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Synthesis and properties of UV-curable polyurethane acrylates containing fluorinated acrylic monomer/vinyltrimethoxysilane

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Abstract A series of UV-curable polyurethane acrylates containing fluorinated acrylic monomer (heptadecafluorodecyl methacrylate, PFA, 6 wt%)/vinyltrimethoxysilane (VTMS, 0–9 wt%) [FPUA6/0, FPUA6/3, FPUA6/6 and FPUA6/9, where the numbers indicate the wt% of PFA/VTMS] were synthesized from a reactive urethane oligomer (40 wt%) and diluents (60 wt%). This study examined the effect of bulky VTMS (0–9 wt%)/bulky IBOA (34–25 wt%) weight ratio on the properties of the UV-curable polyurethane acrylates for transparent anti-fouling coating materials. In the wavelength range of 400–800 nm, the transmittance % of the FPUA film samples increased markedly up to nearly 100 % with increase in the VTMS content up to 9 wt%. As the VTMS content increased, the storage modulus/tensile modulus/hardness of the UV-cured film samples increased significantly and the tensile strength/glass transition temperature increased a little; however, the elongation at break decreased significantly. XPS showed that the film–air surface of the UV-cured polyurethane acrylate film had a higher fluorine content than the film–dish interface indicating the gradient concentration of fluorine in the structure of the film from the film–air surface to the film–glass interface. As the VTMS content increased from 0 to 9 wt%, the surface tension of the UV-cured urethane acrylate films decreased from 17.2 to 15.9 mN/m, whereas the water/methylene iodide contact angles of the film–air surface increased significantly from 107.9/80.9° to 114.2.9/84.2°. These results suggest that the UV-curable polyurethane acrylate containing 9

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wt% of VTMS has strong potential as a coating material for transparent antifouling applications.

Keywords Fluorinated polyurethane acrylate · UV curable · Antifouling coating

Introduction

The UV-curable polyurethane acrylate system is typically composed of reactive polyurethane acrylate oligomer (prepolymer), reactive diluents and a photoinitiator. Various liquid reactive diluents miscible with the oligomer can be used to decrease the viscosity of the viscose oligomer and to control the properties of UV-cured materials. 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 [1–4], protective coatings for optical fibers [5, 6] and photolithography [7].

Fluorinated polymers have many useful and desirable features, such as unique surface properties (low surface tension, high soil resistance), good insulating/gas barrier properties and high resistance to thermal/chemical/weather attack, owing to the low polarizability, strong electronegativity of fluorine atoms and high strength of the C–F bond. The most common commercially available fluorine polymers (fluoropolymers) are based on the monomers of tetrafluoroethylene, vinylidene fluoride and chlorotrifluoroethylene. Polytetrafluoroethylene is a polymeric solid with a very low surface energy. The surface tension/water contact angle of polytetrafluoroethylene which consisted of closed-packed perfluoroalkyl-CF_2 group was 18.5 mNm/108° [8]. The lower critical surface energy of many polymers containing fluorocarbon side chains has been attributed to the higher content of CF_3 groups on their surfaces [9–12]. Fluoroalkyl acrylate homopolymers with long side chains have very low critical surface tension, ranging from 10 to 11 mN/m [9]. Generally, the surface energy (tension)/contact angle of a material is used as a criterion for the antifouling property.

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 energy (water/oil repellency). 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 [13–15]. The fluorinated side groups in fluorinated acrylic copolymers have emerged preferentially at the coating–air surface [16–20]. Fluorinated acrylic copolymer films not only retain the original properties of polyacrylate films, such as good adhesion to the matrix, but also have better durability as well as good antifouling property. Therefore, water-based acrylic copolymer dispersions containing perfluoroalkyl groups have been available for some time and are used widely in coatings for textiles/carpets [21] and leathers [22].

Generally, longer alkyl and perfluoroalkyl moieties increase the tendency for microphase separation in the bulk and surfaces [23, 24]. Comb-shaped polymers containing fluorinated 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 [25]. 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 on the surface layer.

On the other hand, hydrophobic vinylalkoxysilanes are some of the functional groups that can introduce self-cross-linking structure during the film formation process [26, 27]. Some studies have reported the synthesis and properties of self-cross-linkable fluorinated acrylate copolymer emulsions [21, 28, 29], but there has been little research on the optimum content of hydrophobic bulky alkoxysilanes for improving the water/oil repellency (low surface tension) and mechanical properties. In an earlier investigation of the synthesis and surface properties of self-cross-linking core–shell acrylic copolymer emulsions containing fluorine/silicone in the shell, we found that the optimum vinyltriethoxysilane (VTES) content was about 6 wt% to obtain a high water/oil repellent coating material [30].

Acrylic polymers are generally considered to be inexpensive with good water and weathering resistance, proper mechanical properties and gloss, but exhibit poor elasticity and abrasion resistance. Polyurethane has attracted particular attention in coatings, because it is easy to control its properties, such as toughness, flexibility, adhesion on substrate and abrasion resistance, etc. As a result, various formulators have examined ways of combining the advantages of waterborne polyurethane and acrylic polymer. Polyurethane/polyacrylate hybrid emulsions have been studied [31–35].

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, low water absorptivity (water resistance), attractive surface properties, excellent flexibility, good wearability and high weatherability [12, 36–40].

Some studies have examined the UV-curable waterborne polyurethane/polyurethane acrylate [41–43], but there are few reports on UV-curable fluorinated poly(urethane acrylate)s using fluorinated urethane [44, 45]. However, there has been little work on UV-curable copolymers of urethane acrylate oligomer with acrylate monomer/acrylate monomer possessing perfluoroalkyl groups. Moreover, studies on UV-curable polyurethane acrylate using PFA and VTMS have not been published. In our earlier study on the preparation and properties of a series of UV-curable polyurethane acrylates containing perfluoroalkyl groups, we found that the surface energy of the UV-cured film samples improved markedly with increase in the PFA content, but their transmittance % and mechanical properties decreased markedly [46].

In this study, the bulky monomer MMA was used to increase the hardness of the material, the rigid bulky cycloalkyl group contained monomer IBOA to increase the toughness, the bulky alkoxysilane group contained monomer VTMS to increase the transparency and surface/mechanical properties and the long perfluoroalkyl group

contained monomer perfluoroalkyl acrylate (PFA) to increase surface tension. This study focused on the effect of VTMS/IBOA weight ratio on properties such as surface tension, transparency and mechanical properties of UV-cured polyurethane acrylate films. The objective of this study is to enhance these properties by using VTMS containing bulky side groups. Therefore, in this study, the effect of the VTMS 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 VTMS for good transparent 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), dibutyltin dilaurate (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), isobornyl acrylate (IBOA, Aldrich Chemical, Milwaukee, WI), methyl methacrylate (MMA, Aldrich Chemical, Milwaukee, WI), 1-hydroxycyclohexyl acetophenone (Irgacure 184, Aldrich Chemical, Milwaukee, WI) and vinyltrimethoxysilane (VTMS, Aldrich Chemical, Milwaukee, WI) were used as received.

Preparation of UV-curable polyurethane acrylates and their films

Scheme 1 shows the preparation process of UV-curable 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_{12}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 prepolymer was cooled to 45 °C and HEMA was added dropwise. To obtain the vinyl-terminated urethane prepolymer, 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 (2,270 cm^{-1}). The UV-curable fluorinated urethane acrylate mixtures were formulated from viscous prepolymer (40 wt%), diluents and photoinitiator Irgacure 184 (1.5 wt% based on the prepolymer/diluents). A series of UV-curable fluorinated urethane acrylates mixtures (prepolymer/diluents/photoinitiator) were formulated by adding the
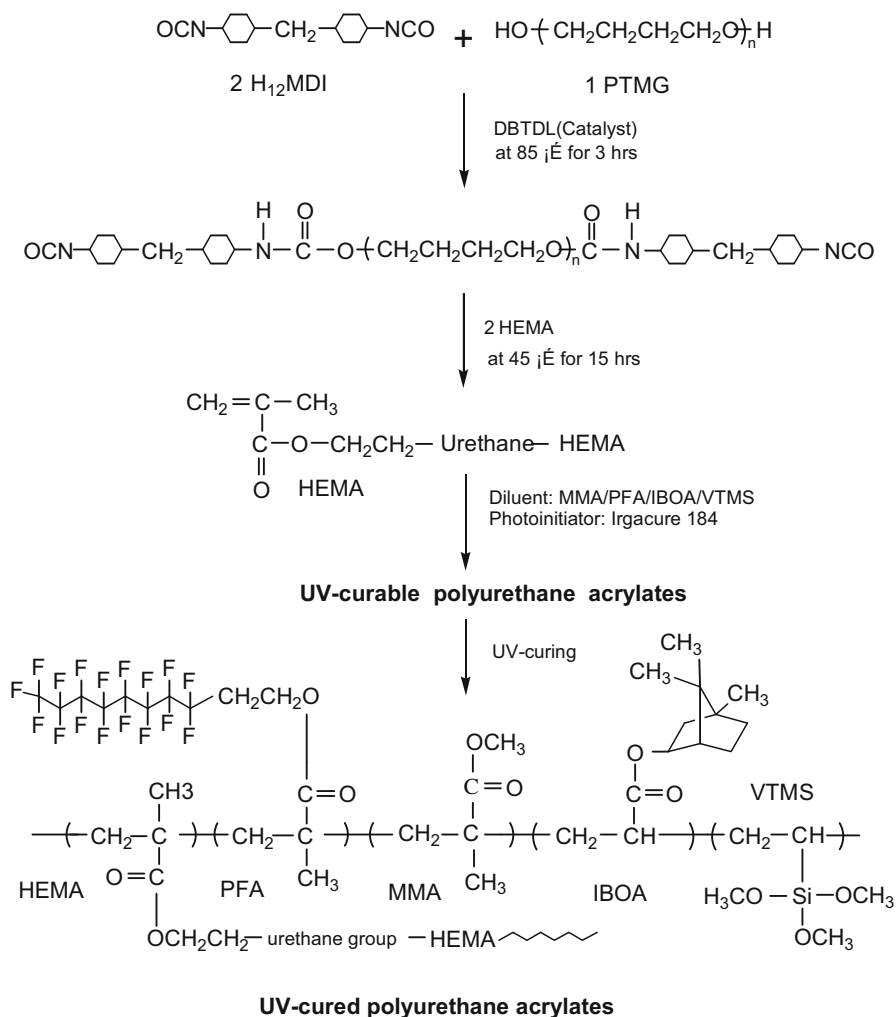
Scheme 1 Preparation process of UV-curable polyurethane acrylates and UV-cured polyurethane acrylates

acrylate diluents [methyl methacrylate (MMA, 20 wt%)/isobornyl acrylate (IBOA, 34–25 wt%)/heptadecafluorodecyl methacrylate (PFA, 6 wt%)/vinyltrimethoxysilane (VTMS, 0–9 wt%), total diluents: 60 wt%] and photoinitiator Irgacure 184 (1.5 wt%) to the viscose urethane acrylate prepolymer (40 wt%) and mixing them at 45 °C for 3 h. Table 1 lists the sample designation and composition of the UV-curable fluorinated urethane acrylate containing various contents of VTMS.

The UV-cured fluorinated urethane acrylate 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 a main wavelength of 365 nm.

Table 1 Sample designation and composition of UV-curable polyurethane acrylates

Sample designation	Composition							
	Prepolymer (molar ratio)			Prepolymer (wt%)	Diluent (wt%)			
	$H_{12}MDI$	PTMG	HEMA		MMA	IBOA	PFA	VTMS
FPUA 6/0	2	1	2	40	20	34	6	0
FPUA 6/3	2	1	2	40	20	31	6	3
FPUA 6/6	2	1	2	40	20	28	6	6
FPUA 6/9	2	1	2	40	20	25	6	9

Irgacure184*(photoinitiator): 1.5 wt% based on prepolymer/diluents mixture

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 chemical components of the UV-cured fluorinated polyurethane acrylate film samples containing various contents of VTMS were confirmed by 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, U. K) 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 in 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:

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

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

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 [47].

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 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 obtained using a UV–visible spectrophotometer (T70 + UV/VIS Spectrometer, PG Instruments, England).

Results and discussion

Composition of UV-curable polyurethane acrylate (prepolymer/diluents mixture)

Table 1 lists the sample designation, composition of prepolymer and prepolymer/ diluents of UV-curable polyurethane acrylates [prepolymer (40 wt%/diluents (60 wt%)/photoinitiator (1.5 wt%)]. In this study, the oligomer (prepolymer) was kept at a constant molar ratio, and the UV-curable urethane acrylate had a fixed weight ratio of oligomer (prepolymer)/diluents (40/60 wt%) and MMA/PFA/(20/6 wt%.), whereas the weight ratio of IBOA/VTMS was 34/0, 31/3, 28/6, 25/9 and 25/9 wt%. The reaction process is shown in Scheme 1. In this study, the effect of VTMS content (0–9 wt%) on the transparency, surface properties and mechanical properties of UV-cured polyurethane acrylate film was investigated to find the optimum content of VTMS for transparent antifouling coating materials.

Identification of chemical structure of UV-cured film samples

Most commonly, the process of photopolymerization reactions of acrylic materials was followed by monitoring the disappearance of the reactive acrylic groups present in the monomers and oligomers. Figure 1 shows the FT-IR spectra of the UV-cured
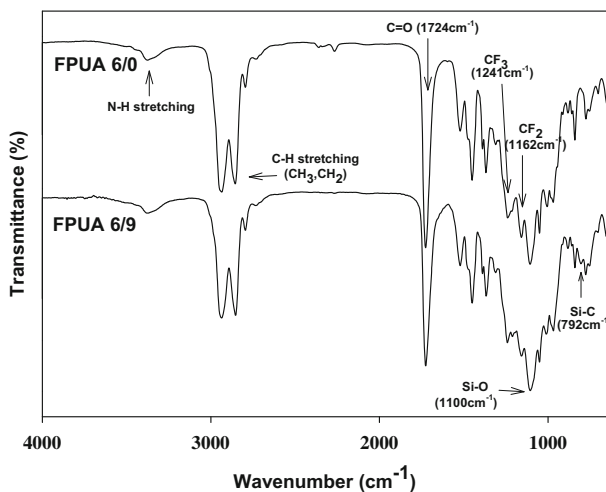

Fig. 1 FT-IR spectra of typical UV-cured film samples (FPUA6/0 and FPUA6/9)

FPUA6/0 FPUA6/9 film samples. The UV-cured PUA6/0 and FPUA6/9 film samples had no C=C peak at 1630–1640 cm^{-1}, indicating the complete reaction of all vinyl groups. The ester carbonyl (C=O) group of the PUA6/0 and FPUA6/9 films was identified by the characteristic peaks at approximately 1724 cm^{-1}. The stretching vibrations of the –CF$_2$ group at 1162 cm^{-1} and –CF$_3$ group at 1,241 cm^{-1} were all detected in the FPUA6/0 and FPUA6/9 film samples. The characteristic bands at approximately 1100 cm^{-1} and 792 cm^{-1} confirm the Si–O and Si–C groups of the FPUA6/9 film sample. The stretching vibrations of the urethane group (N–H) at 3300–3500 cm^{-1} and methylene/methyl group (C–H) at 2853–2962 cm^{-1} were all detected in the FPUA6/0 and FPUA6/9 film samples. On the other hand, many peaks of ether/urethane/acrylate/fluorine/silicone groups 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 surface (film–air interface) of PUA6/0, (b) film–dish interface of FPUA6/0, (c) film–air surface of FPUA6/3, (d) film–air surface of FPUA6/6, (e) film–air surface of FPUA6/9 and (f) film–dish interface of FPUA6/9. The atomic concentration of film samples is shown in Table 2. The surface peak intensity of F$_{1s}$ at 69 eV increased with increase in the VTMS content in FPUAs. By comparing the peak intensities of F$_{1s}$ for film–air surfaces of FPUA 6/0(a) and FPUA6/9(e), and for film–dish interfaces of FPUA6/0 (b)FPUA6/9(f), the relative peak intensity of F$_{1s}$ 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 [30, 34]. This suggests that the long perfluoralkyl group of the PFA component was introduced mainly to the surface layer of the fluorinated material as expected. The curing process should encourage the emergence of PFA/VTMS components (long alkyl/perfluoroalkyl groups) on the coating–air surface. The peak intensity of F1s in the film–air surface increased significantly with increase in the VTMS content. This indicated that the VTMS component containing bulky trimethoxysilane groups turned out be significantly more effective than the IBOA component containing bulky trimethylcycloalkyl group in promoting the emergence of PFA component onto the surface layer. This should be due to the presence of less rigid VTMS containing silicone which makes it easy for fluorine components to migrate over the surface. On the other hand, the peak at 152 eV assigned to Si$_{2p}$ and the peak at 101 eV assigned to Si$_{2p}$ were not observed in the FPUA6/0 film sample. The concentration of Si component in the film–air surface was found to be higher than that in the film–dish interface. The peak intensity/concentration of the Si component for film samples (FPUA6/3, 6/6 and 6/9 samples) were found to increase with increase in the VTMS content.

The transmittance % of UV-cured film samples

Figure 3 shows the UV–visible spectra of the UV-cured film samples (FPUA6/0, FPUA6/3, FPUA6/6, FPUA6/9 and FPUA6/12). The FPUA6/0 film without VTMS showed a low transmittance % of approximately 82 % in the visible range (400–800 nm). The transmittance % of the UV-cured film samples increased
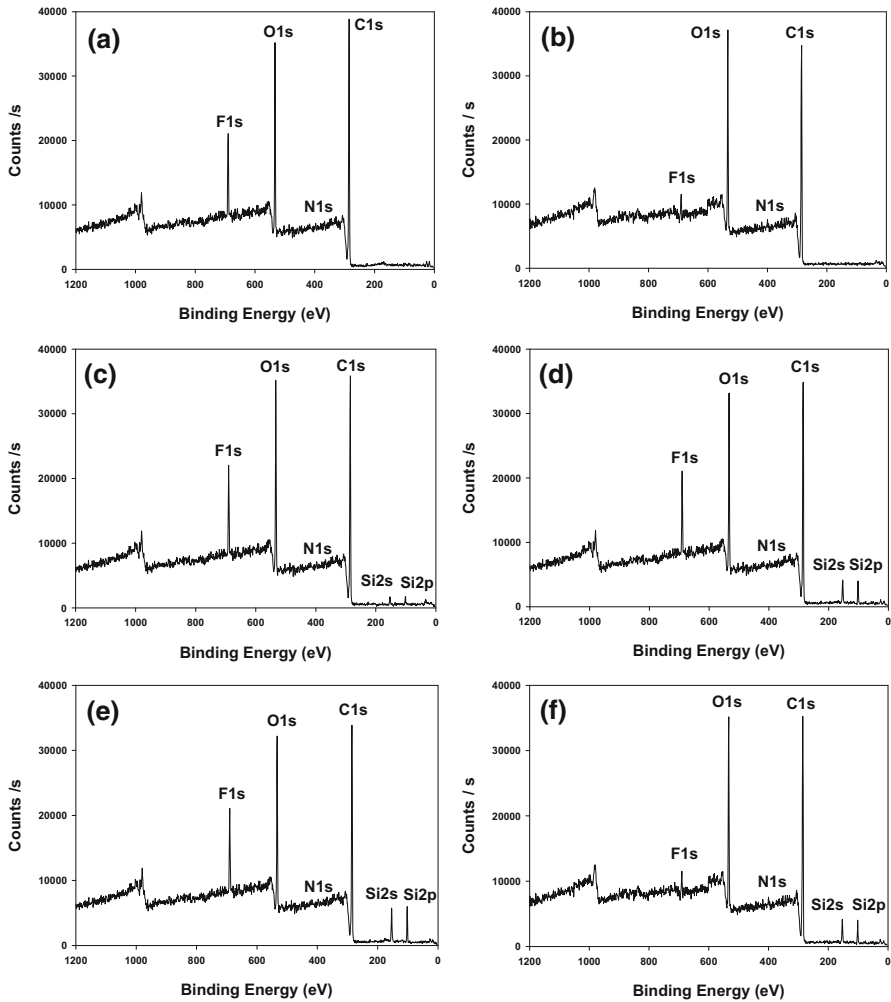
Fig. 2 XP spectra of **a** film–air surface of FPUA6/0, **b** film–dish interface of FPUA 6/0, **c** film–air surface of FPUA 6/3, **d** film–air interface of FPUA 6/6, **e** film–air surface of FPUA 6/9 and **f** film–dish interface of FPUA 6/9

markedly up to near 100 % with increase in the VTMS content up to 9 wt%. The increase in transmittance % should be due to the increases of amorphous region of film samples. The increase of amorphous region was caused by the incorporation of bulky VTES component into ordered region of polyol PTMG and acrylate components, which led to the decrease of the total ordered region. From these results, it was found that the FPUA6/9 film sample had near-perfect glassy (amorphous) morphology.

Table 2 Atomic concentration of film–air surface and film–dish interface free for film samples (FPUA6, FPUA6/3, FPUA6/6 and FPUA6/9)

Sample designation	Surface/interface	Atomic concentration (%)					
		C1s	N1s	O1s	F1s	Si2s	Si2p
FPUA 6/0	Film–air surface	70.70	0.23	22.78	6.29	0	0
	Film–dish interface	69.30	2.28	26.04	2.38	0	0
FPUA 6/3	Film–air surface	69.15	0.35	20.60	6.81	1.27	1.82
FPUA 6/6	Film–air surface	67.84	0.31	19.13	7.25	2.32	3.15
FPUA 6/9	Film–air surface	66.29	0.28	17.78	7.12	3.97	4.56
	Film–dish interface	70.30	1.92	21.52	2.21	1.84	2.21
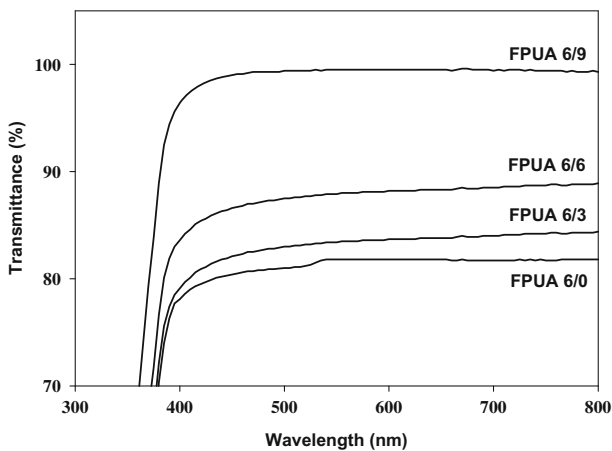
Fig. 3 UV–visible spectra of UV-cured film samples (FPUA 6/0, FPUA 6/3, FPUA 6/6 and FPUA 6/9)

DMA properties of UV-cured film samples

Figure 4 shows the storage modulus and tan delta of the UV-cured film samples. The film sample containing a higher VTMS content had a higher storage modulus. As the VTMS content increased, the Tgα of the film sample increased from 41.0 to 46.2 °C, whereas the broad peak at approximately −50 °C assigned to the soft segment Tg was almost unchanged. The increase of Tgα also might be due to the bulky trimethoxysilane group of VTMS. This suggests that the VTMS in vinyl monomers mainly affects the alpha amorphous region.

Mechanical properties and hardness of UV-cured polyurethane acrylate film samples

Figure 5 shows the stress–strain curves of UV-cured acrylate film samples. Table 3 lists the Young modulus, tensile strength, elongation at break and hardness of the film samples. As VTMS content increased, the tensile modulus and hardness
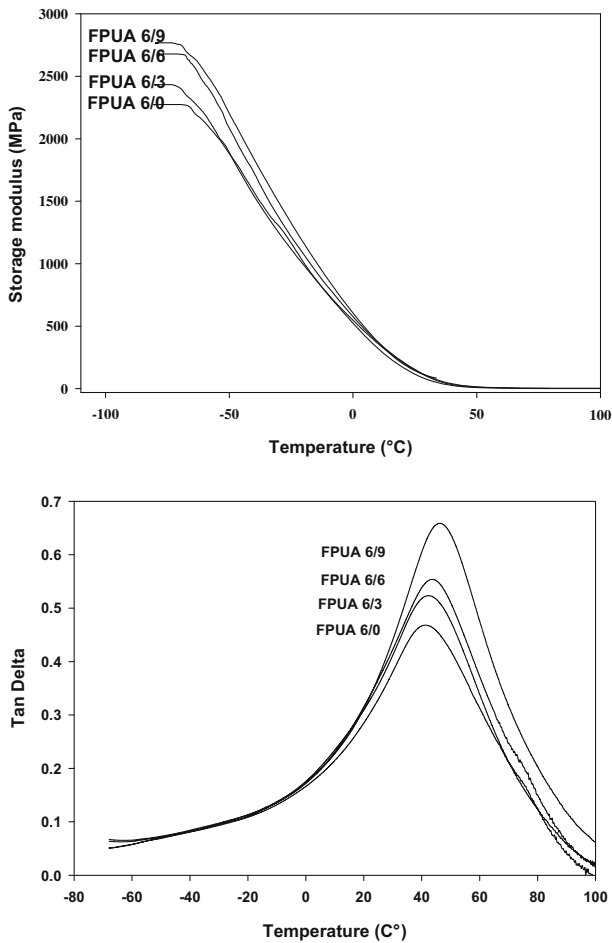
Fig. 4 Storage modulus and tan delta of UV-cured film samples (FPUA 6/0, FPUA 6/3, FPUA 6/6 and FPUA 6/9)

increased significantly and the tensile strength increased a little; however, the elongation at break decreased significantly. These results might be due to not only the increase of entanglement of the bulky trimethoxysilane side group, but also the increase of self-cross-linking of trimethoxysilane group exposed to water vapor during sample preparing/UV-curing processes under room environment containing a certain amount of water vapor. The specific influence of water vapor on the self-cross-linking of alkoxysilane will be studied in a future research.

Surface properties of UV-cured polyurethane acrylate film samples

Wettability of solid surface with liquid (water/oil) in air is a very important phenomenon in our daily life as well as in various industrial processes. Generally,
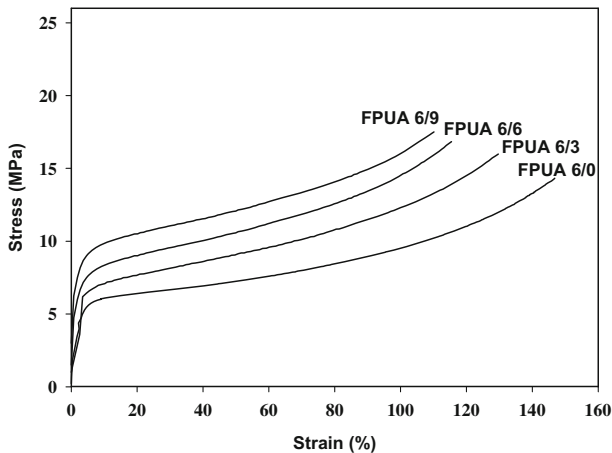
Fig. 5 Stress–strain curves of UV-cured film samples (FPUA 6/0, FPUA 6/3, FPUA 6/6 and FPUA 6/9)

Table 3 Water and methylene iodide contact angle, surface tension, mechanical properties and shore A hardness of UV-cured film samples

Sample designation	Contact angle (°)		Surface tension (mN/m)	Mechanical properties			Hardness (shore A)
	Water	Methylene iodide		Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)	
FPUA 6/0	107.9	80.9	13.8	14.3	146.8	106	90
FPUA 6/3	110.1	82.1	16.7	16.0	129.7	121	92
FPUA 6/6	112.4	83.4	16.2	16.8	115.5	143	94
FPUA 6/9	114.2	84.2	15.9	17.5	110.2	162	95

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). Table 3 and Fig. 6 show the water/methylene iodide contact angles and the surface tension of UV-cured polyurethane acrylates containing a range of VTMS contents (0–9 wt%). The water/methylene iodide contact angles of the UV-cured film samples FPUA6/0, FPUA6/3, FPUA6/6 and FPUA6/9 were 107.9/80.9°, 110.1/82.1°, 112.4/83.4° and 114.2/84.2°, respectively, whereas the surface tensions of these film samples were 17.2, 16.7, 16.2 and 15.9 mN/m, respectively. The surface tension and contact angles changed significantly with increase in the VTMS content. This might be due to the increase of migration of the hydrophobic PFA component to the film surface layer by increase in the bulky trimethoxysilane groups of VTMS, as mentioned in XPS analysis results. Generally, a self-assembled micro-domain 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 a surface. Usually, the higher root mean square roughness (RMS)
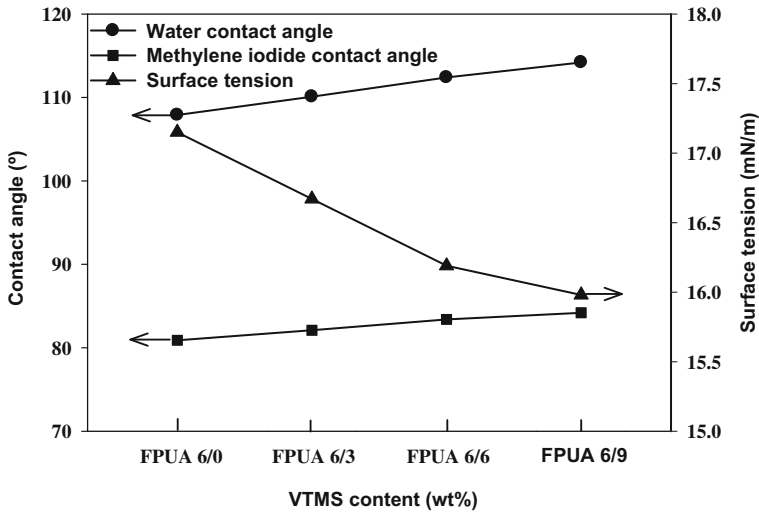
Fig. 6 Effect of VTMS content on the water/methylene iodide contact angles and surface tension

values determined using AFM implies surface change from smooth to rough. In our previous study, we found that the RMS value (surface roughness) increased with increase in fluorinated component content in fluorinated polyurethanes [48]. Therefore, the increase of contact angles/decrease of surface tension of film samples prepared here with increasing VTMS content should be attributed to not only the lower attractive force of fluorine/silicone components in the uppermost surface, but also the surface roughness.

Conclusion

UV-curable polyurethane acrylates containing fluorinated acrylic monomer (heptadecafluorodecyl methacrylate, PFA, 6 wt%)/vinyltrimethoxysilane (VTMS, 0–9 wt%) [FPUA6/0, FPUA6/3, FPUA6/6 and FPUA6/9, where the numbers indicate the wt% of PFA/VTMS] were synthesized 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%)/PFA (6 wt%)/isobornyl acrylate (IBOA, 34–25 wt%)/VTMS (0–9 wt%), total diluents: 60 wt%]. The effect of bulky VTMS/IBOA weight ratio on the properties of the UV-cured polyurethane acrylates was assessed for potential transparent antifouling coating applications. The transmittance % of UV-cured FPUA6/0 film sample containing 6 wt% PFA without VTMS was about 81.7 %; however, the transmittance % of the UV-cured FPUA6/9 film sample containing 9 wt% of VTMS was found to be near 100 %, indicating almost perfect transparency over the wavelength range of 400–800 nm (visible light). The storage modulus and hardness increased significantly with increasing

VTMS content, but the elongation at break decreased. By XPS analysis, it was found that the film–air surface of the UV-cured polyurethane acrylate film samples had a higher fluorine content than the film–dish interface. As the VTMS content increased from 0 to 9 wt%, the water/methylene iodide contact angles of UV-cured film samples increased from 107.9/80.9° to 114.2/84.2°, whereas the surface tension of these film samples decreased significantly from 17.2 to 15.9 mN/m. These results point to the strong potential of UV-curable polyurethane acrylate (FPUA6/9) with PFA/VTMS contents (6/9 wt%) as a coating material with the lowest surface energy (the highest contact angles) and the highest transparency. Overall, the FPUA6/0, FPUA6/3 and FPUA6/6 and FPUA 6/9 samples have better antifouling properties than polytetrafluoroethylene.

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