Surface Modification with Waterborne Fluorinated Non-ionic Polyurethane Dispersion

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Abstract: Waterborne fluorinated non-ionic polyurethane dispersions (FNPUDs) were synthesized from tris(6-isocyanatoxethyl) isocyanurate (TIIIH), N-ethyl-N-2-hydroxyethyl-perfluorooctanesulfonamide (HFA), poly(oxyethylene glycol) (PEG) and 1,4-butanediol (BD). Waterborne polyurethane dispersion (PUD) was synthesized from isophorone diisocyanate (IPDI), poly(oxytetramethylene glycol) (PTMG), dimethylolpropionic acid (DMPA) and ethylenediamine (EDA). Fluorine PUD mixtures (FPDs) were prepared by blending the FNPUDs into the PUD. The particle size of the FNPUDs was measured by using dynamic light scattering (DLS), and the surface energy estimation and thermal property of the FPDs were studied by using a contact angle analyzer and differential scanning calorimetry (DSC). The particle size and glass transition temperature (Tg) of the FNPUDs tended to increase as the fluorine content in the FNPUD increased. When the fluorine content was 0.087 wt%, based on the total solid content, the surface energies of the FPDs exhibited the lowest values. In the same fluorine content in the FPDs, the surface energies of FPDs containing a higher fluorine content in the FNPUD exhibited a lower surface energy than those containing a lower fluorine content in the FNPUD. The thermal properties of the FPDs were found to be similar to the pure PUD. Accordingly, these results indicate that the phase separation and thermal behavior of the FNPUDs did not appear due to the compatibility of the polyether type PUD and the FNPUDs.

Keywords: waterborne fluorinated polyurethane dispersion, waterborne polyurethane dispersion, surface energy, glass transition temperature, compatibility

Introduction

Waterborne polyurethane dispersions (PUDs) can be prepared in an ionomer or nonionomer form. Nonionomer types contain hydrophilic soft segments, such as poly(oxyethylene glycol)s (PEGs), whereas ionomer types contain pendant acid or tertiary nitrogen groups, which are neutralized to form salts. The soft segments generally consist of polyether or polyester polyl, whereas the hard segments are usually formed by the chain extension of the diisocyanate with a low molecular polyl or amine [1-3].

PUDs have many useful features. From an environmental point of view, the industrial application of PUDs is highly acceptable since water does not pollute the environment. Also, PUDs exhibit excellent mechanical properties such as abrasion resistance, toughness, tensile strength, film-forming properties, adhesion, and so on. However, the application of PUDs is limited due to a decrease in solvent and water resistance, high-temperature performance and chemical resistance, if the PUD does not form a chemical crosslinked structure. Therefore, to increase the application and functionality of PUDs, research on a functional polymer that includes water and oil repellency has been conducted to protect the surface or bulk structure of a PUD when high temperature or chemical resistance is required [4-6].

The surface properties such as water repellence, abrasion resistance and pollution resistance are all related with the chemical structure and molecular arrangement of the polymer surface. Among organic components with such a characterization, fluorine has been successfully utilized for surface modification. Several investigations on the surface modification of PUDs have already been carried out [7-14]. Yet, previous research on the fluorine...
surface modification of PUDs is sparse in open literature. In previous work, the current authors synthesized waterborne fluorinated anionic polyurethane dispersions (FAPUDs) using two different neutralizing agents (TEA or Na₂CO₃) according to an acetone process and pure PUD. The particle size of the FAPUDs and thermal property of the FAPUD films were observed according to the fluorine content and degree of neutralization (DN). The surface modification and thermal property of the FOM films prepared by blending the FAPUDs into pure PUD were also discussed [15].

In the current study, waterborne fluorinated polyurethane dispersions (FNPUUDs) and pure PUD were synthesized. The particle size of FNPUUDs and thermal property of the FNPUUD films relative to the PEG molecular weight and fluorine content were observed. Finally, we discussed the surface modification and thermal property of the FPM films prepared by blending the FNPUUDs into pure PUD.

**Experimental**

**Materials**

For the synthesis, isophorone diisocyanate (IPDI, Aldrich Co.), tris(6-isocyanatohexyl) isocyanurate (TIHI, BASF Co.), dimethylolpropionic acid (DMPA, TRIMET Technical Products Inc.), triethylamine (TEA, Samchun Pure Chemical Co.), ethylenediamine (EDA, JANSSEN CHEMICA Co.), N-methyl-2-pyrrolidone (NMP, Samchun Pure Chemical Co.), and dibutyldilaurate (DBTDL, Nine Chemical Co.) were used as received. N-ethyl-2-hydroxyethyl-perfluorooctanesulfonamide (HFA, 3 M Co.) was used after recrystallization from toluene. Tetrahydrofuran (THF, Samchun Pure Chemical Co.) and 1,4-hexanediol (BD, Junsei Chemical Co.) were dried over 4 Å molecular sieves before use. Also, poly(oxytetramethylene glycol) (PTMG, $M_n=2000$ g/mol, BASF Co.) and poly(oxyethylene glycol) (PEG, $M_n=1000$ g/mol, KANTO Chemical Co., $M_n=2000$ g/mol, SHINYO Pure Chemical Co.) were dried and vacuumed at 60°C before use.

**Synthesis of Waterborne Polyurethane Dispersion (PUD)**

A 2000 mL plate-bottomed, four-necked separated flask with a mechanical stirrer, thermometer, and condenser with drying tube was used as the reactor. The reaction was carried out in a constant-temperature oil bath. DMMP (0.1342 mole) and PTMG (0.09868 mole) dissolved in NMP (10 wt% based on the total solid content) were charged into the dried flask. While stirring, the mixture was heated to 70°C for about 30 min, followed by the addition of IPDI (0.34932 mole) 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 using TEA and stirred for about 30 min. The PUD was prepared by a chain extension [(NCO)/(OH) molar ratio 1.0] as EDA (0.11644 mole) dissolved in water after adding water to the neutralized prepolymers. The resulting product was a pure PUD with a solid content of about 30 wt%. The molecular weight of the PUD was observed at about 110000 g/mol, while the particle size of the pure PUD was observed at about 69.3 nm.

**Synthesis of Waterborne Fluorinated Non-Ionic Polyurethane Dispersions (FNPUUDs)**

The FNPUUDs were synthesized according to the following reaction. Above all, fluorine modified disiocyanate (FMD) was prepared from TIHI and HFA dissolved in THF (with a solid content of about 30 wt%), and the addition of DBTDL (0.03 wt% based on the total solid content) into a dried flask. At this point, the change of NCO value during the reaction was determined using a standard dibutylamine back-titration method. A similar FMD preparation method was already in the previous other work [16]. Fluorine modified polyurethane (FPU) was obtained by adding PEG and BD as chain extender into the FMD and leaving it to react for about 3 h. The FNPUUDs were obtained by adding water to the FPU. After the emulsification was completed, THF was distilled off at 50°C, and the solid content in the final product (FNPUUDs) was around 10 wt%. The process used to synthesize the FNPUUDs is illustrated in Figure 1, and the recipe used to prepare the FNPUUDs is listed in Table 1.

**Measurements**

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

Infrared spectra were obtained on a Bio-Rad FTS-7 fourier transform infrared spectrometer (FTIR) in a 4 cm⁻¹ resolution mode. An average of sixteen scans were performed on each sample. Each sample for infrared analysis was prepared by coating a thin film on a KBr window from resolving solution in THF.

The particle size of the PUD and the FNPUUDs was measured by using a dynamic light scatter (DLS) of the OTSUKA ELECTRONICS corporation (LPA-3000, 3100).

Films were prepared to observe the thermal and surface properties. Fluorine PUD mixtures (FPMs) were made
Table 1. Recipe for Preparing the FNPUDs and Variation of Molecular Weight (MW) of the FNPUDs

<table>
<thead>
<tr>
<th>Sample (FNPUD)</th>
<th>Materials &amp; MW</th>
<th>TIHI (mole)</th>
<th>HFA (mole)</th>
<th>PEG 2,000 (mole)</th>
<th>PEG 1,000 (mole)</th>
<th>BD (mole)</th>
<th>Molecular weight</th>
<th>Polydispersity (PDI)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\langle M_w \rangle$</td>
<td>$\langle M_n \rangle$</td>
</tr>
<tr>
<td>FNPUD 1K 23</td>
<td></td>
<td>0.05341</td>
<td>0.05341</td>
<td>0.01404</td>
<td>0.039</td>
<td>0.047</td>
<td>$3.5 \times 10^4$</td>
<td>$1.1 \times 10^4$</td>
</tr>
<tr>
<td>FNPUD 1K 24</td>
<td></td>
<td>0.05573</td>
<td>0.05573</td>
<td>0.01107</td>
<td>0.045</td>
<td>0.050</td>
<td>$3.3 \times 10^4$</td>
<td>$1.1 \times 10^4$</td>
</tr>
<tr>
<td>FNPUD 1K 25</td>
<td></td>
<td>0.05806</td>
<td>0.05806</td>
<td>0.00809</td>
<td>0.050</td>
<td>0.055</td>
<td>$3.0 \times 10^4$</td>
<td>$1.1 \times 10^4$</td>
</tr>
<tr>
<td>FNPUD 1K 26</td>
<td></td>
<td>0.06038</td>
<td>0.06038</td>
<td>0.00510</td>
<td>0.055</td>
<td></td>
<td>$3.2 \times 10^4$</td>
<td>$1.1 \times 10^4$</td>
</tr>
<tr>
<td>FNPUD 2K 23</td>
<td></td>
<td>0.05341</td>
<td>0.05341</td>
<td>0.00669</td>
<td>0.047</td>
<td></td>
<td>$2.6 \times 10^4$</td>
<td>$9.8 \times 10^3$</td>
</tr>
<tr>
<td>FNPUD 2K 24</td>
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<td>0.05573</td>
<td>0.05573</td>
<td>0.00527</td>
<td>0.050</td>
<td></td>
<td>$2.9 \times 10^4$</td>
<td>$9.8 \times 10^3$</td>
</tr>
<tr>
<td>FNPUD 2K 25</td>
<td></td>
<td>0.05806</td>
<td>0.05806</td>
<td>0.00389</td>
<td>0.054</td>
<td></td>
<td>$3.0 \times 10^4$</td>
<td>$9.8 \times 10^3$</td>
</tr>
<tr>
<td>FNPUD 2K 26</td>
<td></td>
<td>0.06038</td>
<td>0.06038</td>
<td>0.00245</td>
<td>0.058</td>
<td></td>
<td>$3.0 \times 10^4$</td>
<td>$9.8 \times 10^3$</td>
</tr>
</tbody>
</table>

*: molecular weight of polystyrene (K=1000g/mol), #: fluorine content (wt%); in solid FNPUD

![Process for synthesis of the FNPUDs](image)

Figure 1. Process for synthesis of the FNPUDs.
from blending the FNPUDs into PUD (with a solid content of about 30 wt%) based on the fluorine content. Films were prepared by casting the FPMS on the Teflon plate after mixing for about 24 h. The solvent of FPMS was evaporated off at room temperature for about 24 h. Evaporated FPMS 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 pressure for about 24 h. The resulting 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 by using a contact angle analyzer, Kruss G-10 and carried out by measuring water and methylene iodide drop contact angles at the FPMS film / air interface. The measurement samples were prepared by attaching the FPMS film on the slide glass cleaned with acetone.

The thermal properties were measured by using a differential scanning calorimetry (DSC) 2010 of the TA corporation. The measurement samples were pre-cooled to -100°C using liquid nitrogen, and then the experiments were carried out at a heating rate of 10°C/min under a dry nitrogen purge. Data collection for the pure PUD, FNPUDs and FPMS was carried out between -100°C and 100°C. The sample weight of the DSC specimens was approximately 10 ± 1 mg.

Results and discussion
Identification of the PUD and FNPUD Synthesis
The synthesis of the PUD and the FNPUDs containing variable fluorine contents (23, 24, 25 and 26 wt% based on the total solid content) was characterized by FTIR and GPC. Figure 2 shows FTIR spectra of the PUD, FMD and FNPUDs. The spectrum of the PUD is shown in curve (1). The strong C-O-C peak was observed at 1112 cm⁻¹, and the carbonyl peak (C=O) of the urethane was formed at 1712 cm⁻¹. The FMD illustrated by curve (2) exhibited a spectrum that measured after reacting HFA and THDI based on a standard dibutylamine back-titration method. After the reaction with HFA, the asymmetric and symmetric stretching vibration of S=O was shown at 1386 cm⁻¹ and 1151 cm⁻¹ respectively, the stretching vibration of the perfluoroalkyl group was observed at 1210 cm⁻¹, N-H stretching and bending vibration of urethane resulting from the reaction of NCO and OH was showed at 3330 cm⁻¹ and 1520 cm⁻¹ respectively, and the carbonyl peak (C=O) was observed between 1638 cm⁻¹ and 1766 cm⁻¹. The strong peak formed at 2270 cm⁻¹ was the NCO peak of the FMD. Curve (3) represents a spectrum of the FNPUDs. Due to the reaction with ether polyl C-O-C peak was found at 1110 cm⁻¹, while no NCO peak was observed at 2270 cm⁻¹. GPC was used in order to identify the molecular weight and extent of reaction. The molecular weight of the FNPUDs was observed within a range of 26000 g/mol ~ 35000 g/mol and shown in Table 1. From results of the FTIR and GPC analysis, the synthesis of the PUD, FMD and FNPUDs was successfully accomplished.

Particle size of the FNPUDs
The particle sizes of the FNPUDs prepared from PEG with different molecular weights (2000 g/mol, 1000 g/mol) are shown in Figure 3. In the case of a molecular weight 1000 g/mol (FNPUD 1K series), the particle sizes increased from 183.3 nm to 358.4 nm as the fluorine content in the FNPUD increased, and when a molecular weight 2000 g/mol (FNPUD 2K series) was used the particle sizes increased from 117.6 nm to 682.7 nm. In the case of FNPUD with the fluorine content between 23 wt% and 25 wt%, the particle sizes of the FNPUD 1 K were larger than those of the FNPUD 2 K. Because the difference in these particle sizes was governed by the molecular weight of PEG. In other words, the hydrophilicity of the molecular weight 2000 g/mol was superior to that of the molecular weight 1000 g/mol. However, when the fluorine content in the FNPUD was more than 25 wt%, the particle size of the FNPUD 2 K series rapidly increased from 204.4 nm to 682.7 nm.
Therefore, in this case, the difference in the particle size resulted from PEG content rather than the effect of PEG molecular weight. Consequently, the factors determining the particle sizes were found to be the molecular weight and content of PEG. The particle sizes of the FNPUDs were governed by the hydrophilicity related to the molecular weight and content of PEG.

Surface Energy Estimation of the FPM Films

Figure 4 shows the surface energies estimated from the contact angle data for the surface property of the FPM films. Wetting liquids used for the contact angle measurement were water and methylene iodide, which of surface tensions were suggested by Owens and Wendt. The total surface energies and their polar and dispersion components were calculated by Fowkes’ equation as follows [17].

\[
\gamma_{LV}(1 + \cos \theta) = 2\left[ (\gamma_S^d)^{1/2} (\gamma_{LV}^d)^{1/2} + (\gamma_S^p)^{1/2} (\gamma_{LV}^p)^{1/2}\right]
\]

Where p and d are the polar and dispersion components of each surface energy, \(\theta\) is the contact angle, \(\gamma_{LV}\) is the interfacial tension at liquid-vapor, and \(\gamma_S\) is the sum of the surface tension components (\(\gamma_S^d + \gamma_S^p\)). By measuring the contact angles on a solid surface with two wetting liquids 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.

In Figure 4, the PUD showed a high surface energy of about 40.95 dyne/cm due to the presence of the carboxyl group on the surface of the film. FPM 2 K 23 exhibited a much higher surface energy than FPM 2 K 25. FPM showed the mixtures of FNPUD and PUD, contant presented the molecular weight (K=1000 g/mol) of PEG used for preparing the FNPUDs and the fluorine content in the FNPUDs. Also, the surface energy of FPM 2 K 23 tended to increase with the fluorine content above 0.087 wt%, while that of FPM 2 K 25 unchanged nearly. This reason seems that the increase of PEG content in the FPMs affected to the surface energy with the same fluorine content. When the surface energies of FPM 2 K 25 and FPM 1 K 25 were compared with the fluorine content under 0.087 wt%, the surface energy of FPM 1 K 25 was lower than that of FPM 2 K 25. Thus, it would seem that the large molecular weight of PEG had more effect on limiting the fluorine arrangement toward the surface with the fluorine content under 0.087 wt%. However, in the same fluorine content over 0.087 wt%, the surface energy of FPM 1 K 25 were higher than that of FPM 2 K 25 due to the increase of PEG content in FPM 1 K 25. However, the difference between the surface energies was a little.

Differential Scanning Calorimetry (DSC)

Thermal properties were studied to determine whether the presence of the FNPUDs blended in the FPMs influenced the bulk microdomain structure of the pure PUD. Figure 5 and 6 show DSC thermograms for the variation of fluorine contents in the FNPUD 1 K and FPMs. In Figure 5, the glass transition temperature (\(T_g\)) of the pure FNPUD 1K tended to increase as the fluorine content in the FNPUD 1 K increased. Because of the urethane bond combined in the FNPUD backbone, the soft segment \(T_g\) of the FNPUD 1 K increased. In addition, the soft segment \(T_g\) of the FNPUD 2 K (not shown) was observed at a higher temperature about 1 ~ 5°C than that of the FNPUD 1 K, yet the thermal behavior of the FNPUD 2 K was similar to that of the FNPUD 1 K. Accordingly, it would seem that the increase of hard segment and the decrease of soft segment resulting from a decrease the PEG content affected to the variation of the FNPUD thermal
Figure 6. DSC thermograms of PUD and FPM 1 K 25 with different fluorine contents (F). (1) PUD; (2) Fe-0.044; (3) Fe-0.087; (4) Fe-0.26; (5) Fe-0.44; (6) Fe-0.61.

transitions. Figure 6 shows the thermograms of the pure PUD and FPMs relative to the fluorine content. In Figure 6, the soft segment $T_g$ of the pure PUD was observed at about -74.76°C. Even though the fluorine content in the FPMs increased from 0.044 wt% to 0.61 wt%, the soft segment $T_g$ of the FPMs were found to be similar to that of the PUD. In addition, the thermal behavior of the FNPUDs was not observed in FPMs. These thermal properties seem that the phase separation and thermal behavior of the FNPUDs did not appear due to the compatibility of the polyether type PUD and the FNPUD backbone, in spite of increasing the fluorine content in the FPMs.

Conclusion

The FNPUDs in the current work were synthesized in order to alter the surface chemistry of pure PUD. The pure PUD and the FNPUDs were respectively synthesized using a NCO-terminated prepolymer mixing process and aceton process. The molecular weight ($M_n$) and particle size of the prepared PUD were observed about 110000 g/mol and 69.3 nm respectively. The particle size of the FNPUDs tended to increase as the fluorine content increased. These particle sizes of the FNPUDs were influenced by the balance of hydrophilicity and hydrophobicity. Thus, it would seem that the balance of hydrophilicity and hydrophobicity was governed by the fluorine used as a hydrophobic, and the molecular weight and content of PEG used as a hydrophilic. FPM films prepared by blending the FNPUDs into the PUD were observed based on the surface and thermal properties relative to the fluorine content. In the case of the surface energy, the pure PUD showed a high surface energy (40.95 dyne/cm) due to the presence of a carboxyl group on the surface of the film. However, when the FNPUDs were added, the FPM films were observed a low surface energy due to the surface arrangement of fluorine. These surface energies of the FPMs were dependent on the fluorine content and PEG content in the FNPUD. Even though the concentration of the FNPUDs in the FPMs was increased, the thermal behavior of the pure PUD was unchanged. Accordingly, the surface modification was accomplished without any morphological variation of the pure PUD.

Acknowledgement

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References