Preparation and properties of UV-curable fluorinated polyurethane acrylates containing crosslinkable vinyl methacrylate for antifouling coatings

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ABSTRACT: To obtain highly effective antifouling coatings, a series of UV-curable polyurethane acrylates containing diluents [heptadecafluorodecyl methacrylate (PFA, 6 wt %)/isobornyl acrylate (IBOA, 34 wt %)/methyl methacrylate (MMA, 20-5 wt %)/vinyl methacrylate (VMA, 0–15 wt %)] were prepared. This study examined the effect of bulky MMA (20-5 wt %)/crosslinkable VMA (0–15 wt %) weight ratio on the properties of the UV-curable polyurethane acrylates. The fluorine concentration in UV-cured film surface increased with increasing VMA content up to 9 wt % and then decreased. The $T_{g\alpha}$, transparency, elasticity, and mechanical properties of the UV-cured film samples increased with increasing VMA content. The water/methylene iodide contact angles and surface tension of samples increased from 107/79 to 121/91° and decreased from 17.8 to 12.7 mN/m with increasing VMA content up to 9 wt % and then decreased/increased, respectively. From these results, it was found that the optimum VMA content was 9 wt % to obtain a high-performance antifouling coating. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42168.

INTRODUCTION

UV curing saves energy and reduces or eliminates solvent emission compared with solvent-based systems, since most formulations are 100% reactive oligomers and diluents. This technique has been applied commercially in printing, thin film coatings, and adhesives. The reactive diluents are mostly acrylic monomers that are added to modify the properties and to reduce the viscosity of the viscous reactive oligomer. Their 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,[1–3] protective coatings for optical fibers,[4,5] coatings for textiles/carpets/leathers,[6] and photolithography.[7]

The low surface tension of coating material is an important factor for the application of fouling release coatings. Fluorinated polymers (fluoropolymers) have unique surface properties (low surface tension and high stain resistance), good insulation/gas barrier properties, and have a lot of useful and desirable features such as high resistance to thermal/chemical/weather attack, owing to the low polarizability, strong electronegativity of fluorine atom, and high strength of C—F bond. The most common commercially available fluoropolymer is based on the mono-

mers of tetrafluoroethylene, vinylidene fluoride, and chlorotrifluoroethylene.[8] Polytetrafluoroethylene is a polymeric solid with a very low surface energy. The surface tension/water contact angle of polytetrafluoroethylene that consists of closed packed perfluoroalkyl —CF_2 group is known to be 18.5 mN/m/108°. The low surface energy of polymer containing fluorocarbon side chains should be due to large amount of CF_3 groups protruded on the surface.[9–12] Homopolymers of fluoroalkyl acrylates with long side chains have a very low critical surface tension, ranging from 10 to 11 mN/m.[9] In general, the surface tension/contact angle of the material is used as the basis for the antifouling properties. The main drawback of fluorinated polymer is the relatively high cost of fluorinated monomers. Therefore, while maintaining a reasonable surface energy (water/oil repellency), the content of the fluorinated monomer should be minimized.

Acrylic copolymers with fluorine-containing groups or perfluoroalkyl groups can provide materials with low surface energies, and the acrylic groups confirm that the copolymer can adhere well to a range of substrates. Hence, they have been used a progressively greater extent in surface coatings for water/oil repellency for textile/carpets and leather.[13–16] In general, longer alkyl

and perfluoroalkyl moieties, increases the tendency of micro-phase separation in the bulk and surface.[17,18] The extent to which the polymer surface energy is reduced depends not only on the surface coverage by fluorocarbon segments but also on the degree of ordering in the surface layer. In particular, the low surface energy of these copolymers is attributed that the fluorinated side groups in the fluorinated acrylic copolymer is preferentially appears in the coating-air surface.[19–23]

It is well known that less expensive acrylic polymers have good water resistance, weather resistance, suitable mechanical properties, and gloss; however, they have exhibited poor elasticity and abrasion resistance. Polyurethane has attracted particular attention in coatings because it is easy to control the properties, such as toughness, flexibility, adhesion on substrate, abrasion resistance, *etc.* As a result, formulators have found ways to combine the advantages of polyurethane and acrylic polymer.[24–28] A combination of polyurethane with an acrylic copolymer containing fluorine is expected to be efficient in improving 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, low water absorptivity (water resistance), attractive surface properties, excellent flexibility, good wearability, and high weatherability.[12,29–33]

In our previous study on the preparation and properties of UV-curable fluorinated polyurethane acrylates, we found that the surface energy of the UV-cured film samples improved markedly with increasing PFA content but their transmittance %, shelf stability, and mechanical properties decreased markedly.[34] In addition, the solubility threshold (dilution capacity) of diluents decreased with increasing PFA content in diluents.

Vinyl methacrylate (VMA), a commercially available asymmetrical difunctional monomer with two different double bonds, which can be polymerized by radicals, generally produces insoluble products (crosslinked materials) by conventional radical polymerization at relatively low monomer conversions, because both methacryloyl and vinyl ester groups can participate in the radical propagation.[35–37] The reason for using VMA was its high compatibility with other diluent monomers (IBOA/PFA/MMA). Some research on the UV curable aqueous polyurethane/polyurethane–acrylate[38–40] was performed, but there are few reports on the UV-curable fluorinated polyurethane acrylates.[34,41,42] Moreover, there has been little research on the UV-curable polymer of a urethane acrylate oligomer with acrylate monomer/acrylate monomer containing perfluoroalkyl group.[34] In addition, the study of UV-curable polyurethane acrylate using PFA/IBOA/MMA/crosslinkable VMA monomers has not been announced.

In this study, the rigid bulky cycloalkyl group contained monomer IBOA to raise toughness, vinyl group contained acrylic monomer VMA as a crosslinking agent and bulky MMA to improve transparency/surface properties, and long perfluoroalkyl group contained monomer perfluoroalkyl acrylate (PFA) to expand surface tension, are used. This study focused on the effect of VMA/MMA weight ratio on the properties such as contact angle/surface tension, transparency, elastic recovery, and

mechanical properties of UV-cured polyurethane acrylates films. The objective of this study is to enhance these properties using vinyl group containing acrylic monomer VMA as a crosslinking agent. Therefore, in this study, the effect of the VMA content on the properties of UV-cured fluorinated polyurethane–acrylates with a fixed urethane prepolymer content (40 wt %) and a fixed PFA content (6 wt %) was investigated to find the optimum content of VMA for high performance antifouling coatings having low surface tension.

EXPERIMENTAL

Materials

Poly(tetramethylene glycol) (PTMG M_n = 2000 g/mol; Aldrich Chemical, Milwaukee, WI) was dried at 90°C under 1–2 mmHg for 3 h before use. 4,4'-Dicyclohexymethanediisocyanate (H_{12}MDI, Aldrich Chemical, Milwaukee, WI), dibutyltindilaurate (DBTDL, 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-heptadecafluorodecyl methacrylate (PFA, Aldrich Chemical, Milwaukee, WI), iso-bornyl acrylate (IBOA, Aldrich Chemical, Milwaukee, WI), methyl methacrylate (MMA, Aldrich Chemical, Milwaukee, WI), 1-hydroxycyclohexyl acetophenone (Irgacure 184, Aldrich Chemical, Milwaukee, WI), VMA and (Tokyo Chemical Industry, Japan) were used as received.

Preparation of UV-Curable Polyurethane Acrylates and Their Films

The preparation process of UV-curable polyurethane acrylates is shown in Scheme 1. 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_{12}MDI was dropped slowly into the flask, and the reaction mixture was allowed to react at 85°C until the theoretical isocyanate group (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 prepolymer 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 prepolymer with HEMA was continued until the NCO-content reached zero, as evidenced by the disappearance of the IR NCO peak (2270 cm^{-1}). The UV-curable fluorinated urethane-acrylate mixtures were formulated from a viscous oligomer (40 wt %), diluents, and photoinitiator Irgacure 184 (2 wt % based on the prepolymer/diluents). A series of UV-curable fluorinated urethane acrylates mixtures (prepolymer/diluents/photoinitiator) were formulated by adding the acrylate diluents [MMA (20-5 wt %)/IBOA (34 wt %)/PFA (6 wt %)/VMA (0–15 wt %), total diluents: 60 wt %] and photoinitiator Irgacure 184 (2 wt %) to the viscose urethane acrylate prepolymer (40 wt %) and mixing them at 45°C for 3 h. In this study, the UV-curable polyurethane acrylates samples [FPUA6/0, FPUA6/3, FPUA6/6, FPUA6/9, FPUA6/12, and FPUA6/15, where the numbers indicate the wt % of PFA/VMA] were prepared from a reactive oligomer [4,4'-H_{12}MDI/PTMG/2-hydroxyethyl
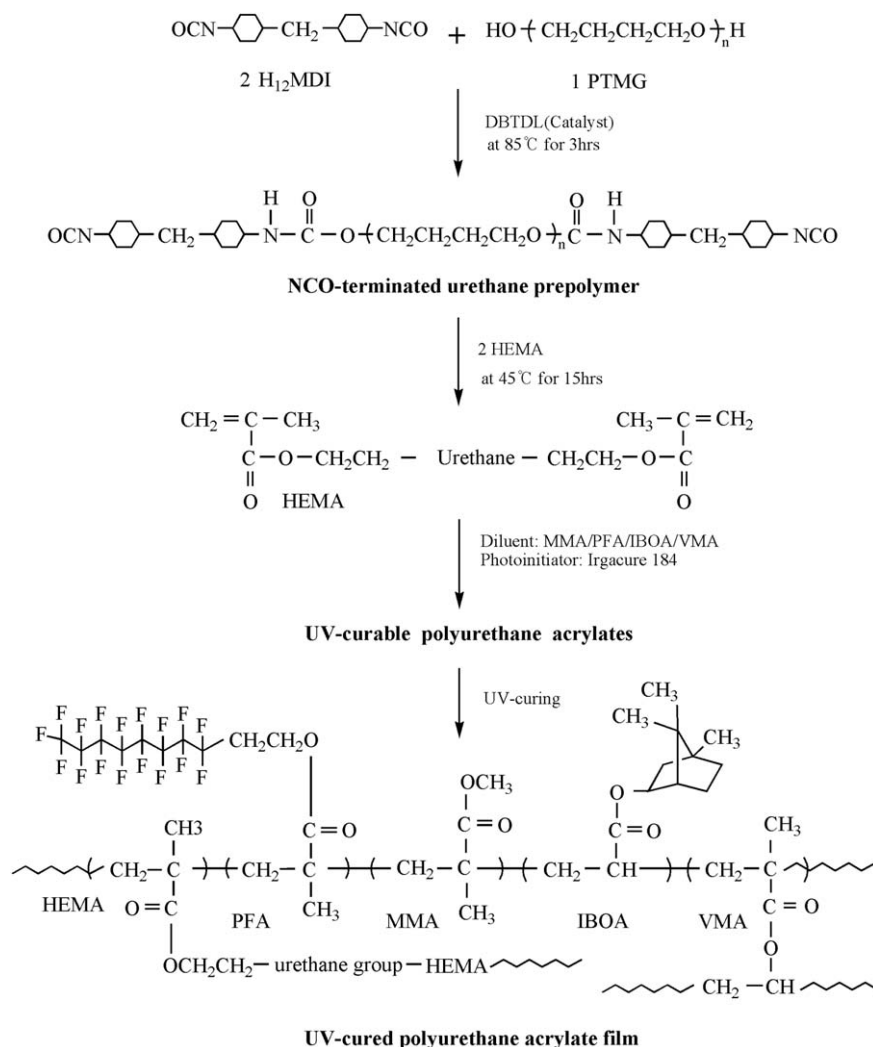
Scheme 1. Preparation process of UV-curable polyurethane acrylates and UV-cured polyurethane acrylates film.

methacrylate (HEMA): 2/1/2 molar ratio, prepolymer: 40 wt %] and diluents. Table I lists the sample designation and composition of the UV-curable fluorinated urethane-acrylate containing various contents of VMA. All the samples formulated in this study were stored in dark condition at room temperature before irradiation (curing).

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 II+, USA). The measurements were performed at 100 rpm using a spindle RV-3.

The chemical components of the UV-cured fluorinated polyurethane–acrylates film samples containing various contents of VMA 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^{-1} using an ATR (ZnSe crystal) apparatus at a resolution of 4 cm^{-1} 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 Ka X-ray source (15 kV, 150 W) and a spot size of 400 μm. 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 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 surface tension. The surface tension of the solid film can be determined using the following equation:

Table I. Sample Designation, Composition and Viscosity of UV-Curable Urethane Acrylate (Oligomer/Diluents Mixture/Crosslinking Agent) Containing Various MMA/VMA Contents

Sample designation	Composition									
	Oligomer (molar ratio)			Oligomer (wt %)	Diluent (wt %)			Crosslinking agent (wt %)	Irgacure[a] (wt %)	Viscosity (cP, 25°C)
	H_{12}MDI	PTMG	HEMA		PFA	IBOA	MMA	VMA		
FPUA6/0	2	1	2	40	6	34	20	0	2	417.2
FPUA6/3	2	1	2	40	6	34	17	3	2	423.5
FPUA6/6	2	1	2	40	6	34	14	6	2	435.5
FPUA6/9	2	1	2	40	6	34	11	9	2	452.4
FPUA6/12	2	1	2	40	6	34	8	12	2	487.4
FPUA6/15	2	1	2	40	6	34	5	15	2	494.2

[a] Irgacure 184: 2 wt % based on prepolymer/diluents mixture/crosslinking agent.

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

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

where γ_s is the surface energy of the 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 methylene iodide (L2), and their γ_{L1}^d, γ_{L1}^p, γ_{L2}^d, and γ_{L2}^p were 21.8, 51.9, 1.3, and 49.5 mN/m, respectively.[43] The dynamic mechanical properties of film samples were measured at 3 Hz using dynamic mechanical thermal analyzer (DMA, TA-Q 800; TA Instrument, USA) with a heating rate of 10°C/min in the temperature range from −100 to 100°C. The tensile properties were measured at room temperature with a 5582 system 3 using a universal testing machine (Instron, USA) according to ASTM D 638. A cross-head speed of 10 mm/min was used throughout these investigations to determine the ultimate tensile strength, modulus, and elongation at break for all samples. Tensile recovery test was carried out using a universal testing machine on dumbbell specimens of 50 × 5 mm² area at room temperature. The samples were clamped and subjected to successive given elongation in 10%. The number of cycling was four times, and the cross-head speed was 50 mm/min. 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 as the test. The values quoted are the mean of five measurements. The UV–Visible spectra were obtained using a UV–Visible spectrophotometer (T70+UV/VIS Spectrometer, PG Instruments, England).

RESULTS AND DISCUSSION

Composition, Viscosity, and Shelf Stability of Mixture Solutions of UV-Curable Polyurethane Acrylate (Oligomer/Diluents/Photoinitiator)

The sample designation, composition, and viscosity of UV-curable polyurethane acrylates [oligomer (40 wt %)/diluents (60 wt %)/photoinitiator Irgacure 184 (2 wt %) [FPUA6/0, FPUA6/3, FPUA6/6, FPUA6/9, FPUA6/12 and FPUA6/15, where the numbers indicate the wt % of PFA/VMA] are shown in Table I. The perfluoroalkyl group contained PFA was fixed at a relatively low content (6 wt %), because the high content of PFA in

diluents disimproves the shelf-stability of UV-curable liquid mixture and the price of PFA is relatively high. In this study, the urethane 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 composition of MMA/VMA (20/0, 17/3, 14/6, 11/9, 8/12, and 5/15 weight ratio) was varied to investigate its effect on the properties. The chemical structure of UV-cured samples is shown in Scheme 1. The difference is that MMA has methyl group, while VMA has vinyl group. The viscosity of UV-curable polyurethane acrylate increased a little with increasing VMA content in MMA/VMA. This increase might be due to the higher bulkiness of VMA vinyl group than MMA methyl group. All the liquid samples (oligomer/diluents/photoinitiator mixtures) with different content of MMA/VMA were found to be stable after 5 months in dark condition at room temperature, indicating that the weight ratio of MMA/VMA does not have any effect on shelf life of the prepared coating.

Identification of Chemical Reactions and Structures

In this study, the chemical reactions between the functional groups were checked by monitoring the disappearance of the
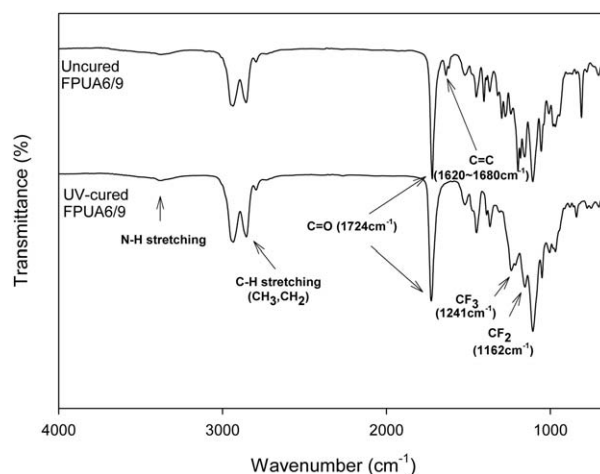
Figure 1. FT-IR spectra of typical uncured FPUA6/9 sample and UV-cured FPUA6/9 film sample.
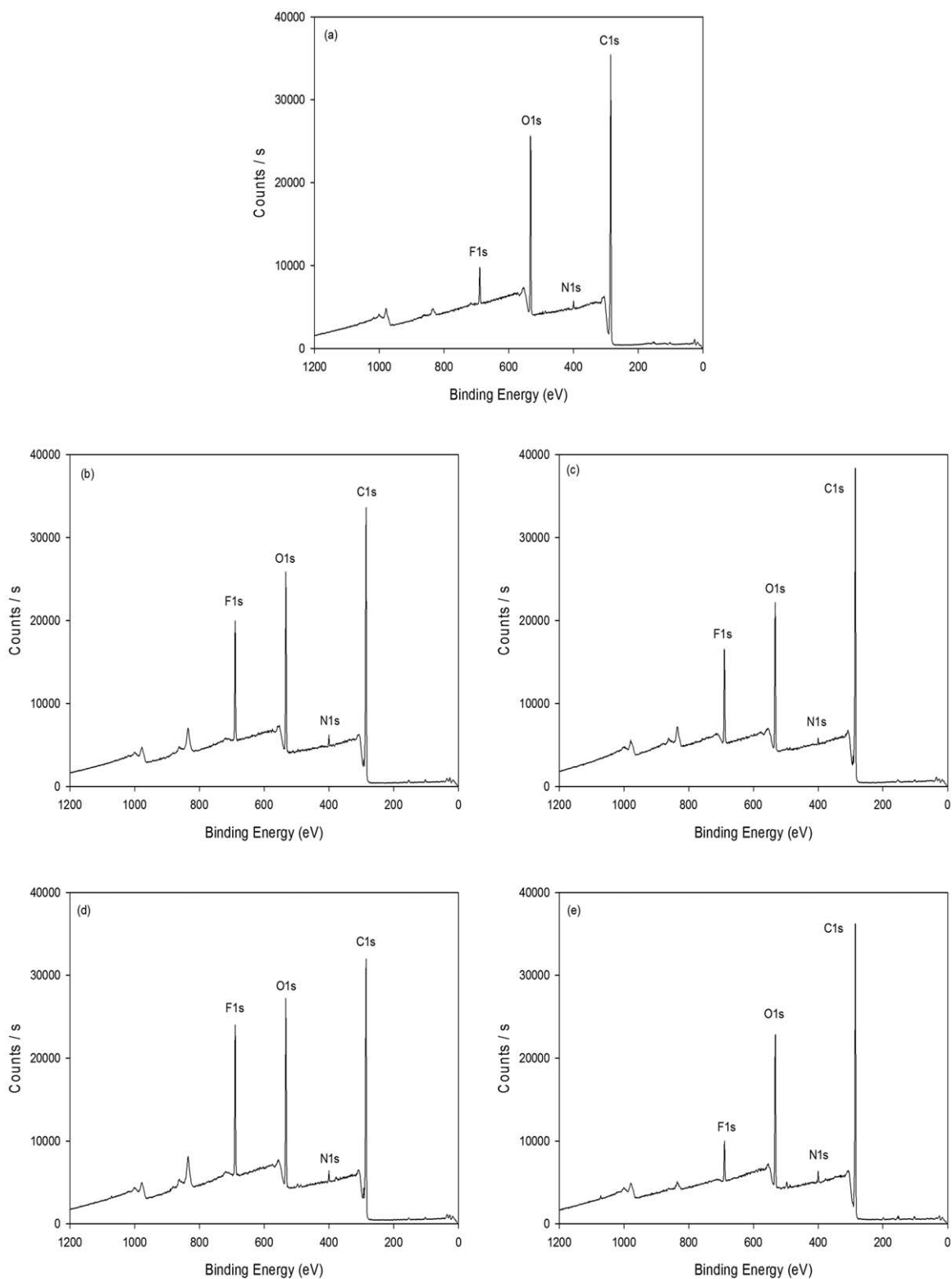
Figure 2. XP spectra of typical UV-cured film samples. (a) film-air surface of FPUA6/0, (b) film-air surface of FPUA6/6, (c) film-dish interface of FPUA6/6, (d) film-air surface of FPUA6/9, and (e) film-dish interface of FPUA6/9.

reactive groups present in the monomers and oligomers. The capping reaction of the NCO-terminated urethane prepolymer with HEMA was confirmed by the disappearance of NCO peak at 2270 cm^{-1}. Figure 1 shows the FT-IR spectra of the uncured

FPUA6/9 liquid sample and UV-cured FPUA6/9 film sample. The FT-IR spectrum of the uncured FPUA6/9 sample showed the characteristic C=C peaks at 1620–1680 cm^{-1} but the UV-cured FPUA6/9 film samples had no C=C peak indicating the

Table II. The Atomic Concentration of the Surface and Interface of UV-Cured Polyurethane Acrylate Film Samples

Sample designation	Surface/ interface	Atomic concentration (%)			
		C1s	N1s	O1s	F1s
FPUA6/0	Surface	72.8	1.2	21.9	4.1
FPUA6/6	Surface	71.3	1.5	18.5	8.7
	Interface	73.4	2.7	17.9	6.0
FPUA6/9	Surface	68.7	1.7	18.5	11.1
	Interface	74.4	2.8	18.0	4.8
FPUA6/12	Surface	70.8	1.6	18.6	9.0
FPUA6/15	Surface	71.2	1.6	18.7	8.5

Figure 3. Storage modulus and tan delta of UV-cured film samples (FPUA 6/0, FPUA 6/3, FPUA 6/6, FPUA 6/9, FPUA 6/12, and FPUA 6/15).

complete reaction of all vinyl groups. The characteristic bands at approximately 1713, 1082, 1105, and 3300–3500 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 cm^{-1} was found to overlap with urethane carbonyl group in the range of 1802–1651 cm^{-1}. The stretching vibrations of —CF$_2$ group at 1150 cm^{-1}, —CF$_3$ group at 1230–1240, 1206 cm^{-1}, and a combination of rocking and wagging vibration of the CF$_3$ group at 656 and 701 cm^{-1} in the fingerprint region, are all detected in two samples. On the other hand, many peaks of ether/urethane/acrylate/fluorine groups were found to be 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 2 presents the XP spectra of (a) film-air surface of FPUA6/0, (b) film-air surface of FPUA6/6, (c) film-dish interface of FPUA6/6, (d) film-air surface of FPUA6/9, and (e) film-dish interface of FPUA6/9. The atomic concentration of film samples is shown in Table II. The surface peak intensity of F$_{1s}$ at 690 eV increased with increasing VMA content in FPUA samples. This indicated that the crosslinking of VMA component containing crosslinkable vinyl groups turned out be significantly more effective than the MMA component containing methyl group in promoting the emergence of PFA component onto the surface layer. By comparing the peak intensities of F$_{1s}$ for film-air surfaces of FPUA 6/0 (a), FPUA6/6 (b), and FPUA6/9 (d), and for film-dish interfaces of FPUA6/6 (c) and FPUA6/9 (e), the relative peak intensity of F$_{1s}$ in the film-air surface was higher than that in the film-dish interface indicating the gradient concentration of the fluorine in the structure of the film from the film-air surface to the film-glass interface. This also indicated that the long perfluoralkyl group of PFA component was introduced mainly to the surface layer of the fluorinated material as expected. This means that the curing process should encourage the emergence of PFA components (perfluoroalkyl groups) on the coating-air surface during film formation. By curve fitting analysis, our previous studies that covered this subject showed the same results.[28,34] The peak intensity of F$_{1s}$ in
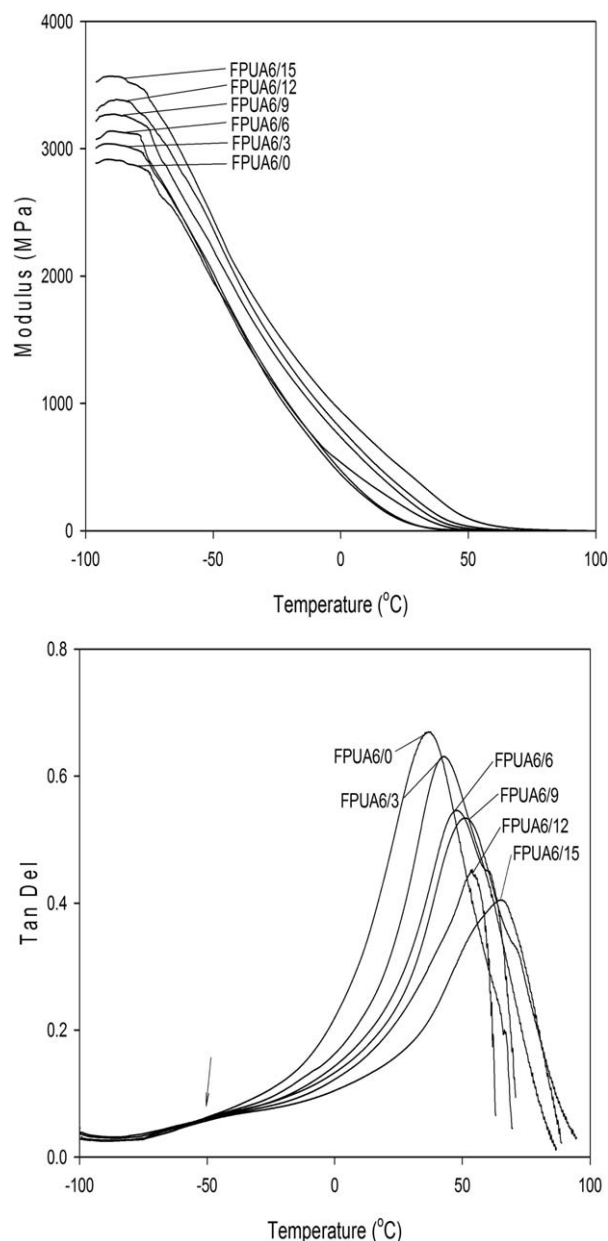
film-air surface increased significantly with increasing VMA content up to 9 wt %, and then decreased. This indicated that the increase in crosslinking until a certain amount of crosslinkable VMA (9 wt %) encouraged the emergence of long perfluoroalkyl group contained PFA component onto the film surface and then discouraged. This means that the excessive crosslinking interferes the emergence of PFA component onto the film surface. However, the reason why the critical point exists is not clear at the present moment. More detailed studies should be conducted. Anyhow, these changes will relate the change in surface properties (contact angles and surface tension) of the UV-cured film samples with a range of FPA contents, as described later.

Table III. T_g, Water and Methylene Iodide Contact Angle, Surface Tension, Mechanical Properties, and Shore A Hardness of UV-Cured Polyurethane Acrylate Film Samples

| Sample designation | DMA results | | Contact angle (°) | | Surface tension (mN/m) | Mechanical properties | | | Hardness (Shore A) |
	$T_g\beta$ (°C)	$T_g\alpha$ (°C)	Water	Methylene iodide		Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)	
FPUA6/0	−49.1	36.4	107.2	79.6	17.8	18.2	170.0	288.7	87
FPUA6/3	−49.9	42.9	109.7	81.8	16.7	19.8	143.2	331.9	88
FPUA6/6	−50.2	47.0	113.4	85.3	15.1	20.5	132.5	410.8	89
FPUA6/9	−51.1	51.2	121.3	91.1	12.7	21.7	115.4	434.7	93
FPUA6/12	−50.5	53.3	116.5	87.8	14.1	22.3	109.5	479.9	95
FPUA6/15	−50.9	64.9	111.7	86.0	16.6	22.9	88.7	523.6	97

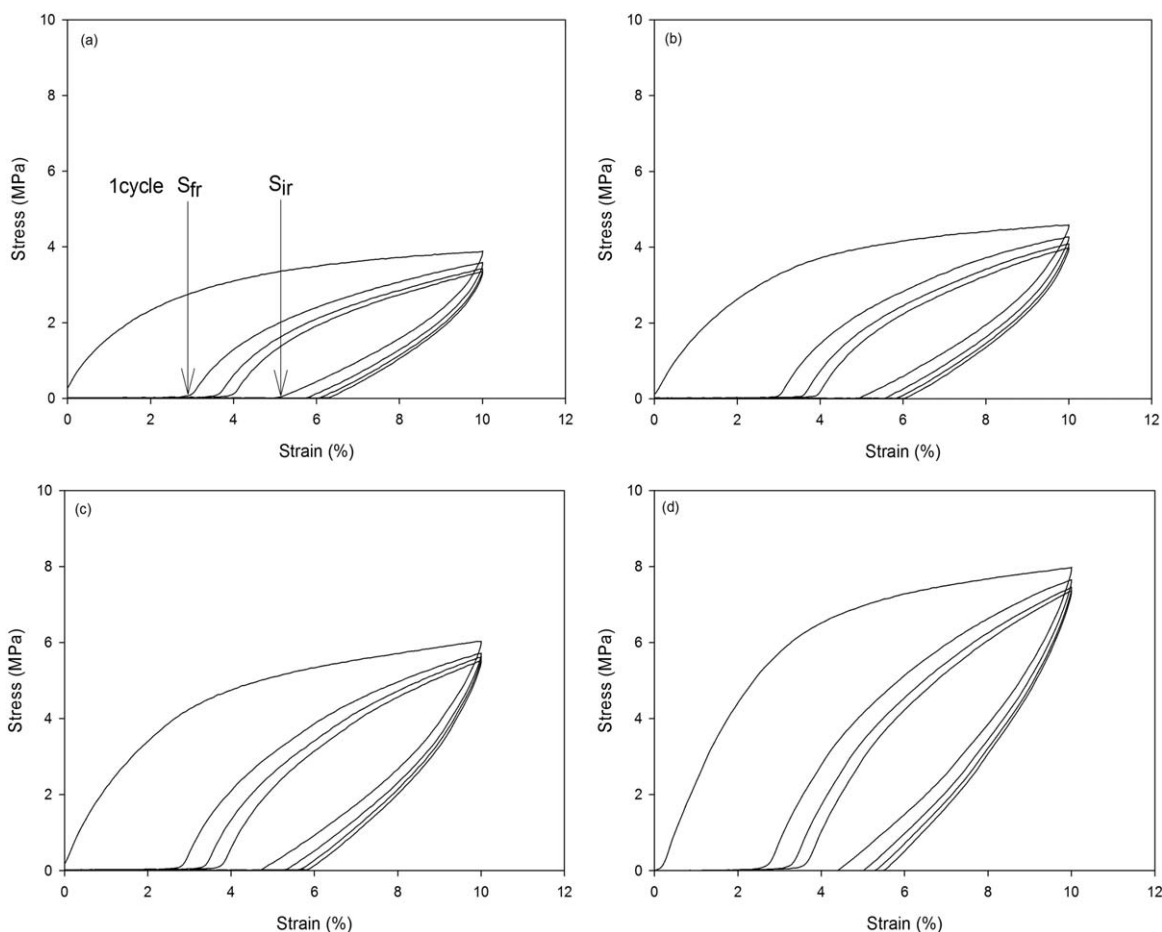**DMA Properties of UV-Cured Film Samples (FPUA0, FPUAs)**
The storage modulus and tan delta of the UV-cured film samples are shown as a function of temperature in Figure 3. The film sample containing a higher VMA content had a higher storage modulus. Generally, in two-phase system where the phases are well separated, there are two glass transitions instead of the usual one. It is well known that waterborne polyurethanes and polyurethane acrylates are amorphous polymers having two phases assigned to $T_{g\alpha}$ and $T_{g\beta}$. The glass transition temperatures (T_gs) determined from tan delta peaks are shown in Table III. As the crosslinkable VMA content increased, the higher temperature broad peak ($T_{g\alpha}$) of the film sample increased significantly from 36.4 to 64.9°C, whereas the broad peak at approximately −50°C assigned to the soft segment T_g ($T_{g\beta}$) was almost unchanged. The rise of $T_{g\alpha}$ according to increasing VMA content also must be attributable to the increase in crosslinking density. From these results, it was found that the crosslinking of VMA component in copolymer chains affects just only to the alpha amorphous region. The shift of $T_{g\alpha}$ suggests that the hard segment of polyurethane is miscible with acrylic components including VMA.

The miscibility should be attributable to the intimate molecular mixing through the formation of homogeneous solution of diluent monomer/urethane-acrylate oligomer and the existence of the polyurethane–polyacrylate copolymer as a compatibility agent.

Visible Light Transmittance Percentage of UV-Cured Film Samples
Figure 4 shows the UV–visible spectra of the UV-cured film samples (FPUA6/0, FPUA6/3, FPUA6/6, FPUA6/9, FPUA6/12, and FPUA6/15). Most often, the inhomogeneity renders the product turbid or at least milky (low transmittance %). However, system with closely matching indices of refraction or with a very small domain size can be quite transparent. The FPUA6/0 film sample without VMA showed a low transmittance % of approximately 83.9% in the visible range (400–800 nm). The transmittance % of the UV-cured film samples increased a little up to near 90% with increasing VMA content up to 15 wt %. The increase in transmittance % should be due to the decrease in amorphous domain region in UV-cured film samples by increasing bulky crosslinked VMA component.
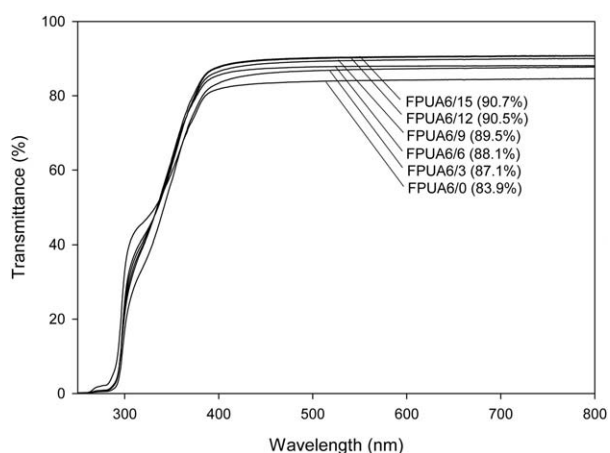
Figure 4. UV-visible spectra of UV-cured film samples (FPUA6/0, FPUA6/3, FPUA6/6, FPUA6/9, FPUA6/12, and FPUA6/15).
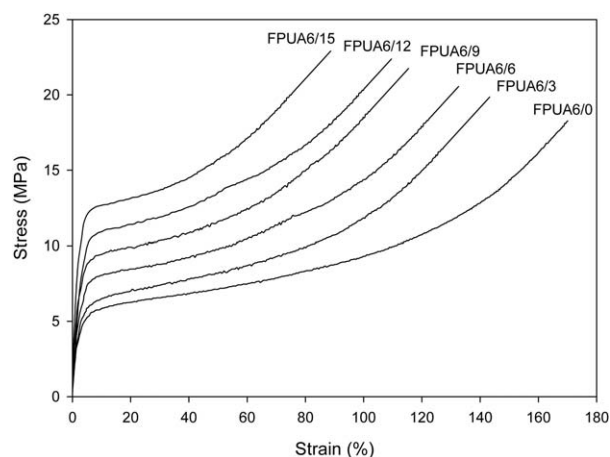
Figure 5. Stress–strain curves of UV-cured film samples (FPUA 6/0, FPUA 6/3, FPUA 6/6, FPUA 6/9, FPUA 6/12, and FPUA 6/15).

Figure 6. Stress–strain hysteresis loops of UV-cured film samples. (a) FPUA 6/0, (b) FPUA 6/6, (c) FPUA 6/9, and (d) FPUA 6/15.

Tensile Properties/Elastic Properties and Hardness of UV-Cured Film Samples

Figure 5 shows the stress–strain curves of UV-cured acrylate film samples. The initial tensile modulus, tensile strength, elongation at break, and hardness of the film samples are shown in Table III. Generally, the stress–strain behavior of a polymeric material depends on various parameters such as molecular characteristics, microstructure, strain-rate, and temperature. As the crosslinkable VMA content increased, the tensile modulus/strength increased, however, the elongation at break decreased. The increase in tensile modulus/strength and decrease in elongation at break were understandably due to the increase in

crosslinking density by increasing crosslinkable VMA content. The changing trend of the initial modulus was found to be coincident with that of the storage modulus.

Stress–strain hysteresis loops of UV-cured film samples for a given strain (10%) are shown in Figure 6. Table IV lists the instant elastic recovery strain (S_{ir}) and finally recovery strain (S_{fr}) of UV-cured film samples. The stress to extend the fixed strain (10%) increased with increasing crosslinkable VMA content. The S_{ir} at zero stress and S_{fr} decreased with increasing VMA content. This indicates that the UV-cured film samples containing higher content of crosslinkable VMA show higher elastic recovery as expected. It was also found that the elastic

Table IV. Instant Elastic Recovery Strain (S_{ir}) and Finally Recovery Strain (S_{fr}) of Typical UV-Cured Film Samples

Sample designation	Instant elastic recovery Strain, S_{ir} (%)				Finally recovery strain, S_{fr} (%)		
	1 Cycle	2 Cycle	3 Cycle	4 Cycle	First	Second	Third
FPUA6/0	5.08	5.77	6.08	6.24	2.97	3.58	3.96
FPUA6/6	4.97	5.59	5.85	6.04	2.97	3.57	3.91
FPUA6/9	4.74	5.32	5.67	5.83	2.80	3.35	3.77
FPUA6/15	4.40	5.02	5.29	5.49	2.64	3.24	3.57
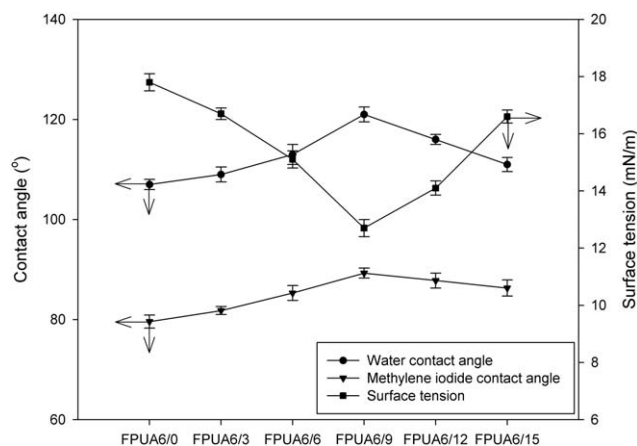
Figure 7. Effect of VMA content on the water/methylene iodide contact angles and surface tension of UV-cured film samples.

recovery decreased with increasing the number of cycle. The hardness (Shore A) of the UV-cured film samples increased with increasing VMA content (Table III). The increase in hardness also should be due to the increase in crosslinking.

Surface Properties of UV-Cured Polyurethane Acrylate Film Samples

The surface tension and water/methylene iodide-contact angles of UV-cured polyurethane acrylates containing a range of VMA contents (0–15 wt %) are shown in Figure 7 and Table III. The water/methylene iodide contact angles of the UV-cured film samples FPUA6/0, FPUA6/3, FPUA6/6, FPUA6/9, FPUA6/12, and FPUA6/15 were 107.9/79.6, 109.1/81.8, 113.4/85.3, 121.2/93.1, 116.5/87.8, and 111.2/86.0°, respectively, whereas the surface tensions of these film samples were 17.8, 16.7, 15.2, 12.8, 14.2, and 16.6 mN/m, respectively. The water/methylene iodide contact angles of the film-air surface increased significantly from 107/79 to 121/91° with increasing VMA content up to 9 wt %, and then decreased. It was found that the chaining trend of contact angles was coincident with that of fluorine concentration as mentioned in XPS result. The surface tension of the UV-cured urethane acrylates films decreased from 17.8 to 12.8 mN/m with increasing VMA content up to 9 wt % and then increased. From these results, the optimum VMA content was found to be 9 wt % to obtain a high performance water/oil repellent coating materials. The increase in contact angle and the decrease in surface tension might be due to the increase in migration of the hydrophobic PFA component to the film surface layer during curing process.

In addition, wettability of solid surface with liquid (water/oil) in air is very important phenomenon in our daily life and in various industrial processes. Generally, wettability is governed by two factors: the chemical factor of the solid/liquid (attractive force) and the geometrical factor of the solid surface (morphology: surface roughness). Generally, a self-assembled microdomain with the fluorinated side chain standing up on the uppermost surface has been proposed for polyurethane with higher fluorinated component content. Atomic force microscopy (AFM) is a powerful technique for characterizing surface. Usually the higher root-mean-square (RMS) roughness values deter-

mined using AFM implies the surface changed from smooth to rough. In our previous study, we found that the RMS value (surface roughness) increased with increasing fluorinated component content in fluorinated polyurethanes.[44] Therefore, the increase in contact angles/decrease in surface tension of film samples prepared here with increasing VMA content should be attributed to not only the lower attractive force of fluorine component in uppermost surface but also the surface roughness.

CONCLUSIONS

A series of UV-curable polyurethane acrylates containing fluorinated acrylic monomer (PFA, 6 wt %)/vinyl methancryalte (VMA, 0–15 wt %)[FPUA6/0, FPUA6/3, FPUA6/6, FPUA6/9, FPUA6/12, and FPUA6/15, where the numbers indicate the wt % of PFA/VMA] were prepared from a reactive oligomer [4,4′-H_{12}MDI/PTMG/2-hydroxyethyl methacrylate (HEMA): 2/1/2 molar ratio, prepolymer: 40 wt %] and diluents [PFA (6 wt %)/IBOA (34 wt %)/MMA (20-5 wt %)/VMA (0–15 wt %), total diluents: 60 wt %]. The effect of bulky MMA (20-5 wt %)/bulky VMA (0–15 wt %) weight ratio on the properties of the UV-curable polyurethane acrylates for anti-fouling coating materials was investigated. The visible light transmittance % of the FPUA film samples increased up to near 90% with increasing VMA content up to 15 wt %. XPS result showed that the film-air surface of the UV-cured polyurethane acrylate film had a higher fluorine content than the film-dish interface. The fluorine concentration in the film surface of UV-cured film sample increased with increasing VMA content up to 9 wt %, and then decreased. As the VMA content increased, the T_g/storage modulus/tensile modulus and strength/hardness/elastic recovery of the UV-cured film samples increased significantly, while the elongation at break decreased. The water/methylene iodide contact angles of the UV-cured film samples FPUA6/0, FPUA6/3, FPUA6/6, FPUA6/9, FPUA6/12, and FPUA6/15 were 107.9/79.6, 109.1/81.8, 113.4/85.3, 121.2/93.1, 116.5/87.8, and 111.2/86.0°, respectively, whereas the surface tensions of these film samples were 17.8, 16.7, 15.2, 12.8, 14.2, and 16.6 mN/m, respectively. The surface tension of the UV-cured urethane acrylates films decreased with increasing VMA content up to 9 wt %, and then increased. The water/methylene iodide contact angles of the film-air surface increased from 107/79 to 121/91° with increasing VMA content up to 9 wt %, and then decreased. These results suggest that the UV-curable polyurethane acrylate containing 9 wt % of VMA (FPUA6/9) has strong potential as a coating material for antifouling applications.

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