Surface Modification with Waterborne Fluorinated Anionic Polyurethane Dispersions

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ABSTRACT: Waterborne fluorinated anionic polyurethane dispersions (FAPUDs) were synthesized from tris(6-isocyanatohexyl) isocyanurate, *N*-ethyl-*N*-2-hydroxyethyl-perfluorooctanesulfonamide, poly(oxytetramethylene glycol) (PTMG), dimethylolpropionic acid (DMPA), hexamethylene diisocyanate, 1,4-butanediol, and two different neutralizing agents (triethylamine and sodium carbonate). Waterborne polyurethane dispersions (PUDs) were synthesized from isophorone diisocyanate, PTMG, DMPA, and ethylenediamine as chain extenders. The particle size of the FAPUDs, based on the fluorine content and degree of neutralization (DN), was measured with dynamic light scattering. So that the surface modification and morphology variations of the PUDs through the addition of the FAPUDs could be observed, the surface energy and thermal properties of the blending films [fluorine PUD mixtures (FPMs)] were measured with contact-angle analysis and differential scanning calorimetry. The particle size of the FAPUDs increased as the fluorine content in the FAPUDs increased and decreased as the DN increased. The surface energy of the FPM films made from the blending of the FAPUD T series (neutralization with triethylamine) gradually decreased above the critical fluorine concentration (0.02797 wt %). However, for the blending of the FAPUD 25Na series (neutralization with sodium carbonate), the surface energy increased above the critical fluorine concentration (0.02797 wt %) because of the increase in Na salts. The FAPUDs showed the native thermal behavior of the fluorine. However, the thermal properties of the blending films were like those of pure PUDs. This showed that the morphology of the PUDs was rarely unchanged when the FAPUDs were added. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3322–3330, 2002

Key words: polyurethanes; dispersions; morphology; modification

INTRODUCTION

Because waterborne polyurethane dispersions (PUDs) are nontoxic and nonflammable and do not pollute the air, they are widely encountered in coatings and adhesives for flexible substrates (textiles, leather, paper, and rubber), wood, and glass fibers.[1]

PUDs can be prepared in ionomeric and nonionomeric forms. Among these polyurethane dispersions, anionic dispersions are commercially predominant. Sulfonate and carboxylate groups are most often incorporated into polyurethane anionomers. The acid group is subsequently neutralized with a base, typically triethylamine (TEA), and this results in the formation of a polyurethane anionomer. Polycarboxylates provide good hydrophilic character. Among dihydroxylcarboxylic acids, dimethylolpropionic acid (DMPA) is most often encountered in the literature as a potential ionic center.[2–4]

These PUDs have commercially important applications. However, the application of PUDs is limited by decreasing solvent and water resistance, high-temperature performance, and chemical resistance. Therefore, so that the applications and functionality of PUDs might be increased, research into functional polymers characterized by such qualities as water and oil repellency has been required for preventing surface or bulk structures of PUDs when PUDs are exposed to high temperatures or chemical materials.[5–7]

These surface properties, such as water repellency, abrasion resistance, and pollution resistance, are closely related to the chemical structure and molecular arrangement of the polymer surface. Among the organic components with this characterization, fluorine is usefully employed for the surface modification. At present, investigations into the surface modification of PUDs have been carried out.[8–15] However, works on the fluorine surface modification of PUDs are sparse in the open literature.

In our previous study, we prepared waterborne fluorinated nonionic polyurethane dispersions containing hydrophilic polyols such as poly(ethylene glycol). However, in this study, we synthesized waterborne fluorinated anionic polyurethane dispersions (FAPUDs) with two different neutralizing agents [TEA or sodium carbonate (Na$_2$CO$_3$)] according to an acetone process and pure PUD. We observed the particle size of the FAPUDs and thermal properties of the FAPUD films according to the fluorine content and degree of neu-

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tralization (DN). The concentration of fluorine and DN were design variables used to control the properties. Finally, the surface modification and thermal properties of the fluorine PUD mixture (FPM) films prepared by the blending of FAPUD with pure PUD were examined.

EXPERIMENTAL

Materials

For the synthesis, isophorone diisocyanate (IPDI; Aldrich Co., USA), tris(6-isocyanatohexyl) isocyanurate (TIHI; BASF Co., Germany), DMPA (TRIMET Technical Products, Inc., USA), TEA (Samchun Pure Chemical Co., Korea), ethylenediamine (EDA; Janssen Chemica Co., Belgium), N-methyl-2-pyrrolidone (NMP; Samchun Pure Chemical), dibutyltindilaurate (DBTDL; Nine Chemical Co., Korea), Na_2CO_3 (JIN Chemical Co.), and hexamethylene diisocyanate (HDI; Aldrich) were used as received. N-Ethyl-N-2-hydroxyethyl-perfluorooctanesulfonamide (HFA; 3M Co., USA) was used after recrystallization from toluene. Tetrahydrofuran (THF; Samchun Pure Chemical, Korea) and 1,4-butanediol (BD; Junsei Chemical Co., Japan) were dried over 4-Å molecular sieves before use. Also, poly(oxytetramethylene glycol) [PTMG, number-average molecular weight (M_n) = 2000 or 1000 g/mol; BASF] was dried and vacuumed at 60°C before use.

Synthesis of the PUDs

A 2000-mL, plate-bottomed, four-necked separated flask with a mechanical stirrer, a thermometer, and a condenser with a drying tube was used as a reactor. The reaction was carried out in a constant-temperature oil bath. DMPA (0.1342 mol) dissolved in NMP (10 wt % based on the total solid content) and PTMG (M_n = 2000 g/mol, 0.09868 mol) were charged into the dried flask. With stirring, the mixture was heated to 70°C for about 30 min, and this was followed by the addition of IPDI (0.34932 mol) and DBTDL (0.03 wt % based on the total solid content) to the homogenized mixture. After about 3 h, NCO-terminated prepolymers ([NCO]/[OH] molar ratio = 1.5) were obtained. After cooling, the prepolymers were neutralized with TEA and stirred for about 30 min. The PUD was prepared by chain extension ([NCO]/[OH] molar ratio = 1.0) with EDA (0.11644 mol) dissolved in water after the addition of water to the neutralized prepolymers. The resulting product was a pure PUD with a solid content of about 30 wt %. The weight-average molecular weight (M_w) of the PUD was about 8.0×10^4 g/mol, and the particle size of the pure PUD was about 39.3 nm.

Synthesis of the FAPUDs

The FAPUDs were synthesized with the following reaction. First, fluorine-modified diisocyanate (FMD) was prepared from TIHI and HFA dissolved in THF (with a solid content of ca. 30 wt %) and from the addition of DBTDL (0.03 wt % based on the total solid content) to the dried flask. At this point, the change in the NCO value during the reaction was determined with a standard dibutylamine back-titration method. A similar FMD preparation was reported in a previous study.[16] A fluorine-modified polyurethane (FPU) was obtained by the addition of PTMG (M_n = 1000 g/mol), DMPA and HDI or BD as a chain extender to the FMD and by about 3 h of reaction. After cooling, the FPU was neutralized with TEA or Na_2CO_3 and stirred for about 30 min. After the completion of emulsification, THF was distilled off at 50°C, and the solid content in the final product (FAPUD) was around 20 wt %. The process for the synthesis of the FAPUD is illustrated in Figure 1, and the recipe for preparing the FAPUD is shown in Table I.

Measurements

The molecular weights were determined by the gel permeation chromatography (GPC) methods of Waters Corp (USA). The operating temperature was 35°C, the mobile phase was THF, the flow rate was 1.0 mL/min, and the detector was refractive-index. Polystyrene standards were used to generate calibration.

Infrared spectra were obtained on a Bio-Rad FTS-7 Fourier transform infrared (FTIR) spectrometer (USA) in the 4-cm^{-1} resolution mode. Sixteen scans were averaged for each sample. Each sample for infrared analysis was prepared by the coating of a thin film on a KBr window from a resolving solution in THF.

The particle sizes of the PUD and FAPUD were measured with the dynamic light scattering method of Otsuka Electronics Corp., Japan (LPA 3000 and 3100).

Films were prepared for observing the thermal and surface properties. FPMs were made from the blending of the FAPUD with the PUD (with a solid content of ca. 30 wt %) according to the fluorine content. Films were prepared by the casting of the FPMs on a Teflon plate after mixing for about 24 h. The solvent of the FPMs was evaporated off at room temperature for about 24 h. Evaporated FPM films were dried in an oven at 60°C for about 24 h and then further dried in a vacuum oven under 2–3 mmHg of pressure for about 24 h. The final films were annealed at 100°C for about 3 h and were approximately 0.35 ± 0.05 mm thick.

The contact-angle measurements were obtained with a contact-angle analyzer (Kruss G-10, USA) and were carried out by the measurement of the water and methylene iodide drop contact angles at the FPM film–
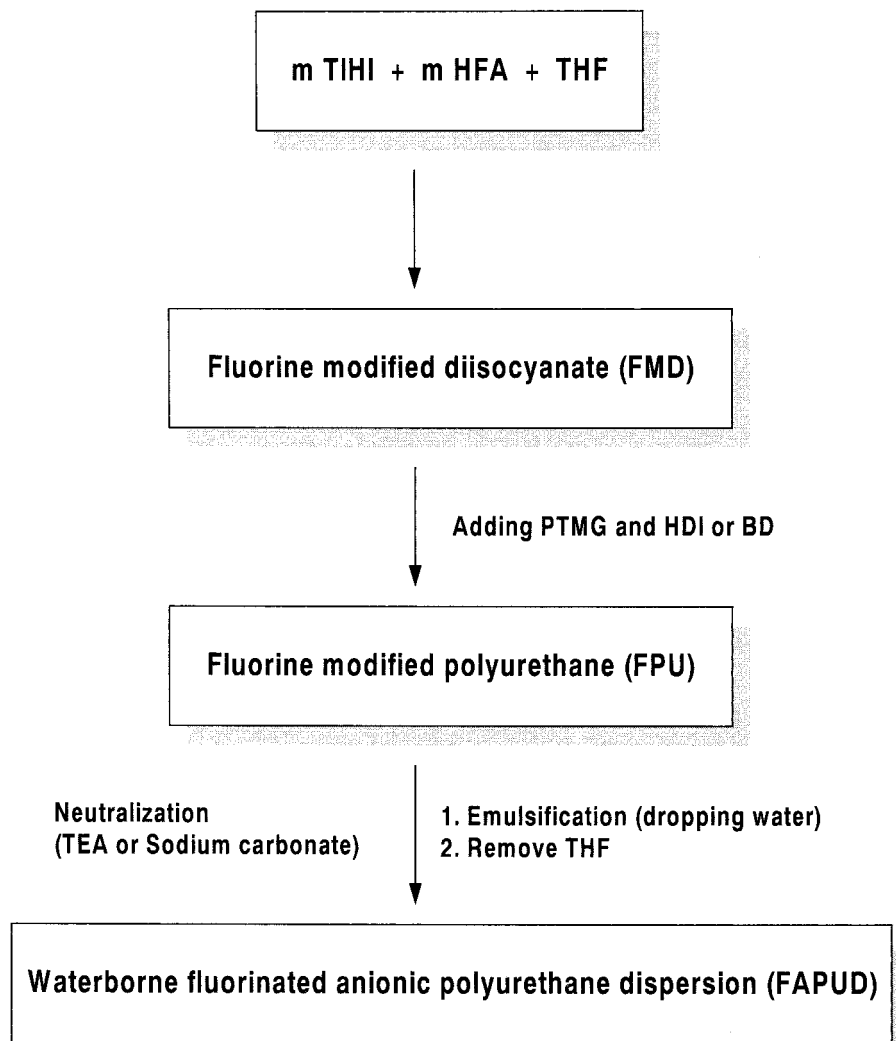
Figure 1 Process for the synthesis of the FAPUDs.

TABLE I
Recipe for the Preparation of FAPUDs and Variation of the Molecular Weight of FAPUDs

Sample	TIHI (g)	HFA (g)	PTMG (g)	DMPA (g)	HDI (g)	BD (g)	TEA (g)	Na$_2$CO$_3$ (g)	Molecular weight	
									M_w	Polydispersity Index
FAPUD 13[a]T[b]-100[c]	15.22	17.24	24.05	4.5	10.71	3.28	3.39	—	1.2×10^4	1.83
FAPUD 15T-100	17.55	19.89	28.49	4.5	4.57	—	3.39	—	1.05×10^4	1.92
FAPUD 20T-100	23.41	26.52	19.47	4.5	1.11	—	3.39	—	1.29×10^4	2.13
FAPUD 25T-100	29.26	33.15	6.46	4.5	—	1.63	3.39	—	1.35×10^4	2.13
FAPUD 25Na[d]-100	29.26	33.15	6.46	4.5	—	1.63	—	1.78	1.0×10^4	1.92
FAPUD 25Na-90	29.26	33.15	6.46	4.5	—	1.63	—	1.6	8.0×10^3	2.15
FAPUD 25Na-80	29.26	33.15	6.46	4.5	—	1.63	—	1.42	7.6×10^3	1.88
FAPUD 25Na-70	29.26	33.15	6.46	4.5	—	1.63	—	1.24	7.1×10^3	1.79

[a] Fluorine content in FAPUD.
[b] TEA used as neutralizing agent.
[c] DN.
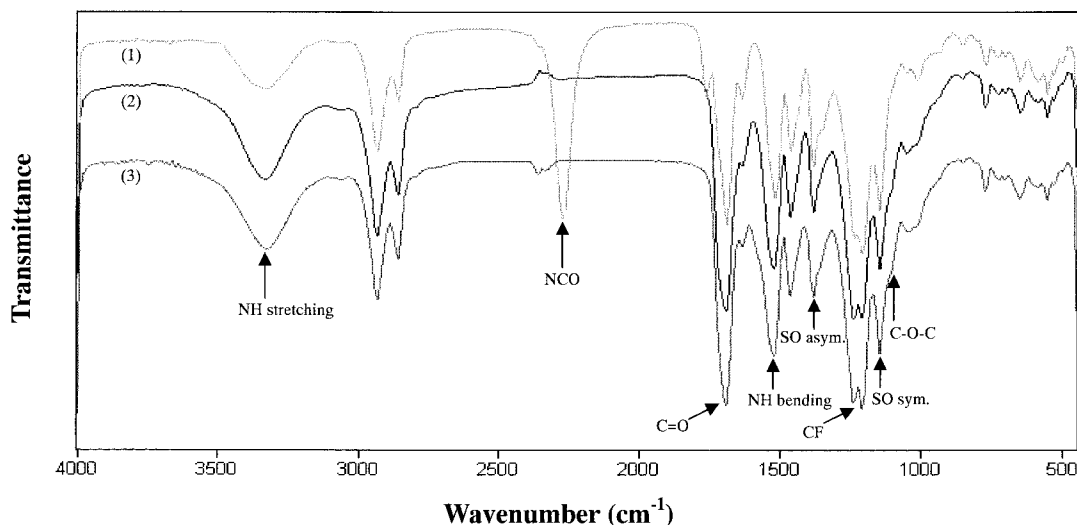[d] Na$_2$CO$_3$ used as neutralizing agent.

Figure 2 FTIR spectra of (1) FMD, (2) FAPUD 25T, and (3) FAPUD 25Na-100.

air interface. Measuring samples were prepared by the FPM film being attached to a slide glass cleaned with acetone.

The thermal properties were measured with differential scanning calorimetry (DSC; TA Corp. 2010, USA). Measuring samples were precooled to $-100°C$ with liquid nitrogen, and the experiments were carried out a heating rate of $10°C/min$ under a dry nitrogen purge. Data collection for the pure PUD, FAPUD, and FPMs was carried out between -100 and $100°C$. The sample weight of the DSC specimens was approximately 10 ± 1 mg.

RESULTS AND DISCUSSION

Identification of the FAPUD synthesis

The synthesis of the FAPUD T series containing variable fluorine contents (15, 20, and 25 wt % based on the total solid content) and the FAPUD 25Na series with respect to the DN was characterized by FTIR and GPC. Figure 2 shows the FTIR spectra of FMD, FAPUD 25T-100, and FAPUD 25Na-100, where T and Na represent TEA and Na_2CO_3, respectively, used as neutralizing agents; the first number shows the fluorine content in the FAPUD T and FAPUD Na series, and the second (e.g., 100) shows the DN. Curve 1 is an FMD spectrum measured after the reaction of HFA and TIHI through the NCO value identified with a standard dibutylamine back-titration method. By the reaction with HFA, the asymmetric and symmetric stretching vibrations of S=O appeared at 1386 and 1151 cm^{-1}, respectively, and the stretching vibration of —C—F— was observed at about 1210 cm^{-1}. The N—H stretching and bending vibrations of urethane that resulted from the reaction of NCO and OH appeared at about 3300 and 1520 cm^{-1}, respectively, and

a carbonyl peak (C=O) was observed at about 1640 cm^{-1}. The strong peak forming at 2270 cm^{-1} was a NCO peak of the FMD. Curves 2 and 3 are spectra of FAPUD 25T-100 and FAPUD 25Na-100, respectively. The spectra show the C—O—C peak at 1106 cm^{-1} and no NCO peak at 2270 cm^{-1}. GPC was used to identify the molecular weight and the reaction conversion. The molecular weights of the FAPUD T and FAPUD 25Na series were observed at 1.05×10^4 to 1.35×10^4 g/mol and at 7.1×10^3 to 1.0×10^4 g/mol, respectively, as shown in Table I.

Particle sizes of the FAPUDs

In these experiments, the DMPA concentration was fixed at 6 wt % based on the total solid content. Figures 3 and 4 show the particle sizes of the FAPUDs prepared from neutralizing agents (TEA or Na_2CO_3). Figure 3 shows the particle sizes of the FAPUD T series prepared with TEA as a function of the fluorine content in the FAPUDs. The particle sizes of FAPUD T increased from 174.3 to 239.7 nm as the fluorine content in the FAPUDs increased. The variation of these particle sizes was mostly governed by the fluorine content in the FAPUDs because we fixed the DN and external condition such as the temperature and revolutions per minute of the reactor.

Figure 4 shows the particle sizes of the FAPUD 25Na series prepared with Na_2CO_3 as a function of the DN. In this series, the DN was varied from 70 to 100%. The particle sizes of FAPUD 25Na decreased from 269.8 to 81.7 nm with increasing DN. Because the DN was the only variable in these experiments, the variation in the particle size with increasing DN was due to the increased hydrophilicity from the increased ionic content.[1] The variation of these particle sizes was dependent on the DN.
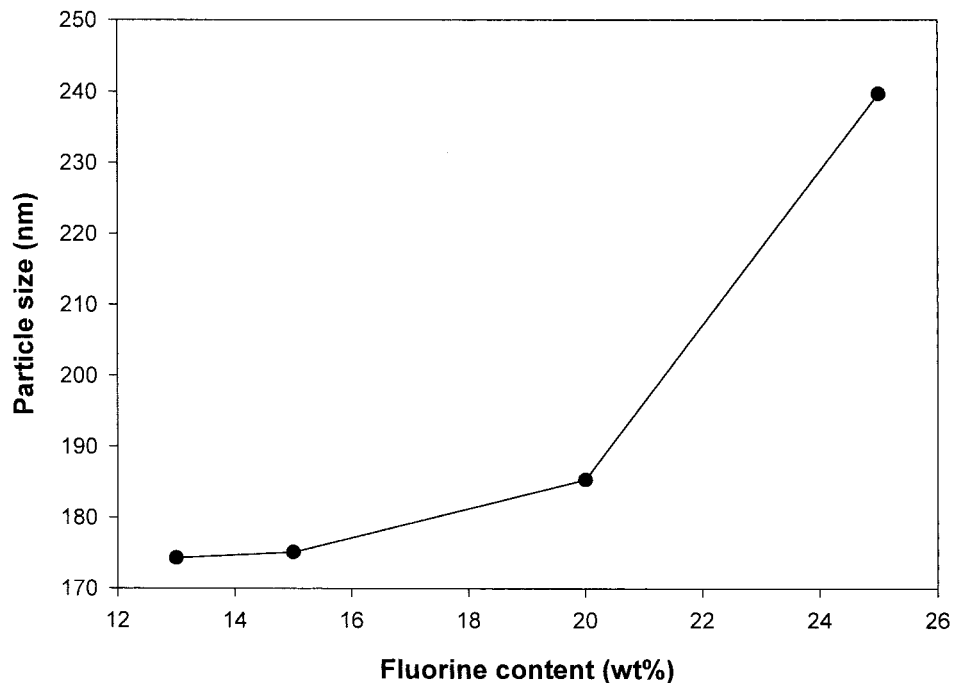
Figure 3 Particle size of the FAPUD T series with different fluorine contents.

Surface properties of the FPM films

Figures 5 and 6 show the surface energies estimated from contact-angle data for the surface properties of films of the FPM T-100 and FPM 25Na series, respectively. The wetting liquids used for the contact-angle measurements were water and methylene iodide, the surface tensions of which were suggested by Owens and Wendt.[17] The total surface energies and their polar and dispersion components were calculated by Fowkes' equation as follows:

$$\gamma_{LV}(1 + \cos\theta) = 2\lfloor (\gamma_S^d)^{1/2}\,(\gamma_{LV}^d)^{1/2} + (\gamma_S^P)^{1/2}\,(\gamma_{LV}^P)^{1/2} \rfloor$$

where p and d are the polar and dispersion components, respectively, of each surface energy, θ is the
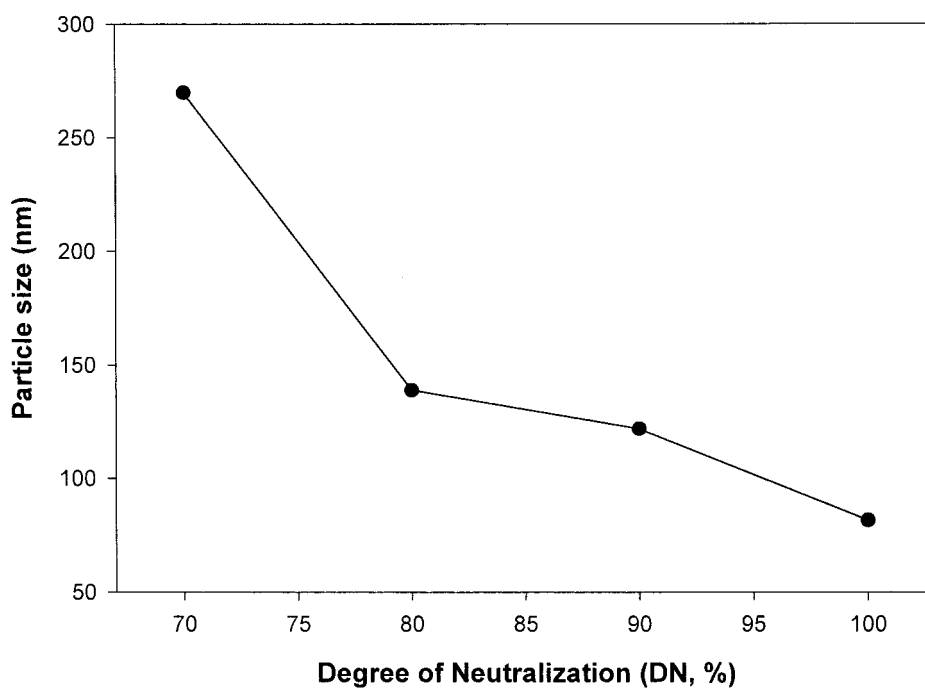

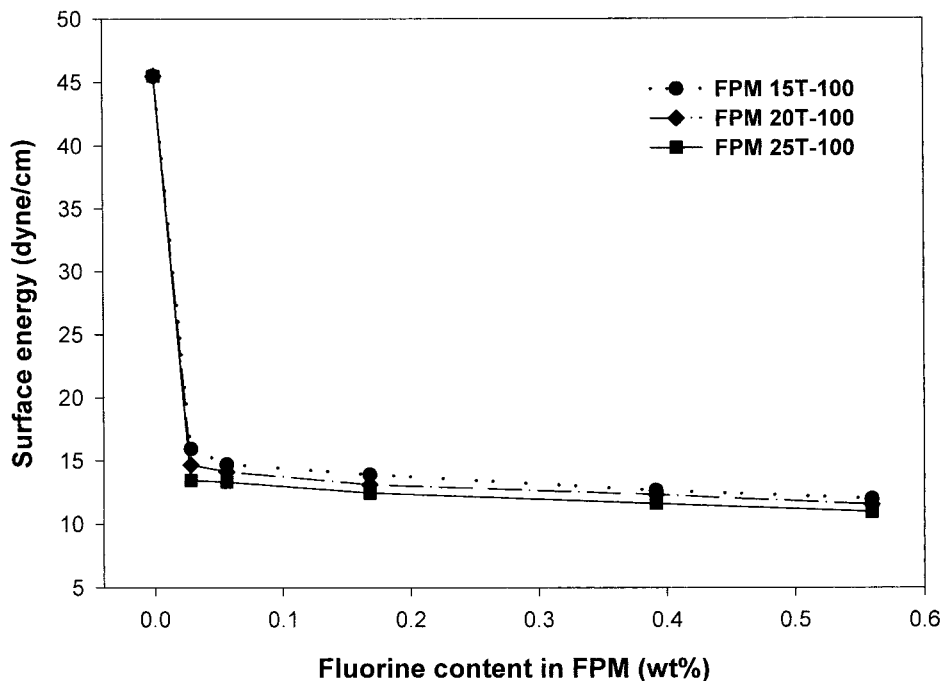**Figure 4** Particle size of the FAPUD 25Na series with the DN.

Figure 5 Surface energy diagrams of the FPM T series estimated with the Owens–Wendt general equation.

contact angle, γ_{LV} is the interfacial tension at the liquid vapor, and γ_S is the sum of the surface tension components ($\gamma_S^d + \gamma_S^p$). By measurement of the contact angles on a solid surface with two wetting liquids so that the polar and dispersion components of the surface tensions are known, the total surface energy of a solid and its components can be calculated.

Figure 5 shows the surface properties of FPM T films obtained from the blending of the FAPUD T series with pure PUD. FPM T represents the mixture of FAPUD T and pure PUD, and the number shows the fluorine content in the FPM films. The pure PUD showed a high surface energy of about 40.95 dyn/cm due to the presence of hydrophilic properties, such as
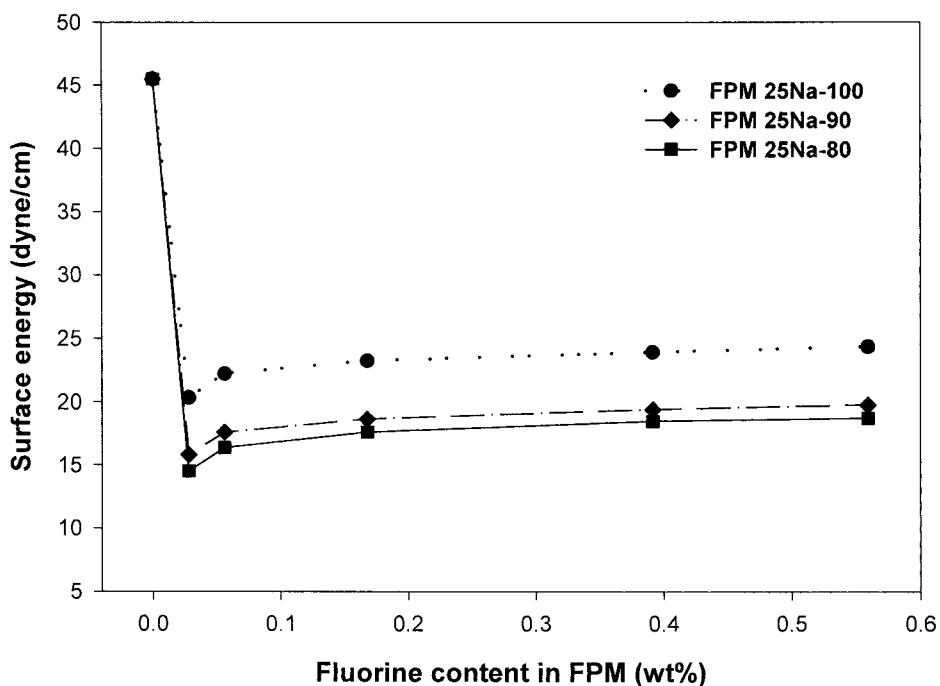

Figure 6 Surface energy diagrams of the FPM 25Na series estimated with the Owens–Wendt general equation.
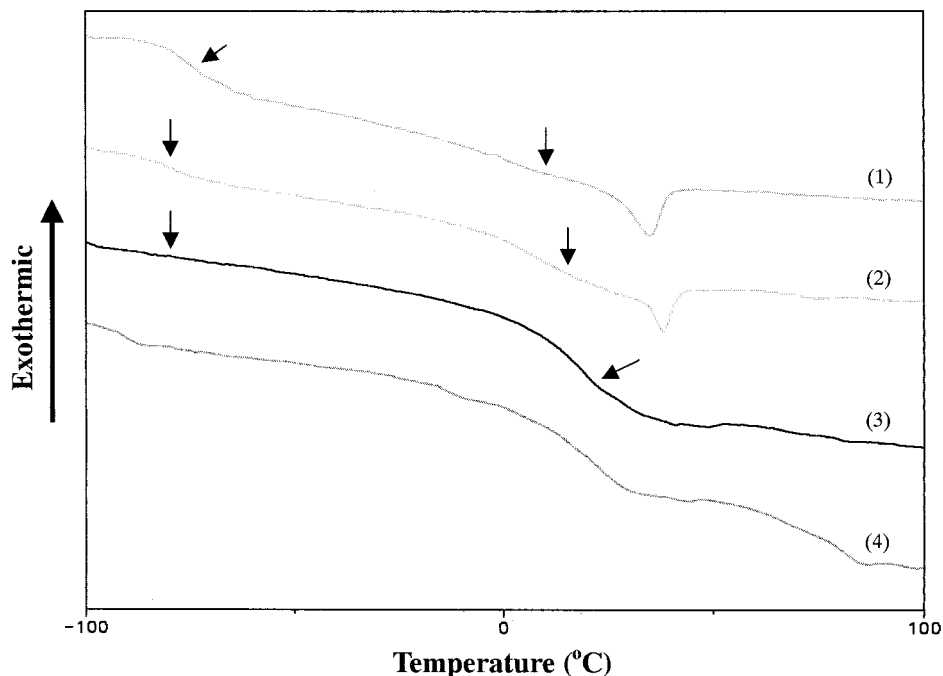
Figure 7 DSC thermograms of the FAPUD T series with different fluorine contents: (1) FAPUD 15T, (2) FAPUD 20T, (3) FAPUD 25T, and (4) FAPUD 25Na-100.

the carboxyl group on the surface of the film. With increasing fluorine content, the surface energies of FPM films tended to decrease. In addition, FPM 25T had the lowest surface energy with the same fluorine content of the FPM films because of the extent of the difference in the surface arrangement of fluorine in the FAPUDs.

Figure 6 shows the surface properties of FPM 25Na films, which were obtained from the blending of the FAPUD 25Na series with pure PUD. The number (e.g., 100, 90, and 80) represents the DN. The surface energies of the films rapidly decreased until 0.02797 wt %. However, the surface energies of the films continuously increased above 0.02797 wt %. It seems that the salt inside the FPM films prevented the surface arrangement of the fluorine on the FPM films. Also, the surface energy was increased above 0.02797 wt %. It seems that the fluorine did not regularly arrange toward the film surface because the salt augmentation of films inside increased.

DSC

DSC thermograms of the FAPUD T series and FAPUD 25Na-100 are shown in Figure 7. The soft-segment glass-transition temperature (T_{gs}) of FAPUD 15T-100 was about $-74.08°C$. However, T_{gs} of FAPUD T disappeared as the fluorine content in FAPUD increased gradually. In FAPUD 15T-100, the hard-segment glass-transition temperature (T_{gh}) of FAPUD was not observed, but in FAPUD 25T-100, T_{gh} was observed at

about 18.21°C. In addition, the amount of the polyol (PTMG) decreased with the increase in the fluorine content. Therefore, in FAPUD 15T-100, the melting temperature (T_m) and melting enthalpy (ΔH_m) of PTMG were about 35°C and 1.964 J/g, respectively, whereas T_m of PTMG was not observed in FAPUD 25T-100 because of the sudden increase in the fluorine content. The aforementioned results can be demonstrated as follows. The variations of T_{gs} and polyol T_m resulted from decreasing polyol due to the increase in the fluorine content in FAPUD. Also, variations of T_{gh} were observed. It seems that the increase in the hard domains resulted from the use of short-chain diols. Therefore, T_{gh} was observed for FAPUD 20T-100 and FAPUD 25T-100. In FAPUD 25T-100 and FAPUD 25Na-100 with the same fluorine content, T_{gh} of FAPUD 25Na-100 was higher than that of FAPUD 25T-100 because of the interaction of salt and ionic groups. T_{gs}, T_{gh}, T_m, and ΔH_m of the FAPUDs are listed in Table II.

Figure 8 shows the thermograms of FPM films made from the blending of FAPUD 25T with the PUD. T_{gs} of the PUD was observed at about $-74.76°C$. Even though the fluorine content in the FPMs increased, the T_{gs} value of the FPMs was like that of the pure PUD. In addition, the thermal behavior of the FAPUDs was not observed in the FPMs. The thermal properties of the FPMs prepared from the blending of other FAPUD series were like those of the PUD as well (not shown). These thermal properties show that the phase separation and thermal behavior of the FAPUDs did not

TABLE II
Thermal Property Data of the FAPUD Series

	Soft phase			Hard phase
Sample (FPUD)	T_{gs} (°C)	T_m (PTMG) (°C)	ΔH_m (PTMG) (J/g)	T_{gh} (°C)
FAPUD 15T-100	−74.08	26.88	1.964	—
FAPUD 20T-100	−79.13	33.79	1.167	3.71
FAPUD 25T-100	—	—	—	18.21
FAPUD 25Na-100	—	—	—	22.13

appear because of the compatibility of the polyether-type PUD and FAPUD backbone, despite the increasing fluorine content in the FPMs.

CONCLUSIONS

The FAPUDs in this work were synthesized to alter the surface chemistry of pure PUD. The pure PUD and FAPUD were synthesized by an NCO-terminated pre-polymer mixing process and an acetone process, respectively. The M_w value and particle size of the prepared PUD were about 8.0×10^4 g/mol and 39.3 nm, respectively. The particle size of the FAPUD T series tended to increase as the fluorine content increased, whereas the particle size of the FAPUD 25Na series tended to decrease with increasing DN. The variation of these particle sizes was governed by the fluorine content in the FAPUDs and the DN. The thermal properties of the FAPUD T series and FAPUD 25Na-100 were observed as follows. As the fluorine content increased, the soft-phase T_{gs} of the FAPUD T series

gradually disappeared; however, the hard-phase T_{gh} of FAPUD 20T-100 and FAPUD 25T-100 was observed because of the increase in the hard domains with the decrease in the polyol. In addition, the FAPUD 25Na-100 T_{gh} was observed at a higher temperature than the FAPUD 25T-100 T_{gh} because of the interactions between the salt and ionic groups. FPM films prepared by the blending of the FAPUD T series or FAPUD 25Na series with the PUD were observed for their surface and thermal properties with the fluorine content. As for the surface energy, the pure PUD showed a high surface energy (40.95 dyn/cm) because of the presence of a carboxyl group on the surface of the film. When an FAPUD was added, the FPM T series showed low surface energies because of the surface arrangement of fluorine. However, the surface energy of the FPM 25Na series films increased above the critical fluorine concentration because of the increase in salt. Even though the concentration of the FAPUDs in FPM films increased, the thermal behavior of the
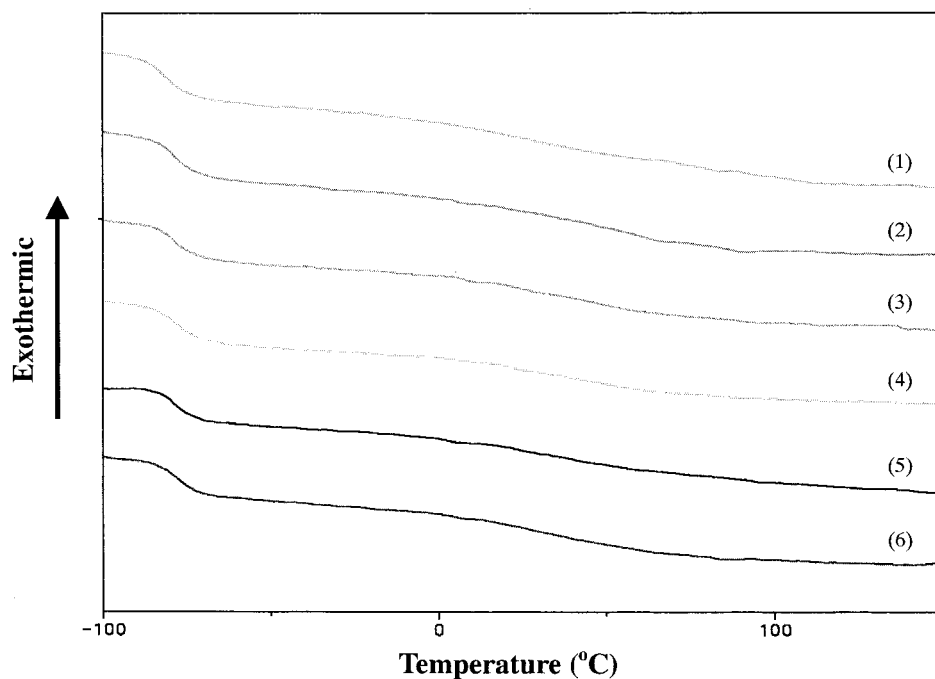

Figure 8 DSC thermograms of PUD and FPM 25T with different fluorine contents: (1) PUD only and (2) 0.02707, (3) 0.05594, (4) 0.16782, (5) 0.39158, and (6) 0.5594 fluorine contents.

pure PUD was unchanged. Therefore, the surface modification was accomplished without morphology variations of the pure PUD.

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