

## Preparation and Properties of UV-Curable Fluorinated Polyurethane Acrylates

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**ABSTRACT:** A series of UV-curable polyurethane acrylates (PUA0, FPUA3, FPUA6, FPUA 9 FPUA12, FPUA15, where the numbers indicate the wt % of perfluoroalkyl acrylate), were prepared from a reactive oligomer [4,4'-dicyclohexymethanediisocyanate(H12MDI)/ poly(tetramethylene glycol)(PTMG)/2-hydroxyethyl methacrylate (HEMA): 2/1/2 molar ratio, prepolymer:40 wt %] and diluents [methyl methacrylate (MMA, 20 wt %)/ isobornyl acrylate (IBOA, 40–25 wt %)/heptadecafluorodecyl methacrylate (PFA, 0–15 wt), total diluents: 60 wt %]. This study examined the effect of PFA/IBOA weight ratio on the properties of the UV-curable polyurethane acrylates for antifouling coating materials. The as-prepared UV-curable coating material containing a 15 wt % PFA content in diluents (MMA/IBOA/PFA) form a heterogeneous mixture, indicating that a PFA content of approximately 15 wt % was beyond the limit of the dilution capacity of diluents for the oligomer. In the wavelength range of 400–800 nm, the UV-cured PUA0 film sample was quite transparent (transmittance%: near 100%). On the other hand, the transmittance% of the FPUA film sample decreased markedly with increasing PFA content. XPS showed that the film-air surface of the UV-cured polyurethane acrylate film had a higher fluorine content than the film-glass dish interface. As the PFA content increased from 0 to 12 wt %, the surface tension of the UV-cured urethane acrylates decreased from 26.8 to 15.6 mN/m, whereas the water/methylene iodide contact angles of the film-air surface increased from 90.1/63.6° to 120.9/87.1°. These results suggest that the UV-curable polyurethane acrylates containing a PFA content up to 12 wt % have strong potential as fouling-release coating materials. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40603.

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### INTRODUCTION

Generally, polyurethane acrylates are composed of soft segment formed of polyol chains, acrylic structure unit formed from the reaction of hydroxyl acrylate and reactive acrylate monomers (diluents) and/or hard segments formed from diisocyanate and low molecular diol. The versatility of these materials can be attributed to the ability of UV-light to transform a solvent-free, liquid mixture (oligomer/acrylate monomer) to a solid almost instantaneously, with a range of properties available through the judicious choice of coating components. This high production rate/energy efficiency and versatility of properties have made them ideal materials for use in a wide range of applications, including thin film coatings,<sup>1–4</sup> protective coatings for optical fibers,<sup>5,6</sup> and photolithography.<sup>7</sup>

The low surface tension of coating material is an important factor for the application of fouling-release coatings. One of the most popular and successful strategies for reducing the surface

tension of a film is the incorporation of fluorine into the polymer molecules. Fluorinated polymers (fluoropolymers) are becoming increasingly important because of their unique surface properties (high hydrophobic/oleophobic properties: very low surface tension, and water- and oil-repellent properties) and are predestined for use as soil-repellent coating systems. The most common commercially available fluoropolymers are based on the monomers of tetrafluoroethylene, vinylidene fluoride, and chlorotrifluoroethylene. Polytetrafluoroethylene is a polymeric solid with a very low surface tension. Therefore, its critical surface tension/water contact angle of wetting of 18.5 mN/m/108° is characteristic of a surface consisting essentially of closed packed perfluoromethylene-CF<sub>2</sub>-groups.<sup>8</sup> Fluoroalkyl acrylate homopolymers with long side chains have very low critical surface tension, ranging from 10 to 11 mN/m.<sup>9</sup> The lower critical surface tension of many polymers containing fluorocarbon side chains has been attributed to the higher content of CF<sub>3</sub> groups on their surfaces.<sup>9–12</sup> Generally, the surface energy

(tension)/contact angle of a material is used as a criterion of the antifouling property.

Acrylic copolymers containing perfluoroalkyl side chains have been the focus of many studies because of the good reactivity of perfluorinated acrylate with fluorine-free acrylate and good adhesion to the matrices. Generally, longer alkyl and perfluoroalkyl moieties increase the tendency for microphase separation in the bulk and surfaces.<sup>13–15</sup> The long fluorinated side groups in fluorinated acrylic copolymers have emerged preferentially at the coating-air surface.<sup>16–19</sup> The reason for the very low surface tension of perfluoroalkyl polymer is the orientation of hydrophobic/oleophobic perfluoroalkyl groups to the outmost layer of the polymer-air surface. Comb-shaped polymers with fluorocarbon segments in their side chain are used as surface modification agents, such as water and oil repellents, and soil release on different substrates, such as textiles, paper, leather and carpets, as well as nonwoven and building materials.<sup>20</sup> The extent to which the polymer surface tension is reduced depends not only on the surface coverage by fluorocarbon segments but also on the degree of ordering in the surface layer. However, the main disadvantage of the fluorinated monomer is the relatively high cost. Therefore, the content of fluorinated monomers should be minimized while maintaining a reasonable surface tension (water/oil repellency).

A combination of polyurethane with an acrylic copolymer containing fluorine is expected to be effective in increasing the performance of the resulting materials. These materials combine some of the virtues of polyurethane and fluorinated acrylate/acrylate polymer, such as high thermal stability, good chemical resistance, excellent flexibility, good low temperature properties, low water absorptivity (water resistance), attractive surface properties (low surface tension: antifouling property), good wearability, good optical properties, and high weatherability.<sup>12,21–25</sup> Polyurethane/polyacrylate hybrid emulsions have been studied.<sup>26–31</sup>

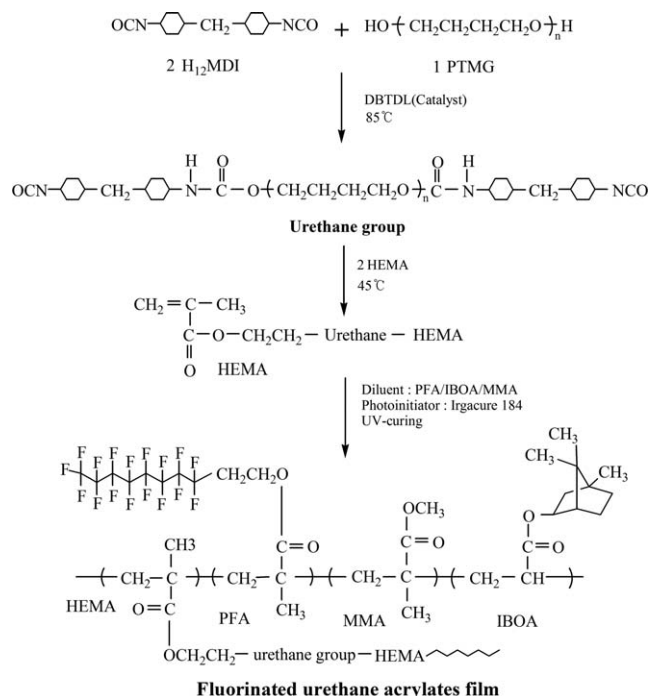
Some studies have examined the UV-curable waterborne polyurethane/polyurethane-acrylate<sup>32–34</sup> but there are few reports on UV-curable fluorinated poly(urethane acrylate)s using fluorinated urethane.<sup>35,36</sup> Moreover, there has been little work on UV-curable copolymers of urethane-acrylate oligomer with acrylate monomer/ acrylate monomer possessing perfluoroalkyl groups.

In this study, the bulky monomer MMA was used to increase the hardness of material, rigid bulky cycloalkyl group contained monomer IBOA to raise toughness, and long perfluoroalkyl group contained monomer perfluoroalkyl acrylate (PFA) to expand surface tension. This study focused on the effect of PFA/IBOA weight ratio on the properties of stable UV-curable fluorinated polyurethane-acrylates with a fixed urethane oligomer content (40wt %) to find the optimum content of the fluorinated acrylic monomer for good antifouling coatings having high hydrophobic/oleophobic (water-/oil-repellent) properties.

## EXPERIMENTAL

### Materials

Poly(tetramethylene glycol) (PTMG Mn = 2000 g/mol; Aldrich Chemical, Milwaukee, WI) was dried at 90°C under 1–2 mmHg



**Scheme 1.** Synthesis process of UV-curable fluorinated urethane acrylates films.

for 3 h before use. Dibutyltindilaurate (DBTDL, Aldrich Chemical, Milwaukee, WI), 4,4'-dicyclohexylmethanediisocyanate (H<sub>12</sub>MDI, Aldrich Chemical, Milwaukee, WI), N,N-dimethyl formamide (DMF, Duksan, Kyungkido, Korea), toluene (Aldrich Chemical, Milwaukee, WI), 2-hydroxyethyl methacrylate (HEMA, Aldrich Chemical, Milwaukee, WI), 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl methacrylate (PFA, Aldrich Chemical, Milwaukee, WI), isobornyl acrylate (IBOA, Aldrich Chemical, Milwaukee, WI), methyl methacrylate (MMA, Aldrich Chemical, Milwaukee, WI), 1-hydroxycyclohexyl acetophenone (Irgacure 184, Aldrich Chemical, Milwaukee, WI) were used as received.

### Preparation of UV-Curable Fluorinated Polyurethane Acrylates and Their Films

Scheme 1 shows the preparation process of UV-curable fluorinated polyurethane-acrylates. PTMG was 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 heating jacket, and was degassed in a vacuum at 90°C for 1 h. PTMG was allowed to cool to 45°C with moderate stirring (125–150 rpm). H<sub>12</sub>MDI was dropped slowly into the flask, and the reaction mixture was allowed to react at 85°C until the theoretical NCO content was reached. The change in NCO value during the reaction was determined using the standard dibutylamine back-titration method (ASTM D 1638). The reaction mixture of the NCO-terminated urethane oligomer was cooled to 45°C, and HEMA was added dropwise. To obtain the vinyl-terminated urethane oligomer, the capping reaction of the NCO-terminated urethane oligomer with HEMA was continued for 15 h until the NCO-content reached near zero, as evidenced by the disappearance of the IR NCO peak (2270 cm<sup>-1</sup>). The UV-curable fluorinated urethane-acrylate mixtures were

**Table I.** Sample Designation, Composition, Viscosity and Stability of UV-Curable Urethane Acrylate (Prepolymer/Diluents Mixture) Containing Various PFA Content

Sample Designation	Composition									
	PUA prepolymer (molar ratio)			PUA prepolymer (wt %)	Diluent (wt %)			Irgacure <sup>a</sup> (wt %)	Viscosity (cP/25°C)	State of mixture <sup>b</sup>
	H <sub>12</sub> MDI	PTMG	HEMA		MMA	IBOA	PFA			
PUA0	2	1	2	40	20	40	0	1.5	1579	Stable
FPUA3	2	1	2	40	20	37	3	1.5	1608	Stable
FPUA6	2	1	2	40	20	34	6	1.5	1657	Stable
FPUA9	2	1	2	40	20	31	9	1.5	1691	Stable
FPUA12	2	1	2	40	20	28	12	1.5	1702	Stable
FPUA15	2	1	2	40	20	25	15	1.5	-	Unstable

<sup>a</sup>Irgacure184 : 1.5 wt % based on prepolymer/diluents mixture.

<sup>b</sup>Stable: Homogeneous mixture, Unstable: Heterogeneous mixture.

formulated from a viscous oligomer (40 wt %), diluents and photoinitiator Irgacure 184 (3 wt % based on the oligomer / diluents). A series of UV-curable fluorinated urethane acrylates mixtures (oligomer /diluents/photoinitiator) were formulated by adding the acrylate diluents [methyl methacrylate (MMA, 20 wt %)/ isobornyl acrylate (IBOA, 40–25 wt %)/ heptadecafluorodecyl methacrylate (PFA, 0–15 wt), total diluents: 60 wt %] and photoinitiator Irgacure 184 (1.5 wt %) to the viscose urethane acrylate oligomer (40 wt %) and mixing them at 45°C for 3 h. Table I lists the sample designation and composition of the UV-curable fluorinated urethane-acrylate.

The UV-cured fluorinated urethane acrylates films (thickness: 0.3 mm) were prepared by casting the above-formulated mixture onto a glass plate at room temperature followed by curing using a medium pressure mercury lamp (80 W/cm). Radiation curing was carried out using UV light with the main wavelength of 365 nm. The distance between lamp and sample was 20 cm. Sufficient UV curing time of 3 min was used for complete curing in this study.

### Characterization

The viscosity of the UV-curable fluorinated polyurethane-acrylates dispersion and hybrid emulsions was measured at 25°C using a Brookfield digital viscometer (Brookfield LVDV|+, USA). The measurements were performed at 100 rpm using a spindle RV-3. The chemical components of the UV-curable fluorinated polyurethane-acrylate film samples were confirmed by the Fourier transform infrared (FT-IR, NICOLET iS5, Thermo scientific, USA) spectroscopy. The FT-IR spectra of the samples were recorded in the range, 4000–650 cm<sup>-1</sup> using an ATR (ZnSe crystal) apparatus at a resolution of 4 cm<sup>-1</sup> and 32 scans. A constant compression load was applied to the samples. Surface analysis was performed by X-ray photoelectron spectroscopy (XPS, Theta Probe AR-XPS System, Thermo Fisher Scientific, UK) equipped with a monochromated Al K $\alpha$  X-ray source (15 kV, 150 W) and a spot size of 400  $\mu$ m. The samples for XPS were prepared by casting the polymer onto a clean glass disc. The disc was placed into an oven at 60°C for 12 h and 60°C for 6 h under vacuum.

The gel content of UV-cured film samples was determined by the Soxhlet extraction method using toluene/DMF for 24 h. The gel contents of the UV-cured film samples were determined from the difference in dry weight before and after the extraction experiment. It was found that the gel content of all UV-cured film samples prepared in this study had a very high molecular weight (crosslink-like structure).

The water and methylene iodide contact angles were measured at 25°C using a contact angle goniometer (Erma Contact Angle Meter, Japan), and 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 tension of the solid film can be determined using the following equation:

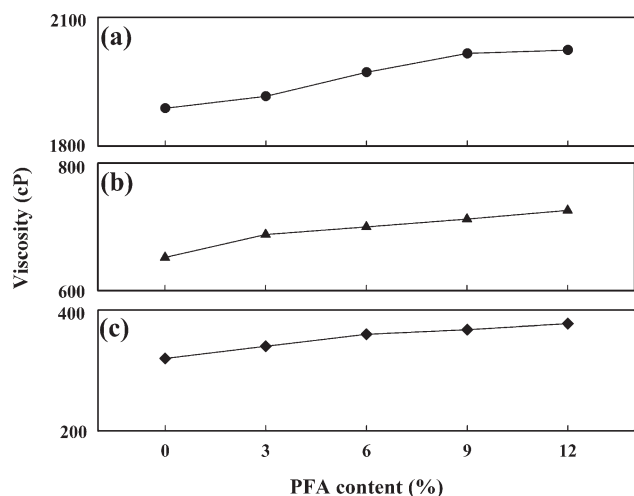
$$\gamma_s = \gamma_s^d + \gamma_s^p$$

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

where  $\gamma_s$  is the surface tension of the solid film,  $\gamma_s^d$  is the dispersion force, and  $\gamma_s^p$  is the polarity force. The testing liquids used were water (L1) and methylene iodide (L2), and their  $\gamma_{L1}^d$ ,  $\gamma_{L1}^p$ ,  $\gamma_{L2}^d$ , and  $\gamma_{L2}^p$  were 21.8, 51.9, 1.3, and 49.5 mN/m, respectively.<sup>37</sup>

The dynamic mechanical properties of film samples were measured at 3 Hz using dynamic mechanical thermal analyzer (DMA, TA-Q800; TA Instrument, USA) with a heating rate of 10°C/min in the temperature range from -100°C to 100°C.

The tensile properties were measured at room temperature using a Universal Testing Machine (UTM, WL2100, WITHLAB). A cross-head speed of 10 mm/min was used throughout these investigations to determine the ultimate tensile strength, modulus, and elongation at break. The hardness was measured using a shore A type durometer (Asker, Kobunshi Keiki, Japan) according to ASTM D 2240. The films were overlapped and used in the test. The values quoted are the mean of five measurements. The UV-Visible spectra were measured using a



**Figure 1.** Viscosity versus PFA content of UV-curable samples (PUA0, FPUAs 3, 6, 9 and 12) at various temperatures: (a) at 20°C, (b) at 40°C, and (c) at 60°C.

UV-Visible spectrophotometer (T70+UV/VIS Spectrometer, PG Instruments, England).

## RESULTS AND DISCUSSION

### Preparation and Stability of Mixture Solutions of UV-Curable Urethane Acrylate (Oligomer/Diluents Mixture)

Table I lists the sample designation, composition of oligomer and oligomer/diluents, viscosity, and stability of UV-curable urethane acrylate (oligomer/diluents mixture). In this study, the oligomer was kept at a constant molar ratio, and the UV-curable urethane acrylate had a fixed weight ratio of oligomer/diluents (40/60 wt %), whereas the compositions of IBOA/PFA in the diluents (MMA(20 wt %)/IBOA/PFA) were changed from 40/0 wt % to 25/15 wt %. The solubility threshold (dilution capacity) of diluents decreased with increasing PFA content in diluents. Oligomer/diluents mixtures containing 0–12 wt % of PFA had an apparently homogeneous system. On the other hand, the oligomer/diluents mixture containing 15 wt % of PFA was heterogeneous, suggesting that almost 15 wt % of PFA in the diluents (MMA/IBOA/PFA) was beyond the limit of the dilution capacity of the diluents for the oligomer. The decrease in dilution capacity using the mixed diluents with a high PFA content might be because of the lower surface tension of the PFA component containing hydrophobic/oleophobic perfluoroalkyl moieties. This also should be because of the increases in the PFA domain (domain size and content) and micro-phase separation, attributable to the low dilution capacity of the diluents containing PFA, which led to low compatibility between the PFA-contained diluents and oligomer. These phenomena will affect the properties of the UV-cured polyurethane-acrylate film samples with a range of PFA contents, as described later.

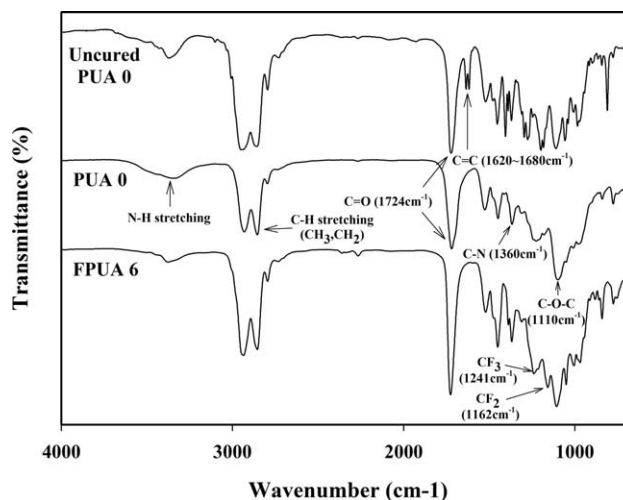
Generally, the viscosity is one of the most important properties of a fluid and plays very prominent roles (the easiness of processing and the control of thickness) in the coating industry. Figure 1 shows the viscosity vs. PFA content at various temperatures (20°C, 40°C, 60°C). The viscosity of UV-curable urethane

acrylate decreased markedly with increasing temperature. As the PFA content increased from 0 to 15 wt %, the viscosity was increased significantly from 1888 to 2024 cP at 20°C, from 650 to 726 cP at 40°C and from 296 to 342 cP at 60°C, respectively. This also should be because of the poor miscibility of the PFA component.

### Identification of Chemical Structure of UV-Cured Film Samples (PUA0, FPUAs)

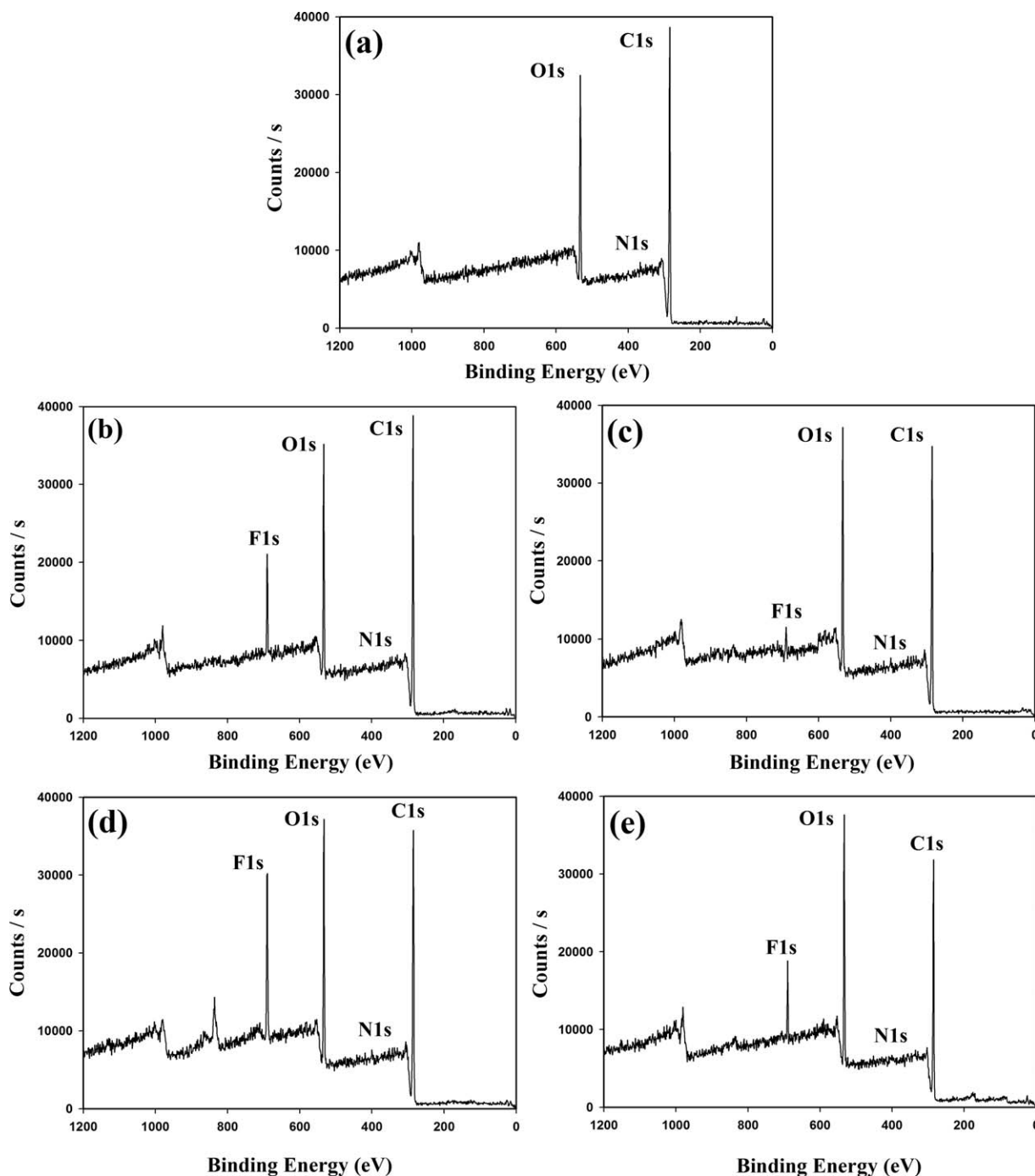
ost commonly, the process of the photopolymerization reactions of acrylic materials was followed by monitoring the disappearance of the reactive acrylic groups present in the monomers and oligomers. Figure 2 shows the FT-IR spectra of the uncured PUA0, UV-cured PUA0 film, and typical FPUA6 film samples. The FT-IR spectrum of the uncured PUA0 showed the characteristic C=C peaks at 1630–1640  $\text{cm}^{-1}$  but the UV-cured film samples PUA0 and FPUA6 had no C=C peak indicating the complete reaction of all vinyl groups. The characteristic bands at approximately 1713, 1082, 1105, 3300–3500  $\text{cm}^{-1}$  confirm the carbonyl group of urethane, C-O-C(=O) in ester group, ether group (C-O-C) of PTMG, and N-H of urethane group, respectively. The peak of ester carbonyl (C=O) group at 1730  $\text{cm}^{-1}$  was found to overlap with urethane carbonyl group in the range of 1802–1651  $\text{cm}^{-1}$ . The stretching vibrations of -CF<sub>2</sub> group at 1150  $\text{cm}^{-1}$ , -CF<sub>3</sub> group at 1230–1240, 1206  $\text{cm}^{-1}$ , and a combination of rocking and wagging vibration of the CF<sub>3</sub> group at 656 and 701  $\text{cm}^{-1}$  in the fingerprint region, are all detected in the FPUA6 film. On the other hand, many peaks of ether/urethane/acrylate/fluorine groups were overlapped with each other.

XPS is a surface chemical analysis technique for analyzing the surface chemistry of a material in the as-received state or after some treatment. Figure 3 presents the XP spectra of (a) film surface (film–air interface) of PUA0, (b) film–air surface of FPUA6, (c) film–dish interface of FPUA6, (d) film–air surface of FPUA12, and (e) film–dish interface of FPUA12. The peak at 690 eV assigned to F<sub>1s</sub> was not observed in pristine PUA0. The peak intensity of F<sub>1s</sub> increased with increasing PFA content in



**Figure 2.** FT-IR spectra of typical samples (uncured PUA0, UV-cured PUA0, and FPUA6 films).



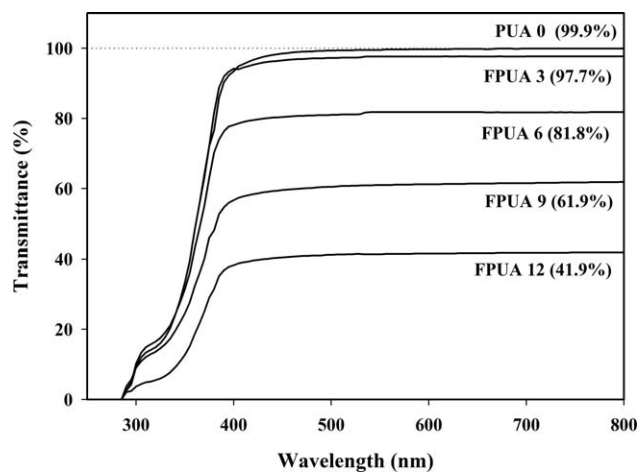


**Figure 3.** XPS spectra of (a) film–air surface of PUA0, (b) film–air surface of FPUA6, (c) film–dish interface of FPUA6, (d) film–air surface of FPUA12, and (e) film–dish interface of FPUA12.

FPUAs. By comparing the peak intensity of F<sub>1s</sub> for (d) film–air surface of FPUA12 and (e) film–dish interface of FPUA12, the relative peak intensity of F<sub>1s</sub> in the film–air surface was higher than that in the film–dish interface. By curve fitting analysis, our previous studies that covered this subject showed the same result.<sup>30,38</sup> This suggests that the long perfluoroalkyl group of PFA component was introduced mainly to the surface layer of the fluorinated material as expected.

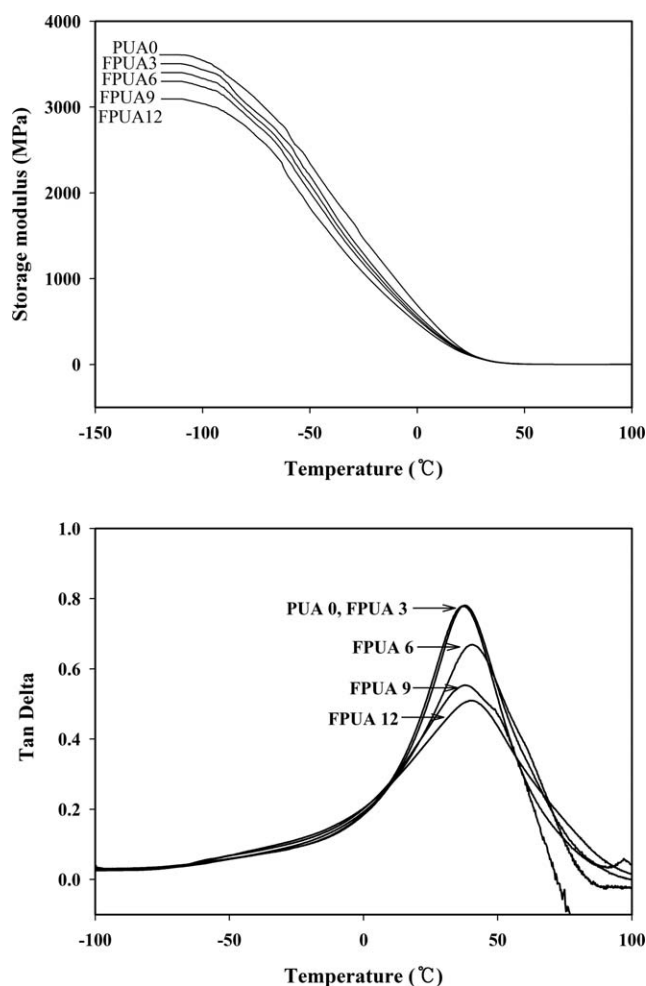
#### The Transmittance% of UV-Cured Film Samples (PUA0, FPUAs)

Figure 4 shows the UV-visible spectra of the cured film samples (PUA0, FPUA3, FPUA6, FPUA9, and FPUA12). The PUA0 film showed a high transmittance% of near 100% in the visible range. The transmittance% of the UV-cured film samples decreased markedly with increasing PFA content. The decrease in transmittance might be because of increases in the PFA

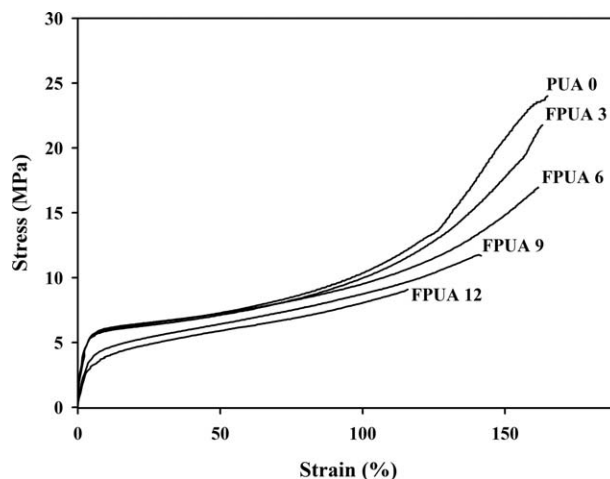


**Figure 4.** UV-visible spectra of UV-cured film samples (PUA0, FPUAs 3, 6, 9, and 12 films).

domain (domain size and content) and microphase separation<sup>13–15</sup> following the increase in PFA content. The increases in such domain and phase separation were caused by the low dilution capacity of the diluents containing hydrophobic/oleophobic



**Figure 5.** Storage modulus and tan delta of UV-cured film samples (PUA0, FPUAs 3, 6, 9, and 12).



**Figure 6.** Stress–strain curves of UV-cured film samples (PUA0, FPUAs 3, 6, 9, and 12).

PFA, which led to low compatibility between the PFA-contained diluents and oligomer. From these results, the high PFA content ( $\sim 15$  wt %) was beyond the limit of the dilution capacity for the oligomer, which led to the heterogeneous system of UV-curable urethane acrylate (oligomer/diluents mixture), as described above. These results suggest that the PFA component lowers the mechanical properties of the UV-cured polyurethane acrylate film samples but increases their contact angles, i.e. decreases their surface tension.

#### DMA Properties of UV-Cured Film Samples (PUA0, FPUAs)

Figure 5 shows the storage modulus and tan delta of the UV-cured film samples. The UV-cured urethane acrylate film sample containing a higher PFA content had a lower storage modulus. This might be because of the decrease of rigid IBOA monomer content and the incompatibility of the PFA component with the urethane oligomer. As the PFA content increased, the  $Tg\alpha$  of the film sample increased from  $37.2^\circ\text{C}$  to  $40.3^\circ\text{C}$ , whereas the broad peak at approximately  $-50^\circ\text{C}$  assigned to  $Tg\beta$  (the soft segment Tg) was almost unchanged. This suggests that the PFA/IBOA weight ratio in acrylic monomer mainly affects the alpha amorphous region. However, the reason why  $Tg\alpha$  increases with increasing PFA and with decreasing IBOA is not clear at the present moment. More detailed studies should be conducted.

#### Mechanical Properties and Hardness of UV-Cured Urethane Acrylate Film Samples

Figure 6 shows the stress–strain curves of UV-cured urethane acrylate film samples. Table II lists the Young modulus, tensile strength, elongation at break, and hardness of the film samples. The PUA0 sample exhibited a high extraordinary high tensile strength (24.0 MPa) and modulus (110.0 MPa). As anticipated, the tensile strength/modulus and hardness of the film samples decreased with increasing PFA content. The tensile strength/modulus decreased markedly from 24.0/110.0 MPa to 9.1/61.2 with increasing PFA content from 0 to 12 wt %. This was attributed not only to the low compatibility between the PFA-contained diluents and oligomer but also to the decrease of rigid IBOA component containing bulky cycloalkyl group.

**Table II.** Water and Methylene Iodide Contact Angle, Surface Energy, Mechanical Properties and Shore A Hardness of Acrylate Copolymer Containing Various Fluorine Contents

Sample designation	Contact angle(°)			Mechanical properties			
	Water	Methylene iodide	Surface Energy (mN/m)	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)	Hardness (Shore A)
PUA0	90.1	63.6	26.8	24.0	165.0	110.0	96
FPUA 3	100.5	77.8	18.8	21.8	163.3	108.2	93
FPUA 6	107.9	80.9	17.2	17.0	161.6	106.1	90
FPUA 9	113.8	83.3	16.5	11.7	141.6	75.1	86
FPUA 12	120.9	87.1	15.6	9.1	115.9	61.2	83

### Surface Properties of UV-Cured Urethane Acrylate Film Samples

Table II and Figure 7 show the surface tension and water/methylene iodide contact angles of UV-cured urethane acrylates containing a range of PFA contents. The water/ methylene iodide contact angles of the PUA0, FPUA3, FPUA6, FPUA9, FPUA12 UV-cured film samples were 90.1/63.6, 100.5/77.8, 107.9/80.9°, 113.8/83.3°, and 120.9/87.1°, respectively, whereas the surface energies of these film samples were 26.8, 18.8, 17.2, 16.5, and 15.6 mN/m, respectively. The surface tension and contact angles changed markedly with increasing PFA content. This might be because of migration of the hydrophobic/oleophobic PFA component to the film surface layer.

### CONCLUSIONS

A series of UV-curable polyurethane acrylates were prepared from a oligomer and diluents and assessed as high performance antifouling materials. The as-prepared UV-curable coating material containing 15 wt % PFA in the diluents (MMA/IBOA/PFA) formed a heterogeneous mixture, suggesting that a PFA content of ~ 15 wt % was beyond the limit of the dilution capacity for the oligomer. The effects of the PFA content on the properties of the UV-cured polyurethane acrylates were assessed for potential antifouling coating applications. The UV-cured PUA0 film sample was quite transparent (transmittance%: near 100%) over the wavelength range of 400–800 nm but the transmittance% of

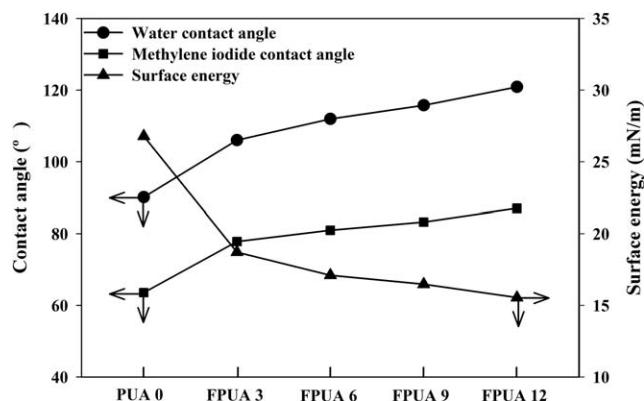
the FPUA film sample decreased significantly with increasing PFA content. The storage modulus, tensile strength and modulus, elongation at break, and hardness of the UV-cured film samples decreased significantly with increasing PFA content. The film–air surface of the UV-cured polyurethane acrylate film had a higher fluorine content than the film–dish interface. As the PFA content increased up to ~ 12 wt %, the water/methylene iodide contact angles of UV-cured film samples increased markedly up to 120.9/87.1°, whereas the surface tensions of these film samples decreased sharply up to 15.6 mN/m. These results suggest that UV-curable polyurethane acrylates with a higher PFA content have strong potential as coating materials for antifouling material applications. Overall, the FPUA6, FPUA9, and FPUA12 samples have better antifouling properties than polytetrafluoroethylene.

### ACKNOWLEDGMENTS

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**Figure 7.** Effect of fluorine content on the water/methylene iodide contact angles and surface free energy. The inserted picture indicates the water drops on the film samples.

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