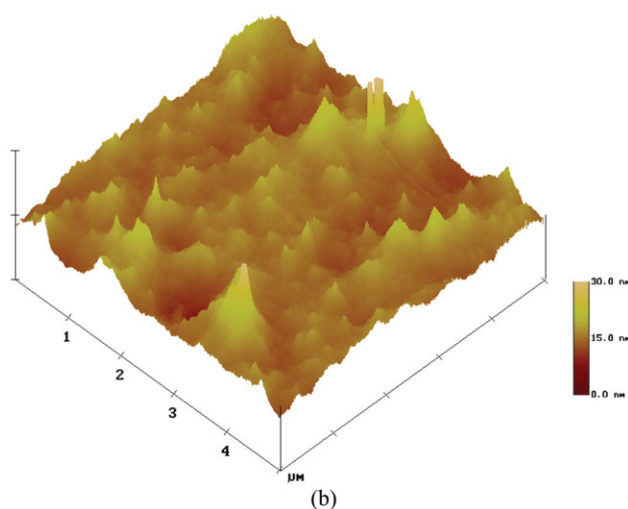
PDPCD was synthesized from 1,4-cyclohexanedicarboxylic acid + DEPD and was used to prepare

TABLE IV
Atomic Compositions Calculated from the XPS Intensities for PUD Cast Films

Peak/designation	A30Z0	A30Z50	C30Z0	C30Z50
C 1s	77.63	66.20	79.86	79.86
O 1s	20.77	16.80	17.17	17.17
N 1s	1.60	3.73	2.95	2.91
F 1s	–	13.25	–	3.19



(a)



(b)

Figure 6 3D AFM images of A30Z50 (RMS = 18.743 nm) (a) and C30Z50 (RMS = 5.819 nm) (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PUDs which were subsequently modified with fluoro oligomer (Zonyl BA-N) and tested for various properties.

The XPS and AFM measurements showed that fluoro segments effectively modified the PUD cast films at the free surfaces forming a fluoro-rich layer, and the effect was more pronounced with PDPAD-based PU than the PDPCD-based one because of its higher mobility at the test conditions.

PDPCD provides PUD with higher tensile property and better hydrolytic stability than PDPAD. In addition, the cycloaliphatic structure gave greater ability to physically impede the nucleophilic attack of water molecule presumably due to the interconversion of chair and boat conformations.

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