



UV-curable low surface energy fluorinated polycarbonate-based polyurethane dispersion

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ABSTRACT

UV-curable low surface energy fluorinated polycarbonate-based polyurethane dispersions were synthesized by incorporating a hydroxy-terminated perfluoropolyether (PFPE) into the soft segment of polyurethane. The effects of the PFPE content on the UV-curing behavior, physical, surface, thermal properties and refractive index were investigated. The UV-curing behavior was analyzed by photo-differential scanning calorimetry. The surface free energy of the UV-cured film, which is related to the water or oil repellency, was calculated from contact angle measurements using the Lewis acid–base three liquids method. The surface free energy decreased significantly with increasing fluorine concentration because PFPE in the soft segment was tailored to the surface and produced a UV-cured film with a hydrophobic fluorine enriched surface, as confirmed by X-ray photoelectron spectroscopy. With increasing the fluorine content, the refractive indices of UV-cured films decreased. However, the UV-curing rate and final conversion was decreased with increasing contents of PFPE, which resulted in the decrease of the glass transition temperature (T_g), crosslink density, tensile strength and surface hardness.

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1. Introduction

Coating technologies have been developed to produce more environmental friendly coatings to meet the growing consumer demands, such as good for health, excellent performance and lower cost. Moreover, environmental regulations and government legislation have been passed to enforce these developments. Many coatings technologies have been developed to satisfy these requirements, and traditional solvent-borne coatings have been replaced by environmental friendly coatings [1,2].

In this situation, waterborne UV-curable coatings are considered to be important coating technologies due to the combined advantages of UV curing technology and waterborne system [3,4]. The disadvantage of UV-curing systems arisen from the unreacted monomers can be solved by incorporation of dispersion technology. UV-curable dispersions are based on high molecular weight binders that make it possible to obtain the low viscosity necessary for spray applications independent of the molecular weight of the dispersed polymer. Moreover, the disadvantages of waterborne coating systems can be improved by the incorporation of a crosslinked structure formed by UV-curing [5,6]. However, the properties of waterborne UV-curable coatings are inferior to the 100% liquid UV-curing system [7,8].

In this study, UV-curable low surface energy fluorinated polycarbonate-based polyurethane dispersions were synthesized by incorporating a hydroxy-terminated perfluoropolyether (PFPE) into the soft segment of polyurethane. The incorporation of PFPE into the soft segments of the polyurethane backbone was performed by a reaction between NCO and OH groups in the diisocyanates and hydroxy-terminated PFPE.

To produce the polyurethane dispersion, polycarbonate diols have been selected as polyols to achieve better mechanical properties for surface coatings applications. In particular, linear aliphatic polycarbonates are used as both binders in high-quality polyurethane coatings and in the production of polyurethane binders or polyurethane dispersions [9,10].

Generally, PFPE has excellent properties, such as low friction coefficient, high thermal and chemical resistance, and non-wetting property [11,12]. In addition, the PFPE chain is quite flexible without a crystallization tendency and the T_g of the PFPE homopolymer is quite low [13,14]. The effects of the PFPE content on the UV-curing behavior, physical, surface, thermal properties and refractive index were examined. The UV-curing behavior was analyzed by a photo-differential scanning calorimetry. The surface free energy of the UV-cured film, which is related to the water or oil repellency, was calculated from contact angle measurements using the Lewis acid–base, three liquids method.

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2. Experimental

2.1. Materials

Table 1 lists the chemical structures and basic information of the raw materials used for the synthesis. A polycarbonate diol (PCDL, Asahi Kasei Chemicals Corp.) and dimethylol propionic acid (DMPA, Across Organics) were dried and degassed at 80 °C under vacuum for 6 h prior to use. A hydroxy-terminated perfluoropolyether (PFPE, Fluorolink D10H, fluorine content = 61%, Solvay Solexis) was used as received. Isophorone diisocyanate (IPDI, Bayer Material Science) and triethylamine (TEA, Samchun Pure Chemical) were dried using a 4 Å molecular sieve prior to use. 2-Hydroxyethylmethacrylate (2-HEMA, Junsei Chemicals) was used as the end-capping agent without further purification. A radical-type photo-initiator (Irgacure 500, Ciba Specialty Chemicals) was used as received.

2.2. Synthesis of UV-curable fluorinated polycarbonate-based polyurethane dispersion

Five different compositions of UV-curable fluorinated polycarbonate-based polyurethane dispersions were synthesized according to the process and formulation shown in Fig. 1 and Table 2, respectively. The reaction time was determined by observing the changes in the FT-IR peak at 2265 cm⁻¹ (NCO peak), which decreased with

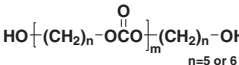
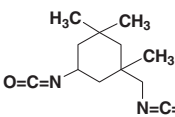
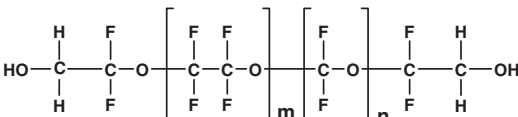
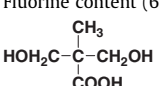
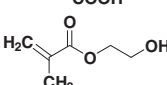
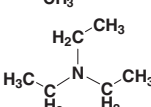
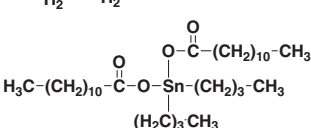
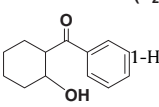
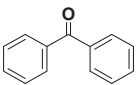
the progression of the polyurethane reaction. A 300 ml round bottom flask equipped with a four-necked separable flask with a mechanical stirrer, thermometer and condenser with a drying tube and N₂ inlet was used as a reactor. A constant temperature heating mantle was used to control the reaction temperature at each reaction step. In the first step, IPDI was charged into a dried reactor and the temperature was increased to 70 °C. The PCDL with some of the catalyst (dibutyltin dilaurate, approximately 500 ppm) was added dropwise over a 2 h period and maintained for further 1 h. A hydroxy-terminated PFPE was added dropwise and reacted for 2 h. Before adding into reactor, DMPA was dissolved in dimethylacetamide (5 wt.% based on the total weight) at 40 °C for 0.5 h. Then, DMPA was added dropwise for 1.5 h and reacted for 1 h. The reaction temperature was cooled to 50 °C, and 2-HEMA was added dropwise over a 2 h period and reacted for 3 h until the NCO peak had almost disappeared. After cooling to ambient temperature, TEA was then added as a neutralizing agent and the resulting mixture was stirred for a further 0.5 h. In the final step, water was added and stirred at 3000 rpm for 1 h. Irgacure 500 (3 wt.%) was then added as a radical type photo-initiator for the initiation of UV-curing. The solid content of dispersions was about 35%.

2.3. Coating and curing process

Fluorinated polycarbonate-based polyurethane dispersions were applied onto glass plates using an applicator at a 40 µm

Table 1

Raw materials used for the synthesis of UV-curable fluorinated polycarbonate-based polyurethane dispersions.

Function	Materials	Abbreviation	Chemical structure	Molar mass (g/mol)	Supplier
Polyol	Polycarbonate diol	PCDL		500	Asahi Kasei Chemicals Corp.
Isocyanate	Isophorone diisocyanate	IPDI		222	Bayer Material Science
Surface energy modifier	Hydroxy-terminated perfluoropolyether	PFPE		1400	Solvay Solexis
Ionomer	Dimethylol propionic acid	DMPA		134	Acros Organics
End-capping agent	2-Hydroxyethylmethacrylate	2-HEMA		130	Samchum Chemicals
Neutralizing agent	Triethylamine	TEA		101	Samchum Chemicals
Catalyst	Dibutyltin dilaurate	DBTDL		631.6	Alfa Aesar
Photoinitiator	Irgacure 500	I500		204	Ciba Specialty Chemicals
				182	

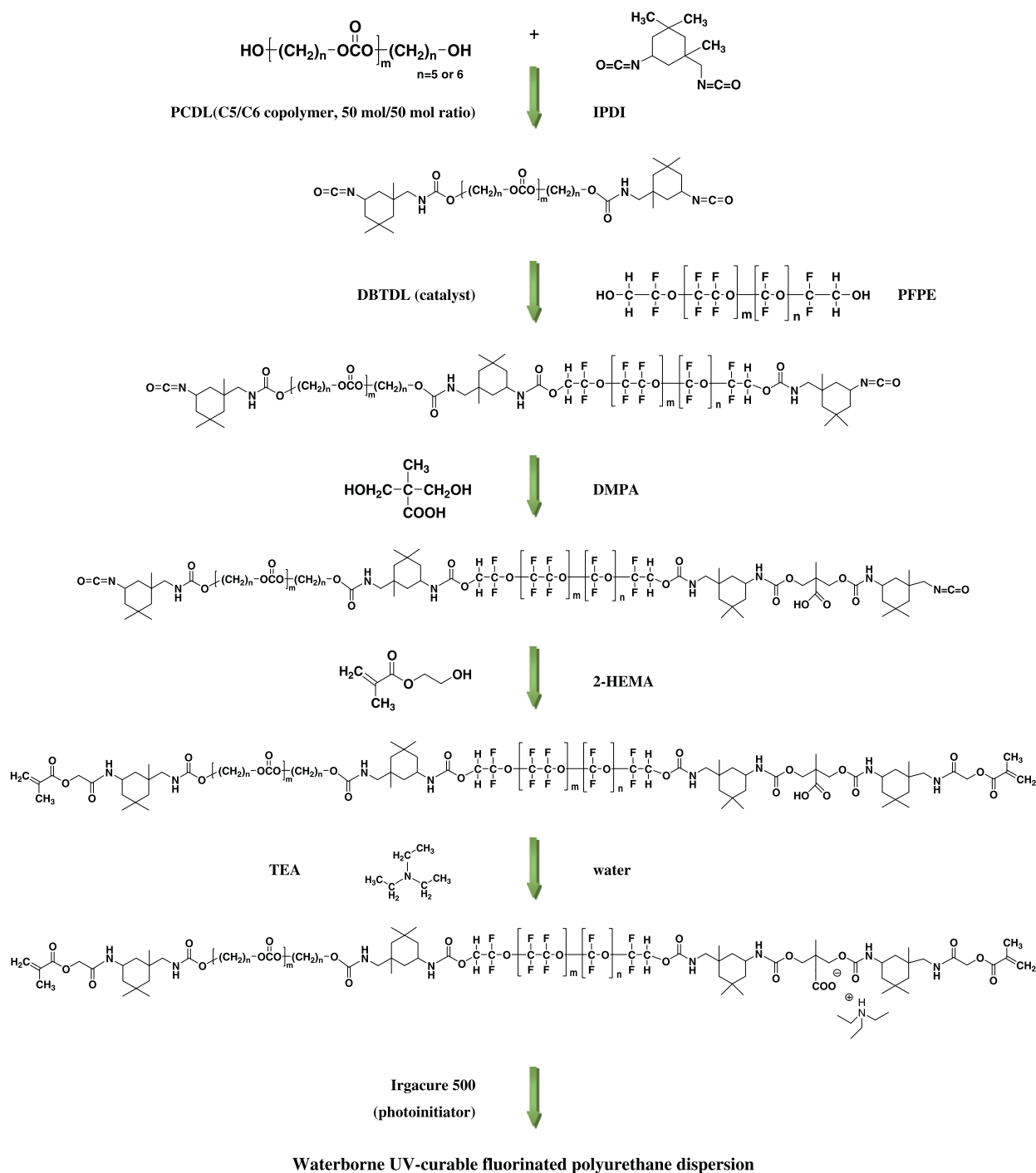


Fig. 1. Synthesis process of UV-curable fluorinated polycarbonate-based polyurethane dispersions.

thickness and dried in an oven at 80 °C for 5 min. The tack-free dried films were cured by passing under a conveyor type UV-curing machine equipped with medium pressure mercury UV-lamps (100 W/cm, main wave length: 365 nm). The irradiated UV-doses used to examine the surface hardness were 250, 500, 1000, 1500, 2000 and 3000 mJ/cm². Only 3000 mJ/cm² was used to examine the surface free energy. The UV doses were measured using an UV radiometer (IL 390C Light Bug, International Light Inc.). To prepare the free standing film samples for the dynamic mechanical analysis, tensile strength, thermogravimetric analysis, XPS measurements and refractive index the dispersions were cast on an aluminum pan and dried at ambient temperature for 1 day

and then in an oven at 60 °C for another 1 day. The thickness of the fully dried film was approximately 500–600 μm. The dried films were then cured using a conveyor type UV-curing machine at a UV dose of 3000 mJ/cm².

2.4. Curing behavior and characterization properties

2.4.1. Average particle size of the dispersions

The average particle size of the dispersion was measured at ambient temperature using an electrophoretic light scattering spectrophotometer (ELS-8000, Otsuka Electronics). The dispersion

Table 2

Formulations used for the synthesis of UV-curable fluorinated polycarbonate-based polyurethane dispersions (units in mole).

Sample	PCDL ^a	IPDI ^b	PFPE ^c	2-HEMA ^d	DMPA ^e	TEA ^f
WPCU-L500-1MA	0.1852	0.4444		0.1852	0.0926	0.0926
WPCU-L500-F(0.1)-1MA	0.1842	0.4444	0.0010	0.1852	0.0926	0.0926
WPCU-L500-F(0.25)-1MA	0.1827	0.4444	0.0025	0.1852	0.0926	0.0926
WPCU-L500-F(0.5)-1MA	0.1802	0.4444	0.0050	0.1852	0.0926	0.0926
WPCU-L500-F(1.0)-1MA	0.1752	0.4444	0.0100	0.1852	0.0926	0.0926

^a Polycarbonate diol.^b Isophorone diisocyanate.^c Hydroxy-terminated perfluoropolyether.^d 2-Hydroxyethylmethacrylate.^e Dimethylol propionic acid.^f Triethyl amine.

was diluted to approximately 1% concentration with deionized water, and the measurements were carried out twice.

2.4.2. UV-curing behavior by photo differential scanning calorimetry (photo-DSC)

The photo-DSC experiments were carried out using a DSC (Q-1000, TA Instruments) equipped with a photocalorimetric accessory (Novacure 2100), which used the light from a 100 W medium-pressure mercury lamp (main wave length: 250–650 nm) to examine the UV-curing behavior. The light intensity was determined by placing an empty DSC pan on the sample cell. The UV light intensity at the sample was 50 mW/cm². The sample weight was approximately 2 mg and the sample was placed in an open aluminum DSC pan. The water contained in the dispersion was evaporated off at 50 °C for 10 min prior to UV-curing. The measurements were carried out at 30 °C in flowing N₂ gas at 50 ml/min.

2.4.3. Surface free energy

The surface free energy of the UV-cured films was evaluated from the static contact angles measured using a contact angle analyzer (SEO 300A, Surface & Electro-Optics Corp.). The temperature and relative humidity were 23 ± 2 °C and 50 ± 3%, respectively. The equilibrium contact angle is defined as the angle between the solid surface and a tangent, drawn on the drop-surface, passing through the atmosphere–liquid–solid triple-point [15].

The surface free energy from contact angles was calculated based on Young's equation. In this study, the three liquids method was employed. This method was suggested by Good and van Oss and has been used widely to examine the surface free energy of polymeric coating films. The test liquids used in this study were distilled water, formamide and diiodomethane. From these contact angles of the liquids, the surface free energy can be calculated using the following equations:

$$\begin{aligned}\gamma_{LV}(1 + \cos \theta_1) &= 2\sqrt{\gamma_S^{LW}\gamma_{LV1}^{LW}} + \sqrt{\gamma_S^+ \gamma_{LV1}^-} + \sqrt{\gamma_S^- \gamma_{LV1}^+} \\ \gamma_{LV}(1 + \cos \theta_2) &= 2\sqrt{\gamma_S^{LW}\gamma_{LV2}^{LW}} + \sqrt{\gamma_S^+ \gamma_{LV2}^-} + \sqrt{\gamma_S^- \gamma_{LV2}^+} \\ \gamma_{LV}(1 + \cos \theta_3) &= 2\sqrt{\gamma_S^{LW}\gamma_{LV3}^{LW}} + \sqrt{\gamma_S^+ \gamma_{LV3}^-} + \sqrt{\gamma_S^- \gamma_{LV3}^+} \\ \gamma &= \gamma_S^{LW} + \gamma_S^{AB} = \gamma_S^{LW} + 2\sqrt{\gamma_S^+ \gamma_S^-}\end{aligned}\quad (1)$$

where *LW* means the Lifshitz-van der Waals and *AB* means the acid–basic interaction, γ is the surface free energy contributed by Lifshitz-van der Waals (γ^{LW}) and acid–base interaction (γ^{AB}). γ^+ and γ^- are the Lewis acid parameter and the Lewis base parameter of the surface free energy, respectively. In the same manner, γ_{LV} is the surface tension of the liquid in equilibrium with its own vapor

and subscripts 1, 2 and 3 represent liquids 1, 2 and 3, respectively. γ_{LV}^{LW} , γ_{LV}^+ , γ_{LV}^- , γ_{LV} are all available, the surface tension γ could be obtained by solving Eq. (1) [16,17].

2.4.4. X-ray photoelectron spectroscopy (XPS)

XPS was carried out to analyze the surface composition of the fluorinated UV-cured films with an ultra-high vacuum (UHV) multipurpose surface analysis system (Sigma Probe, Thermo VG Scientific) operating at a base pressure <10^{−9} mbar. The photoelectron spectra were excited by an Al K α (1486.6 eV) anode operating at a constant power of 100 W (15 kV and 10 mA), which was used to irradiate a 400 μ m diameter spot size of the samples. Constant analyzer energy (CAE) mode was employed at a pass energy of 30 eV, and a step of 0.1 eV at a take-off angle of 90° to acquire higher resolution spectra of fluorine 1s (F_{1s}), carbon 1s (C_{1s}), nitrogen 1s (N_{1s}) and oxygen 1s (O_{1s}). The fluorine to carbon (F/C) ratio on the surfaces was determined from the peak areas using the standard atomic sensitivity factors (*S_F*).

2.4.5. Viscoelastic properties by dynamic mechanical analysis (DMA)

The glass transition temperature and viscoelastic properties of the UV-cured films were analyzed using a DMA (Q800, TA Instruments). Rectangular specimens, 12 mm in length, 6.6 mm in width and 0.5 mm in thickness were prepared. The measurements were taken in tension mode at a frequency of 1 Hz and strain of 0.1%. The temperature ranged from −100 °C to 150 °C at a scanning rate of 2 °C/min. The storage modulus (*E'*), loss modulus (*E''*) and loss factor (tan δ) of the UV-cured films were measured as a function of temperature.

2.4.6. Pendulum hardness

The surface hardness of the UV-cured film as function of the UV-dose was measured using a pendulum hardness tester (Ref. 707PK, Sheen Instruments Ltd.) according to the König method (ASTM D 4366) at 23 ± 2 °C and 50 ± 3% R.H.

2.4.7. Tensile strength

The tensile strength was measured using a Universal Testing Machine (Zwick Corp.) at ambient temperature with a crosshead speed of 100 mm/min. The UV-cured films were prepared as rectangular specimens, 20 mm in length (span length), 6.6 mm in width and 0.5 mm in thickness. Five measurements were taken with the mean value used for further analysis.

2.4.8. Thermogravimetric analysis (TGA)

The thermal stability and decomposition profiles of the UV-cured films were measured using a thermogravimetric analyzer (Q-5000 IR, TA Instruments). Five milligram of the UV-cured sample was loaded into a ceramic pan, and heated from 30 °C to 600 °C at a constant heating rate of 10 °C/min in an inert

nitrogen atmosphere. The balanced and sample purge flows were 10.0 ml/min and 25.0 ml/min, respectively.

2.4.9. Refractive index

The refractive index of the UV-cured films were determined by the prism coupler (2010/M, Metricon) at the wavelengths of 404 nm, 532 nm, 632.8 nm, and 829 nm with tolerance of ± 0.001 .

3. Results and discussion

3.1. Average particle size of the dispersions

The particle size of a dispersion depends primarily on the viscosity of the dispersant, which is related to the prepolymer molecular weight, ionic group content and molecular structure. The main chain flexibility and molecular structure also affect the particle size. For example, an increase in the concentration of hydrophilic units or chain flexibility results in a decrease in particle size of the polyurethane dispersion [18]. The characteristic feature of functional materials employed in the dispersion system for special use, such as polydimethylsiloxane, fluorine, clay and carbon nanotubes, also affected the particle size of the dispersion [19–22].

Fig. 2 shows the effect of the PFPE content on the particle size of the dispersion. The average particle size of the dispersions increased with increasing PFPE content in the soft segment. The particle size of WPCU-L500-1MA (not contain PFPE), WPCU-L500-F(0.1)-1MA (0.1 mol% of PFPE) and WPCU-L500-F(0.25)-1MA (0.25 mol% of PFPE) was 85.8 nm, 98.8 nm and 130.3 nm, respectively. Increasing the level of PFPE incorporation to 0.5 mol% (WPCU-L500-F(0.5)-1MA) resulted in an increase in particle size to 273.2 nm, which was approximately three times higher than that of WPCU-L500-1MA. In the case of WPCU-L500-F(1.0)-1MA, the aggregation and precipitation of the dispersion began after 2 or 3 weeks due to the much larger particle size (598.9 nm). These results show that the hydrophobic features of fluorine in the PFPE segment increased the average particle size of the dispersion.

3.2. UV-curing kinetics by photo-DSC

Photo-DSC test is a convenient method for examining UV-curing reactions because it can determine the kinetic parameter, degree of conversion, curing rate and reaction enthalpy during an extremely rapid UV-curing reaction. The UV-curing behavior depends on the intensity and dose of UV-light, species and content of

photo-initiator, reaction temperature, and reactivity of the functional groups [23].

In this study, photo-DSC measurements were carried out to examine the effect of the PFPE content on the UV-curing behavior of fluorinated polyurethane dispersions. Fig. 3 shows the isothermal UV-curing heat enthalpy and conversion profiles of UV-curable fluorinated polyurethane dispersion by photo-DSC. The exothermic heat flow (cal/g s) vs. curing time (Fig. 3a) is the only result by photo-DSC measurements. In all samples, the early onset of auto-acceleration by the activation of radicals was confirmed to be a steep increase at the beginning of the reaction, which was followed by auto-deceleration, as indicated in the rapid dropping curves [24]. The exothermic heat flows decreased with increasing PFPE content. This shows that increase in the content of hydrophobic fluorine has an adverse effect on the UV-curing reaction.

Fig. 3b–d are the results of further calculations. The reaction enthalpy was determined by integrating the area under the exothermic peak and the degree of conversion was determined using the following equation [23,25]:

$$\alpha = \frac{\Delta H_t}{\Delta H_0^{\text{theor}}} \quad (2)$$

where ΔH_t is the reaction heat enthalpy released at time t and $\Delta H_0^{\text{theor}}$ is the theoretical heat enthalpy for complete conversion. $\Delta H_0^{\text{theor}}$ of methacrylate is 54.4 kJ/mol or 13.1 kcal/mol [26,27]. The heat of polymerization of each sample ($\Delta H_0^{\text{theor}}$ (sample)) was calculated using the following equation:

$$\Delta H_0^{\text{theor}}(\text{sample}) = \frac{\Delta H_0^{\text{theor}}(\text{methacrylate})}{MW^{\text{theor}}} \times \text{Functionality} \quad (3)$$

where MW^{theor} is the theoretical molecular weight of the repeating unit. Table 3 lists the theoretical reaction enthalpy of each sample. The rate of polymerization (R_p) is related directly to heat flow (dH/dt) using the following equation [23,25]:

$$R_p = \frac{d\alpha}{dt} = \frac{(dH/dt)}{\Delta H_0^{\text{theor}}} \quad (4)$$

where $d\alpha/dt$ is the conversion rate or polymerization rate, $\Delta H_0^{\text{theor}}$ is the total exothermic heat of the reaction and dH/dt is the measured heat flow at a constant temperature. Fig. 3b presents the conversion of each sample calculated using Eqs. (3) and (4). The final conversion decreased with increasing PFPE content as the following order: WPCU-L500-F(1.0)-1MA (62.5%) < WPCU-L500-F(0.5)-1MA (66.0%) < WPCU-L500-F(0.25)-1MA (69.6%) < WPCU-L500-F(0.1)-1MA (73.0%) < WPCU-L500-1MA (83.9%). Fig. 3c and Table 4 shows the curing rate as function of time and the peak time with the maximum curing rate. Fig. 3d shows plots of the curing rate vs. conversion.

The curing rate peak of WPCU-L500-1MA appeared first at 1.90 s and the maximum curing rate was 20.8%/s. On the other hand, the peak time and maximum curing rate of WPCU-L500-F(1.0)-1MA were 3.05 s and 8.0%/s, respectively, which were much lower than those of WPCU-L500-1MA. Therefore, the curing rate decreased with increasing PFPE content, resulting in low final conversion because steric hindrance and the hydrophobicity of fluorine restricted the UV-curing reaction.

3.3. Surface free energy

Fig. 4 shows the contact angles of three testing liquids on each UV-cured film as function of the PFPE content. Fig. 5 shows the surface energy calculated by Lewis acid–base three liquids method. These results are summarized in Table 5. The contact angle of the film surface increased with increasing PFPE content, which was incorporated to increase the film hydrophobicity. The water

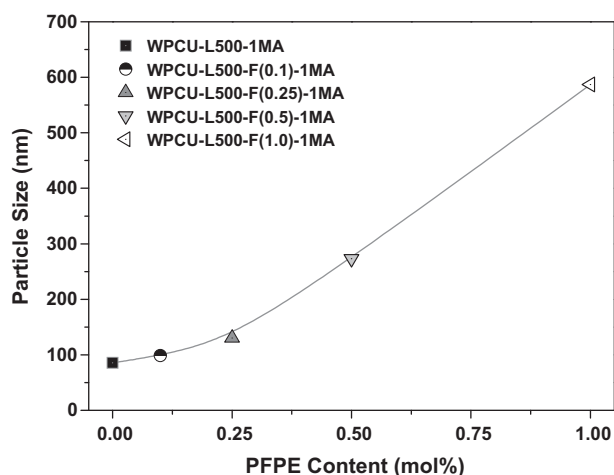


Fig. 2. Average particle size of UV-curable fluorinated polycarbonate-based polyurethane dispersions according to PFPE content.

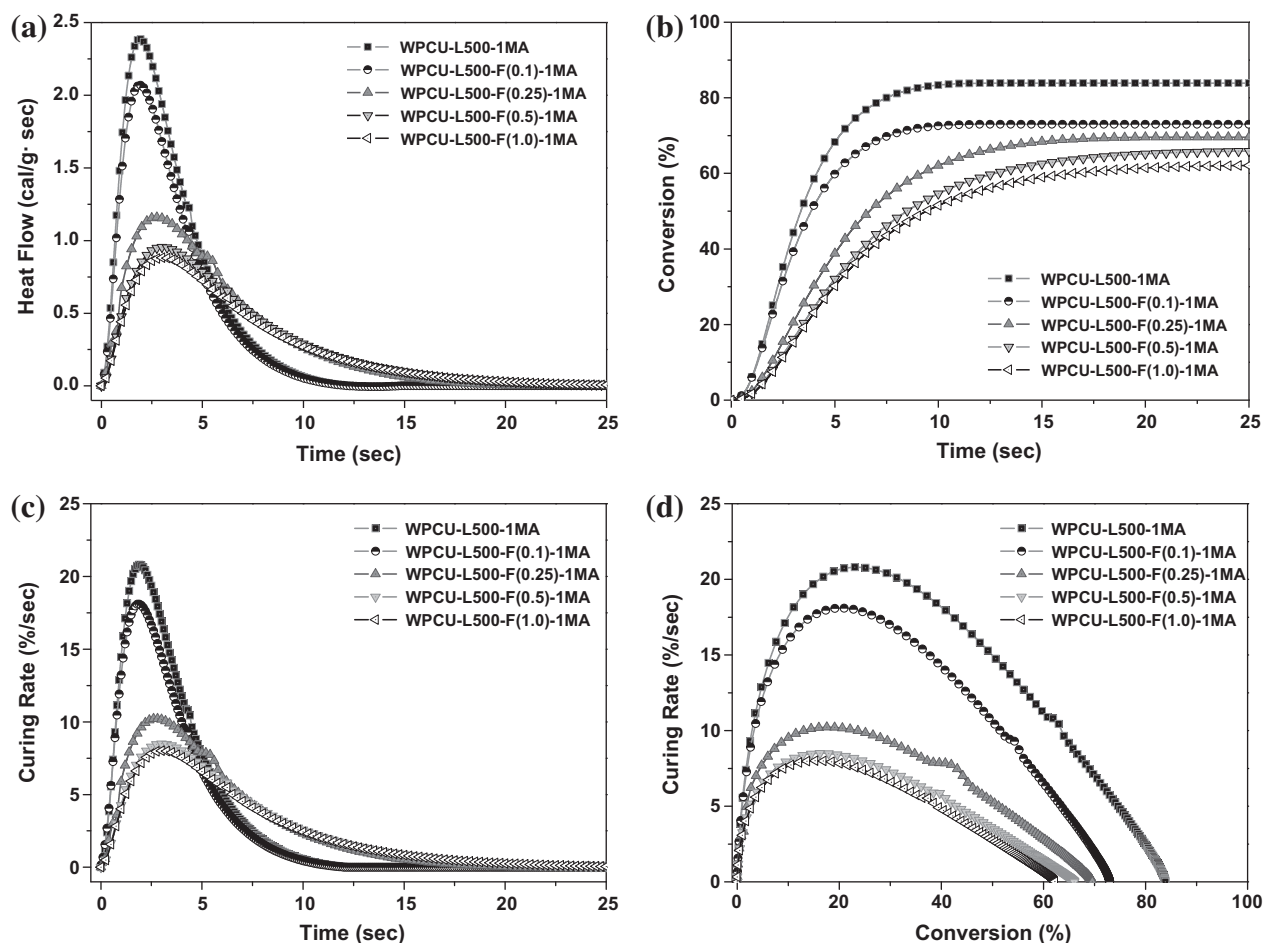


Fig. 3. Isothermal UV-curing heat enthalpy and conversion profiles for UV-curable fluorinated polycarbonate-based polyurethane dispersions by photo-DSC. (a) Heat flow vs. time, (b) conversion vs. time, (c) conversion rate vs. time, and (d) conversion rate vs. conversion.

Table 3

Calculated theoretical reaction enthalpy of UV-curable fluorinated polycarbonate-based polyurethane dispersions.

Samples	Theoretical molecular weight of repeating unit	Functionality	Theoretical reaction enthalpy			
			kJ/mol	J/g	kcal/mol	cal/g
WPCU-L500-1MA	2284	2 Methacrylate	108.8	47.646	26.2	11.474
WPCU-L500-F(0.1)-1MA	2293	2 Methacrylate	108.8	47.440	26.2	11.424
WPCU-L500-F(0.25)-1MA	2308	2 Methacrylate	108.8	47.144	26.2	11.353
WPCU-L500-F(0.5)-1MA	2332	2 Methacrylate	108.8	46.653	26.2	11.235
WPCU-L500-F(1.0)-1MA	2381	2 Methacrylate	108.8	45.701	26.2	11.005

Table 4

Peak time of the curing rate, maximum curing rate, conversion at peak, and final conversion of UV-curable fluorinated polycarbonate-based polyurethane dispersions by photo-DSC.

Samples	Peak time of curing rate (s)	Maximum curing rate (%/s)	Final conversion (%)
WPCU-L500-1MA	1.90	20.8	83.9
WPCU-L500-F(0.1)-1MA	2.00	18.1	73.0
WPCU-L500-F(0.25)-1MA	2.65	10.2	69.6
WPCU-L500-F(0.5)-1MA	3.00	8.5	66.0
WPCU-L500-F(1.0)-1MA	3.05	8.0	62.5

contact angle and surface free energy of WPCU-L500-1MA were 66.9° and 51.0 m N/m, respectively. With the incorporation of only 0.1 mol% (0.3 wt.%) PFPE, the contact angle increased dramatically to 93.3° and the surface free energy decreased to 27.0 m N/m. Only

a very small amount of PFPE affected significantly the surface free energy. These results suggest that the CF₂ groups in the soft segment tailor the outermost surface and produce UV-cured films with a hydrophobic fluorine enriched surface [13].

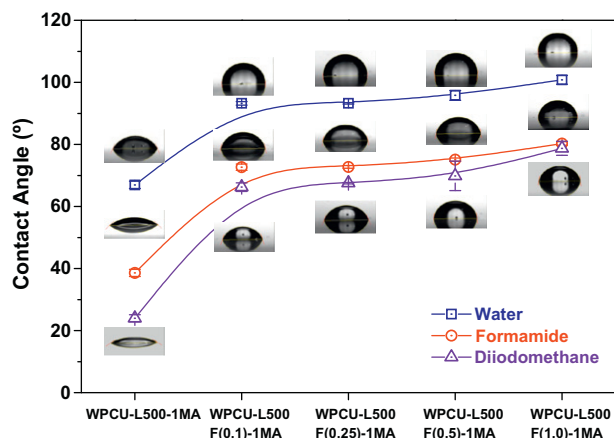


Fig. 4. Contact angle of the UV-cured films according to PFPE content.

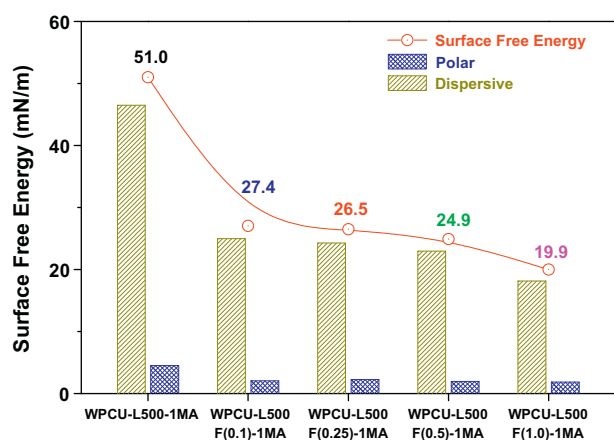


Fig. 5. Surface free energy of the UV-cured films according to PFPE content.

3.4. X-ray photoelectron analysis

Contact angle measurements cannot provide direct information on the species and relative concentration of different atoms because this method reflects the interface characteristics as well as the thermodynamic interactions with the surface roughness. The thermodynamic interactions are related to the composition up to a few angstroms from the surface. On the other hand, XPS provides the composition of the outermost layer (2–3 nm) of the coatings in a high vacuum atmosphere independent of the surface characteristics of hybrid materials [28]. The photo-emission spectra also provide both quantitative and qualitative analysis, such as the surface concentrations and functional group identification, respectively [13,21].

Fig. 6 shows the XPS spectra of the UV-cured films according to the PFPE content. The photoemission peaks of the F_{1s} , O_{1s} , N_{1s} and C_{1s} core levels can be observed with bonding energies of 688, 532, 399, 285 eV, respectively [29]. The fluorine peak was not seen in the photoemission curve of WPCU-L500-1MA not containing PFPE. The fluorine to carbon ratio increased with increasing PFPE content, as shown in Fig. 7 [30]. These results agreed with the trend of the surface free energy.

The surface enrichment factor (S_F) is defined as the ratio of the fluorine content measured experimentally at the top surface of the dried film ($F_{surface}$) to the estimated atomic% fluorine in the film solids, assuming a uniform and random distribution (F_{bulk}) as the follows [21]:

$$S_F = \frac{F_{surface}}{F_{bulk}} \quad (5)$$

Table 6 lists the PFPE and fluorine content of the experimental formulation and surface enrichment factor. The fluorine surface enrichment ranged from 14 to 24-fold with respect to the bulk composition. All the samples containing PFPE showed a higher fluorine atomic content at the surface than that estimated in the bulk. Therefore, the fluorine chain in the soft segment can easily tailor the surface owing to the thermodynamic driving force of the PFPE segments related to their very low surface energy [28].

3.5. Viscoelastic properties by DMA

Dynamic mechanical measurements can be used to determine the visco-elasticity from the behavior of UV-cured polymeric materials stressed under cyclic loading [31]. A polymeric sample subjected to a sinusoidal dynamic stress will exhibit a sinusoidal tension that lags behind the applied stress with a phase angle δ_0 [32]. The glass transition temperature (T_g), which is determined from the temperature associated with the peak magnitude of the loss factor ($\tan \delta$) and storage modulus (E'), provide information on the viscoelastic properties of the polymer, degree of cure and crosslink density [24].

Fig. 8 shows the effect of the PFPE content on the viscoelastic properties of the UV-cured films. As shown in Fig. 8a, the storage modulus decreased rapidly near T_g due to vibrations of the molecular segments, which continued until reaching a rubbery plateau. The chemical crosslink structure restricted further progress to the flowing region. Fig. 8b shows the $\tan \delta$ curves of each sample with different PFPE content. The T_g of WPCU-L500-F(1.0)-1MA, WPCU-L500-F(0.5)-1MA, WPCU-L500-F(0.25)-1MA, WPCU-L500-F(0.1)-1MA and WPCU-L500-1MA was 57.2 °C, 59.0 °C, 66.7 °C, 67.7 °C and 71.3 °C, respectively. All the samples showed a single T_g due to the good miscibility between the hard and soft segments as well as the complete phase mixing of polyurethane [33]. Increasing the PFPE content led to a shift in the T_g to a lower temperature because the incorporation of PFPE has an adverse effect on the curing reaction and reduces the film stiffness.

Table 5

Contact angle and surface free energy of UV-curable fluorinated polycarbonate-based polyurethane dispersions.

Samples	Contact angle (°)			Surface free energy (m N/m)		
	Water	Formamide	Diiodomethane	γ_s	γ_s^{LW}	γ_s^{AB}
WPCU-L500-1MA	66.9 ± 1.2	38.6 ± 1.4	24.0 ± 1.1	51.0	46.5	4.5
WPCU-L500-F(0.1)-1MA	93.3 ± 0.6	72.7 ± 1.0	66.2 ± 1.4	27.0	25.0	2.0
WPCU-L500-F(0.25)-1MA	93.2 ± 0.2	72.7 ± 0.4	67.5 ± 0.3	26.5	24.3	2.2
WPCU-L500-F(0.5)-1MA	95.8 ± 1.6	75.1 ± 0.6	69.9 ± 2.7	24.9	23.0	1.9
WPCU-L500-F(1.0)-1MA	100.8 ± 1.4	80.3 ± 0.6	78.7 ± 2.3	19.9	18.1	1.8

γ_s = surface free energy.

γ_s^{LW} = Lifshitz-van der Waals (dispersive component).

γ_s^{AB} = acid–basic interaction (polar component).

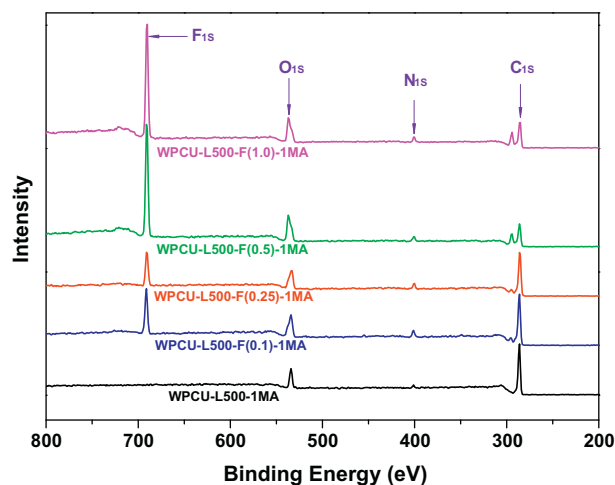


Fig. 6. X-ray photoelectron spectroscopy of the UV-cured films.

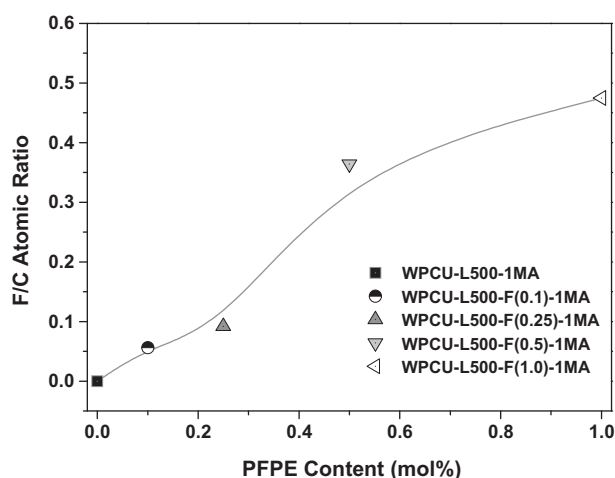


Fig. 7. The fluorine/carbon atomic composition of the UV-cured films.

The crosslink density is expressed as ν (mol/g; $0 \leq \nu$) or the degree of crosslinking (X_c ; $0 \leq X_c \leq 1$). The theoretical molecular weight between the crosslinks (M_c) is a reciprocal of X_c , which can be calculated using the following equation:

$$M_c = \frac{M_0}{pf_0 - 2} \quad (6)$$

where M_0 is the average molecular weight, f_0 is the average functionality, and p is the fraction of converted groups ($p \leq 1$) [7]. Table 7 lists the calculated results. The final conversion by photo-DSC measurements was used as p to calculate the theoretical M_c

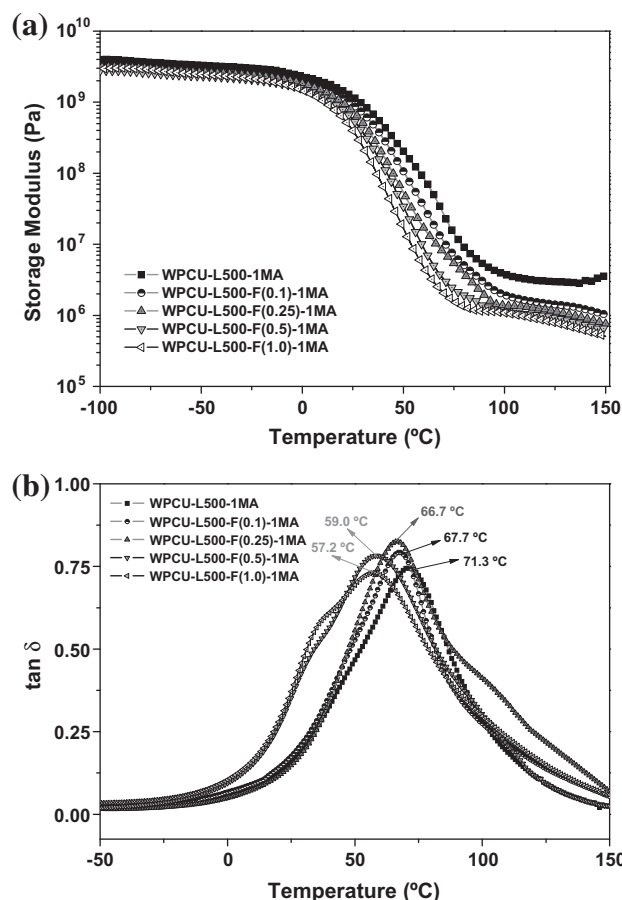


Fig. 8. Viscoelastic properties of the UV-cured films. (a) Storage modulus, (b) $\tan \delta$.

and X_c . The crosslink density can also be determined experimentally by DMA based on the theory of rubber elasticity using the following equation [34,35]:

$$G_N^0 = \frac{\rho RT}{M_c} \quad (7)$$

where G_N^0 is the rubbery plateau modulus, ρ is the density, T is the absolute temperature and R is the gas constant. Table 7 also lists the actual M_c and X_c calculated using Eq. (7).

Judging from the theoretical and actual M_c and X_c , the T_g and crosslink density of the UV-cured films decreased with increasing PFPE content. There were some differences between methods but the order of the crosslink density was WPCU-L500-F(1.0)-1MA < WPCU-L500-F(0.5)-1MA < WPCU-L500-F(0.25)-1MA < WPCU-L500-F(0.1)-1MA < WPCU-L500-1MA. These results suggest that the hydrophobicity and steric hindrance of fluorine in the PFPE segment reduced the activity of UV-curing, which resulted in a

Table 6
PFPE and fluorine content of the experimental formulation and surface enrichment factor.

Samples	wt.% of PFPE in total formulation	Estimated atomic% fluorine in UV-cured film (F_{bulk})	Atomic% fluorine at the surface measured by XPS ($F_{surface}$)	Surface enrichment (S_F)
WPCU-L500-1MA	0	0	0	0
WPCU-L500-F(0.1)-1MA	0.300	0.183	4.420	24.2
WPCU-L500-F(0.25)-1MA	0.740	0.451	6.910	15.3
WPCU-L500-F(0.5)-1MA	1.470	0.897	20.080	22.4
WPCU-L500-F(1.0)-1MA	2.930	1.787	25.230	14.1

Table 7
Calculated theoretical molecular weight between the crosslinks (M_c) and degree of crosslinking (X_c) of UV-curable fluorinated polycarbonate-based polyurethane dispersions using the final conversion measured by photo-DSC, actual M_c and X_c measured by DMA.

Samples	Theoretical molecular weight	Functionality	Theoretical M_c and X_c by photo-DSC			Actual M_c and X_c by DMA	
			Final conversion (%)	M_c (g/mol)	$X_c (\times 10^3)$	M_c (g/mol)	$X_c (\times 10^3)$
WPCU-L500-1MA	2284	4 (2 double bond)	83.9	1688	0.593	1081	0.925
WPCU-L500-F(0.1)-1MA	2293	4 (2 double bond)	73.0	2505	0.399	2200	0.455
WPCU-L500-F(0.25)-1MA	2308	4 (2 double bond)	69.6	2975	0.336	2706	0.370
WPCU-L500-F(0.5)-1MA	2332	4 (2 double bond)	66.0	3704	0.270	3303	0.303
WPCU-L500-F(1.0)-1MA	2381	4 (2 double bond)	62.5	4927	0.203	3890	0.257

decrease in the final conversion. As a result, a network structure with a lower crosslink density was produced and the T_g also shifted to a lower temperature. In addition, the molecular weight of PFPE (1400 g/mol) was higher than that of the PCDL (800 g/mol), which also affected the decrease in crosslink density.

3.6. Pendulum hardness

The pendulum hardness depends strongly on the T_g and crosslink density of the cured UV-films, and ranges from 30 s for soft elastomeric materials up to 400 s for very hard and glassy polymers [36]. Fig. 9 shows the effect of the PFPE content on the surface hardness as function of the UV-dose. Only after a UV-dose of 250 mJ/cm² was the pendulum hardness of most samples >100 s because the physical dried film had already a tack-free surface due to the high molecular weight of the dispersions. With increasing UV-dose, the pendulum hardness of all samples increased due to an increase in the crosslink density formed by chemical crosslinking.

The order of pendulum hardness after a UV-dose of 3000 mJ/cm² was as follows: WPCU-L500-F(1.0)-1MA (153 ± 4.5 s) < WPCU-L500-F(0.5)-1MA (166 ± 8.9 s) < WPCU-L500-F(0.25)-1MA (188 ± 9.3 s) < WPCU-L500-F(0.1)-1MA (192 ± 7.2 s) < WPCU-L500-1MA (195 ± 8.6 s). The pendulum hardness decreased with increasing PFPE content due to the decreased T_g and crosslink density of the UV-cured films containing PFPE.

3.7. Tensile strength

Fig. 10 shows the effects of the PFPE content on the strain-stress behavior (a) and the maximum tensile strength and elongation at break (b). With increasing PFPE content, the maximum tensile strength and initial modulus (slope of the curve) decreased and

the elongation at break increased. WPCU-L500-1MA showed a tensile strength of 15.5 MPa with 110.8% elongation. However, with the incorporation of 1.0 mol% PFPE (WPCU-L500-F(1.0)-1MA), the tensile strength decreased to 4.5 MPa and the percent elongation increased to 289.8%. The network with a lower crosslink density due to PFPE incorporation had poor resistance to external extension force, which lead to a lower tensile strength and higher elongation at break. In addition, the PFPE chain is quite flexible, highly hydrophobic and oleophobic without a crystallization tendency. The T_g of PFPE homopolymers, in which the molecular weight ranged from 1000 to 2000, was reported to be −92.0 °C and −110.0 °C, respectively [12,37]. The flexibility of the PFPE chain was also responsible for reducing the mechanical properties. The tensile behavior was in accordance with the other mechanical tests, such as the pendulum hardness and modulus of DMA. The mechanical properties of the UV-cured film were correlated with

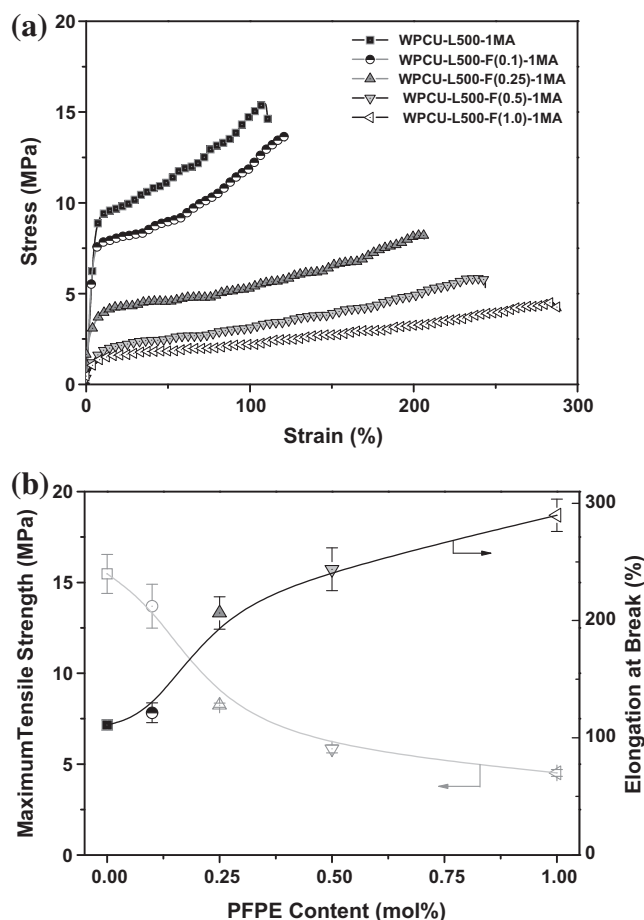


Fig. 10. Tensile behavior of the UV-cured films. (a) Strain–stress curves, (b) maximum tensile strength and elongation at break.

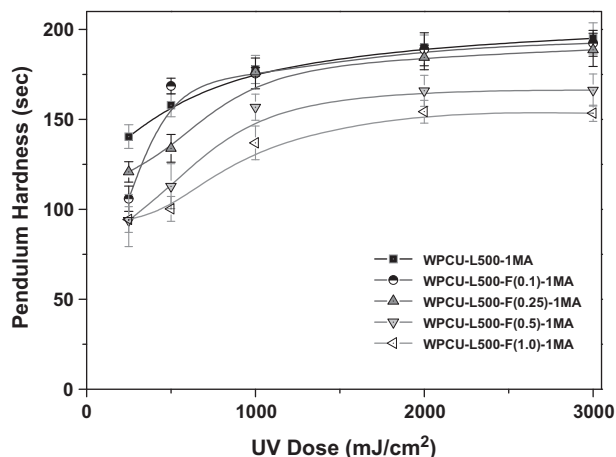


Fig. 9. Pendulum hardness of the UV-cured films with increasing UV-dose.

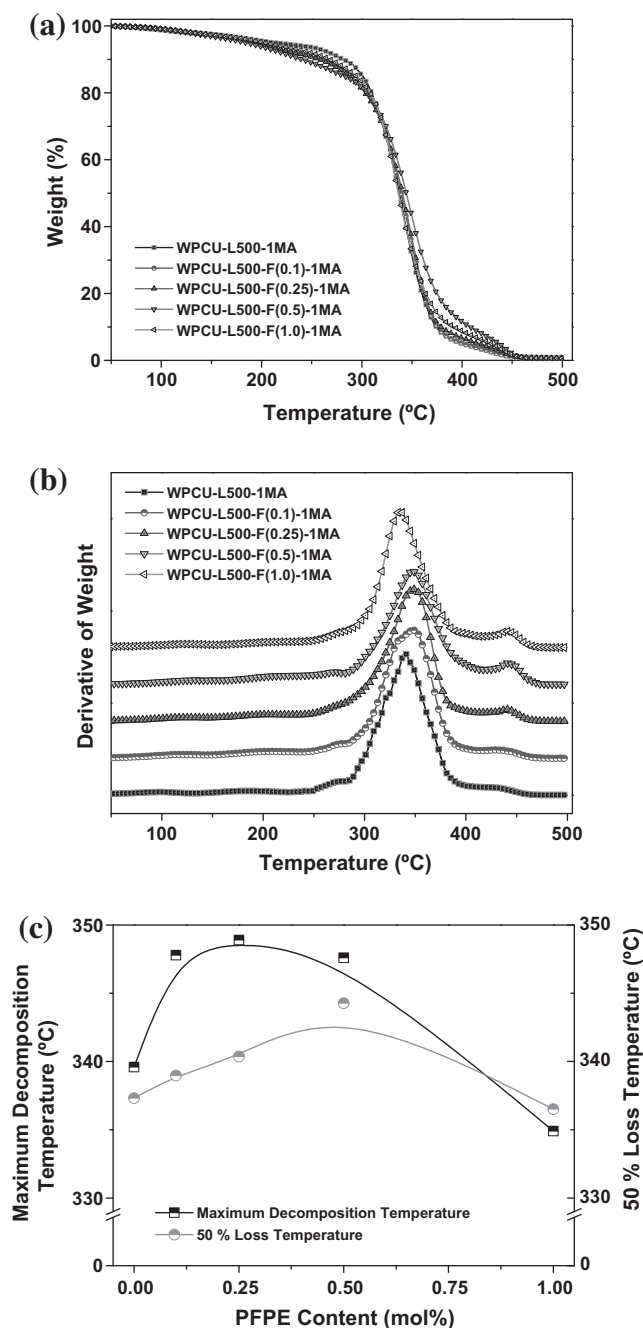


Fig. 11. Thermogravimetric analysis of the UV-cured films. (a) Weight loss curve, (b) derivative of weight loss curve, (c) maximum peak temperature of derivative weight and 50 wt.% loss temperature.

the elastic modulus and T_g of the crosslinked polymer [38].

Table 8

Characteristic thermal decomposition data of the UV-cured films.

Samples	Weight loss			Maximum decomposition temperature		
	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	wt.% at 440 °C	T_{max1} (°C)	T_{max2} (°C)	T_{max3} (°C)
WPCU-L500-1MA	281.4	337.3	1.68	270.6	339.6	
WPCU-L500-F(0.1)-1MA	259.5	339.0	1.60	273.2	347.8	435.8
WPCU-L500-F(0.25)-1MA	257.7	340.4	2.56	270.5	348.9	441.4
WPCU-L500-F(0.5)-1MA	240.9	344.3	4.33	271.6	347.6	441.8
WPCU-L500-F(1.0)-1MA	268.2	336.5	3.24	273.0	334.9	440.2

$T_{10\%}$; 10 wt.% loss temperature, $T_{50\%}$; 50 wt.% loss temperature, T_{max} ; maximum decomposition temperature.

3.8. Thermal property by TGA

The thermal stability of the UV-cured films was measured by TGA at temperatures ranging from 30 °C to 600 °C. Fig. 11a and b shows the weight loss curves and derivative of the weight profiles of each sample, respectively. Table 8 lists the characteristic thermal decomposition temperatures: the temperature of the initial 10% mass loss ($T_{10\%}$), temperature of 50% mass loss ($T_{50\%}$), weight percent at 440 °C (decomposition temperature related to the PFPE segment), and maximum decomposition temperature (T_{max}). The thermal degradation mechanism of polyurethane is well established. The urethane groups first undergo depolymerization to the individual monomers, which then react further to produce carbon dioxide. Generally, there are two distinct stages in the thermal degradation of polyurethane. The first and second stages are due to degradation of the hard and soft segments of polyurethane linkages, respectively [13,14,39].

The UV-cured film without PFPE (WPCU-L500-1MA) was decomposed in two steps in a similar manner to general polyurethane decomposition. The first part of degradation (270–273 °C) indicates the hard segment (IPDI–DMPA–HEMA segment) of the polyurethane linkage, and the second peak was assigned to the degradation of the soft segment (PCDL) (335–350 °C) [40,41]. On the other hand, the UV-cured films incorporated with PFPE decomposed in three steps. The first and second regions were assigned to the degradation of hard and soft segments, respectively. The third region at approximately 435–442 °C correlated with the fluorine in the PFPE chain. The maximum thermal decomposition of the PFPE chains occurred at approximately 440 °C.

Fig. 11c shows the maximum decomposition temperature and 50 wt.% loss temperature according to the PFPE content. The thermal stability of the UV-cured film increased slightly until 0.5 mol% PFPE due to the excellent thermal stability of fluorine [13,42]. However, the thermal stability of WPCU-L500-F(1.0)-1MA incorporated with 1.0 mol% PFPE decreased despite the increase in PFPE content. PFPE reduced the final conversion and produced a UV-cured film with a low T_g and crosslink density, which also reduced the thermal stability.

3.9. Refractive index

There are some materials that have influences on the refractive index. For example, with the weight percentage of TiO_2 incorporated in the hybrid coatings varied from 10% to 50%, the refractive indices increased from 1.502 to 1.663 [43]. The refractive index of the nanocomposite coating increases with increasing ZrO_2 content. Refractive index of 1.78 was attained for the nanocomposite containing 60 wt.% of ZrO_2 [44].

The effect of PFPE on the refractive index was measured by the prism coupling method. Fig. 12 shows the variation of the refractive index as a function of wavelength (a), and PFPE content (b) for the UV-cured films. The refractive indices were in the range of 1.5018–1.5249, 1.4929–1.1589, 1.4914–1.5151, 1.4843–1.5115 and 1.4865–1.5084 for WPCU-L500-1MA, WPCU-L500-F(0.1)-

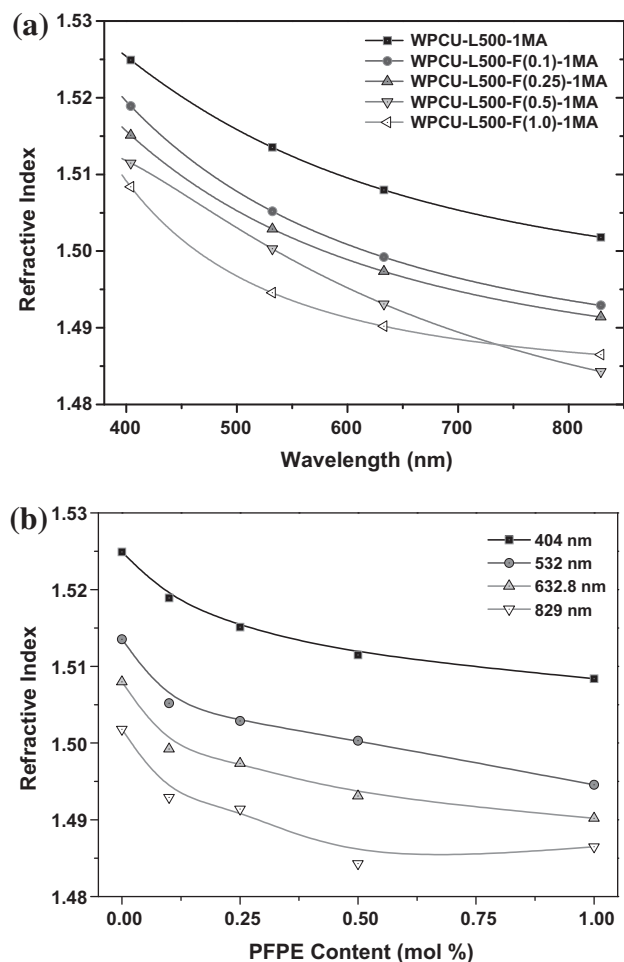


Fig. 12. Refractive index of the UV-cured films according to different PFPE content. (a) Refractive index vs. wavelength, and (b) refractive index vs. PFPE content.

1MA, WPCU-L500-F(0.25)-1MA, WPCU-L500-F(0.5)-1MA, and WPCU-L500-F(1.0)-1MA, respectively. With increasing the fluorine content, the refractive indices of UV-cured films decreased. The incorporation of PFPE even at a small amount decreased effectively the refractive index of the UV-cured films. The decrease of refractive indices attributed to the smaller electronic polarizability and larger free volume of the C–F compared to C–H bonds [45,46].

In fact, a good linear relationship is observed between refractive indices and PFPE content as shown in Figs. 5–12b. This nearly linear relationship represented good control of the refractive indices by varying the content of PFPE [47].

4. Conclusions

Hydroxy-terminated PFPE was incorporated into the soft segment of polycarbonate-based polyurethane dispersions with different concentrations. The surface free energy of the UV-cured films decreased with increasing PFPE concentration. The very low concentrations of PFPE resulted in an efficient decrease in surface free energy to 19–27 m N/m because the PFPE in the soft segment was tailored easily to the surface. A hydrophobic UV-cured film surface enriched with fluorinated species was also confirmed by XPS. The thermal stability was improved slightly with the incorporation of PFPE. The incorporation of PFPE with the low electronic polarizability and high free volume even at a small amount

decreased effectively the refractive index of UV-cured film. On the other hand, the UV curing rate and final conversion decreased with increasing PFPE content, which resulted in a decrease in T_g , crosslink density, tensile strength and surface hardness, due to the unique flexibility of the PFPE chain and the higher molecular weight of PFPE (1400 g/mol) than PCDL (500 g/mol). In conclusion, the surface and thermal properties of waterborne UV-curable coatings can be modified by incorporating PFPE.

Acknowledgments

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