

UV-Curable Fluorinated Crosslinkable Polyurethane-Acrylates for Marine Antifouling Coatings

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Abstract

To prepare UV-curable polyurethane-acrylate oligomer, NCO-terminated urethane prepolymers with trimethylolpropane, [TMP; 0 (0), 0.1 (0.021) and 0.2 (0.043) mole (mole fraction)] as crosslinkable tri-functional chain extender were end-capped with pentaerythritol triacrylate [PETA; 2.0 (0.400), 1.7 (0.354) and 1.4 (0.304) mole (mole fraction)] with one hydroxyl group/three vinyl functionalities. The stable as-formulated UV-curable polyurethane-acrylates [stable mixtures of PETA-capped oligomer/reactive acrylic monomer diluents without/with heptadecafluorodecyl methacrylate (PFA; 0, 6 and 9 wt%)] were formed up to 0.2 (0.043) mole (mole fraction) of TMP content in the prepolymer, while homogeneous-mixing failed at 0.3 (0.068) mole (mole fraction), in which the crosslink density in NCO-terminated urethane prepolymer was too high to enable the formation of stable mixture. This study examined the effect of TMP/PETA molar ratio and heptadecafluorodecyl methacrylate (PFA) content (wt%) on the properties of UV-cured polyurethane-acrylates as marine antifouling coating materials. The properties of UV-cured polyurethane-acrylate were found to be significantly dependent on the crosslinkable TMP/PETA ratio and PFA content. With the increasing of the TMP and PFA contents, the contact angles increased, and consequently the surface tension decreased. The adhesion of algae/barnacles to PFA contained film samples were found to be sufficiently weak to allow their easy removal. These results suggest that the UV-cured samples containing PFA have strong potential as coating materials for antifouling applications.

Keywords : UV-curable polyurethane-acrylate, Coatings, Antifouling, Crosslinkable trimethylolpropane and pentaerythritol triacrylate

1. Introduction

Polyurethanes are unique materials, which have a wide range of applications because their properties can be readily tailored by the variation of their components [1-3]. Polyurethane-acrylates are made up of relatively long and flexible soft segments composed of polyol chains, highly polar hard segments formed from diisocyanate and chain extender (low molecular weight diol/diamine), and acrylic structure unit formed from hydroxyethyl acrylate (or hydroxyethyl methacrylate) and reactive acrylate monomers. The phase separation and properties of polyurethane and polyurethane-acrylate are commonly controlled by the physical and chemical crosslink. Chemical crosslink can be incorporated into either soft segments using multi- (tri- or tetra-) functional polyols or hard segments using multi-functional chain

extenders. Many studies have examined the effects of chemical crosslink on the properties of polyurethane such as tensile properties [4-8], swelling [7-10], thermal properties [4,6,9,10] and morphology [10,11]. The chemical crosslinks in the hard segment have important effects on the properties of the segmented polyurethanes [11,12]. Fan and Xiao have investigated the effect of crosslinkable TMP content on the structure and properties of semi-IPNs based on polyurethane/nitrogum [13].

Recently, preparation and properties of castor oil/PETA-based UV curable waterborne polyurethane acrylate has been investigated by Li et al. [14] Our previous reports have shown that the wet state adhesive strength of waterborne polyurethane-acrylates for footwear adhesives can be improved by using PETA [15,16]. Park et al. studied the effect of self-crosslinkable vinyl triethoxysilanes content on the properties of waterborne

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polyurethane-acrylic hybrids for high-performance water-repellent coating materials [17]. The effects of crosslinking agents such as vinyltrimethoxysilane and vinylmethacrylate on the properties of UV-curable polyurethane-acrylates containing fluorinated acrylic monomer for antifouling coating materials were investigated by Jeon et al. and Park et al. [18,19]. They found that chemical crosslinks in acrylic copolymer region is very important to improve water-resistance and thermal/mechanical properties of polyurethane-acrylates.

Fluorinated polymers have many unique properties including low surface tension/high soil resistance, good insulating/gas barrier properties and high resistance to thermal/chemical/weather attack, because of the low polarizability, strong electronegativity of fluorine atoms and high strength of the C-F bond. The main disadvantage of the fluorinated monomer is the relatively high cost. Therefore, the content of the fluorinated monomers should be minimized while maintaining a reasonable surface tension. Acrylic copolymers containing perfluoroalkyl side chains have been focus of many studies, because of the good reactivity of perfluorinated acrylate with fluorine-free acrylate and the good adhesion of acrylate component to the various substrates [20,21].

Many formulators have examined ways of combining the advantage of polyurethane and acrylic polymer. The properties of polyurethane-acrylic hybrid emulsions have been studied [22-25]. 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 and high weatherability [26,29]. Some studies have examined the properties of UV-curable waterborne polyurethane-acrylate [30,31] and the performance of UV-curable fluorinated polyurethane-acrylate using fluorinated urethane [32,33]. Teflon [34] and silicon rubber [35] would be used as alternatives to the self-polishing paints (tributyltin based paints). However, their adhesion to ship hulls was sufficiently weak to allow their easy removal by water jets or simply by the friction of sea water in the case of fast ships. To overcome the problem of lack of adhesion of these materials to ship hulls, UV-curable crosslinkable polyurethane-acrylates containing fluorine component, whose adhesion to ship hulls was strong enough, was synthesized in this study. However, studies on UV-curable polyurethane-acrylate containing chemical crosslinking component TMP and PETA and reactive diluents with fluorinated acrylic monomer PFA have not been issued. Thus, the aim of this study was to improve the surface antifouling properties and mechanical properties of crosslinked polyurethane-acrylate by introducing crosslinkable three vinyl groups contained PETA and internal

crosslinkable TMP and fluorinated acrylic monomer PFA.

In this study, the rigid bulky cycloalkyl group contained monomer isobornyl acrylate (IBOA) to raise toughness/rigidity, long-alkyl chain group contained acrylic monomer butyl acrylate (BA) to raise flexibility/hydrophobicity, long perfluoroalkyl group contained monomer perfluoroalkyl acrylate (PFA) to expand surface tension, three vinyl groups/one hydroxyl group contained PETA as an end capping agent as well as a crosslinking/multi-branching agent for acrylate monomer, and TMP as an internal cross-linker for PU hard segment, are used in this study. This study focused on the effects of TMP/PETA molar ratio and PFA content on the properties such as mechanical properties, thermal properties, contact angle, surface tension and antifouling property of UV-cured polyurethane acrylates with a fixed urethane oligomer content (40 wt%) to find the optimum composition for outstanding antifouling materials.

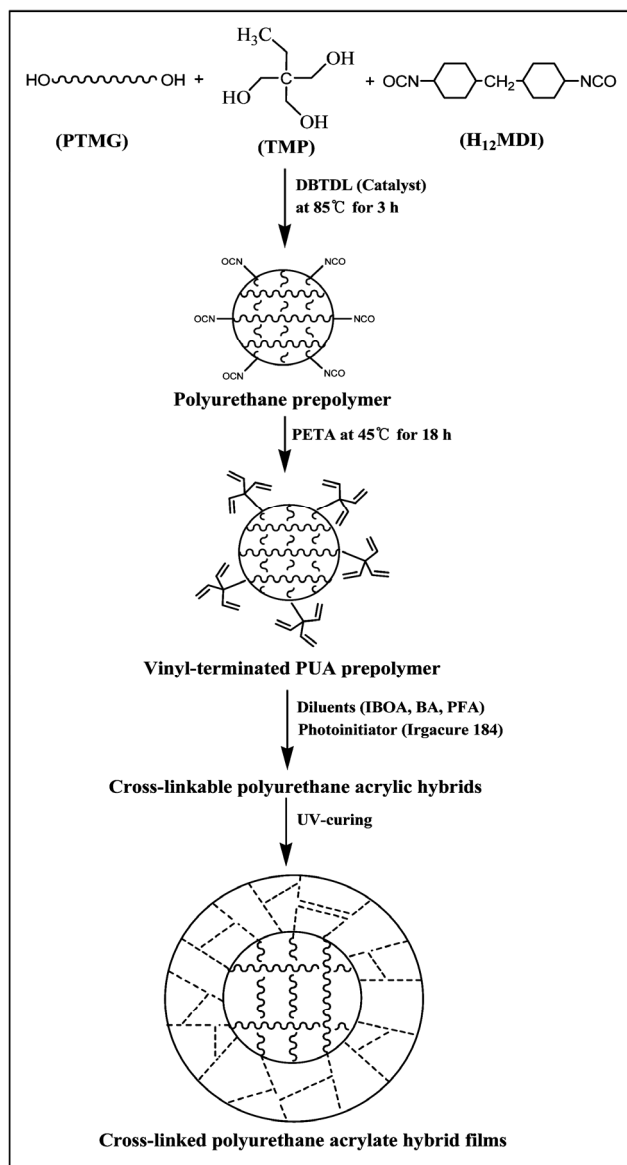
2. Materials and methods

2.1. 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'-Dicyclohexymethane-diisocyanate (H_{12} MDI, Aldrich Chemical, Milwaukee, WI), dibutyltindilaurate (DBTDL, Aldrich Chemical, Milwaukee, WI), trimethylol propane (TMP, Aldrich Chemical, Milwaukee, WI), pentaerythritol triacrylate (PETA, 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), butyl acrylate (BA, Aldrich Chemical, Milwaukee, WI) and 1-hydroxycyclohexyl acetophenone (Irgacure 184, Aldrich Chemical, Milwaukee, WI) were used as received.

2.2. Preparation of cross-linked polyurethane acrylate hybrids and their films

The preparation process of cross-linked polyurethane acrylates is shown in Scheme 1. First, PTMG and TMP were 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 were degassed in a vacuum at 90 °C for 1 h. The mixture were allowed to cool to 60 °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 PETA was added dropwise.



Scheme 1. Synthesis process of cross-linked polyurethane acrylate hybrid films.

To obtain the vinyl-terminated urethane acrylate prepolymer, the capping reaction of the NCO-terminated urethane prepolymer with PETA 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 (60 wt%) and photoinitiator Irgacure 184 (2 wt% based on the prepolymer/diluents). A series of UV-curable fluorinated polyurethane acrylates mixture (prepolymer/diluents/photo-initiator) were formulated by adding the acrylate diluents [isobornyl acrylate (IBOA, 40 - 31 wt%)/ butyl acrylate (BA, 20 - 11 wt%), heptadecafluorodecyl methacrylate (PFA, 6 - 9 wt%), total diluents: 60 wt%] and photo-initiator Irgacure 184 (2 wt%) to the viscous urethane acrylate prepolymer (40 wt%) and mixing them at $45\text{ }^{\circ}\text{C}$ for 3 h. Table 1 lists the sample designation and composition of the UV-curable fluorinated urethane-acrylate containing various contents of TMP, PETA and PFA. All the samples formulated in this study were stored in dark condition at room temperature before irradiation (curing).

The UV-curable 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^2). 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.

2.3. Characterizations

The viscosity of the formulated UV-curable polyurethane acrylates was measured at $25\text{ }^{\circ}\text{C}$ using a Brookfield digital viscometer (Brookfield LVDVII+, USA). The measurements were performed at 100 rpm using a spindle RV-4.

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

Sample designation	Composition										Viscosity (cP/25 °C)
	Oligomers [mole (mole fraction)/wt%]				Oligomer (wt%)	Reactive acrylic monomers (Diluents, wt%)			Diluent (wt%)	Irgacure (wt%)	
	H ₁₂ MDI	PTMG	TMP	PETA		IBOA	BA	PFA			
PUA-T/P (0/2.0)	2.0(0.400) /16.8	1.0(0.200) /64.1	0(0)/0	2.0(0.400) /19.1	40	40	20	0	60	2	824
PUA-T/P (0.1/1.7)	2.0(0.417) /17.2	1.0(0.208) /65.7	0.1(0.021) /0.4	1.7(0.354) /16.7	40	40	20	0	60	2	1061
PUA-T/P (0.2/1.4)	2.0(0.435) /17.7	1.0(0.217) /67.4	0.2(0.043) /0.9	1.4(0.304) /14.1	40	40	20	0	60	2	1357
PUA-T/P (0.2/1.4)-F6	2.0(0.435) /17.7	1.0(0.217) /67.4	0.2(0.043) /0.9	1.4(0.304) /14.1	40	40	14	6	60	2	1430
PUA-T/P (0.2/1.4)-F9	2.0(0.435) /17.7	1.0(0.217) /67.4	0.2(0.043) /0.9	1.4(0.304) /14.1	40	40	11	9	60	2	1510

The chemical components of the UV-curable polyurethane acrylate film samples were confirmed by the Fourier transform infrared (FTIR, NICOLET iS5, USA) spectroscopy. The FTIR 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.

The dynamic mechanical properties of film samples were measured at 3 Hz using dynamic mechanical thermal analyzer (DMA, TA-Q 800; Instrument, USA) with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ in the temperature range from -100 to 150 $^{\circ}\text{C}$.

The tensile properties were measured at room temperature using a universal testing machine (Instron, USA) with a 5582 system according to ASTM D 638. A cross-head speed of 10 mm min^{-1} was used throughout these investigations to determine the ultimate tensile strength, modulus, and elongation at break for all samples.

For swelling test of UV-cured film samples in water, the films were immersed in water for 48 h at room temperature and the swelling percentage was determined from the weight increase.

$$\text{Swelling (\%)} = [(W - W_0) / W_0] \times 100 \quad (1)$$

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

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.

The water and methylene iodide contact angles were measured at 25 $^{\circ}\text{C}$ 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 surface wettability, was used to determine the hydrophobicity and hydrophilicity. The surface tension of the solid film can be determined using the following equation:

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (2)$$

$$\gamma_L(1 + \cos\theta_L) = 2(\gamma_L^d \gamma_s^d)^{1/2} + 2(\gamma_L^p \gamma_s^p)^{1/2} \quad (3)$$

where γ_s is the surface energy of 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^{-1} , respectively [36].

Field tests in seawater were performed from September 2015 (78 days) located at Dadaepo in Busan, Korea. The film samples

that were mounted onto the PVC supports were immersed into the seawater at depths of about 1 m below the surface. The samples faced the open ocean and were not caged. Periodically, the samples were removed, washed with a stream of fresh water that was aimed perpendicularly to the substrate (distance \sim 20 cm), and photographed.

3. Results and Discussion

3.1. Composition, stability and viscosity of formulated UV-curable polyurethane acrylates (polyurethane-acrylate oligomers/diluents/photoinitiator)

Table 1 lists the sample designation, composition and viscosity of UV-curable polyurethane acrylates [polyurethane-acrylate prepolymer (40 wt%)/diluents (60 wt%)/photoinitiator Irgacure 184 (2 wt%)]. In this study, the UV-curable polyurethane-acrylate had a fixed weight ratio of polyurethane-acrylate prepolymer (oligomer)/diluents (40/60 wt%), whereas the compositions of TMP/PETA and BA/PFA were changed. The as-formulated UV-curable polyurethane acrylate containing up to 0.2 (0.043) mole (mole fraction) of TMP in the prepolymer was found to form stable homogeneous mixtures. However, the UV-curable polyurethane acrylate with 0.3 (0.068) mole (mole fraction) of TMP was found to be unstable, indicating that 0.3 (0.068) mole (mole fraction) of crosslinkable TMP content was beyond the limit value of crosslink density to form homogeneous mixture (polyurethane-acrylate oligomer/diluent/photoinitiator). This means that between 0.2 (0.043) and 0.3 (0.068) mole (mole fraction) of TMP content leads to unstable mixture. 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. The viscosity of UV-curable polyurethane-acrylate increased significantly from 824 to 1357 cP with increasing crosslinkable TMP content from 0 (0) to 0.2 (0.043) mole (mole fraction). The viscosity of UV-curable polyurethane-acrylate increased from 1357 to 1510 cP with increasing FPA content from 0 to 9 wt%. The increases of viscosity should be due to both the increase of crosslink density and fluorinated long side chain content.

3.2. Identification of chemical reactions and structure

Figure 1 shows the FTIR spectra of typical samples (NCO-terminated PU prepolymer, vinyl-terminated PUA prepolymer, PUA-T/P (0/2.0), PUA-T/P (0.2/1.4) and PUA-T/P (0.2/1.4)-F9. In this study, the chemical reactions between the functional groups were checked by monitoring the disappearance of the reactive functional groups present on the monomers and prepolymer. The capping reaction of the NCO-terminated urethane prepolymer with PETA was confirmed by the disappearance of NCO peak

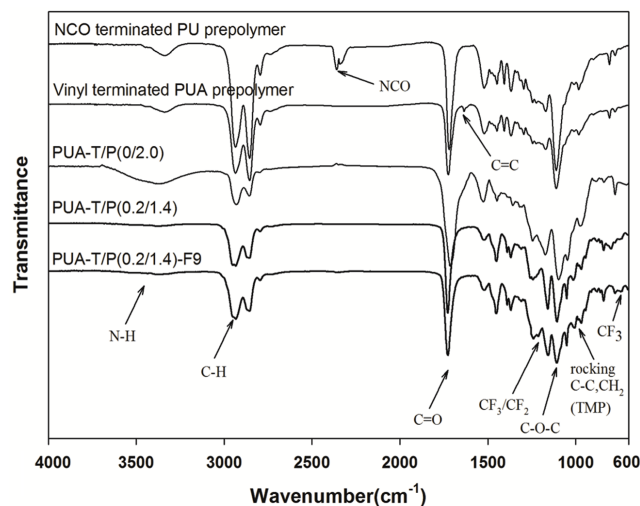


Figure 1. FTIR spectra of typical samples (NCO terminated PU prepolymer, vinyl terminated PUA prepolymer, PUA-T/P (0/2.0), PUA-T/P (0.2/1.4) and PUA-T/P (0.2/1.4)-F9).

at 2270 cm^{-1} . The FTIR spectrum of the vinyl terminated PUA prepolymer showed the characteristic C=C peaks at $1620\text{--}1640\text{ cm}^{-1}$ but the UV-cured film samples (PUA-T/P (0/2.0), PUA-T/P (0.2/1.4) and PUA-T/P (0.2/1.4)-F9) had no C=C peak indicating the complete reaction of all vinyl groups. The characteristic bands at $1002\text{--}1012\text{ cm}^{-1}$ confirm the stretching/rocking vibrations of the C-C/CH₂ groups in TMP of PUA-T/P (0.2/1.4) and PUA-T/P (0.2/1.4)-F9 samples. The characteristic bands at approximately 1713 , 1082 , 1105 and $3000\text{--}3500\text{ cm}^{-1}$ 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 cm^{-1} was found to overlap with urethane carbonyl group in the range of $1802\text{--}1651\text{ cm}^{-1}$. The stretching vibrations of -CF₂, -CF₃ groups at 1206 cm^{-1} , and a combination of rocking and wagging vibration of the CF₃ group at 701 cm^{-1} in the fingerprint region, are all detected in the PUA-T/P (0.2/1.4)-F9 film sample. On the other hand, many peaks of ether/urethane/acrylate/fluorine groups were overlapped with each other.

3.3. DMA properties of UV-cured film samples

In general, polyurethanes have hard and soft segment phases, and polyurethane-acrylates have hard/soft/acrylic copolymer segment phases. The glass transition temperatures of these phases are very important characteristics of polyurethanes/polyurethane-acrylates. Generally, the T_g of these phases depends on the chemical composition, phases mixing/separation and molecular weight of these phases. The storage modulus (E') and tan delta of the UV-cured polyurethane-acrylate film samples are shown in Figure 2. The E' of film samples was maintained constant

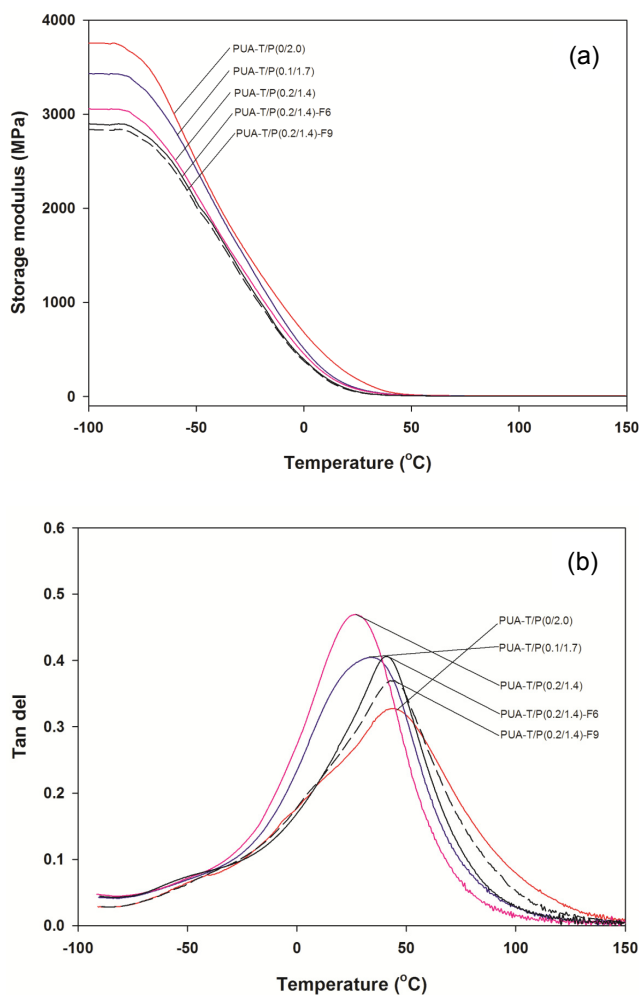


Figure 2. (a) Storage modulus and (b) tan delta of cross-linked polyurethane hybrid film samples [PUA-T/P (0/2.0), PUA-T/P (0.1/1.7), PUA-T/P (0.2/1.4), PUA-T/P (0.2/1.4)-F6 and PUA-T/P (0.2/1.4)-F9].

in the glassy plateau region ($-100\text{--} -47\text{ }^{\circ}\text{C}$), and then it was sharply decreased owing to the glass transition of soft segment PTMG. The E' value of UV-cured film samples decreased with increasing TMP/PETA molar ratio. This indicated that the modulus (rigidity: $1/\text{softness}$) of film samples was mainly dependent on the amount of three bulky vinyl groups contained PETA and not the content of TMP as an internal cross-linker in urethane hard segment. This might be due to the higher contents [2.0 (0.400), 1.7 (0.354), 1.4 (0.304) mole (mole fraction)] of cross-linking bulky PETA component in acrylic component. The film sample containing a higher PFA content had a lower storage E' . This might be because of the incompatibility of the bulky flexible hydrophobic PFA component with the acrylic/urethane components. The T_{gs} (T_{gu} and T_{gp}) of the UV-cured polyurethane-acrylate film samples are shown in Table 2. The loss $\tan\delta$ peak of UV-cured polyurethane-acrylate film samples at about $-55.5\text{ }^{\circ}\text{C}$ is assigned to the glass transition temperature (T_{gp}) of soft

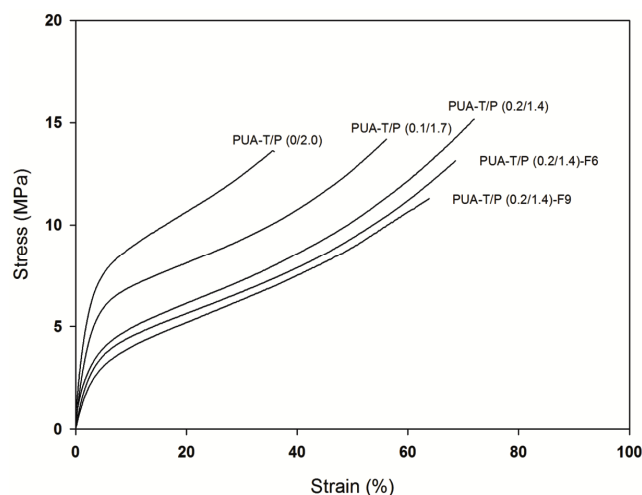
Table 2. DMA results and mechanical properties of UV-cured polyurethane acrylate film samples

Sample designation	DMA results		Mechanical properties		
	$T_{g\beta}$ (°C)	$T_{g\alpha}$ (°C)	Tensile strength (MPa)	Elongation at break (%)	1% Strain Modulus (MPa)
PUA-T/P (0/2.0)	-40.3	43.8	13.6	35.8	333.5
PUA-T/P (0.1/1.7)	-	33.5	14.2	56.1	232.4
PUA-T/P (0.2/1.4)	-	26.7	15.2	71.9	175.2
PUA-T/P (0.2/1.4)-F6	-	40.6	13.1	68.6	132.8
PUA-T/P (0.2/1.4)-F9	-	44.7	11.3	63.9	109.6

segment (PTMG) of polyurethane component. As the PETA and PFA contents were increased, the $T_{g\beta}$ was almost not changed. This indicated that the soft segment PTMG component was almost not mixed with hard segment/acrylic components. The loss $\tan\delta$ peak of UV-cured polyurethane-acrylate film samples at in the range of 27 ~ 45 °C should be assigned to the T_{ga} (the T_g of mixed phase of polyurethane hard segment/acrylic components (PETA/IBOA/BA/PFA)). The T_{ga} of the film sample increased from 26.7 to 43.8 °C with increasing PETA content from 1.4 (0.304) to 2.0 (0.400) mole (mole fraction)/decreasing TMP content from 0.2 (0.043) to 0 (0) mole (mole fraction). The shift of T_{ga} suggests that the hard segment of polyurethane containing TMP is miscible with acrylic copolymer segments containing PETA. The miscibility should be attributable to the intimate molecular mixing through the formation of acrylic monomer absorbed urethane prepolymer. The increase of T_{ga} was also found to be depended on the amount of PETA containing three bulky vinyl groups. In addition, the T_{ga} of UV-cured film samples containing PFA increased from 26.7 to 44.7 °C with increasing bulky PFA content from 0 to 9 wt%.

3.4. Mechanical properties of UV-cured film samples

Figure 3 shows the stress-strain curves of UV-cured polyurethane acrylate film samples. The initial tensile modulus, tensile strength, elongation at break of the film samples are shown in Table 2. As the TMP (crosslinking agent in polyurethane hard segment) content increased from 0 (0) to 0.2 (0.043) mole (mole fraction)/PETA (branching/crosslinking agent in acrylic component) content decreased from 2.0 (0.400) to 1.4 (0.304) mole (mole fraction), the tensile modulus decreased significantly from 333.5 to 175.2 MPa. This result also indicated that the modulus (rigidity: 1/softness) of film samples was mainly depen-

**Figure 3.** Stress-strain curves of cross-linked polyurethane acrylate hybrid film samples [PUA-T/P (0/2.0), PUA-T/P (0.1/1.7), PUA-T/P (0.2/1.4), PUA-T/P (0.2/1.4)-F6 and PUA-T/P (0.2/1.4)-F9].

dent on the amount of three bulky vinyl groups contained PETA and not the content of TMP as an internal cross-linker for polyurethane hard segment component. However, the tensile strength and the elongation at break increased significantly from 13.6 to 15.2 MPa and from 35.8 to 71.9%, respectively, with increasing TMP content from 0 (0) to 0.2 (0.043) mole (mole fraction). As opposed to the modulus (rigidity) result, this result indicated that the effect of TMP on the tensile strength/elongation at break was higher than that of PETA. As anticipated, the initial tensile modulus, tensile strength and elongation at break decreased with increasing hydrophobic/oleophobic bulky heptadecafluorodecyl/methyl group contained PFA content.

3.5. Water swelling and gel content of UV-cured film samples

The water uptake% (water swelling%) and gel content% of UV-cured polyurethane-acrylates film samples containing crosslinkable TMP/PETA and PFA are shown in Table 3. The absorbed water in polymer network has a devastating influence on the properties of coating materials, therefore, the water uptake behavior of coatings is of great interest to determine their end application performance. It was found that all the prepared samples containing crosslinkable components (PETA and TMP)/PFA absorb water almost zero. This means that all the prepared samples are highly water resistant materials. The UV-curing of crosslinkable polyurethane-acrylates prepared in this study led to the formation of more compact interpenetrating networks. The crosslinked three-dimensional network of UV-cured polyurethane-acrylates may induce the decrease of free volume in the coating materials, thereby avoiding entry of water molecules. The very

Table 3. Water swelling, gel content and surface properties of UV-cured polyurethane acrylate film samples

Sample designation	Water swelling (%)	Gel content (%)	Contact angle (°)		Surface tension (mN m ⁻¹)
			Water	Methylene iodide	
PUA-T/P (0/2.0)	~0	~100	93.5	69.6	23.4
PUA-T/P (0.1/1.7)	~0	~100	95.3	72.3	21.8
PUA-T/P (0.2/1.4)	~0	~100	99.5	77.4	19.0
PUA-T/P (0.2/1.4)-F6	~0	~100	105.1	84.3	15.4
PUA-T/P (0.2/1.4)-F9	~0	~100	113.1	87.1	14.2

low level water uptake for crosslinked polyurethane-acrylates prepared here may be attributed to the prevention of water penetration into the polymeric bulk due to the crosslinking of the PETA-capped prepolymer containing TMP/acrylic monomers particles.

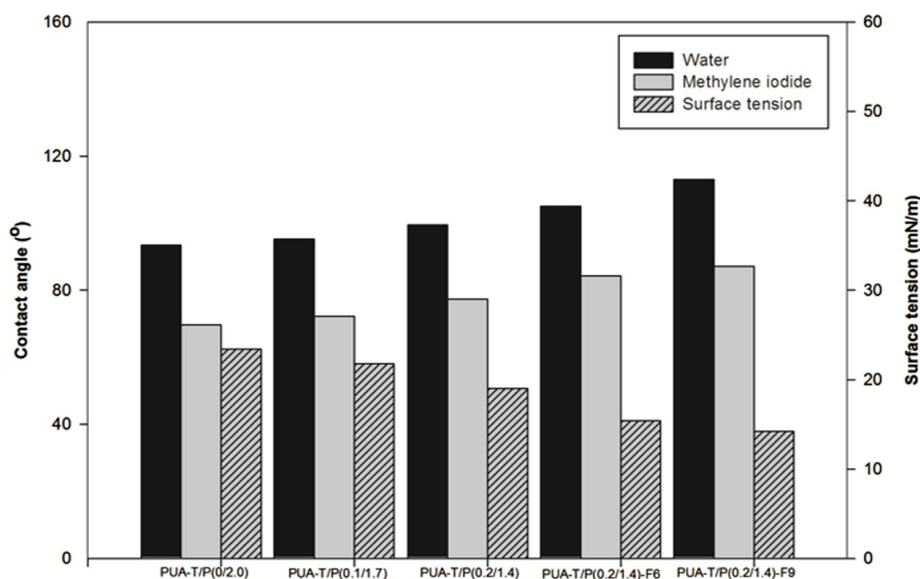
The gel content (%) is a measure of curing and crosslinking of the UV-curable coating materials. It was found that the gel content of all UV-cured film samples was near 100%, indicating that the UV-cured film samples prepared in this study had a very high molecular weight (crosslink-like structure). The difference of effect of PETA/TMP/PFA contents on the gel content was negligible. This should be due to the sufficiently high enough crosslink density of UV-cured polyurethane-acrylates containing different contents of PETA/TMP/PFA components.

3.6. Surface properties of UV-cured film samples

Table 3 and Figure 4 show water/methylene iodide-contact angles and surface tension of UV-cured polyurethane acrylates containing different contents of TMP, PETA and PFA. As the TMP content increased from 0 (0) to 0.2 (0.043) mole (mole fraction)/the PETA content decreased from 2.0 (0.400) to 1.4 (0.304) mole (mole fraction), the water and methylene iodide contact angles of UV-cured polyurethane-acrylate film samples increased from 93.5 to 99.5°, and from 69.6 to 77.4°, respectively. Thus, the surface tension decreased from 23.4 to 19.0 mN/m. As expected, the water contact angle/methylene iodide contact angle/surface tension of film samples increased markedly from 99.5/77.4 to 113.1°/87.1° with increasing PFA content from 0 to 9 wt%. Therefore, the surface tension decreased from 19.0 to 14.2 mN/m. The migration of the hydrophobic/olephobic PFA component to the film surface layer during curing leads to a relatively low free energy at the surface. This phenomenon has been confirmed by many analyses [17,24,25]. This is very useful to improve the water and soil repellency of coating materials.

3.7. Antifouling properties

The antifouling properties of UV-cured polyurethane-acrylate film samples were investigated through a simple visual observation of the immersed coated panels. We also verified the adhesion properties of algae/barnacles by visual inspection. All the prepared samples were used for comparing antifouling properties. The pictures corresponding to the pristine film, films immersed in sea-water for 20 days, 36 days and 78 days, and 78 days - im

**Figure 4.** Water/methylene iodide-contact angles and surface tension of cross-linked polyurethane hybrid film samples [PUA-T/P (0/2.0), PUA-T/P (0.1/1.7), PUA-T/P (0.2/1.4), PUA-T/P (0.2/1.4)-F6 and PUA-T/P (0.2/1.4)-F9].

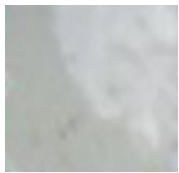




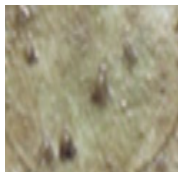
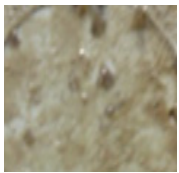

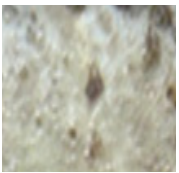



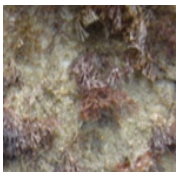

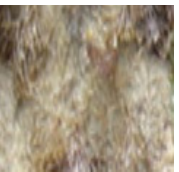


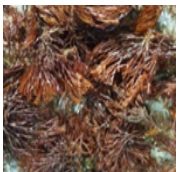



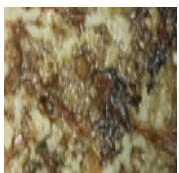



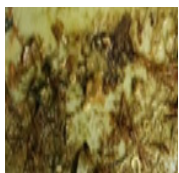




Sample designation	PUA-T/P (0/2.0)	PUA-T/P (0.1/1.7)	PUA-T/P (0.2/1.4)	PUA-T/P (0.2/1.4)-F6	PUA-T/P (0.2/1.4)-F9
Pristine film					
Film immersed seawater for 20 days					
Film immersed seawater for 36 days					
Film immersed seawater for 78 days					
78 days immersed film after manually peeling off the algae/barnacles					
78 days immersed film after scrapping off the algae/barnacles using 0.5 kgf/cm ² plastic square bar					

Figure 5. Photographs of coated samples after immersion in sea water.

mersed film after manually peeling off the algae/barnacles and 78 days-immersed film after scrapping off the algae/barnacles using a plastic square bar (0.5 kgf cm^{-2}) are presented in Figure 5. The amount of algae/barnacles adhered to the film surface increased markedly with increasing elapsed time. The adhesion of algae/barnacles to PUA-T/P (0.2/1.4)-F6 and PUA-T/P (0.2/1.4)-F9 film samples containing fluorinated acrylate monomer (PFA) was found to be sufficiently weak to allow their easy removal. This indicates that the temporary fixing of algae/barnacles to antifouling coatings on ship hulls was weak to allow their easy removal by water jets or simply by the friction of sea water in the case of fast ships. This should be due to the lower surface tension of these samples.

4. Conclusions

A series of stable UV-curable polyurethane acrylates were formulated from PETA [2.0 (0.400) - 1.4 (0.304) mole (mole fraction) - capped oligomers (40 wt%) containing TMP [0 (0) - 0.2 (0.043) mole (mole fraction)] as a crosslinkable tri-functional chain extender and diluents [IBOA (40 wt%)/BA (20 wt%) and IBOA (40 wt%)/BA (14/11 wt%)/PFA (6/9 wt%)]. The effects of the TMP/PETA molar ratios (0/2.0, 0.1/1.7 and 0.2/1.4) and PFA contents (6 and 9 wt%) on the properties of the UV-cured polyurethane acrylates were investigated. The stable as-formulated UV-curable polyurethane-acrylates [the stable mixtures of PETA-capped oligomer (40 wt%) and acrylic monomer diluent (IBOA/

BA 40 wt%/20 wt%)/photoinitiator] were formed up to 0.2 (0.043) mole (mole fraction) of TMP content in the oligomer, while homogeneous-mixing failed at 0.3 (0.068) mole (mole fraction), in which the crosslink density in NCO-terminated urethane oligomer was too high to enable the formation of homogeneous mixture. This indicates that between 0.2 (0.043) and 0.3 (0.068) mole (mole fraction) of TMP content lead to unstable mixture of oligomer/diluent/photoinitiator. The viscosity of PETA-capped oligomer/diluent mixture increased significantly with increasing multi-functional chain extender TMP in place of PETA as well as fluorinated monomer PFA content. As the TMP content increased/the PFA content decreased, the tensile strength/elongation at break of film samples increased, however, the tensile modulus of film sample decreased. The T_{gu} of film sample decreased with increasing PETA content, but the T_{gu} increased with increasing PFA content in diluents. However, the soft segment T_g (T_{gs}) was not changed with varying PETA/TMP ratio and PFA content, indicating that the soft segment domain in urethane component was not mixed with the hard segment domain as well as acrylic polymer domain. With the increasing of the TMP and PFA contents, the contact angles increased, and consequently the surface tension decreased. All of the prepared samples were almost not swelling in water and not dissolved in solvents (DMF and toluene). Water/methylene iodide contact angles increased with increasing TMP content/decreasing PETA content up to 0.2/1.4, however, the emulsion stability decreased with increasing TMP content. Therefore, the optimum content of TMP/PETA was found to be about 0.2 (0.043)/1.4 (0.304) mole (mole fraction). The samples containing PFA exhibited a greatly improved foul release behavior compared to others samples without PFA. These results suggest that the UV-curable crosslinkable polyurethane acrylate samples containing PFA have strong potential as coating materials for antifouling applications.

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