Evaluating the Properties of a Coating Material with Polycaprolactone-Degradable Fluorinated Silicon-Containing Waterborne Polyurethane

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Abstract: This study successfully synthesized fluorinated silicon-containing waterborne polyurethanes (FSWPUs) by using polycaprolactone (PCL) diol, 2,2,3,3-Tetrafluoro-1,4-butanediol, and [3-(2-Aminoethylamino)propyl] trimethoxysilane (AEAPTES). The FSWPU’s particle size was examined using dynamic light scattering. After the FSWPUs were processed into a dry film, their molecular weight and basic properties were analyzed using gel permeation chromatography (GPC), Fourier-transform infrared spectroscopy (FTIR), and energy-dispersive X-ray spectroscopy (EDS). Additionally, the thermal stability of the FSWPUs was inspected by thermogravimetric analysis and dynamic mechanical analysis. The tensile strength and elongation at the break of the FSWPUs before and after hydrolysis were also analyzed, using a tensile testing machine. Subsequently, FSWPU emulsions were cast between the tiles, and hydrophilicity, hydrophobicity, and surface tension were then measured on a contact-angle measurement instrument. The tensile testing machine was again employed to test the sheer strength of the FSWPUs between the tiles, and a tape test was conducted to analyze their adhesion to the tiles. The results revealed that AEAPTES functional groups can reinforce the thermal stability, tensile strength, and water resistance of FSWPUs. Moreover, the AEAPTES functional groups increased the adhesion of FSWPUs to the tiles and reduced the surface energy of the tiles.

Keywords: polyurethane; fluorinated; silicon-containing; tiles

1. Introduction

In 2018, 359 million tons of plastic were produced, and the demand for polyurethane (PU) worldwide was 7.9%. To resolve the waste problem, 29.1 million tons of plastic waste were collected in Europe (including Norway and Switzerland), and 24.9% of these plastics were buried [1]. With the rising awareness of the crucial environmental problem of difficult-to-decompose plastics [2], the application of degradable materials has been widely discussed [3,4]. For instance, degradable segments can be included in PU synthesis to increase its degradability [5]. PU is generally synthesized using soft-segment diols, hard-segment diisocyanates, and chain extenders, while the degradable segments (e.g., polycaprolactone (PCL) and poly (tetramethylene ether) glycol (PTMG)) can be used as PU soft segments that enable PU to be degradable and, thus, addresses the global problem of buried and undegradable plastics. Therefore, to reduce the environmental hazards that result from plastic burial, this study used PCL as a substrate for synthesizing PU. Currently, volatile organic compounds (VOCs), such as dimethylacetamide and dimethylformamide, are commonly used in PU synthesis [6]; however, due to its impact on climate change and increased environmental awareness, concerns for reducing VOC use have been accentuated [7,8]. By passing the Clean Air Act [9], the United States
Environmental Protection Agency strengthened the regulation of VOC emissions, which encouraged the development of various nonsolvent systems in coating and painting materials [10]. To this end, relevant research on a water-based system was presented in 2015 [11], and waterborne PU (WPU) became more well-developed [12]. The most common WPU synthesis method is structural modification; specifically, internal hydrophilic functional groups are applied to modify the hydrophobicity of the PU structure [13], and WPU dispersions are created with emulsification by adding deionized (DI) water [14]. Water is generally considered an inexpensive, safe, and nontoxic solvent [15]; therefore, WPU can effectively limit VOCs in the atmosphere.

Compared with conventional PU or epoxy, WPU has inferior mechanical properties, water resistance, and hydrophobicity, as well as limited applications [16,17]. Common solutions for enhancing the function of WPU films include the addition of organic fluoride or natural products [18]. Despite fluorinated PU having advanced adhesion and water- and weather-resistant properties, its cost is very high, which limits its applicability [19]. Other materials, such as organosilicon that has a low surface energy and cost, are used extensively in waterproofing coatings (SPU) [20], however, its substandard oil resistance and adhesion limit its applications. A relevant study indicated that using a compound composed of Si and F in a crosslinking reaction of PU modification (FSPU) is a constructive strategy that can be used to enhance waterproofing and other functions (e.g., thermal stability, water resistance, and optical transparency) and can retain the improvement of mechanical properties [21]. Studies have mostly used acrylic acid functional groups for free-radical polymerization and have added nanoparticles to simultaneously import F and Si elements into the PU [22,23]. However, when using free-radical polymerization, the produced fluorinated silicon-containing waterborne polyurethanes (FSWPU) may result in excessively high crosslinking, which would make the FSWPUs unsuitable for further processing [24]. Moreover, added nanoparticles are likely to gather and cause an uneven distribution [25]. Accordingly, in this study, silicon compounds and fluorinated compounds with two functional groups, which can react with NCO, were imported into WPU to resolve these concerns. Such chemical combinations could not only avoid the aggregation or precipitation of nanoparticles commonly occurring in traditional mixing methods, but could also effectively increase the stability of the aqueous polyurethane lotion. Silicon compounds with two functional groups were added to allow the silicon compounds and fluorinated compounds to be introduced into the main segment, which enabled the silicon and fluorine elements to be distributed evenly in the polyurethane and achieve effectiveness by only adding a small amount of additives.

This study used degradable segments as PU soft segments to improve its performance for environmental protection, and imported silicon compounds and fluorinated compounds with two functional groups to produce FSWPU emulsions. The particle size of the FSWPU emulsions were then analyzed. After the emulsions were processed into a dried film, gel permeation chromatography (GPC), Fourier-transform infrared spectroscopy (FTIR), and energy-dispersive X-ray spectroscopy (EDS) were conducted to analyze the film’s molecular weight and basic properties. Subsequently, the thermal stability of FSWPU was measured by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA), and a tensile testing machine was employed to inspect the film’s mechanical properties before and after hydrolysis. Then, FSWPU emulsions were cast between the tiles and tested for hydrophilicity, hydrophobicity, and surface tension with a contact-angle measuring instrument. A tensile testing machine was used to analyze the sheer strength of the FSWPUs between the tiles, and an ASTM D3359 test was conducted to assess the adhesion of the FSWPUs to the tiles.

2. Materials and Methods (Experimental)

2.1. Materials

Methyl Ethyl Ketone (MEK), N-methyl-2-pyrrolidone (NMP) from Mallinckrodt, and solvents were dehydrated with 4-A molecular sieves for 2 days. Polycaprolactone diol (PCL, Mw = 530), Dimethylolpropionic acid (DMPA), [3-(2-Aminoethylamino) propyl] trimethoxysilane (AEAPTES), and
Triethylamine (TEA) were sourced from Aldrich, while Isophorone diisocyanate (IPDI) was obtained from Tokyo Chemical Industry Co. (Tokyo, Japan). Other materials, such as Ethylenediamine (EDA) and 2,2,3,3-Tetrafluoro-1,4-butanediol (TF), were purchased from TEDIA and Matrix Scientific, respectively.

2.2. Synthesis of FSWPUs

First, PCL, TF, and 5 mL of NMP were dispersed in a 500 mL three-necked flask for 30 min. Subsequently, IPDI was added, while nitrogen was introduced into the flask for 30 min and heated to 75 °C. The contents were then mixed by a mechanical mixer at 300 rpm for 2 h. DMPA was added for prepolymerization for a 2-h reaction time. To control the stickiness, 10 mL of butanone was also added into the mixture, and after the WPU prepolymer was cooled down to 50 °C, AEAPTES was added and TEA was utilized for a 20-minute neutralization. In order to disperse FSWPUs (Scheme 1), deionized (DI) water and ethylenediamine (EDA) were blended in and the solution was left to stand 1 h. The extracted FSWPUs solution was stored in a vacuum serum bottle for a 1-day defoaming before being dried in an oven on a Teflon plate. The recipe and symbols of the FSWPU films are shown in Table 1.

![Scheme 1](image_url)

Scheme 1. Formula for the fluorinated silicon-containing waterborne polyurethanes (FSWPUs).

Table 1. Formulas of the fluorinated silicon-containing waterborne polyurethanes (FSWPUs).

| Designation | PCL ^1 (moles) | IPDI ^2 (moles) | TF ^3 (mole) | DMPA ^4 (moles) | TEA ^5 (moles) | AEAPTM ^6 (moles) | EDA ^7 (moles) | Si ^8 (%) |
|-------------|----------------|-----------------|-------------|----------------|----------------|-------------------|---------------|----------|
| FSWPU-01    | 2.2            | 4               | 0.3         | 0.8            | 0.8            | 0                 | 0.7           | 0        |
| FSWPU-02    | 2.1            | 4               | 0.3         | 0.8            | 0.8            | 0.1               | 0.7           | 1        |
| FSWPU-03    | 2              | 4               | 0.3         | 0.8            | 0.8            | 0.2               | 0.7           | 2        |

^1 PCL: Polycaprolactone diol. ^2 IPDI: Isophorone diisocyanate. ^3 TF: 2,2,3,3-Tetrafluoro-1,4-butanediol. ^4 DMPA: Dimethylolpropionic acid. ^5 TEA: Triethylamine. ^6 AEAPTS: [3-(2-Aminoethylamino)propyl]trimethoxysilane. ^7 EDA: Ethylenediamine. ^8 Si: Silicon.
2.3. Dynamic Light Scattering (DLS)

The particle size of the FSWPU aqueous dispersion was measured with a Zetasizer (Model Nano-Zs90).

2.4. Gel Permeation Chromatograph (GPC)

The molecular weights of the FSWPUs, which are relative to polystyrene standards, were measured using the Waters Instruments Model ACQUITY APC with a refractive index detector (ACQUITY) and two ACQUITY APC XT Columns (200Å and 450Å) in series at 45 °C. The tetrahydrofuran, with a flow rate of 0.8 mL/min, was used as a carrier solvent.

2.5. Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared spectroscopy measurements of the FSWPUs were accomplished on a Digilab Variant FTS 1000 FTIR-ATR (Hopkinton, MA, USA). The spectra of the samples were recorded by averaging 16 scans on each curve of the FSWPUs in a range of 4000 to 650 cm\(^{-1}\) with a spectral resolution of 2 cm\(^{-1}\).

2.6. Energy-Dispersive X-ray Spectroscopy (EDS)

Elemental compositions of the FSWPUs were analyzed using energy-dispersive X-ray spectroscopy (Horiba, Model 7021-H) with conductive adhesive tape. In order to improve the image resolution, each sample was coated with a thin layer of platinum.

2.7. Thermogravimetric Analysis (TGA)

The heat weight loss curve of the FSWPUs was performed on a TA instruments Q-500 (New Castle, DE, USA). The samples were heated to 700 °C at a heating rate of 10 °C/min under a nitrogen environment.

2.8. Dynamic Mechanical Analysis (DMA)

The tan delta of the FSWPUs was measured using a DMA Q800 machine (TA Instruments) at 1 Hz with a 5 µm amplitude, and the data were collected at a heating rate of 3 °C/min over a temperature range of −50 to 50 °C. The peak temperature of the glass transition region was the dynamic glass transition temperature in the tan δ curve.

2.9. Stress-Strain Testing

The mechanical properties of the FSWPUs were measured on a universal testing machine (CY-6040A8) with ASTM D638, in which the dimensions of the film specimens were 45 mm × 8 mm × 0.2 mm.

2.10. Hydrolytic Stability

A hydrolytic stability test was performed by immersing the FSWPUs in deionized water at room temperature for 30 days. The weight loss rate was determined using the following equation:

\[
\text{Weight loss rate (\%)} = \frac{W_0 - W_t}{W_0} \times 100\%
\]

where \(W_0\) is the original weight before immersion and \(W_t\) is the sample weight after immersion in DI water for 30 days.
2.11. Contact Angle Measurements

The surface energies and hydrophobicity of the FSWPUs were calculated using deionized water and diiodomethane on a Sindatek instrument (Model 100SB). The reported contact angle (CA) was the average values for 3–4 water drops.

3. Results and Discussion

3.1. Emulsion and DLS

Figure 1 presents the appearance and dynamic light scattering (DLS) curve of the FSWPU emulsions. The FSWPU emulsions of three different formulas were all creamy white in appearance, which indicated that all three formulas developed in this study emulsified into WPU dispersions successfully. Even though the appearance of the FSWPU-01 emulsion was creamy white, it was detected, through visual observation, that its WPU dispersion was slightly transparent. This transparency phenomenon is mostly affected by the size of WPU micelles. Therefore, this study measured the particle size of the FSWPUs with DLS. The particle sizes of FSWPU-01, FSWPU-02, and FSWPU-03 were 75, 88, and 140 nm, respectively, which indicated that the FSWPU particle size increases with the increase in AEAPTES content. The variations in the WPU emulsions’ particle sizes may have resulted from two phenomena, one of which was changes in the molecular weight. The highly active –NH functional groups at both ends of AEAPTES increase the molecular weight of FSWPU when the AEAPTES content increases, which also increases the viscosity of FSWPU emulsions and reduces their dispersal ability. The other phenomenon was the changes in the ratio of the hydrophilic functional group. Si–OH functional groups generate crosslinking reactions during emulsification and transform into a Si–O–Si network structure. Hence, COO−, the hydrophilic functional group of 4-dimethylaminopyridine in WPUs, encircles the exterior of the micelles, whereas other nonhydrophilic functional groups are in the interior of the micelles. Accordingly, the content of hydrophobic segments within the micelles, which contributes to the growth in the particle size of WPU micelles, increases. These results all correspond to relevant research [26].

![Figure 1. Emulsion and dynamic light scattering (DLS) of (a) fluorinated silicon-containing waterborne polyurethanes-01 (FSWPU-01), (b) fluorinated silicon-containing waterborne polyurethanes-02 (FSWPU-02) and (c) fluorinated silicon-containing waterborne polyurethanes-03 (FSWPU-03).](image)

3.2. Gel Permeation Chromatograph (GPC)

GPC was employed to initially verify the results of the FSWPUs’ molecular weights. As depicted in Figure 2, all samples have a single peak, which indicates that no macromolecules resulted in residues...
during synthesis. The retention time of the peak, shown in Table 2, implies that the retention time decreased as AEAPTES content increased due to the increment of the molecular weight of the FSWPU. Results for number-average molecular weight (Mn), weight-average molecular weight (Mw), and the distribution value of molecular weight (Mw/Mn; polymer dispersity index (PDI)) are also compiled in Table 2. It is clear from this study that AEAPTES content increased, Mn first increased and then decreased, while Mw increased. The possible reason for this variation is that AEAPTES and isocyanate bonds are highly active, hence, both Mn and Mw increase when AEAPTES is initially imported into WPU. When the AEAPTES content increases, the strong activity between –NH and –NCO raises the PDI value, which also explains the increased particle size of FSWPU emulsions.

![Figure 2. GPC curves of the FSWPUs.](image)

Table 2. Gel permeation chromatography (GPC) result of FSWPUs.

| Sample    | Retention Time of the Peak (min) | Mn (x 10^4) | Mw (x 10^4) | Mw/Mn |
|-----------|----------------------------------|-------------|-------------|-------|
| FSWPU-01  | 20.7                             | 1.88        | 2.63        | 1.40  |
| FSWPU-02  | 20.2                             | 2.64        | 3.46        | 1.31  |
| FSWPU-03  | 20.0                             | 2.57        | 3.58        | 1.39  |

3.3. Basic Properties of FSWPUs

Figure 3a displays the FTIR spectrogram of the FSWPUs at a wavenumber range of 4000–650 cm⁻¹. In the spectra, PU-dominant functional groups were observed in five main peaks: –NH (3340 cm⁻¹), CH₂ symmetric and asymmetric stretching vibration peak (3000–2800 cm⁻¹), C = O (1720 cm⁻¹), –NH (amide II) stretching vibration peak (1520 cm⁻¹), and C–O stretching vibration peak (1032 cm⁻¹). The five PU-dominant functional peaks indicate that the typical reaction of PU (–NCO and –OH or –NH functional groups) was properly performed. Furthermore, no free NCO groups were observed in any samples within the wavenumber range of 2240–2275 cm⁻¹, indicating that the –NCO functional group in isophorone diisocyanate (IPDI) was thoroughly reacted. Specifically, the PU formula used in this study could stimulate a typical PU reaction with the –NCO, –OH, and –NH functional groups.
onset, with the corresponding temperatures of the maximum weight-loss rate, as shown in Table 4. The aforementioned phenomena resulted from the high thermal stability of organosilicon in the Si–O functional group, which was imported to the PU’s main chain [28], and the bond energy of Si–O is higher than that of Si–C [29]. Therefore, due to the good thermal stability of SiO2 and the highest silicon content in FSWPU-03, the ratio of residual amounts at 700 °C indicate that organosilicon enables the char yield of FSWPUs at 700 °C to enhance during this process. In addition, the residues generated at 700 °C were dehydrated and condensed into network structures (e.g., Si–O–Si) when AEAPTES increased [27]. The TGA curves of the FSWPUs are presented in Figure 4. Table 4 comprises data on the pyrolysis onset temperature (T_{onset}) which was calculated using three values: (1) Temperature corresponding to the point of tangency between the highest thermogravimetric rate and the initial horizontal segment on the TGA curve; (2) The temperature of the sample at a 10% weight loss (T10); and (3) The residual amounts at 700 °C. The T_{onset} increased from 295.1 °C (FSWPU-01) to 302.8 °C (FSWPU-03) when organosilicon was imported into the FSWPUs. This indicates that the thermal stability of FSWPUs was enhanced during this process. In addition, the residues generated at 700 °C indicate that organosilicon enables the char yield of FSWPUs at 700 °C to increase from 1.7 to 2.9%. Therefore, due to the good thermal stability of SiO2 and the highest silicon content in FSWPU-03, the ratio of residual volume increased from 1.7 to 2.9% under an environment temperature of 700 °C. The derivative thermogram (DTG) curve was subsequently calculated on the basis of the weight-loss curve together with the corresponding temperatures of the maximum weight-loss rate, as shown in Table 4. The temperature of the highest thermogravimetric rate increased with the introduction of organosilicon. The aforementioned phenomena resulted from the high thermal stability of organosilicon in the Si–O functional group, which was imported to the PU’s main chain [28], and the bond energy of Si–O is

![Figure 3. (a) FTIR spectra at the wavenumber range of 4000–650 cm⁻¹ and (b) energy-dispersive X-ray spectroscopy (EDS) results of the FSWPUs.](image)

Figure 3b presents the EDS elemental analysis of the FSWPUs, while the elemental content of the studied samples is listed in Table 3. Elements, such as C, N, and O exhibited irregular variations. It was observed that the F content decreased while the content of Si increased as AEAPTES increased in the main chain of WPU; the reason for this may be that more Si–OH functional groups in the main chain were dehydrated and condensed into network structures (e.g., Si–O–Si) when AEAPTES increased [27]. F chains, at this time, are further inhibited by the network structures and are less likely to be drawn to the film’s surface [21]; hence, the F content decreased.

| Sample Name | C (%) | N (%) | O (%) | F (%) | Si (%) |
|-------------|-------|-------|-------|-------|--------|
| FSWPU-01    | 48.35 | 38.14 | 11.33 | 2.15  | 0.03   |
| FSWPU-02    | 47.21 | 37.35 | 13.67 | 1.73  | 0.04   |
| FSWPU-03    | 48.52 | 38.11 | 12.28 | 1.03  | 0.06   |

3.4. Thermal Properties

The TGA curves of the FSWPUs are presented in Figure 4. Table 4 comprises data on the pyrolysis onset temperature (T_{onset}), which was calculated using three values: (1) Temperature corresponding to the point of tangency between the highest thermogravimetric rate and the initial horizontal segment on the TGA curve; (2) The temperature of the sample at a 10% weight loss (T10); and (3) The residual amounts at 700 °C. The T_{onset} increased from 295.1 °C (FSWPU-01) to 302.8 °C (FSWPU-03) when organosilicon was imported into the FSWPUs. This indicates that the thermal stability of FSWPUs was enhanced during this process. In addition, the residues generated at 700 °C indicate that organosilicon enables the char yield of FSWPUs at 700 °C to increase from 1.7 to 2.9%. Therefore, due to the good thermal stability of SiO2 and the highest silicon content in FSWPU-03, the ratio of residual volume increased from 1.7 to 2.9% under an environment temperature of 700 °C. The derivative thermogram (DTG) curve was subsequently calculated on the basis of the weight-loss curve together with the corresponding temperatures of the maximum weight-loss rate, as shown in Table 4. The temperature of the highest thermogravimetric rate increased with the introduction of organosilicon. The aforementioned phenomena resulted from the high thermal stability of organosilicon in the Si–O functional group, which was imported to the PU’s main chain [28], and the bond energy of Si–O is
higher than that of C–C [29]. Therefore, this study concluded that the thermal stability of PU increases when organosilicon is added into the main chain of PU.

### Table 4. Thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) of the FSWPUs.

| Designation | TGA          | DMA          |
|-------------|--------------|--------------|
|             | T onset (°C) | T max (°C)  | 700 °C Residue | T gd from Tan δ (°C) | Tan δ max |
| FSWPU-01    | 295.1        | 330.6        | 1.7%           | 31.71                  | 0.8845    |
| FSWPU-02    | 300.7        | 333.8        | 2.4%           | 35.59                  | 0.8397    |
| FSWPU-03    | 302.8        | 339.0        | 2.9%           | 44.26                  | 0.7058    |

3.5. Dynamic Mechanical Analysis (DMA)

Figure 5 displays the tan δ graph of the FSWPUs. Tan δ is the ratio of the storage to loss modulus ($E''/E'$), and the temperature corresponding to the maximum value of the tan δ (max tan δ) is defined as the dynamic glass transition temperature ($T_{gd}$). The $T_{gd}$, based on the tan δ curve, of FSWPU-01, FSWPU-02, and FSWPU-03 and max tan δ are shown in Table 4. The increment of AEAPTES raised the dynamic glass transition temperature of FSWPUs by 13 °C, which can be explained by the network structure developed between the Si–O segments of AEAPTES. Additionally, such a structure enables the content of AEAPTM to increase as the max tan δ decreases; more specifically, since tan δ is the ratio of loss to storage modulus, its decrease implies that the FSWPUs become less viscous and more flexible. This advanced flexibility is rather beneficial for preferable mechanical strength.
3.6. Tensile Properties, Shear Stress, and Hydrolytic Stability

Mechanical properties are crucial indicators for coating materials. Figure 6 displays the stress–strain curve of the FSWPUs while the data are compiled in Table 5. The ultimate tensile strengths of FSWPU-01, FSWPU-02, and FSWPU-03 were 2.0, 2.8, and 5.5 MPa, respectively, and the elongations at the breaks were 811%, 724%, and 484%, respectively. This indicates that, as AEAPTES content of FSWPUs increases, the ultimate tensile strength increases, whereas the elongation at the break decreases. The major cause of this result is the condensation reaction of the silanol functional group that forms a Si–O–Si crosslink network in the main chain of PU, which in turn restrains the movement of FSWPU macromolecular chains [30]. Furthermore, the calculated Young’s modulus of FSWPUs indicates that higher AEAPTES content results in stiffer FSWPUs. This result is similar to that of the DMA. An increase in the total area under the stress–strain curve also shows a considerable improvement in FSWPU tenacity.

![DMA Tan δ curves of the FSWPUs.](image)

**Figure 5.** DMA Tan δ curves of the FSWPUs.

![Stress–strain diagram](image)

**Figure 6.** Original and wet physical properties of the FSWPUs.
Table 5. Physical properties of the FSWPUS.

| Sample    | Tensile Strength (MPa) | Elongation at Break (%) | Young’s Modulus (MPa) | Shear Stress (MPa) |
|-----------|------------------------|-------------------------|-----------------------|-------------------|
|           | Original \(^a\) | Wet \(^b\)   | Original \(^a\) | Wet \(^b\)   |                      |                      |
| FSWPU-01  | 2.0                    | 1.1                     | 811                   | 551               | 0.03                | 0.78                |
| FSWPU-02  | 2.8                    | 2.3                     | 724                   | 706               | 0.04                | 1.16                |
| FSWPU-03  | 5.5                    | 5.1                     | 484                   | 495               | 0.11                | 1.41                |

\(^a\) Physical properties before immersion in deionized water. \(^b\) Physical properties after immersion in DI water for 30 days at room temperature.

To understand the hydrolysis stability of the FSWPUs, each sample was immersed in deionized (DI) water for 30 days so as to conduct a tensile test. The stress–strain diagram is depicted in Figure 6, and relevant data are presented in Table 5. The tensile strength of FSWPU-01 decreased significantly after a 30-d hydrolysis, whereas those of FSWPU-02 and FSWPU-03 only decreased slightly. Such results are associated with the different degrees of hydrolysis in the three samples. The calculated weight-loss rate of each sample is displayed in Figure 7. When AEAPTES was added, the weight-loss rate of FSWPU-01 hydrolysis decreased gradually from 40.6 to 9.3% as AEAPTES increased. This is because of the Si–O–Si crosslink network within WPU developed by AEAPTES, which effectively prevents water molecules from entering the interior of PU; in other words, AEAPTES successfully improved the hydrolytic stability of FSWPUs. At the same time, the weight loss ratio of FSWPU-01 after hydrolysis reached 40.6%, thus, the FSWPU-01 film was defective when the tensile test was carried out again, resulting in a significant reduction in fracture strain.

3.7. Adhesion Test

To assess the adhesion of FSWPUs to tiles, FSWPUs were cast between tiles, and a tensile testing machine, as depicted in Figure 8, was employed to evaluate their shear strength. The test results are organized as shown in Table 5. The shear strength of FSWPU-01 without AEAPTES was 0.78 MPa; while those of FSWPU-02 and FSWPU-03, with more AEAPTES, gradually increased and reached a maximum of 1.4 MPa. Subsequently, the ASTM D3359 test method was performed to evaluate the adhesion of the FSWPUs on tiles; the adhesion coefficient between the FSWPUs and the tiles increased from 3B (the FSWPUs are peeled off by 5% to 10% at intersections of cuts) to 4B (the FSWPUs are peeled...
off by less than 5% at intersections of cuts) when AEAPTES were imported into WPU. This indicates that AEAPTES are beneficial for enhancing adhesion to tiles.

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3.8. Surface Contact Angle

The surface contact angles of the FSWPU-cast tiles are illustrated in Figure 9. The contact angle of water on the non-cast tile surface, which is a type of hydrophilic surface that tends to gather dust, was only 41.5 ± 1.8°. The water contact angle on the cast tile without AEAPTES (FSWPUs-01) was 80.4 ± 2.6°. This hydrophilicity is likely influenced by the dimethylol propionic acid (DMPA) hydrophilic segments. Relevant research on the water contact angle measurement of polymers formed on the PCL substrates (Mw = 530) has been performed previously. For instance, Król et al. [31] demonstrated that the surface free energy of PU synthesized from methylene diphenyl diisocyanate, PCL, and 1,4-butanediol was 42.29 mJ/m², whereas Wang [32] observed that the water contact angle of the PCLF synthesized using fumaryl chloride with PCL was only 51°. Accordingly, the hydrophilicity of FSWPU-01 was influenced by DMPA and the degradable segments of PCL. However, the water contact angle gradually increased to 92.1 ± 3.2° because Si can improve the hydrophobicity of polymers when AEAPTES are imported with WPU and cast on tiles (FSWPUs-02, FSWPU-03) [33]. In addition, methylene iodide was used to examine the original tiles and the cast tiles, and the surface contact angle for methylene iodide decreased from 48.5 ± 0.3° to 44.2 ± 0.6° as the AEAPTES content increased. The Owens–Wendt method was performed to calculate the contact angles of the two types of fluids and to determine the surface free energy of the FSWPUs as follows:

\[ \gamma_L (1 + \cos \theta) = 2 \sqrt{\gamma_S \gamma_L^d} + 2 \sqrt{\gamma_S \gamma_L^p} \]  

(2)

where \( \gamma_S \) is the surface free energies of the solid and \( \gamma_L \) is the surface free energies of the pure liquid. The superscripts d and p represent the dispersive and nondispersive contributions to total surface energy, respectively. In this study, water (\( \gamma_L = 72.8 \text{ mJ/m}^2 \), \( \gamma_L^d = 21.8 \text{ mJ/m}^2 \), \( \gamma_L^p = 51 \text{ mJ/m}^2 \)) and diiodomethane (\( \gamma_L = 50.8 \text{ mJ/m}^2 \), \( \gamma_L^d = 48.5 \text{ mJ/m}^2 \), \( \gamma_L^p = 2.3 \text{ mJ/m}^2 \)) [34,35] were used. Subsequently, the surface free energy of the FSWPUs was calculated by employing the following equation:

\[ \gamma_S = \gamma_S^d + \gamma_S^p \]  

(3)
The results in Table 6 reveal that the surface free energy of the original tile was 56.42, while that of tiles cast with FSWPU-01, FSWPU-02, and FSWPU-03 were 37.67, 37.61, and 37.57 mJ/m², respectively. The results demonstrate that importing AEAPTES reduces the wettability of FSWPUs and provide relevant product information for applications in the construction industry.

### Table 6. Contact angle and surface tension of FSWPUs.

| Sample Name | Contact Angle (°) | Surface Free Energy (mJ/m²) |
|-------------|-------------------|-----------------------------|
|             | Water             | CH₂I₂                       | γₛ     | γₛ     | γₛ     |
| Control     | 41.5 ± 1.8        | 48.5 ± 0.3                  | 23.11   | 33.31   | 56.42   |
| FSWPU-01    | 80.4 ± 2.6        | 45.4 ± 0.6                  | 32.82   | 4.85    | 37.67   |
| FSWPU-02    | 84.3 ± 1.3        | 44.3 ± 0.4                  | 34.50   | 3.11    | 37.61   |
| FSWPU-03    | 92.1 ± 3.2        | 44.2 ± 0.6                  | 36.66   | 0.91    | 37.57   |

Comparisons between the findings of this study regarding the contact angles to water and the maximum stress and fracture strain of silicone group and fluorine group polyurethane with those of previous studies on PCL-based polyurethane are given in Table 7. The results show that the stress of PCL, with the lesser degree of polymerization (Mn = 530) used in this study, successfully increased to a similar level to that of polyurethane that utilizes PCL-2000 (Mn = 2000) as a soft segment. As for polyurethane containing PCL-2000 as the base, mixed with carbon nanotubes (CNTs), despite the level that the maximum stress could increase to, the higher content of CNTs would cause defects in the polyurethane and, thus, reduce the level of stress. Likewise, for fluorinated polyurethane mixed with SiO₂ nanoparticles, even though the results showed good mechanical properties and hydrophobicity, several problems occurred, such as the aggregation of nanoparticles or poor shelf life, etc. By means of chemical bonding, a small amount of the elements Si and F were combined into the polyurethane in this study, which not only extended the shelf life of the aqueous polyurethane lotion but also achieved similar effects.
Table 7. Comparison of the mechanical properties and water contact angles of FSWPUs with previously reported PCL-based polyurethanes, or those containing silicon element polyurethane with (or without) fluorinated segments.

| Sample Name   | Soft Segment + Other Auxiliary | Tensile Strength (MPa) | Elongation at Break (%) | Water Contact Angle (°) Ref. |
|---------------|--------------------------------|------------------------|-------------------------|-----------------------------|
| FSWPU-01      | PCL530                         | 2.0                    | 810                     | 41.5 ± 1.8                  | This study |
| FSWPU-03      | PCL530                         | 5.5                    | 484                     | 92.1 ± 3.2                  | This study |
| FPU-1         | PCL2000                        | 5.5 ± 0.2              | 1197                    | –                           | [36]        |
| FPU-3         | PCL2000                        | 7.9 ± 0.4              | 735                     | –                           | [36]        |
| B2            | PCL2000                        | 8.64                   | 715                     | –                           | [37]        |
| C1            | PCL2000                        | 6.82                   | 638                     | –                           | [37]        |
| WBPU-CNT0.5   | PCL2000+ MWCNT a               | ≈12                    | ≈160                    | –                           | [38]        |
| WBPU-CNT1.0   | PCL2000+ MWCNT                 | ≈4                     | ≈260                    | –                           | [38]        |
| FPU-3         | PTMG2000 + SiO₂ NPs c          | 38                     | ≈920                    | 150.6                       | [22]        |
| SiO₂/FWPU-0   | PBA2000 + SiO₂ NPs d           | –                      | –                       | 61.29                       | [23]        |
| SiO₂/FWPU-20  | PBA2000 + SiO₂ NPs             | –                      | –                       | 101.26                      | [23]        |

a as multi-wall carbon nanotube. b as Polytetramethylene glycol (Mn = 2000). c as SiO₂ nanoparticles. d as 1,4-butylene adipate glycol (Mn = 2000).

4. Conclusions

This study successfully synthesized FSWPUs from degradable PCL diol segments, TF, and AEAPTES. The results of the particle size analysis and GPC implies that the addition of AEAPTES increased the molecular weight of FSWPUs and the particle size of FSWPU micelles. The FTIR spectrogram revealed that no stretching vibration peak of –NCO was observed in any samples, which demonstrates that the IPDI in each sample was thoroughly reacted. The TGA results suggest that the organosilicon in AEAPTES enables the pyrolysis onset temperature and the maximum pyrolysis temperature to increase by 7% and 9%, respectively. Relevant data from the DMA and tensile tests demonstrate that, when more AEAPTES was imported into the FSWPUs, the Tgd increased but the tan δmax decreased on account of the formation of a network structure between the Si–O segments, which also shows that the decrease of δmax increases the flexibility of the FSWPU film, thereby enhancing its tensile strength. Additionally, after a 30-day hydrolysis, the FSWPU film decreased considerably in weight after the addition of AEAPTES, and the film’s mechanical properties were maintained at about the same level as they were before hydrolysis. Finally, FSWPUs were cast between tiles, and the results indicate that FSWPUs were not only effective in reducing the surface energy of the tiles but also exhibited excellent adhesion.

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