

Article

Architectural Sustainability and Efficiency of Enhanced Waterproof Coating from Utilization of Waterborne Poly (Siloxane-Imide-Urethane) Copolymers on Roof Surfaces

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Received: 4 May 2020; Accepted: 26 May 2020; Published: 28 May 2020



Abstract: According to Taiwan's Ministry of the Interior, from 2017 to 2019, more than 12% of house-purchase disputes were due to water leakage caused by frequent tropical rains, which have long troubled engineers. The thermal stability resistance, water resistance, and ultraviolet resistance of existing polyurethane formulations have been limited by environmental aging. Thus, the lifespan of commercial PU-coated resins (typical PU) for the waterproofing of roof surfaces is merely two to three years. Accordingly, this study proposed the introduction of siloxane and imide groups to produce waterborne poly(urethane-siloxane-imide) (Si-imide-WPU) copolymers to improve the resistance of environmental aging in typical PU. The waterproof coating resin made of Si-imide-WPU copolymers was environmentally friendly, safe to use, and free of organic solvents. The results showed that the optimal Si-imide-WPU-2 sample in the study made improvements on the defects of polyurethane (PU) including its thermal properties, mechanical properties, environmental resistance, and lifespan which could be extended up to 5.4 years. Consequently, the studied Si-imide-WPU copolymers could reduce material waste while enhancing the sustainability and efficiency of the architecture.

Keywords: waterproofing; sustainable building materials; environmental aging; siloxane; polyurethane; imide; copolymer

1. Introduction

Reinforced concrete (RC) is a composite material that consists of reinforced steel and concrete. RC's higher levels of rigidity allow a building to resist intense swaying during earthquakes. Furthermore, its greater sound insulation and waterproofing function can provide extra comfort in everyday living. Steel-reinforced concrete (SRC), which combines a steel skeleton and reinforced concrete, is used in construction to make the covers of buildings strong in both tension and compression. RC and SRC are currently the predominant building materials in Asia [1,2]. However, due to the tropical and rainy geographical nature of Southeast Asia, the waterproofing of building exteriors is greatly needed. According to statistics provided by Taiwan's Ministry of the Interior [3], from 2017 to 2019 the major disputes about house purchases were due to water leakage. Frequent repairs may impact the occupants' quality of life and reduce a building's lifespan. There are several waterproofing areas of work for a building structure, including its main body, exterior, rooftop surface, caulking, and others. Due to the continuous thermal expansion and contraction of materials on the rooftop caused by solar radiation, the rooftop surface becomes the most critical area for waterproofing. The waterproofing resins developed to date include the likes of polyurethane (PU), rubberized asphalt, polyurea, acrylic acid polymers, and polymerized siloxane silicone [4]. The most frequently used resin for exterior

waterproofing in Taiwan is polyurethane (PU) owing to its ease of use. There are several advantages in the application of PU in construction, including the reduction of seam grinning and embrittlement, toughness enhancement, applicability under ambient temperatures, the convenience of filling holes, low cost, and use of different colors. Nonetheless, problems caused by environmental aging, such as hydrolysis [5], thermal aging [6,7], and ultraviolet (UV) aging [8], affect the performance of the PU and ultimately lead to disputes between builders and consumers.

In the development of various building materials today, it is a trend to replace petrochemicals with natural materials [9] or to develop green building materials using recycled materials [10]. However, it is still necessary to use some petrochemicals for building repair, protection, and reinforcement due to their ability to improve the lifespan and safety of a building (for example, PU can meet the anti-seepage and anti-wear needs of flood discharge infrastructure) [11]. Given that existing waterproofing works have not been able to completely solve leakage problems due to the aging of resins, a sustainable building still faces such issues. Environmental aging of PU typically occurs after two to three years in Taiwan, especially for the rooftops of older houses where permeability exists. Hence, how to combat the environmental aging of PU is a topic of concern. The main cause for environmental aging in typical PU is mainly caused by the insufficient resistance of ether type or ester type soft segment waterproofing to hydrolysis and UV, as well as insufficient thermal stability of the hard segment urethane group. The added antioxidant or ultraviolet absorber in PU gradually dissipates after two to three years, resulting in loss of function.

Several studies have shown that the insufficient thermal stability of typical PU is due to dissipation of the hard segment at high heat (typically 70–90°C) whereas its glass transition temperature threshold is only 70°C, and its softening temperature threshold is below 70°C [6,7,12,13]. The poor mechanism of PU for combating high heat, including both heat resistance and antioxidation, limits its tolerance. The thermal instability of PU in environmental decay can be attributed to the urethane group, while the light instability and hydrolysis are related to the ester or ether polyol soft segment [8,13–15]. Several studies have introduced siloxane groups [13–15] and imide groups [7,16–22] into the PU structure to improve its thermal stability and mechanism. In addition to thermal stability, other characteristics of siloxane-containing polyurethane include hydrolysis resistance, anti-UV properties, antioxidation properties, friction resistance, flexibility, and flame retardancy, as well as acid-base and solvent resistance [23–26]. Therefore, polysiloxane (silicon polymer) has been used for electrical cables [16] and the waterproofing of window seams. A number of studies [18,27,28] have proposed the introduction of imide and siloxane groups into the PU structure to improve its thermal stability, mechanical stability, and water resistance.

The aforementioned literature related to PU-imide copolymers can be summarized as follows: Firstly, the introduced amide imide groups of PU hard segment elevated its initial degradation temperature up to 285 °C. Secondly, the increased amount of tensile strength related to the content of amide imide of PU copolymer reached 44 MPa. Thirdly, the elongation at break increased up to 1120% due to the amide imide groups. Fourthly, polysiloxane was introduced into the PU soft segment to improve the low temperature resistance. Moreover, the glass transition temperature, performed as an index of low temperature resistance, appeared at about –125 °C in differential scanning calorimeter (DSC) analysis. Lastly, not only surface properties, but also thermal stability and resistance to acid and alkali were improved due to the low surface tension of the silicone [29,30]. While both imide and siloxane groups have been introduced into PU backbones for improving the thermal stability, the first stage of thermal degradation was dominated by the hard-segment structure degradation while the second stage was about the degradation of the soft segment [31]. Thus, incorporating imide and siloxane groups into PU raises the thermal mechanical stability. However, the silicon-containing polyurethane-imide copolymers were produced by the solvent method or utilized the poly-blend method, and discussion on their environmental performance is lacking.

Due to its softness, abrasion resistance, resistance to hydrolysis, hydrophobic properties, heat-resistance, UV-resistance, and weatherability, polysiloxane, such as polydimethylsiloxane (PDMS),

is an excellent additive to enhance the soft segment of PU resin for better waterproofing and UV-resistance; moreover, its aromatic imide structure is hard segment and highly heat-resistant, which benefit its thermal and mechanical stability. Accordingly, both aromatic imide and siloxane groups were introduced into the hard and soft segment of the PU structures in this study to develop waterborne poly(urethane-siloxane-imide) (Si-imide-WPU) copolymers with environmental aging resistance that would be applicable for leak-proof resin roof coatings. Additionally, this study adopted the polymerization synthesis of anions to produce waterborne Si-imide-WPU copolymers that were environmentally friendly, free of solvents, and safe to use. This study analyzed the difference between copolymer resins and typical PU resins in water resistance (water pressure and permeability), thermal stability, and tensile strength. Ultimately, it was found that sustainable architecture efficiency could be achieved using the water-based Si-imide-WPU resin on rooftops, resulting in a reduced need for repeated waterproofing, as well as fewer leakage disputes and material waste.

2. Experiment

2.1. Materials

The typical PU (control sample) used in this study was a commercial PU-coated resin (Champward Chemical Ind. Co.) used for roof waterproofing. The waterborne poly(urethane-siloxane-imide) (Si-imide-WPU) copolymers consisted of hard and soft segments. The soft segments of the copolymers utilized OH-terminated polydimethylsiloxane (PDMS, Mw = 1818, Shin-Etsu Co.) while the hard segments of the copolymers were formed by bis(cyclohexy-diisocyanate) (H12MDI, Mw = 262.3, Covestro Co.), ethylenediamine (EA, TCI Co.), and pyromellitic dianhydride (PMDA, Mw = 218, TCI Co.). Dimethylpropionic acid (DMPA Mw = 134, TCI Co.) was used as the anionic center of the Si-imide-WPU while triethylamine (TEA, Mw = 115, TCI Co.) was used as a neutralizer in this study.

2.2. Synthesis of Waterborne Poly(Urethane-Siloxane-Imide) (Si-Imide-WPU) Copolymers

The anion type Si-imide-WPU copolymers in this study were prepared by a prepolymer method for a regular structure of hard and soft segments. The equipment used for synthesis included a sealed 3L four-mouth reaction flask, a high-speed mixer, a heater, and a quantitative pump. As per the stoichiometry shown in Table 1, H12MDI, PDMS, and PMDA were initially added to the reactor at about 120 °C for three hours to obtain NCO-terminated prepolymers for the prepolymerization reaction. Then, DMPA was placed in the reactor for one hour to form anion-type NCO-terminated poly(urethane-siloxane-imide) prepolymers. Subsequently, the reaction was cooled to 45 °C and small amounts of acetone solvent and triethylamine (TEA) were added and stirred for one hour to achieve neutralization. After neutralization, deionized water was added to the reaction through a quantitative pump at 35 °C within six minutes. Then, a 900–1000 rpm stirrer was used to stir the reaction for about 40 min to force emulsification and dispersion. Finally, EA and H₂O were added to carry out the chain extension reaction, which lasted for approximately one hour. After completion of the reaction, the acetone and TEA in the emulsion were removed and replaced by vacuum distillation while the emulsification stability test was performed. The complete process of the reaction is illustrated in Figure 1.

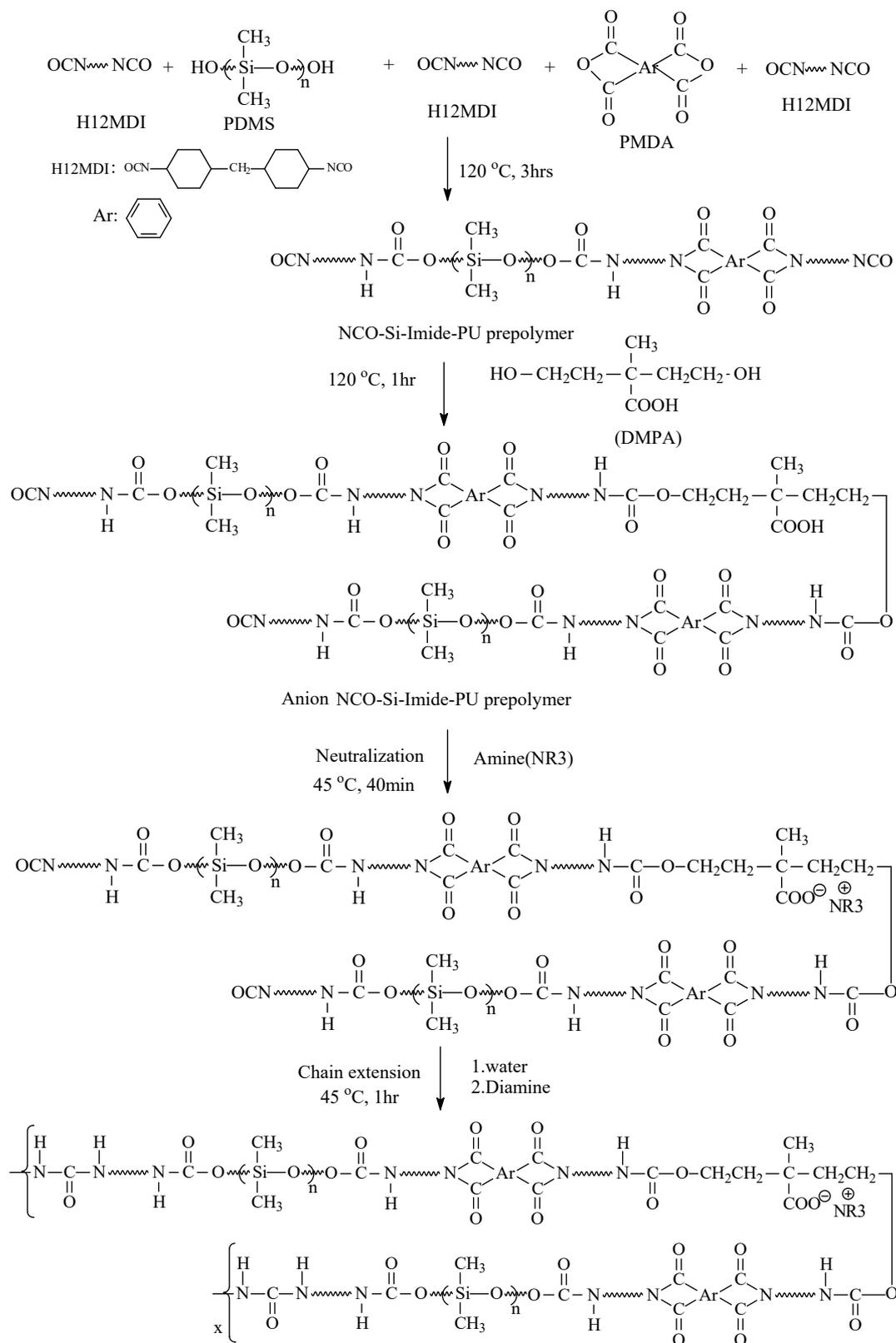


Figure 1. Reaction process for poly(urethane-siloxane-imide) (Si-imide-WPU) copolymers.

Likewise, Table 1 lists the respective components of the monomers of the Si-imide-WPU copolymers. The emulsion stabilization of the Si-imide WPU copolymers was performed via a centrifuge at 3000 rpm for 15 min, as shown in Figure 2.

Table 1. Monomer composition of the synthesis of Si-imide-WPU copolymers.

Code	Monomer Composition	Equivalent Ratio ¹	PDMS (wt%)	PMDA (wt%)	DMPA (wt%)	Hsc ² (wt%)
Si-imide-WPU-1	H12MDI/PDMS-PMDA/DMPA/EA	3/1.5–0.5/0.5/0.5	73.3	2.9	1.8	26.70
Si-imide-WPU-2	H12MDI/PDMS-PMDA/DMPA/EA	3/1.0–1.0/0.5/0.5	62.3	7.5	2.3	37.70
Si-imide-WPU-3	H12MDI/PDMS-PMDA/DMPA/EA	3/0.5–1.5/0.5/0.5	42.9	15.4	3.2	57.10
Si-imide-WPU-4	H12MDI/PDMS-PMDA/DMPA/EA	2/0.75–0.25/0.5/0.5	66.8	2.7	2.1	33.20
Si-imide-WPU-5	H12MDI/PDMS-PMDA/DMPA/EA	2/0.5–0.5-1/0.25/0.5	55.4	6.7	4.1	44.60
Si-imide-WPU-6	H12MDI/PDMS-PMDA/DMPA/EA	2/0.25–0.75/0.25/0.5	36.7	13.2	5.4	63.30

Notes: ¹ Equivalent ratio = synthetic equivalent ratio; ² Hsc = hard segmented content.

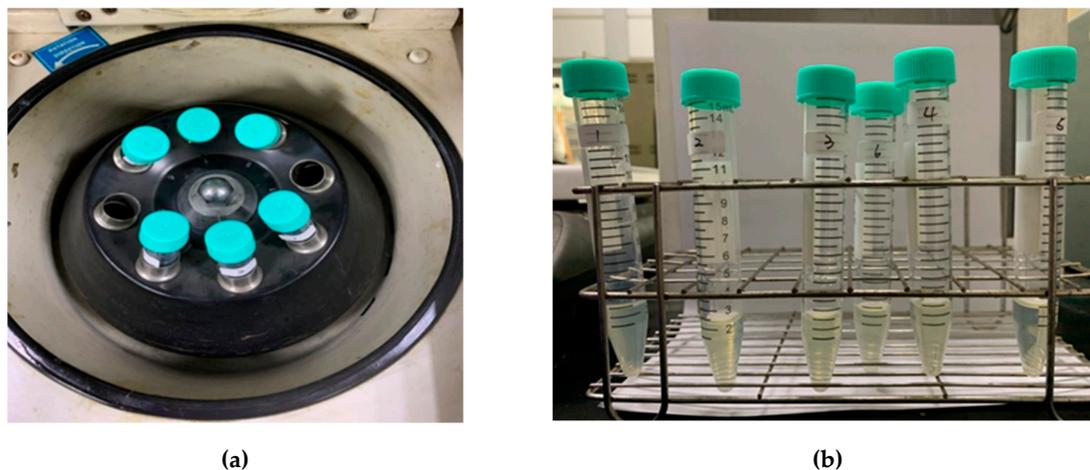


Figure 2. Testing the emulsion stability. (a) Test tubes for centrifuge testing; (b) No precipitation was obtained in the samples after the emulsion stability testing.

For each sample, the copolymer emulsion was considered stable if no sedimentation was detached from the centrifugal test. The emulsion stability of the copolymer was effective for up to six months. After the sample passed the emulsification precipitation test, the FTIR (Fourier-transform infrared spectroscopy), colloidal particle size, molecular weight, and other physical properties were measured.

2.3. Measurements

2.3.1. Emulsion Particle Size and Stability

A Horiba LB-550 laser (JP: Horiba Ltd., Kyoto, Japan) particle size analyzer (1–6000 nm) was used to determine the emulsion particle size and the particle size distribution of the Si-imide-WPU dispersion. The samples were centrifuged at 3000 rpm for 15 min by a centrifuge (BaSO-M500S) to investigate the emulsion stability of Si-imide-WPU.

2.3.2. Fourier-Transform Infrared Spectroscopy (FTIR)

The Si-imide-WPU copolymers and typical PU were coated onto a film and their infrared spectroscopy was recorded by a Perkin Elmer Spectrum One FT-IR Spectrometer (PerkinElmer Inc., Waltham, MA, USA) with a resolution of 4 cm⁻¹ and a scanning range of 500–4000 cm⁻¹.

2.3.3. Weight-Average Molecular Weight

The weight-average molecular weights of the Si-imide-WPU copolymers and typical PU were measured by gel permeation chromatography (GPC) using a Viscotek GPC max VE-2001 (Malvern Panalytical Ltd., Malvern, UK) with dimethylformamide (DMF) as a solvent and polystyrene as a standard control sample.

2.3.4. Thermal Properties

The characteristics of the thermal properties in this study included the phase transition temperature and thermal degradation of the Si-imide-WPU copolymers and typical PU. The phase transition temperature was related to the glass transition temperature (T_g) and the melting temperature (T_m), which were determined by a Perkin–Elmer Pyris-1 (PerkinElmer Inc., Waltham, MA, USA) differential scanning calorimeter (DSC). All DSC scans were performed in the temperature range from -150 to 250 °C at a heating rate of 20 °C/min under nitrogen with a flow rate of 100 mL/min. The thermal degradation characteristics of the Si-imide-WPU copolymers and typical PU were determined using a Perkin Elmer Pyris-1 (PerkinElmer Inc., Waltham, MA, USA) TGA instrument. The test was carried out under a heating rate of 20 °C/min using nitrogen with a flow rate of 100 mL/min, and each sample weighed about 5 mg. The thermal gravity (TG) and differential thermal gravity (DTG) curves for all samples were obtained in the temperature range of 25 to 700 °C.

2.3.5. Tensile Strength

MTS Qtest 5, a tensile machine, (MTS Systems Corp, Eden Prairie, MN, USA), was adopted to test the tensile strength of the Si-imide-WPU copolymers and typical PU under the CNS 6988 standard. The tests were processed at 25 °C with a relative humidity of $60 \pm 5\%$.

2.3.6. Environmental Resistance

The application of the polyurethane (PU) waterproof coating on roof surfaces in an external environment focused on UV resistance, water resistance, and abrasion resistance. For the UV-resistance test, Si-imide-WPU copolymers and typical PU samples sized 5 cm \times 1 cm \times 0.25 mm were placed in Pin Tai UVL-A08, a UV weathering testing machine (Pin Tai Technology Co., Ltd., Tao-Yuan, Taiwan), under UVA-340 nm and a temperature of 50 °C for 24 h; subsequently, the samples went through the same test of measurement of tensile strength. Therefore, the difference in intensity between the samples before and after UV irradiation could be evaluated. The water resistance test included a moisture permeability and hydrostatic pressure test. The moisture permeability (all samples were a thickness of 0.25 mm) was tested using the JIS L1902 B1 method in a programmable temperature and humidity chamber (Pin Tai THP-S225). The hydrostatic pressure test was performed using a Cometech QC-317F hydrostatic head tester (Pin Tai Technology Co., Ltd. Tao-Yuan, Taiwan) and the test method applied was JIS L1902 B. The abrasion resistance of all samples was tested by the CNS 10757 method.

3. Results and Discussion

3.1. FTIR Spectrum

As shown in Figure 3, the characteristic absorption of the urethane group in typical PU (control sample), reacted by isocyanate and hydroxyl, exhibited at about 1730 cm^{-1} . The characteristic groups of the Si-imide-WPU copolymers in the synthetic reaction included urethane, imide, and urea groups. Figure 3 shows their respective FTIR spectrums. The urethane group (C = O stretching vibrations) appeared at about 1730 cm^{-1} and was formed by the reactions of DMPA, H12MDI, and PDMS. The imide group (C = O stretching vibrations) presented at about 1780 cm^{-1} and resulted from the reactions of H12MDI and PMDA. The urea group (C = O stretching vibrations) appeared at 1650 cm^{-1} and was formed by the reactions of H12MDI and EA.

It is noteworthy that the characteristic absorption on the isocyanate group of H12MDI could be displayed at around 2350 cm^{-1} , but the absorption peak of the isocyanate disappeared in the FTIR spectra. The results indicated that the H12MDI had almost completely reacted with the DMPA, PDMS, PMDA, and EA to form Si-imide-WPU copolymers. Furthermore, the characteristic absorption of the PDMS soft segments could be displayed at about 1100 cm^{-1} (-Si-O- stretching vibrations) [32,33]. Other characteristic absorptions of groups in the Si-imide-WPU copolymer could be displayed at 3500 – 3200 cm^{-1} (-NH stretching vibrations), 2940 – 2920 cm^{-1} and 2860 – 2850 cm^{-1} (-CH₂ stretching

vibrations), 1350–1360 cm^{-1} ($\alpha\text{-CH}_3$ bending vibrations), 1400–1450 cm^{-1} ($\alpha\text{-CH}_2$ bending vibrations), 1260 cm^{-1} (-CH_3 stretching absorptions), and 600–700 cm^{-1} (C-H deformation).

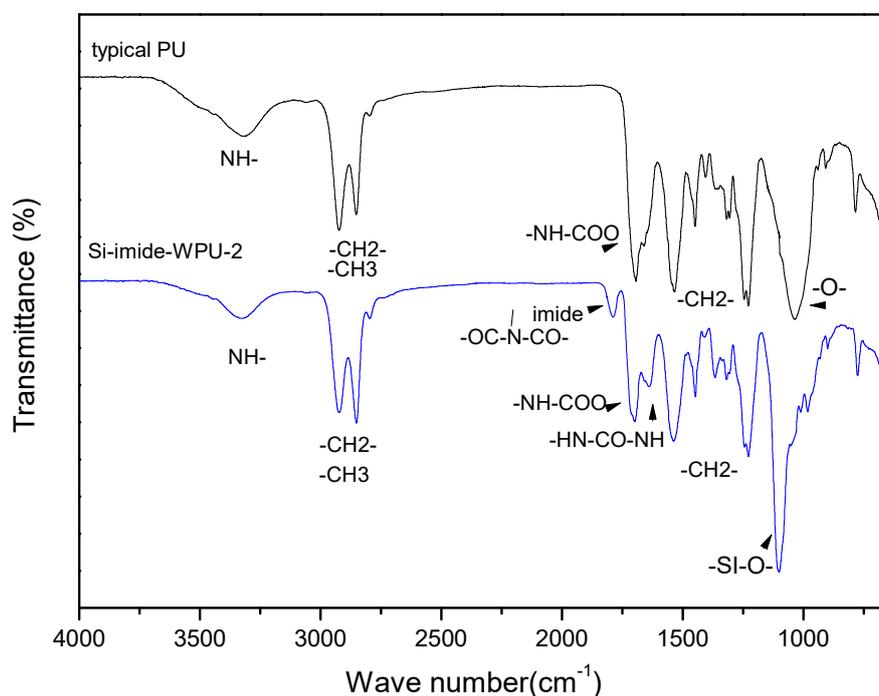


Figure 3. FTIR spectrums of the Si-imide-WPU-2 copolymer and typical PU.

3.2. Emulsion Particle Size and Weight-Average Molecular Weight

Laser particle size analysis was utilized in this study to determine the emulsion particle size of the Si-imide-WPU copolymers and typical PU. Figure 4 indicates that the emulsion particle size distribution of the Si-imide-WPU-3 was between 75 and 700 nm. The distribution and size of the emulsion particles were related to the molecular weight distribution of the copolymer and the uniformity of emulsification in the process of synthesis. The emulsion particle size generally increased when the molecular weight increased but decreased when the monomer content of the anion center (DMPA) of the emulsion polymer increased.

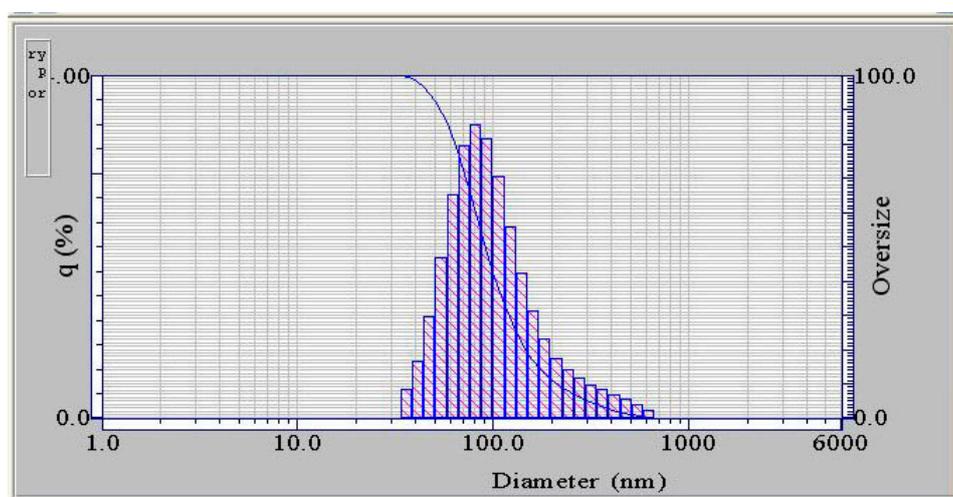


Figure 4. Distribution of the Si-imide-WPU-3 emulsion particle size.

The average particle size of the Si-imide-WPU copolymers emulsion, shown in Table 2, ranged from 100 nm to 140 nm. The average size of the Si-imide-WPU copolymers increased as the molecular weight increased but did not decrease when the monomer content of the anion center increased, which may have been due to the molecular weight having a smaller effect than the DMPA content. On the other hand, the average particle size of the Si-imide-WPU copolymer emulsion increased with the increment in molecular weight, but it did not decrease with the increasing monomer content of the anion center. This may have been due to the molecular weight having a greater effect than the DMPA content.

Table 2. Particle average size of emulsion, intrinsic viscosity, and weight-average molecular weight (Mw) of the Si-imide-WPU copolymers.

Code	Average Size (nm)	Mw $\times 10^3$ (g/mol)
Si-imide-WPU-1	102.5	77.7
Si-imide-WPU-2	127.6	82.7
Si-imide-WPU-3	132.2	86.0
Si-imide-WPU-4	103.7	74.6
Si-imide-WPU-5	109.1	77.0
Si-imide-WPU-6	120.3	84.4
Typical PU ¹	119.5	72.1

Notes: ¹ Typical PU (control sample) = commercial PU-coated resin.

The physical properties of the polymer materials were not only related to molecular weight, but were also influenced by its composition. The average molecular weight, which was measured by GPC, of Si-imide-WPU copolymers was proximate to that of typical PU. As shown in Table 2, the average molecular weight of Si-imide-WPU copolymers was approximately between 77×10^3 and 86×10^3 g/mol, while the weight of typical PU was 72.1×10^3 g/mol. This result shows that the physical properties of typical PU were improved by the introduction of aromatic acetylene and silicone in the molecular segment. Furthermore, in the application of polymer materials, an appropriate molecular weight can enhance not only physical properties, but also processing properties.

3.3. Thermal Properties

3.3.1. Glass transition Temperature

Polyurethane is a two-phase segmented copolymer consisting of a soft segment and a hard segment [7,34]. Therefore, if both phases crystallize, the DSC thermograms may display four transition temperature regions, including the glass transition temperatures of the hard and soft segments (T_{gh} and T_{gs}) and the melting temperatures of the hard and soft segments. The regions of the phase transition temperatures for the PU copolymers were affected by the length and content of the soft and hard segments. In actual use, the T_{gs} and T_{gh} were related to the application of low temperature resistance and softening temperature, respectively.

The DSC curves for the Si-imide-WPU copolymers shown in Figure 5 indicated two phase transition temperature regions. The first region of the phase transition temperature, which was related to the glass transition temperature of PDMS soft segment (T_{gs}), appeared narrowly between -121 and -125 °C. The T_{gs} did not increase significantly when the content of the hard segment increased, hence exhibiting a high degree of phase separation in the copolymers. The second phase transition temperature region of the Si-imide-WPU copolymers appeared between 151 to 192 °C. This was associated with the glass transition temperature of the hard segment (T_{gh}), which consisted of PMDA, DMPA, EA, and H12MDI. The T_{gs} and T_{gh} of Si-imide-WPU copolymers herein are consistent with those of PU-imide copolymer and siloxane-containing PU copolymer shown in previous studies [7,34]. However, the Si-imide-WPU copolymer has a better phase transition temperature, which is caused by

the high degree of phase separation due to the high level of incompatibility between the siloxane and imide group.

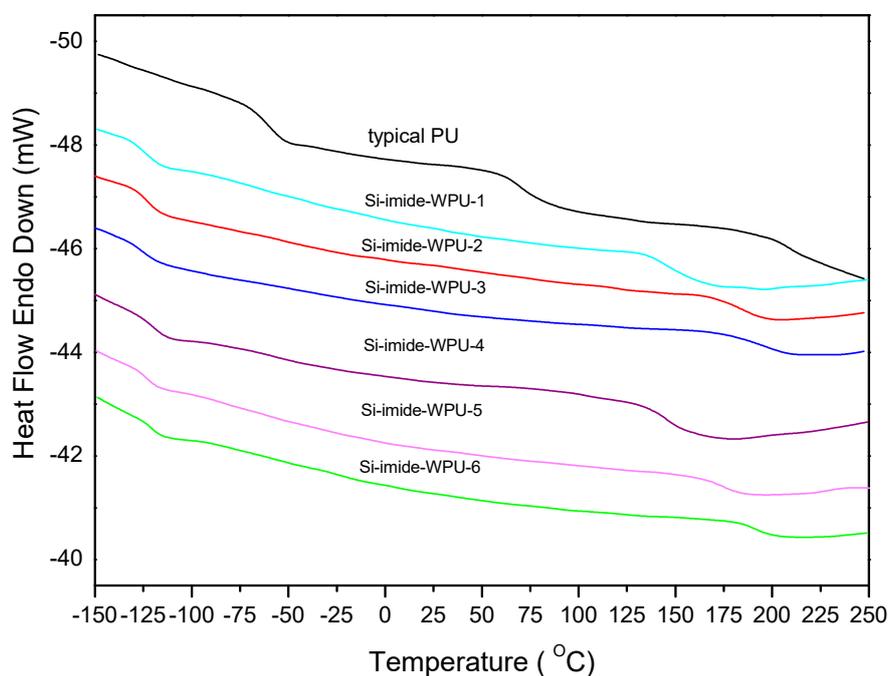


Figure 5. Differential scanning calorimeter (DSC) curves of the Si-imide-WPU copolymers and typical PU.

The Tgh value increased obviously with the increasing imide content (PMDA content), as listed in Table 3. This result indicates that the aromatic imide group could effectively increase the Tgh of the Si-imide-WPU copolymers because of the hindrance to free rotation of segments caused by the aromatic imide groups of the copolymers.

Table 3. Glass transition temperature of the Si-imide-WPU copolymers and typical PU.

Code	Tgs ²	Tgh ³
Si-imide-WPU-1	−125	151
Si-imide-WPU-2	−122	179
Si-imide-WPU-3	−123	192
Si-imide-WPU-4	−124	147
Si-imide-WPU-5	−123	168
Si-imide-WPU-6	−121	183
Typical PU ¹	−64	73

Notes: ¹ Typical PU (control sample) = commercial PU-coated resin; ² Tgs = transition temperature of soft segment; ³ Tgh = transition temperature of hard segment.

The DSC curves shown in Figure 5 also display two regions of phase transition temperatures for the typical PU. The first and second regions, which respectively relate to Tgs and Tgh, both appeared approximately between −64 °C and 73 °C. The results illustrated that the Si-imide-WPU copolymers were more resistant to low or high temperatures compared to the typical PU due to the low Tgs and high Tgh temperature characteristics possessed by the copolymers.

Notably, the Tgh of the Si-imide-WPU copolymers was significantly higher than that of the typical PU, which implied that the Si-imide-WPU copolymers possessed better resistance to softening under higher temperatures than the control sample. Therefore, the Si-imide-WPU copolymers were

indeed more resistant to heat and softening than the typical PU in regard to waterproof coatings on roof surfaces.

3.3.2. Thermogravimetric Analysis

Thermal stability is an important ability for materials, because it determines the appropriate temperature range for material applications. Thermogravimetric analysis (TGA) can be used to evaluate the stability of thermal degradation. Figures 6 and 7 present the TG and DTG curves for the Si-imide-WPU copolymers and typical PU (control sample).

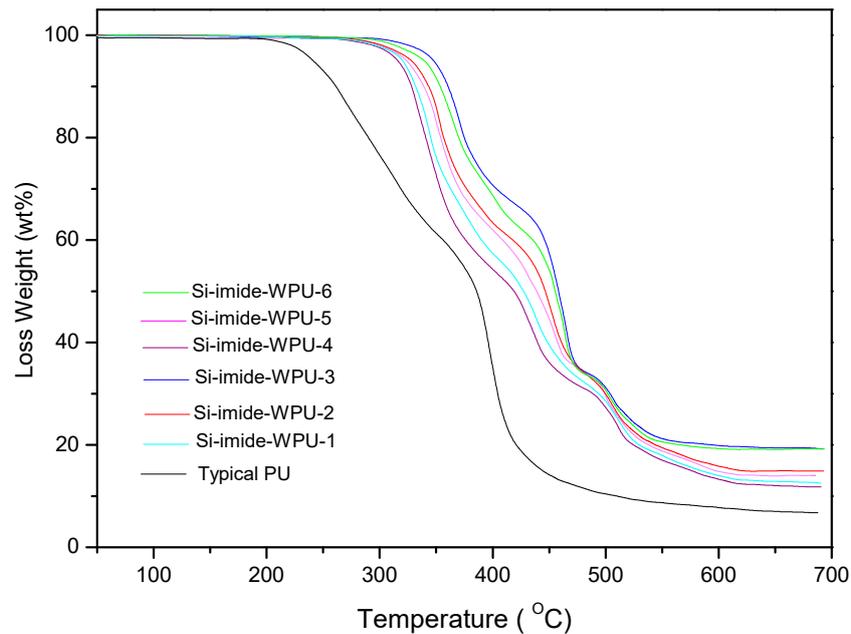


Figure 6. TG curves of the Si-imide-WPU copolymers and typical PU.

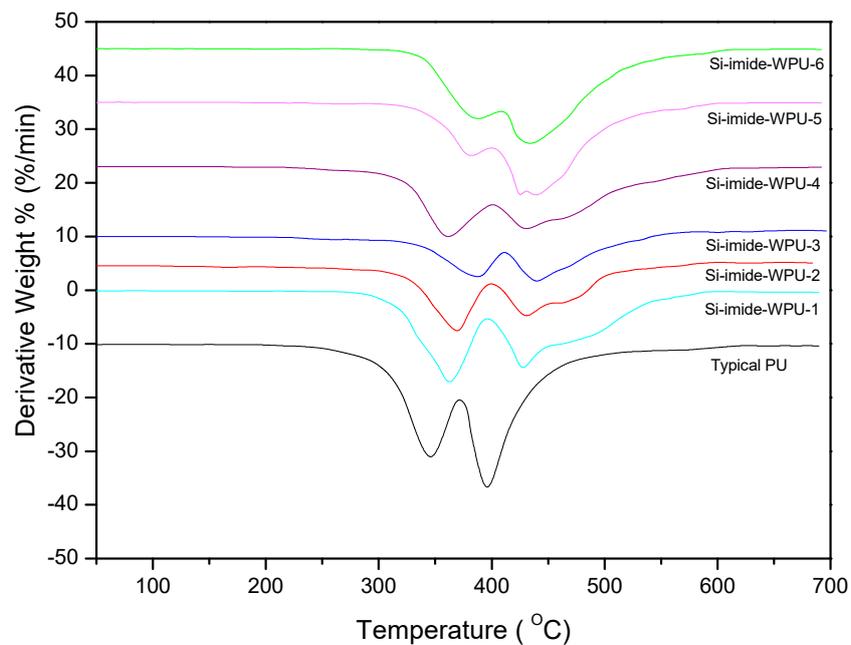


Figure 7. DTG curves of the Si-imide-WPU copolymers and typical PU.

As shown in Figure 6, the TG curves of the Si-imide-WPU copolymers displayed at least three distinct regions of weight loss. These were reflected in the DTG curve (Figure 7) with two peaks and a shoulder peak, indicating that the Si-imide-WPU copolymers had at least three stages of degradation. However, the degradation of the typical PU displayed only two stages of degradation [35]. Since polyurethane is a thermally unstable group, the 5 wt% of weight loss temperature was used as the initial temperature of degradation ($T_{d5\%}$). The onset temperatures of the second and third stage of degradation were represented by T_{2i} and T_{d3i} , respectively. The first, second, and third stage of degradation (stage 1, stage 2, and stage 3) on the TG curves of the Si-imide-WPU copolymers appeared at approximately 316–407 °C, 402–465 °C, and 460–650 °C, as shown in Figure 6. The temperature of the first and second maximum peak (T_{1max} and T_{2max}) at stage 1 and stage 2 respectively corresponded to the temperature of the maximum degradation rate in the stage; however, a shoulder peak was presented in their third stage of degradation, as shown in Figure 6.

Table 4 displays the temperatures of the characteristics in each stage of degradation. It was obvious that the $T_{d5\%}$ of the Si-imide-WPU copolymers was higher than that of the typical PU, as the former ranged from 316 to 347 °C while the latter was only 237 °C. Similarly, the temperatures of T_{1max} , T_{2i} , and T_{2max} at stage 1 and stage 2 for the Si-imide-WPU copolymers also surpassed that of the typical PU. The results indicated that the Si-imide-WPU copolymers had better thermal degradation stability than typical PU. As suggested in previous studies, the thermal stability of Si-imide-WPU in the degradation process was on account of the introduced aromatic imide group in the urethane hard segment [7,31,34].

Table 4. Characteristic thermal degradation temperatures of the Si-imide-WPU copolymers and typical PU.

Code	$T_{d5\%}$ ²	T_{d1max} ³	T_{d2i} ⁴	T_{d2max} ³	T_{d3i} ⁴
Si-imide-WPU-1	320	364	393	426	460
Si-imide-WPU-2	326	371	415	431	463
Si-imide-WPU-3	347	383	417	442	465
Si-imide-WPU-4	316	359	405	430	463
Si-imide-WPU-5	323	378	418	424/439 ⁵	-
Si-imide-WPU-6	346	389	420	435	-
Typical PU ¹	237	345	355	390	-

Notes: ¹ Typical PU (control sample) = commercial PU-coated resin; ² $T_{d5\%}$ = initial temperature of degradation at the first stage of degradation; ³ T_{d1max} , T_{d2max} and T_{d3max} = the temperature of the maximum peak in each stage of degradation corresponding to the degradation temperature of the maximum rate at this stage; ⁴ T_{d2i} and T_{d3i} = the onset temperature of degradation at the second and third stage of degradation; ⁵ 424/439 = split peak: the temperature of the split peak in the DTG curve.

A previous study [11] showed that stage 1 and stage 2 of siloxane-containing PU belong to the degradation of the hard segment and PDMS soft segment, respectively. In addition, stage 3, which appeared as a shoulder peak on the TG and DTG curves, is related to the degradation of non-uniform siloxane chains and macrocyclic siloxanes [15,24]. Notably, a split peak could be observed at 424 °C and 464 °C for the Si-imide-WPU-5, which was possibly affected by the degradation temperature of the aromatic imide group over 400 °C [7]. Therefore, a broad shoulder peak in the other DTG curves of the Si-imide-WPU copolymers was presented at stage 3. Accordingly, it was possible that stage 3 included the degradation of the aromatic imides, non-uniform siloxane chains, and macrocyclic siloxanes. Furthermore, the type and content of the monomer also affected the stability of the Si-imide-WPU copolymers.

Table 4 shows that the copolymers with high PMDA content or high hard segment content (HSC) had higher temperatures of degradation in stage 1 and stage 2, such as Si-imide-WPU-3 and Si-imide-WPU-6. This result was different from that found in the past, reference [6]. The typical PU at stage 1 had low thermal stability due to its high HSC, but it showed an opposite trend at stage 2. However, the Si-imide-WPU copolymers herein in stage 1 and stage 2 presented a high temperature

of degradation due to increased HSC in the imide group caused by DMPA. Thus, the characteristic temperature of degradation in stage 1 and stage 2 was raised with the increment of PMDA content. Similar results have also been reported in past studies of PU-imide copolymers [7,16,17]. This result indicated that the semi aromatic imide group resulting from the reaction of PMDA and H12MDI could improve the thermal degradation stability of the typical PU.

3.4. Mechanical Properties

Tensile strength and abrasion resistance were applied to evaluate the mechanical properties of typical PU (control sample) in waterproof roof coatings. According to the CNS 6988 test standard in Taiwan, commercial PU-coated resins require elongation in excess of 400% and strength in excess of 19.6 MPa (200 kgf/cm²). Table 5 indicates that the breaking strength and elongation of the Si-imide-WPU copolymers had exceeded the values required, and both were higher than that of the typical PU. This result of the study verified that the introduction of imide groups and PDMS soft segments into the polyurethane structure could improve the strength and elongation of typical PU. Additionally, the tensile strength of typical PU is affected by the content and type of soft-hard segments. The breaking strength of the Si-imide-WPU copolymers increased as the PMDA content increased but decreased as the PDMS content increased. Moreover, the stress-strain curve could be used to evaluate the toughness of the materials.

The stress-strain curves of the Si-imide-WPU copolymers shown in Figure 8 illustrate that the curves were closer to the strain axis when there were higher amounts of PDMS and PMDA. PDMS and PMDA have the ability to improve the cohesive energy of hard segment and extensibility of soft segment, respectively. Therefore, the Si-imide-WPU copolymers exhibited higher toughness than typical PU due to the effect of PDMS and PDMA, especially when the amount of HSC was higher, as in Si-imide-WPU-3 and Si-imide-WPU-6. As polymers have better toughness, they usually present higher abrasion resistance. As revealed previously in Table 5, the Si-imide-WPU copolymers showed a lower weight loss of friction than the typical PU in the abrasion test, indicating that the Si-imide-WPU copolymers had better friction resistance in roof waterproofing.

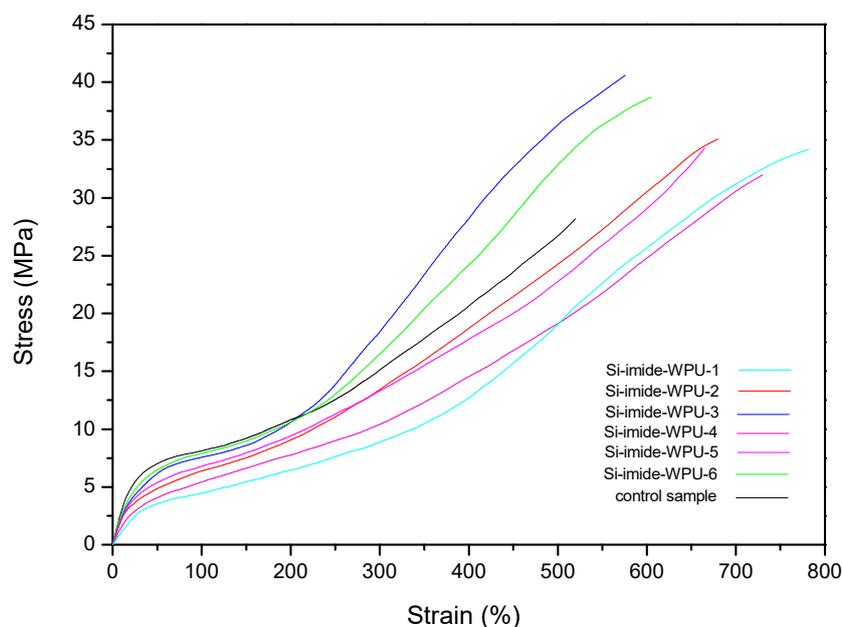


Figure 8. Stress-strain curves of the Si-imide-WPU copolymers.

Table 5. Mechanical properties of the Si-imide-WPU copolymers.

Code	Breaking Strength (MPa)	Elongation at Break (%)	Weight Loss of Friction (g)
Si-imide-WPU-1	34.3	782	0.12
Si-imide-WPU-2	35.1	680	0.32
Si-imide-WPU-3	40.6	576	0.58
Si-imide-WPU-4	32.1	730	0.24
Si-imide-WPU-5	34.3	665	0.46
Si-imide-WPU-6	38.7	605	0.71
Typical PU ¹	28.2	520	0.82

Notes: ¹ Typical PU (control sample) = commercial PU-coated resin.

3.5. Environmental Resistance

It is important to evaluate the water and UV resistance of the PU coating used in waterproof roof coatings. The waterproof tests on the coating resin include water hydrostatic pressure and moisture permeability testing. Table 6 shows that the effect of hydrostatic pressure on the Si-imide-WPU copolymers was beyond that of the typical PU (control sample). This was caused by the imide group that enhanced the strength of the WPU copolymers by intermolecular cohesion along the macromolecule chains.

Table 6. Environmental resistance test.

Code	Breaking Strength after UV Irradiation (MPa)	Elongation at Break after UV Irradiation (%)	Percentage of Decay in Strength after UV Irradiation (%)	Hydrostatic Pressure (cmH ₂ O)	Moisture Permeability (g/m ² × 24 h)
Si-imide-WPU-1	33.7	767	1.8	151	2.1
Si-imide-WPU-2	33.8	636	3.7	164	1.9
Si-imide-WPU-3	36.7	520	9.6	175	2.0
Si-imide-WPU-4	31.2	705	2.8	145	2.3
Si-imide-WPU-5	32.9	618	4.1	153	2.1
Si-imide-WPU-6	34.6	590	10.6	166	2.5
Typical PU ¹	15.1	290	46.4%	135	9.5

Notes: ¹ Typical PU (control sample) = commercial PU-coated resin.

The moisture permeability of a polymer is associated with the hydrophilicity and pores along the macromolecule chains. Compared with the typical PU, the Si-imide-WPU copolymers had obviously lower moisture permeability which ranged from 1.9 to 2.5g/m² × 24 h. This feature was caused by the PDMS segment, which reduced the hydrophilic properties of the copolymer; moreover, the imide group strengthened the intermolecular cohesion and shrank the pores along the macromolecule chains. Accordingly, the waterproofing capabilities of the Si-imide-WPU copolymers in this study had an optimal value, such as the sample of Si-imide-WPU-2. Almost all polymers are exposed to sunlight, which results in the decline in mechanical properties due to ultraviolet aging and thus causes a reduction in the coating's performance. All samples in this study were evaluated for their tensile strength under an exposure of UVA-340 nm and a temperature of 50 °C for 24 h.

Table 6 also shows that the tensile strength of the Si-imide-WPU copolymers was reduced by less than 11% after UV irradiation; however, the strength of the typical PU decreased by approximately 46%. Evidently, the degree of ultraviolet aging decreased with the increase in the PDMS and PDMA content of the copolymer. As mentioned above, the Si-imide-WPU copolymers indeed exhibited good environmental resistance due to the tensile strength enhanced by the imide group and the ultraviolet aging improved by PDMS.

3.6. Evaluation of Si-Imide-WPU Copolymers on the Benefits of Waterproof Coating

Table 7 compares the values of various waterproof coating properties between those of the Si-imide-WPU copolymers and typical PU. Moreover, the degree of improvement in the properties of the waterproof coating is also listed in this table.

Table 7. Properties of the Si-imide-WPU copolymers and typical PU waterproof resin.

Properties	Si-Imide-WPU Copolymers	Typical PU	Percentage of Property Increase (%)
Temperatures of thermal degradation (Td _{5%}) (°C)	316–347	237	33.3–46.4
Glass transition temperature of hard segment (Tgh)(°C)	147–192	73	101.4–163.0
Breaking strength (MPa)	32.1–40.6	28.2	13.8–44
Elongation at break (%)	576–782	520	10.7–50.4
Abrasion resistance (Weight loss) (g)	0.12–0.71	0.82	85.4–1.2
Percentage decrease in intensity (%) after UV irradiation	1.8–10.6%	46.4%	96.0–77.1
Water pressure resistance (cmH ₂ O)	145–175	135	7.4–29.6
Moisture permeability (g/m ² × 24 h)	1.9–2.5	9.5	80.0–73.7

The performances of the three waterproof coating properties were measured as follows:

1. Thermal properties: heat resistance was greatly improved. The Td_{5%} and Tgh of the Si-imide-WPU copolymers rose respectively from 33.3 to 46.4 °C and from 101.4 to 163.0 °C. The improvement of the Tgh, which was related to the softening temperature, could be significantly helpful for the application of waterproof coatings for roof surfaces exposed to high temperatures.
2. Mechanical properties: the breaking strength and elongation at break of the Si-imide-WPU copolymers were slightly higher than that of typical PU, and they complied with the requirements for waterproof coating resins. Moreover, the abrasion resistance of the copolymer also increased approximately from 1.2% to 85.4%, especially for the copolymers with high PDMS content, such as Si-imide-WPU-1.
3. Environmental resistance: water and UV resistance are essential for the evaluation of waterproof roof coatings. To the greatest extent, the hydrostatic pressure and moisture permeability of the Si-imide-WPU copolymers increased by 29.6% and 77.9%, respectively, relative to those of typical PU. Furthermore, the UV resistance grew from 77.1% to 96.0%.

Table 8 lists the growth percentage and average growth percentage of the waterproof coating properties for the Si-imide-WPU copolymers. The factor of thermal degradation was removed because it is not required for waterproof coating resin on a roof surface. Nearly all growth percentages of the properties of Si-imide-WPU-2 were higher than the average percentage, except for the improvement in breaking strength, which was slightly lower than the average percentage. Therefore, the Si-imide-WPU-2 was considered to be the most optimized resin for waterproof roof surface coatings in this study. Regarding current typical PU waterproof coating resins, the main causes of environmental aging are deficiencies in UV resistance, heat resistance stability, and moisture permeability.

The optimized sample (Si-imide-WPU-2) in this study could increase the UV-resistance and thermal stability by 92% and 145.2% respectively, and decrease the moisture permeability by 80%. Based on the general three-year lifespan for typical PU in the application of waterproof roof coatings, it was predicted that the lifespan of coatings based on Si-imide-WPU-2 could be extended to about 5.4 years, even under the lowest growth percentage (the growth percentage of the moisture resistance

for the Si-imide-WPU-2 was 80%; therefore, the lifespan of the Si-imide-WPU-2 was calculated to be three years \times 1.8 = 5.4 years).

Table 8. Percentage of improvement for the Si-imide-WPU copolymers.

Properties	Growth Percentage (%)						Average Percentage (%) of Growth
	Si-Imide-WPU-1	Si-Imide-WPU-2	Si-Imide-WPU-3	Si-Imide-WPU-4	Si-Imide-WPU-5	Si-Imide-WPU-6	
Temperatures of thermal degradation (Td _{5%})	35.0	37.6	46.4	33.3	36.3	46.0	39.1
Glass transition temperature of hard segment (T _{gh})	106.8	145.2	163.0	101.4	130.1	150.7	132.9
Breaking strength	21.6	24.5	44.0	13.8	21.6	37.2	27.1
Elongation at break	50.4	30.8	10.8	40.4	27.9	16.3	29.4
Abrasion resistance	85.4	61.0	29.3	70.7	43.9	13.4	50.6
Percentage decrease in intensity after UV irradiation	96.1	92.0	79.3	94.0	91.2	77.2	88.3
hydrolysis-resistance	11.9	21.5	29.6	7.4	13.3	23.0	17.7
Moisture permeability	-77.9	-80.0	-78.9	-75.8	-77.9	-73.7	-77.4

4. Conclusions

Typical PU resins adopt polyester or polyether soft segments, which can easily cause hydrolysis and aging in waterproof roof coatings under high temperatures and humid conditions. Accordingly, the lifespan of waterproof coatings is restricted. This study successfully employed anionic polymerization synthesis to enhance both the hard and soft segments of typical PU resins by adding PDMS, H12MD1, and PMDA, which eventually produced Si-imide-WPU copolymers. The results indicated that various compositions of Si-imide-WPU waterproofing materials had substantially better environmental aging resistance than typical PU resins. When compared with typical PU, Si-imide-WPU-2, the appropriate copolymer, increased the UV-resistance and thermal stability by 92% and 145.2% respectively, and decreased the moisture permeability by 80%. The lifespan of Si-imide-WPU-2 could also be extended to 5.4 years. Additionally, the water-based Si-imide-WPU resin was nontoxic and free of solvents, thereby indicating it as being environmentally friendly while achieving architectural sustainability.

Although the addition of siloxane and imide groups to the main chain of the PU structure could extend the lifespan of the resin, imperfections still exist due to the unavoidable environmental aging caused by humidity and solar radiation. Continued research on anti-aging organic monomers and the development of new monomers are necessary so as to extend the lifespan of waterproofing materials, either by adding substances to the PU structure or by conducting the hybridization of organic and inorganic compounds. Nonetheless, issues of environmentally friendly solvents and construction friendliness still need to be addressed when developing new coating materials in order to achieve architectural sustainability.

Author Contributions: Y.-T.H. designed and conducted the experiment and was involved in the results discussions; W.-H.W. conducted the literature review, drafted the manuscript and was involved in the results discussions; and W.-H.H. revised the manuscript and was involved in the results discussions. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Baoquan Construction Co., Ltd.

Conflicts of Interest: The authors declare no conflict of interest.

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