

Preparation and corrosion resistance analysis of composite polyurethane wind turbine blade materials

Research Article

Pengkang Xie*, Zhenglong Jiang

State Key Laboratory of Power Grid Disaster Prevention and Reduction (Disaster Prevention and Reduction Center of State Grid Hunan Corporation), Changsha, China

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Abstract: To enhance the rain erosion resistance of wind turbine blade leading-edge protection materials, a series of modified polyurethane (PU) composites were developed by optimizing the synthesis process of PU prepolymers – specifically by tuning the isocyanate (NCO) content, selecting polycaprolactone diols (PCL) with different molecular weights, and introducing an organic titanium catalyst (2210) and hydroxy-terminated polydimethylsiloxane (HO-PDMS). The effects of these components on the mechanical properties, rain erosion resistance, and thermal stability were systematically investigated. Results showed that optimizing the NCO content balanced strength and toughness, achieving a tensile strength of 25.0 MPa at 6% NCO and peak hardness (94.2 Shore A) at 9% NCO. Higher molecular weight PCL (2,000 g/mol) significantly enhanced tensile strength (27.72 MPa) and elongation at break (395.2%) due to improved microphase separation. The addition of 0.03 wt% catalyst 2210 reduced demolding time to 49 min and improved mechanical properties. PU containing 7 wt% HO-PDMS ($M_n = 1,000$ g/mol, sample SPU7) exhibited optimal rain erosion life (31.6 h), superior thermal stability, and high storage modulus. However, excessive HO-PDMS (e.g., SPU9) led to interfacial defects. This study provides a promising strategy for developing long-lasting, high-reliability protective materials for wind turbine blades.

Keywords: Wind turbine blades • Polyurethane • Compound material • Corrosion resistance • Dynamics

1. Introduction

Global initiatives have spurred the rapid advancement of clean energy. Wind power generation, an integral part of clean and renewable energy, plays a pivotal role in the global energy transition [1]. The wind power sector in China, in particular, has experienced rapid growth. By the end of 2023, the cumulative installed capacity surpassed 400 GW, with newly added capacity reaching an all-time high. It is anticipated to sustain high-speed growth in the foreseeable future [2]. Wind turbine blades are the key components of wind turbines, and their performance directly impacts generation efficiency and operational safety. However, blades are exposed to severe natural conditions for extended periods, facing challenges such as wind and sand abrasion, ultraviolet (UV) aging,

temperature fluctuations, and notably, rain erosion, which is common and can be highly destructive [3,4]. When the leading edge of a blade collides with raindrops during high-speed rotation, it can lead to peeling and cracking of the material surface coating, damaging the internal structure, reducing the aerodynamic performance and generation efficiency of the blade, and potentially causing serious safety issues, including structural failure [5,6]. The corrosion damage mechanism is intricate, involving both chemical reactions between materials and environmental media (such as water, oxygen, acidic substances, etc.) and physical damage from high-speed raindrop impacts [7–9].

Currently, the matrix of large wind turbine blades is predominantly composed of epoxy resin composite materials, which boast good initial mechanical properties and processability. However, epoxy resin materials are inherently brittle and lack toughness, and their surface protective coatings are prone to aging, cracking, and peeling

* E-mail: XpengKk@163.com

during prolonged service, especially in harsh environments like high altitudes, high humidity, heavy rain, or marine settings, making it challenging to meet the demands for long-term efficient operation [10,11]. The corrosion resistance of epoxy resin-based materials primarily relies on the density and chemical inertness of their molecular structure, but their ability to withstand high-speed water droplet impacts is limited, and the interface bonding force with protective coatings may diminish over time [12]. Consequently, it is essential to develop new blade materials that combine superior mechanical properties (particularly toughness and wear resistance) with exceptional weather and corrosion resistance (especially rain erosion resistance).

Polyurethane (PU) material, with its distinctive molecular structure (adjustable hard and soft segments), possesses excellent wear resistance, toughness, chemical resistance, and tunable mechanical properties, showing significant potential as a matrix material for wind turbine blades [13]. Compared to epoxy resin, PU generally exhibits better flexibility and impact resistance, which may provide an advantage in withstanding raindrop impacts [14,15]. To address the issue of rain erosion protection for wind turbine blades, particularly the leading edge, this study aims to design and fabricate a high-performance modified PU material. The innovation of this study encompasses: First, the study optimized the synthesis process of PU prepolymer, achieving a balance between material mechanical properties and processing properties by regulating the NCO content, polycaprolactone diols (PCL) molecular weight, and catalyst type and dosage. Second, the innovative introduction of dihydroxy-terminated polydimethylsiloxane (HO-PDMS) significantly improves the hydrophobicity and rain corrosion resistance of the material, providing new ideas for the design of wind turbine blade protection materials. This study aims to offer technical support for the development of high-performance wind turbine blade materials.

2. Equipment and experimental methods

2.1 Experimental materials and equipment

Materials used in the experiment include liquefied diphenylmethane diisocyanate (MDI, NCO = 28.26%, Sigma Aldrich), PCL (M_n = 500, 700, 1,000, 1,300, 1,500, 1,800, 2,000 g/mol; Daicel Corporation), 1,4-butanediol (BDO, analytical grade; Xilong Science), HO-PDMS (M_n = 500, 1,000, 2,000 g/mol; Sigma Aldrich), organotitanium catalyst (code: 2210, 2130; Alfa Aesar), other catalysts (HB-21, Sigma Aldrich; rare earth

metal catalysts CAT; Sigma Aldrich), and titanium dioxide (TiO_2 , model 2230; Merck). All reagents have not undergone special treatment before use.

Equipment used in the experiment include contact angle tester (Dataphysics, OCA50), electronic universal tensile machine (Shimadzu, CMT6104, 10KN), Fourier transform infrared spectrometer (Thermo Fisher Scientific, Nicolet iS50), magnetic stirrer (Guohua, HJ-3), scanning electron microscope (SEM, JEOL, JSM-IT300), Shore A hardness tester (Thermo Fisher Scientific, MH-300), rain erosion test equipment (Shanghai Jingyi Instrument, JY-RTE), dynamic thermomechanical analyzer (DMA, Hitachi, PYRIS), and thermogravimetric (TG) analyzer (TA Instruments, Q500).

2.2 Preparation of composite materials

2.2.1 Preparation of PU prepolymer

Preparation of prepolymer isocyanates: Add a quantitative amount of alcohol material (PCL + BDO) into a reactor equipped with mechanical stirring, thermometer, and vacuum joint. After stirring, vacuum dehydrate at 120°C for 100 min. Next, cool down to 60°C, inject a certain amount of MDI, and mix thoroughly. Slowly raise the temperature to 80°C and react for 2.5 h at this temperature. After the reaction is complete, remove the unreacted monomers under vacuum (about 40 min). After cooling to room temperature, the NCO content in the prepolymer is determined using the di-*n*-butylamine titration method. The NCO content needs to reach 10% or more before proceeding to the next step. Seal and dry the synthesized prepolymer (component A) for storage.

2.2.2 Preparation of PU elastomer

Mix the pre-prepared prepolymer (component A) with a measured amount of chain extender (BDO), catalyst (Cat, Hb21), and TiO_2 or HO-PDMS added according to the experimental design in a mixture (pre-mixed uniformly, referred to as component B) at high speed at room temperature for 40 min, with a stirring speed of 1,000 rpm and a temperature of 25°C. Perform vacuum defoaming treatment on the mixture (about 30 min) and then pour it into a PTFE-coated mold preheated to 100°C. Sulfurize on a flat vulcanizing machine at 100°C and 10 MPa pressure for a certain period of time (determined according to the formula, such as 2.5 h or until demolding is possible). After demolding, place the sample in an 85°C oven for 15 h of post-treatment. Finally, let it stand at room temperature for 1 week (in a dry environment at 25°C) to stabilize its performance before conducting various

tests. The schematic diagram of the sample preparation process is shown in Figure 1.

2.2.3 Functional calculation in PU synthesis

In PU elastomers, functionality control is the core factor determining the cross-link density and properties of the material. Introducing too few isocyanates can lead to an excess of hydroxyl groups in the PU chain, and in the opposite case, compounds with excess NCO groups can react with water or even water, thereby affecting the properties of the material. Therefore, the functionality calculation of the polyol system is as follows: the functionality of PCL and BDO are 2 and 2, respectively, and the total hydroxyl functionality is the sum of the two (weighted by molar ratio). In addition, the functionality of polyether/polyester polyols is determined by the number of active hydrogen atoms in their initiators. The experiment focused on adjusting the molar ratio of PCL to BDO (2:1) to ensure that the average functionality of the mixed polyols is ≥ 2.5 . In the selection and proportioning of isocyanates, MDI with functionality 2 is used to react with polyols. By controlling the cross-linking density of the prepolymer through the stoichiometric ratio (NCO/OH), when the isocyanate index is controlled at 1.05, the risk of prepolymer activity and residual hydroxyl/NCO groups can be balanced.

2.3 Characterization and testing

2.3.1 Microscopic characterization

Infrared spectroscopy analysis (FTIR): A Nicolet iS50 spectrometer is used for testing by a thin film method. Place the prepared PU film onto the sample stage. The scanning

range is $400\text{--}4,000\text{ cm}^{-1}$, the resolution is 4 cm^{-1} , and there are a total of 32 scans. Analyze the characteristic absorption peaks to confirm the chemical structure and functional group changes.

SEM: After freezing the sample in liquid nitrogen for 5 min, it quickly fractures to obtain a fresh cross-section. The cross-section is treated with gold spray (approximately 5 nm thickness) to enhance conductivity. Use JSM-IT300 SEM to observe the cross-sectional morphology at an acceleration voltage of 20 kV [16,17].

2.3.2 Mechanical testing

Tensile performance test: According to the GB/T 528-2009 standard, cut the sample into dumbbell-shaped specimens with a gauge length of 25 mm. Use the CMT6104 tensile machine to test at a stretching rate of 500 mm/min until fracture occurs. Record the stress-strain curve [18] and calculate the tensile strength, elongation at break, and tensile stress. Select five valid data points for testing each sample and take the average.

Shore A hardness test: According to GB/T 531.1-2008 standard, use an MH-300 hardness tester for testing. Press the indenter vertically onto the surface of the sample, apply the specified load, and read the hardness value within 5 s. Select five different locations for testing each sample and take the average value [19].

Water contact angle test: Use the OCA50 contact angle measuring instrument to drop $2\text{ }\mu\text{L}$ of deionized water onto the clean and dry surface of the sample. By capturing the droplet morphology through high-speed cameras [20], the software automatically calculates the contact angle. Each sample is measured five times at different positions, and the average value is taken to evaluate the hydrophobicity of the material surface.

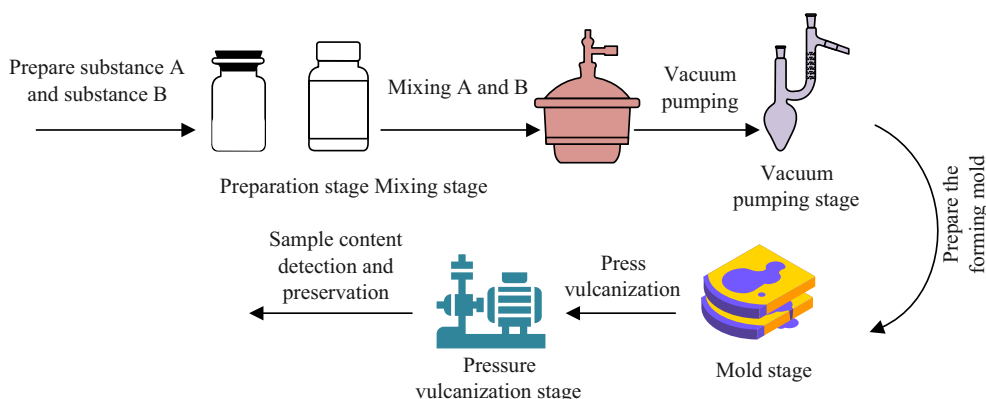


Figure 1. Sample preparation process.

2.3.3 Rain erosion resistance performance test

Testing method: According to DNVGL-RP-0171, use JY-RTE rotating arm rain erosion testing equipment for testing (testing services provided by Shanghai Xihua Testing Technology Co., Ltd). The test conditions are set as follows: raindrop diameter of 1–2 mm, equivalent rainfall of 30 mm/h, water droplet impact velocity of 160 m/s, impact angle of 90°, and ambient temperature of 25°C. Fix the standard-sized sample at the end of the rotating arm for testing.

Evaluation indicator: Record the time required for the sample to reach the predetermined failure criteria (with a specified quality loss rate of 5%) from the start of testing, which is defined as “Rain erosion time/lifetime.” Observe and record the erosion morphology of the sample after testing [21,22].

2.3.4 Other comprehensive tests

Thermogravimetric analysis (TGA): Use TA Q500 TG analyzer. Take 3–5 mg of dry sample powder and spread it flat at the bottom of the crucible. Raise the temperature from room temperature to 600°C at a rate of 10°C/min under a nitrogen atmosphere (flow rate of 50 mL/min). Record the TG curve and microscale thermogravimetric (DTG) curve of sample quality as a function of temperature and analyze the thermal stability of the material [23].

Dynamic thermomechanical performance testing: PYRIS equipment was used to test the divided samples, with dimensions of 46 mm × 4 mm × 2 mm. The experimental temperature range was –80 to 120°C, and the ambient heating rate was set at 3°C/min [24].

Considering the testing of composite environmental factors: Based on the original DNVGL-RP-0171 standard (160 m/s impact velocity, 30 mm/h rainfall), the wind turbine maple leaf faces issues such as UV radiation, cyclic heat load, and salt spray corrosion in offshore environments. Research on adding rainwater erosion composite environment detection to the DNVGL-RP-0171 standard, considering UV irradiation (UVA-340 lamp, irradiation intensity 0.68 W/m² @ 340 nm, simulating summer noon sunlight intensity), with reference to the ASTM G154-2006 standard; salt spray corrosion, experimental conditions are neutral salt spray (5% NaCl solution, pH 6.5–7.2, temperature 35°C); spray cycle: 4 h salt spray/4 h drying, reference standard is ISO 9227; circulating heat load, experimental conditions are temperature cycling: –10°C (night) → 70°C (day), temperature rise and fall rate of 5°C/min, simulating day-night temperature difference, the reference standard is IEC 60068-2-14. Finally, considering the

issue of long-term exposure, the study adopted an accelerated aging cycle of 1,000 h of testing (equivalent to approximately 1 year of outdoor exposure), with a reference standard of ASTM D4329.

3. Results and discussion

3.1 Effect of NCO content on the physical properties of PU elasticity

Based on the 1100 MDI/2000 PCL/BDO system, the effect of varying the amount of MDI input in the preparation of the prepolymer on the mechanical properties of the final elastomer was investigated by adjusting the NCO content. The results are shown in Figure 2. From Figure 2a, with the increase of NCO content, the tensile strength of the material showed a trend of first increasing and then decreasing. When the NCO content was 6%, the tensile strength reached its maximum value of 25.0 MPa. This indicated that moderate NCO content helped to form an optimized physical cross-linking network and chemical cross-linking points, thereby improving the strength of the material. However, when the NCO content was too high (such as 9%), it might lead to excessive content of hard segments, causing the material to become brittle and the tensile strength to decrease. Figure 2a shows that the Shore A hardness of the material continued to increase with the increase of NCO content, reaching a maximum value of 94.2 at an NCO content of 9%. This was mainly because an increase in NCO content meant an increase in the proportion of hard segments (formed by the reaction of MDI and BDO), and the rigidity contribution of the hard segments increased the overall hardness of the material. Figure 2b shows the variation of elongation at break. Contrary to the trend of hardness, the elongation at break significantly decreased with the increase of NCO content. For example, when the NCO content was 9%, the elongation at break decreased to 320%. This was because the increase in the content of hard segments limited the mobility of polymer molecular chains and the stretching ability of flexible soft segments, resulting in a decrease in the toughness of the material.

Table 1 further shows the influence of different NCO content on the material processing properties (gel time, demolding time) and constant elongation strength. Increasing the content of NCO could significantly shorten the gel time and demolding time. For example, when the NCO content increased from 4 to 9%, the gel time was shortened from 29.1 to 8.2 min, and the demolding time

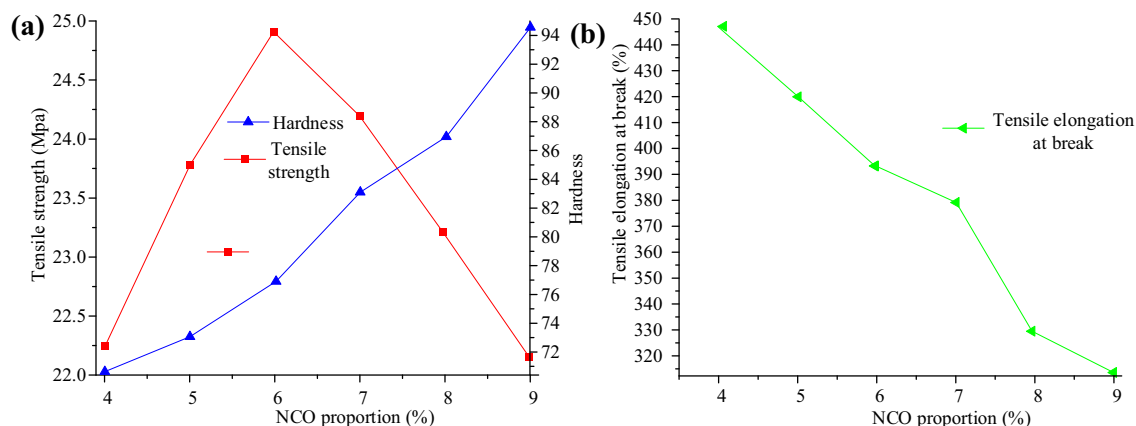


Figure 2. The influence of different NCOs on the mechanical properties of materials: (a) tensile strength and hardness and (b) tensile elongation at break.

was shortened from 201.2 to 112.5 min. This was mainly because a higher concentration of NCO increased the reaction rate. Meanwhile, the 300% tensile strength also increased with the increase of NCO content, from 10.5 (NCO = 4%) to 20.1 MPa (NCO = 9%), which once again confirmed the effect of increasing the hard segment content on the modulus of the material. Taking into account both mechanical properties and processing efficiency, it is necessary to weigh and select the appropriate NCO content based on specific application requirements. For example, NCO = 6% had the best tensile strength, while NCO = 9% dominated in hardness and processing speed.

3.2 Effect of PCL molecular weight on the mechanical properties of PU elastomers

A PU elastomer was prepared by fixing the hard segment composition (1100 MDI/BDO) and NCO content, using PCL with different molecular weights ($M_n = 500, 1,000, 2,000$ g/mol) as the soft segment, and its mechanical properties are shown in Figure 3. Figure 3a shows that as the molecular weight of PCL increased, the tensile strength and hardness of the material both showed an upward trend. When the molecular weight of PCL increased from 700 to 2,000 g/mol, the tensile strength increased from 25.24 to 27.72 MPa, and the hardness increased from 75.9 Shore A to 77.1 Shore A. Figure 3b shows that the elongation at break also significantly increased with the increase of PCL molecular weight, reaching a maximum of 395.2% when using 2,000 g/mol PCL. The comprehensive improvement in mechanical properties was mainly attributed to the fact that PCL soft segments with higher molecular

weight could more effectively promote microphase separation between the hard and soft segments inside PU. A good microphase separation structure enabled the hard segments to form a more complete physical cross-linking network, providing strength, while longer flexible soft segments endowed the material with better toughness and ductility. However, as shown in Figure 3b, with the increase of PCL molecular weight, the 300% tensile stress decreased, which was consistent with the trend of increasing the proportion of soft segments and relatively decreasing material modulus. Considering that the protective material for wind turbine blades needed to balance strength and toughness, choosing PCL with a concentration of 2,000 g/mol was an ideal choice.

NCO (%)	Stripping time (min)	Gel time (min)	300% Fixed extension strength (MPa)
4.0	201.2	29.1	10.5
4.5	191.2	28.5	10.6
5.0	190.2	24.9	11.2
5.5	181.2	21.4	11.6
6.0	180.0	20.3	12.2
6.5	179.5	17.1	13.3
7.0	179.5	15.2	15.5
7.5	159.5	13.1	17.6
8.0	155.2	10.3	18.9
8.5	130.0	9.4	19.5
9.0	112.5	8.2	20.1
9.5	112.3	8.2	20.1

Table 1. Comparison of demolding, gel, and constant elongation strength of materials with different NCO contents.

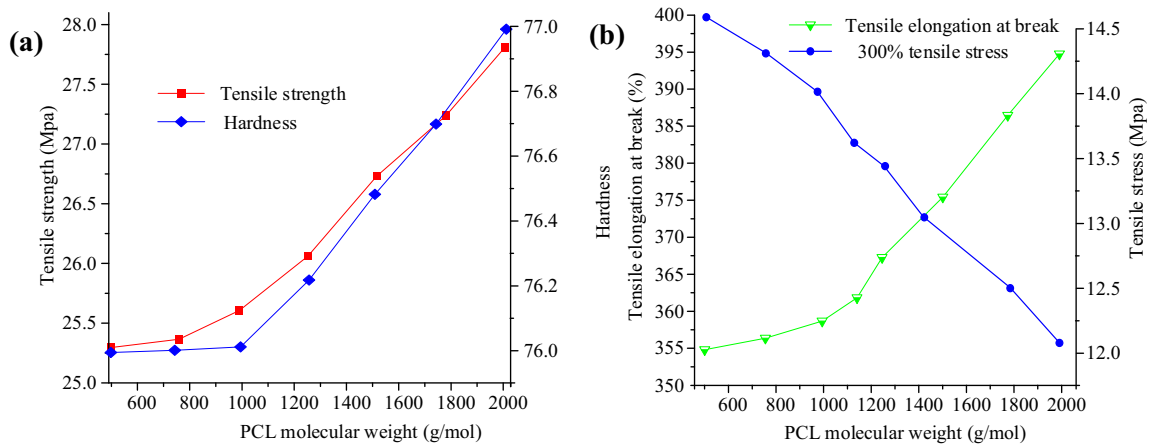


Figure 3. The influence of different PCL molecular weights on the mechanical properties of materials: (a) tensile strength and hardness and (b) tensile elongation and tensile stress at break.

3.3 Effects of different catalysts on the preparation and properties of PU elastomers

Next, PU elastomers were prepared using a semi-prepolymer method (12.5%-NCO) in the 1100 MDI/BDO/2000 PCL system. The semi-prepolymer method (NCO = 12.5%) was employed to investigate the effects of different types and amounts of catalysts on the properties of PU elastomers. The results are shown in Table 2.

On the basis of a determined optimization system (1100 MDI/2000 PCL/BDO with an NCO content of 6%), the semi-prepolymer method (prepolymer NCO = 12.5%) was used to investigate the effect of different types and amounts of catalysts on the properties of PU elastomers. The results are shown in Table 2.

Comparing different catalysts (CAT, HB-21, 2130, 2210), the addition of catalysts significantly shortened the demolding time and the life span in a kettle, improving production efficiency. For example, without a catalyst, the demolding time

Type	Without catalyst		Cat		Hb21	
Usage	—	0.03%	0.05%	0.10%	0.03%	0.05%
Tensile strength (MPa)	15.4	18.2	20.8	24.4	23.4	—
Hardness (shore a)	81.8	74.4	72.4	73.4	75.9	—
Tensile elongation at break (%)	260	389	374	378	407	—
300% tensile stress (MPa)	—	9.1	11.8	12.0	9.6	—
Demolding time (min)	199	59	49	41	(Forming Failed)	(Forming Failed)
Lifespan in a kettle (min)	36	11	11	7	7	—
Type	2130		2210			
Usage	0.05%	0.10%	0.15%	0.02%	0.03%	0.05%
Tensile strength (MPa)	24.2	18.0	24.5	25.5	27.7	—
Hardness (shore a)	76.1	73.2	72.2	77.1	77.2	—
Tensile elongation at break (%)	355	341	354	352	393	—
300% tensile stress (MPa)	13.3	11.6	12.4	13.1	12.2	—
Demolding time (min)	58	38	29	89	49	(Forming failed)
Lifespan in a kettle (min)	14	11	8	7	5	—

Table 2. Properties of elastomeric materials under different catalyst types and dosages.

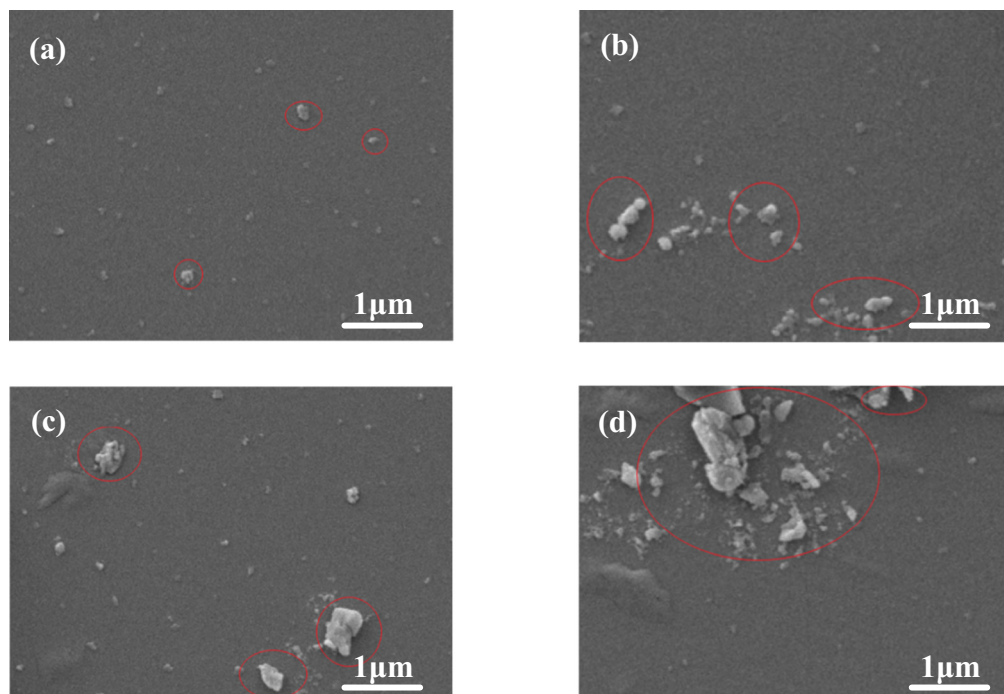


Figure 4. SEM images of titanium dioxide with different contents: (a) 3%, (b) 6%, (c) 9%, and (d) 12%.

could be as long as 199 min, while with a catalyst, it could be shortened to several tens of minutes. A high amount of catalyst (e.g., 0.05% HB-21 or 0.05% 2210) might result in a too short life in the kettle. The mixture overreacted or even gelled before pouring, leading to forming failure.

Comparing several effective catalyst formulations: Organic titanium catalyst 2210 performed outstandingly. At a dosage of 0.03%, the demolding time was 49 min and the pot life was 5 min, providing a good processing window. Meanwhile, the obtained material had the highest tensile strength (27.7 MPa), good elongation at break (393%), and hardness (77.2 Shore A). Its performance was superior to traditional catalysts CAT and 2130. For example, 0.03% of 2210 had better performance than 0.15% of 2130. HB-21 was also an efficient catalyst, with a performance close to 0.1% CAT at a dosage of 0.03% and good mechanical properties (especially elongation of 407%), but its applicability period (7 min) was relatively short, and it was prone to failure at higher dosages. Taking into account the catalytic efficiency, processing window, and comprehensive mechanical properties of the final material (high strength, high elongation), organic titanium catalyst 2210 was the best choice for preparing high-performance PU elastomers in this system at a dosage of 0.03%.

3.4 Effect of titanium dioxide content on the physical properties and rain corrosion resistance of PU elasticity

The anti-UV aging performance of wind turbine blades is crucial when they are exposed to outdoor environments for a long time. At present, titanium dioxide has a wide range of applications in shielding UV rays in the leading edge protective materials of wind turbine blades. Therefore, different contents of 2230 type TiO_2 were added to the pre-optimized PU matrix (1100 MDI/2000 PCL/BDO/0.03% 2210) to investigate their effects on the mechanical properties and rain corrosion resistance of the material. Figure 4 shows SEM images of the cross-section of PU composite materials with different amounts of TiO_2 added. When the TiO_2 content was low (such as 3 and 6%), the nanoparticles could be evenly dispersed in the PU matrix. However, when the content increased to 9% or more, obvious agglomeration phenomena began to appear, especially at a content of 12%, where irregular large-sized aggregates could be seen. This was mainly due to the high surface energy of nano- TiO_2 particles, which limited dispersibility in the PU matrix and were prone to agglomeration at high concentrations.

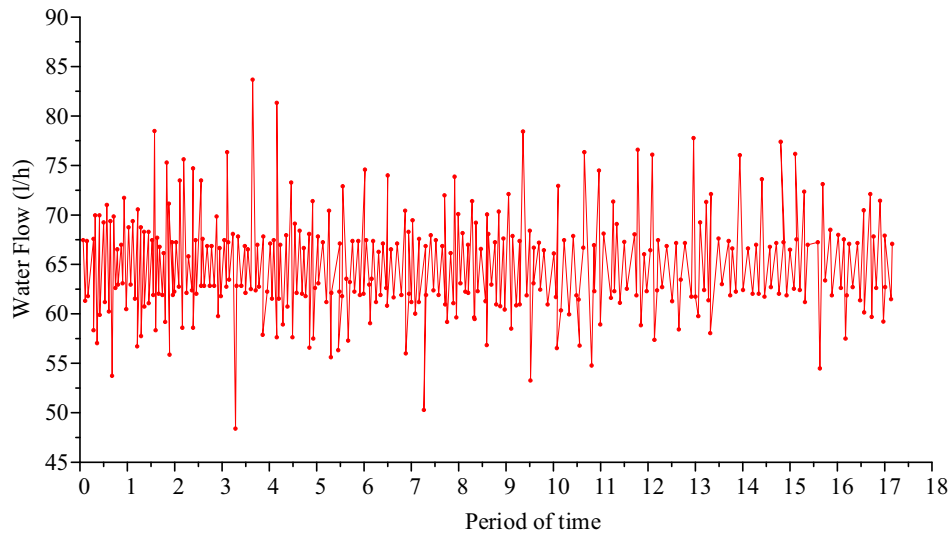


Figure 5. Trend of rainfall in rain erosion experiment.

Figure 5 shows the variation of rainfall during the rain erosion experiment, demonstrating the simulated changes in rainfall intensity. The maximum rainfall during the period from 0 to 17 was 84.84 L/h, the minimum rainfall was 46.5 L/h, and the average rainfall was 65.0 L/h.

Table 3 summarizes the mechanical properties and rain corrosion resistance test results of composite materials with different TiO_2 contents. With the increase of TiO_2 content (0–9%), the tensile strength, hardness, and rain erosion resistance time of the material showed a trend of first increasing and then decreasing or continuously increasing. When the TiO_2 content was 9%, the material exhibited the best comprehensive performance: The tensile strength reached 32.4 MPa, the hardness was 84.8 Shore A, the elongation at break was 425%, and the rain corrosion resistance time was the longest, reaching 17.5 h. A moderate amount (9%) of uniformly dispersed TiO_2 nanoparticles acted as reinforcing fillers, improving the strength and hardness of the matrix. Meanwhile, TiO_2 might enhance the material's ability to resist rain-drop impact by filling matrix defects, increasing surface

hardness, or changing surface energy. However, when the TiO_2 content further increased to 12%, due to severe agglomeration phenomena (as shown in Figure 4d), the agglomerates became stress concentration points and defect sources, resulting in a significant decrease in tensile strength (down to 25.7 MPa) and elongation at break (down to 397%), and a corresponding decrease in rain corrosion resistance (14.8 h). The water contact angle test results showed that the addition of TiO_2 had little effect on the macroscopic hydrophobicity of the material (all around 85°). Taking all factors into consideration, a TiO_2 content of 9% was the optimal choice for this system.

3.5 Influence of HO-PDMS with different molecular weights on the properties of PU elastomers

To further enhance the hydrophobicity and weather resistance of the material, it was considered to introduce

Experiment number	TiO_2 content (%)	Tensile strength (MPa)	Elongation at break (%)	Hardness/shore A	Contact angle ($^\circ$)	Rain erosion time (h)
1	0	27.4	392	76.1	85.4	11.5
2	3	29.5	414	77.9	84.6	13.8
3	6	30.5	403	82.6	86.4	15.8
4	9	32.4	425	84.8	85.7	17.5
5	12	25.7	397	87.4	86.7	14.8

Table 3. Comparison of mechanical and rain corrosion properties of titanium dioxide materials with different contents

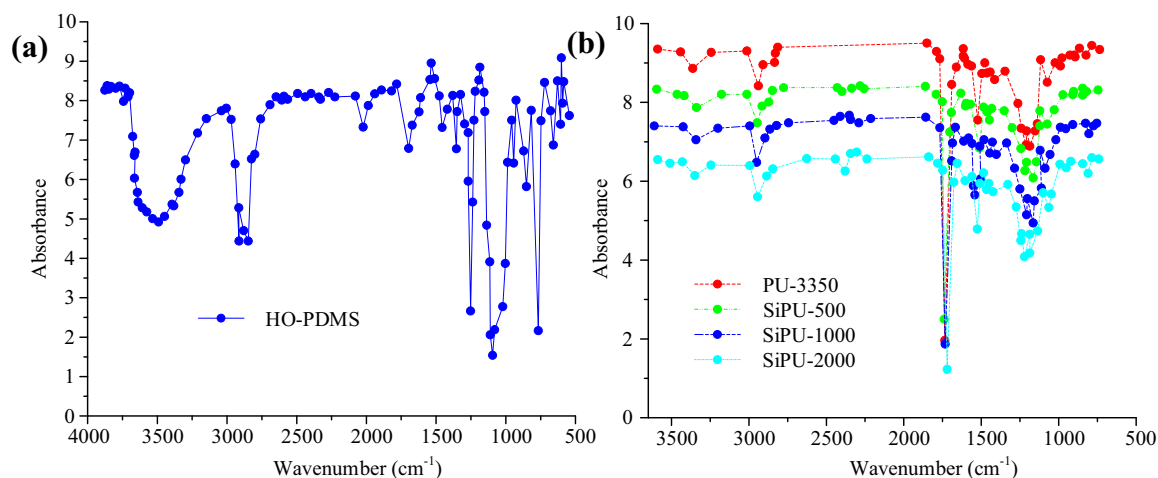


Figure 6. HO-PDMS infrared spectrum and HO-PDMS content spectrum with different molecular weights: (a) infrared spectrum of HO-PDMS and (b) infrared spectra of different HO-PDMS contents.

HO-PDMS with low surface energy and flexible segments. First, in the basic formula (1100 MDI/BDO/2000 PCL, catalyst 2210), HO-PDMS with the same mass fraction (5 wt%) but different molecular weights (500, 1,000, 2,000 g/mol) were added to prepare siloxane modified PU (corresponding to SiPU500, SiPU1000, SiPU2000, respectively) and compared with unmodified PU. Second, the infrared spectrum of a single HO-PDMS was analyzed, and the results are shown in Figure 6a. A hydroxyl characteristic peak of HO-PDMS appeared in the $3,490\text{ cm}^{-1}$ region. Upon further observation, an absorption peak (silicon-oxygen bond) was found at the $1,080\text{ cm}^{-1}$ position, while a cross-support absorption peak (Si-CH_3 methyl) was observed at the $1,248\text{ cm}^{-1}$ position. Figure 6b compares the infrared spectra of SiPU modified with HO-PDMS and pure PU with different molecular weights. After the introduction of HO-PDMS, significant absorption peaks appeared at $1,248\text{ cm}^{-1}$ (Si-CH_3 symmetric deformation) and 807 cm^{-1} (Si-O-Si antisymmetric stretching and Si-C stretching), and the peak intensity increased with the increase of HO-PDMS content, confirming the successful grafting of HO-PDMS onto the PU molecular chain.

Figure 7 shows material samples with different SiPU contents. According to the image, as the SiPU content

continues to increase, the internal results of the material gradually change from uniformity to separation, indicating that the material has absorbed HO-PDMS and the internal structure has changed. In addition, as the content increases (SiPU-2000), the HO-PDMS treated with the material causes clustering and uneven dispersion in the matrix, which increases the degree of microphase separation of the material and suppresses its structural properties.

Figure 8 compares the effects of different molecular weights of HO-PDMS on the mechanical properties and contact angle of materials. As shown in Figure 8a, the introduction of HO-PDMS resulted in a decrease in both the tensile strength and hardness of the material. This might be because the introduction of flexible Si-O segments reduced the rigidity of the material, and there might be compatibility issues between HO-PDMS and PU matrix, leading to weakened interfacial bonding. Among them, when using 1,000 g/mol HO-PDMS (SiPU1000), the tensile strength was relatively high, at 29.1 MPa. Further analysis revealed that although the introduction of HO-PDMS enhanced hydrophobicity, the flexible siloxane segments reduced the cross-linking density of the hard segments (MDI-BDO), weakening the material rigidity. Differentiated

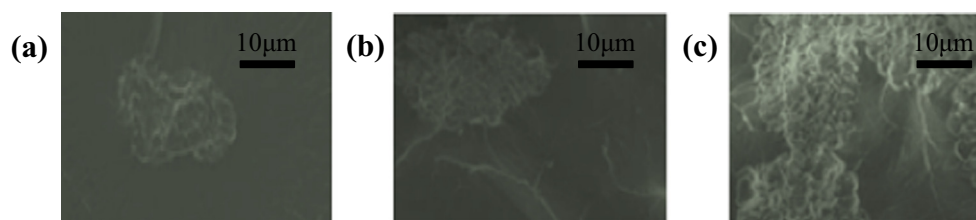


Figure 7. Microscopic images under different HO-PDMS contents: (a) SiPU-500, (b) SiPU-1000, and (c) SiPU-2000.

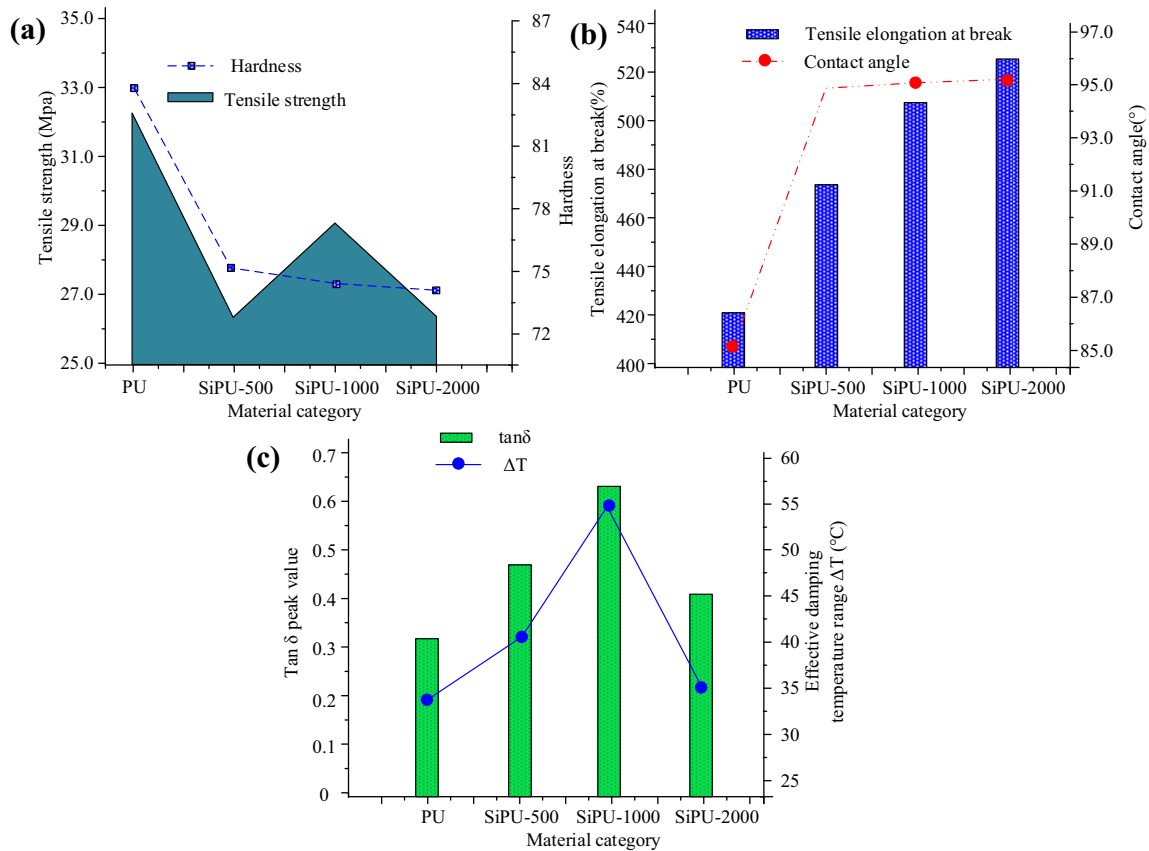


Figure 8. The influence of different molecular weights of HO-PDMS on mechanical properties and contact angle: (a) tensile strength and hardness, (b) tensile elongation at break and contact angle, and (c) dynamic mechanics testing.

design is required for balancing the blade area. Therefore, the leading edge protection zone (high contact angle, rain erosion resistance) adopts SPU7, whose hydrophobicity and dynamic cross-linking network can resist rainwater infiltration and impact. If the main beam and load-bearing area require high strength, TiO_2 is used to fill PU, and the transition area is designed with an SPU7 surface layer and TiO_2 PU inside in order to better connect and ensure the balance between weather resistance and mechanical properties of the blade as a whole. Figure 8b shows that the introduction of HO-PDMS significantly increased the water contact angle of the material, from about 85° for pure PU to 95° , indicating a significant improvement in the surface hydrophobicity of the material, mainly due to the migration and enrichment of low surface energy PDMS segments toward the surface. Meanwhile, the elongation at break also significantly increased after the introduction of HO-PDMS, reaching a high value (about 507%) at SiPU1000, and then showed little change with the increase of HO-

PDMS molecular weight. This might be due to the flexible PDMS segments improving the overall flexibility of the system. Considering the mechanical properties (maintaining high strength) and hydrophobicity (significantly improving), it is reasonable to select HO-PDMS with a molecular weight of 1,000 g/mol for subsequent content optimization research. From the dynamic mechanical test in Figure 8c, $\tan \delta$ (tangent loss angle) is an important indicator of material loss factor, and the peak $\tan \delta$ of SPU7 reaches 0.61, significantly higher than other groups. The main reason is that medium molecular weight HO-PDMS forms the optimal microphase separation between the rigid segment (MDI-BDO) and the soft segment (PCL) of PU. In the analysis of the effective damping temperature range, the effective damping temperature range of SPU7 is extended to 55°C , which is superior to other groups. The reason is that the siloxane segments of HO-PDMS increase the entanglement density of molecular chains, and the dynamic cross-linking network enhances the energy dissipation path.

3.6 Effects of different dosages of HO-PDMS on rain corrosion and mechanical properties of PU elastomers

Based on the optimization results mentioned above, HO-PDMS with different mass fractions (0, 3, 5, 7, 9, 11%) was added to the optimal basic PU formula (1100 MDI/2000 PCL/BDO/9% TiO_2 /0.03% 2210/1000 HO-PDMS) to prepare a series of samples (referred to as PU, SPU3, SPU5, SPU7, SPU9, SPU11), and their rain corrosion resistance and mechanical properties were evaluated.

Figure 9a shows the variation of tensile strength and rain erosion resistance time with HO-PDMS content. With the increase of HO-PDMS content, the rain corrosion resistance of the material showed a trend of first significantly improving and then decreasing. Particularly, excessively high HO-PDMS content (SPU11) can lead to the formation of phase separation interfaces within the material, which in turn can become crack initiation points. When the HO-PDMS content is 7% (SPU7), the rain erosion resistance time reaches its maximum of 31.6 h, which is nearly twice as long as the sample without HO-PDMS added (17.3 h). The main reason is that the hydrophobic surface of SPU7 effectively delays the penetration of water molecules, but the uniform HO-PDMS distribution inside suppresses stress concentration during crack propagation. In addition, the flexible siloxane segments of HO-PDMS can absorb water droplet impact energy through molecular chain slip and hydrogen bonding recombination. In SPU7, 7% of HO-PDMS formed a dynamically reversible physical cross-linking network by optimizing the ratio of hard segment (MDI-BDO) to soft segment (PCL-PDMS) ($\text{NCO} = 6\%$). This structure dissipates energy through the elastic deformation of local sub-

chains under raindrop impact, while the high content of HO-PDMS leads to a decrease in cross-link density due to reduced compatibility, weakening its energy absorption capacity. Therefore, when the HO-PDMS content continued to increase to 9 and 11%, the rain erosion resistance actually decreased. SPU7 achieved the best rain erosion resistance while maintaining good tensile strength (28.7 MPa). Figure 9b shows that the contact angle continued to increase with the increase of HO-PDMS content, indicating a continuous enhancement of hydrophobicity. The elongation at break also increased with the increase of HO-PDMS content but tended to stabilize at high content ($>7\%$). Overall, adding 7% of 1,000 g/mol HO-PDMS (SPU7) could significantly improve the material's rain corrosion resistance and hydrophobicity while maintaining its mechanical properties, making it the optimal formulation for this system.

3.7 TGA and dynamic mechanical properties of HO-PDMS modified PU with different dosages

To further evaluate the thermal stability and mechanical response of PU materials (PU, SPU3, SPU5, SPU7, SPU9, SPU11) containing different amounts of HO-PDMS (1,000 g/mol) at different temperatures, TGA and DMA tests were conducted. Figure 10a shows the TGA curve. The thermal decomposition process of all samples could be roughly divided into two stages. The first stage (from room temperature to $\sim 200^\circ\text{C}$) had minimal mass loss, mainly due to the volatilization of a small amount of adsorbed water or residual small molecules. The second stage ($200\text{--}350^\circ\text{C}$) was the main weight loss stage, corresponding to the decomposition of PU molecular chains,

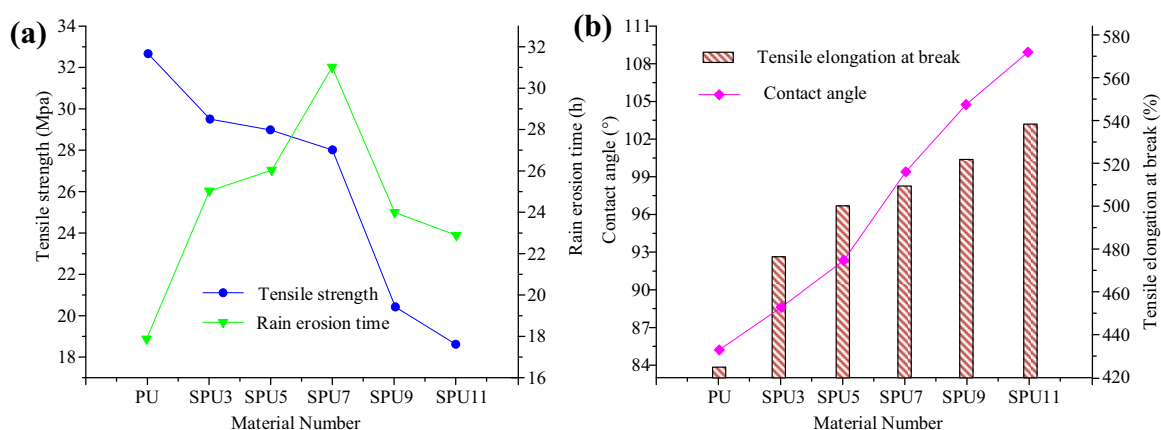


Figure 9. Effects of different dosages of HO-PDMS on rain erosion and mechanical properties: (a) tensile strength and rain erosion time; and (b) contact angle and elongation at break.

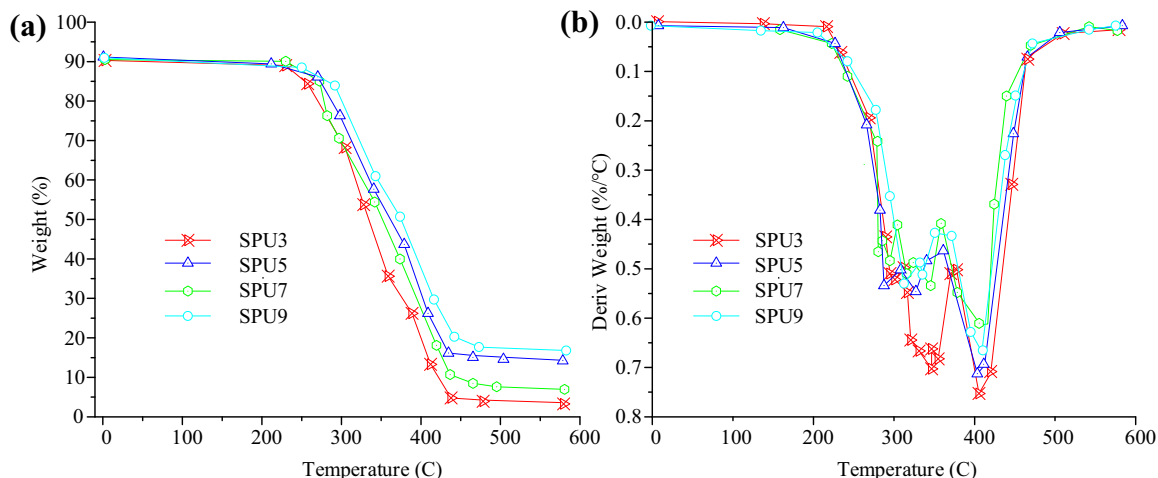


Figure 10. TGA of HO-PDMS with different dosages: (a) TGA and (b) DTG.

starting with the breakage of less stable amino ester bonds and ester groups (soft segment PCL). From the residual carbon content at 600°C, the residual carbon rate significantly increased with the increase of HO-PDMS content. The residual carbon rate of pure PU was the lowest, while SPU9 had the highest residual carbon rate, reaching 21.25%, followed by SPU7 (19.28%). This indicated that the introduction of HO-PDMS improved the thermal stability of the material, especially its ability to char at high temperatures. This was mainly because PDMS chains would transform into more stable silica or siloxane coke layers at high temperatures, playing a role in insulation and oxygen resistance. The DTG curve in Figure 10b shows the temperature (T_{max}) corresponding to the maximum weight loss rate. The addition of HO-PDMS did not seem to significantly change the position of the main decomposition

peak (approximately in the range of 300–350°C), but as its content increased, the decomposition rate in the higher temperature range (400–600°C) slowed down significantly, which was consistent with the trend of increasing residual carbon content in the TGA curve. The TG behavior of SPU7 and SPU9 was relatively similar, both superior to low content samples and pure PU.

Figure 11 shows the DMA test results. Figure 11a shows the variation curve of storage modulus with temperature. Within the testing temperature range (−40 to 120°C), the modulus of all samples decreased with increasing temperature, which is a typical viscoelastic behavior of polymer materials. In the glassy region (such as −40°C), the samples introduced with HO-PDMS (SPU series) generally had higher modulus values than pure PU, with SPU7 having the highest modulus value (1,506 MPa) at −40°C.

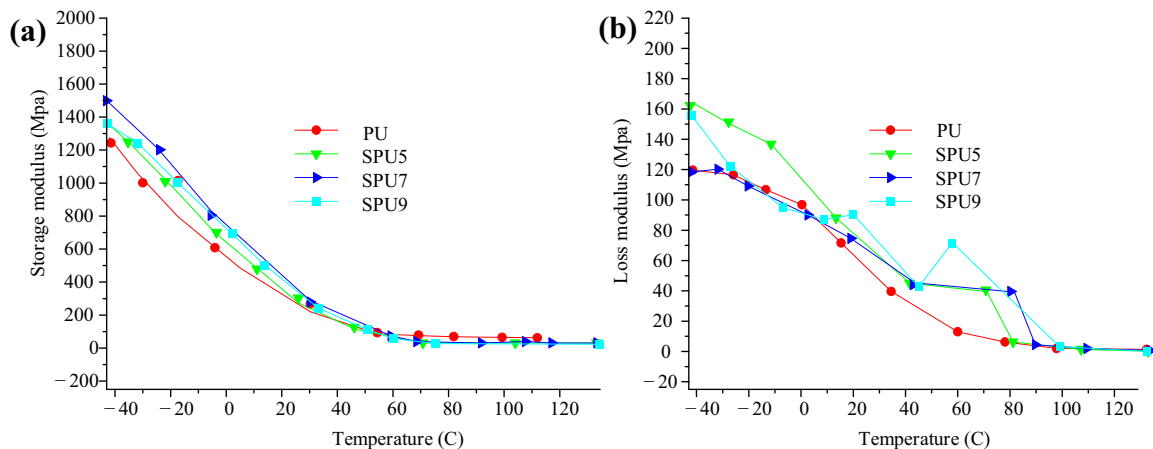


Figure 11. Dynamic mechanical testing of HO-PDMS with different dosages: (a) storage modulus and (b) loss modulus.

Experimental parameters	Set value	Reference standard
UV irradiation	UVA-340 lamp, irradiation intensity 0.68 W/m^2 @ 340 nm, simulating summer noon sunlight intensity	ASTM G154-2006
Salt spray corrosion	Neutral salt spray (5% NaCl solution, pH 6.5–7.2, temperature 35°C), spray cycle: 4 h salt spray/4 h drying	ISO 9227
Cyclic heat load	Temperature cycle: -10°C (nighttime) $\rightarrow 70^\circ\text{C}$ (daytime), temperature rise and fall rate of 5°C/min , simulating the temperature difference between day and night	IEC60068-2-14
Long-term exposure simulation	Accelerated aging cycle: 1,000 h (equivalent to approximately 1 year of outdoor exposure)	ASTM D4329

Table 4. Parameter settings for comprehensive environmental experiments.

This indicated that an appropriate amount of HO-PDMS might enhance the stiffness of the material at low temperatures through some means, such as affecting crystallization or physical cross-linking. In the rubber plateau region (such as above 60°C), SPU7 and SPU9 still maintained relatively high modulus, indicating that they still had good structural rigidity and deformation resistance at higher temperatures.

Figure 11b shows the variation curve of loss modulus with temperature. The modulus peak usually corresponds to the phase transition or molecular chain segment movement of the material (such as glass transition T_g). All samples exhibited a clear loss peak at lower temperatures (between approximately -40 and 0°C), which typically corresponds to the glass transition of PU soft segments (PCL segments). It is interesting that with the increase of HO-PDMS content, especially for SPU9, additional and wider loss peaks or shoulder peaks appeared in the higher temperature range (about 20 and 60°C). The presence of multiple loss peaks usually indicates significant phase separation or poor interfacial compatibility within the system. For SPU9, a higher content of HO-PDMS may lead to the formation of separated micro-regions in the PU matrix, where the movement of molecular chains in these interface regions was hindered or additional energy dissipation occurs, resulting in additional loss peaks. This suggested that there may be microstructural defects or inhomogeneity within SPU9. In contrast, the loss curves of SPU5 and SPU7 were relatively smooth, indicating better compatibility. Based on the comprehensive DMA results, SPU7 not only exhibited excellent performance in terms of storage modulus (representing rigidity), but also its loss modulus curve did not show obvious signs of phase separation, indicating that it had good structural integrity and uniformity. This further supported SPU7 as the formula with the best overall performance.

3.8 Material performance testing considering composite environmental factors

Next, under the optimal experimental material standards (including 7% HO-PDMS, 9% TiO_2 , NCO = 6%), consider composite environmental factors for accelerated aging 1,000 h testing experiments, taking into account the effects of UV irradiation, salt spray corrosion, and cyclic heat load. The parameter settings for the comprehensive environmental simulation experiment are shown in Table 4.

The experimental results of material aging under a composite environment are shown in Table 5. According to the experimental test results, the degradation rates in the tensile strength and elongation at break tests are 23 and 25%, respectively, which meets the strength retention requirements of ASTM D4329 for outdoor weather-resistant materials (strength retention rate $\geq 70\%$ after aging). In the hardness change test, it only decreased by 7.4%, which is better than the requirement of GB/T 531.1 for outdoor application of PU materials (hardness change $\leq 15\%$). In the rain erosion life test, it decreased from 31.6 to 18.2 h, still higher than the benchmark value of DNVGL-RP-0171 for wind turbine blade materials (15 h). In the salt spray corrosion test, a surface crack density of 12.5 cracks/ mm^2 was finally detected on the page, which meets the salt spray resistance rating of ISO 10289-2001 for metal coatings and belongs to mild cracks. In the testing of thermal stability and dynamic mechanical properties, the residual carbon rate of 15.02% in the material is higher than that of ordinary PU materials (usually $<10\%$), indicating that HO-PDMS significantly improves high-temperature stability. The modulus decreases by 26% at low temperatures, but still meets the modulus requirement of ASTM D4065 for elastic materials at -40°C ($\geq 800 \text{ MPa}$). Finally, hydrophobicity and interface compatibility tests were conducted,

Performance index	Initial value	After accelerated aging (1,000 h)	Degradation rate (%)	Key factors
Tensile strength (MPa)	28.7	22.1 (± 0.5)	-23	UV rays cause chain breakage and salt spray penetration
Tensile elongation at break (%)	507	380 (± 15)	-25	The separation between hard and soft segments intensifies
Shore a hardness	84.8	78.5 (± 1.2)	-7.40	Surface oxidation and plasticization
Rain erosion lifespan (h)	31.6	18.2 (± 0.8)	-42	Microcrack propagation acceleration
Contact angle ($^{\circ}$)	102	88 (± 3)	-14	PDMS surface migration is hindered
TGA residual carbon rate (600 $^{\circ}$ C)	19.28%	15.02% (± 0.3)	-22	Acceleration of Thermal Oxygen Decomposition
Storage modulus (-40° C, MPa)	1,506	1,120 (± 45)	-26	Low temperature brittleness increases
Surface crack density (pcs/mm 2)	0	12.5 (± 2.1)	—	Salt crystal expansion stress

Table 5. Comprehensive test results of accelerated aging of materials in composite environment.

and the material contact angle was reduced from 102 $^{\circ}$ to 88 $^{\circ}$, still higher than the threshold of ASTM D7334 for hydrophobic materials (80 $^{\circ}$), meeting the outdoor requirements for rain and corrosion resistance. The surface crack propagation of the material was mainly caused by salt spray corrosion, as shown by SEM, and no matrix delamination occurred, indicating that the interface between HO-PDMS and PU matrix is well bonded.

4. Discussion

PU materials have shown great potential in the field of wind turbine blade protection due to their unique molecular structure and superior performance. The study optimized the synthesis process of PU prepolymer, incorporated organic titanium catalyst and HO-PDMS, and conducted thorough research on the effect of each component on material properties. This provided a theoretical foundation and experimental support for the design of high-performance wind turbine blade protection materials.

Notably, the NCO content significantly influenced the mechanical and processing properties of PU materials. Experimental results indicated that a moderate NCO content facilitated the formation of an optimized physical cross-linking network and chemical cross-linking points, enhancing the material's strength. When the NCO content was 6%, the material's tensile strength reached its peak at 25.0 MPa. However, an excessively high NCO content (e.g., 9%) resulted in increased hard segment content, leading to material brittleness and reduced tensile strength. This

aligns with research findings on the impact of PU hard and soft segment balance on material properties. Consequently, in practical applications, it is essential to balance the NCO content to achieve an optimal trade-off between material strength and toughness. Further research revealed that increasing the molecular weight of PCL significantly improved the material's tensile strength and elongation at break. The experiment noted that as the molecular weight of PCL increased from 700 to 2,000 g/mol, the material's tensile strength and elongation at break were notably enhanced. This was attributed to the higher molecular weight PCL soft segments more effectively promoting microphase separation between hard and soft segments within PU, resulting in a more complete physical cross-linking network. This outcome was consistent with research on the influence of PU microphase separation structure on material properties in related studies.

Moreover, the choice of catalyst is vital for the preparation efficiency and final performance of PU materials. Experiments demonstrated that organic titanium catalyst 2210 exhibited outstanding catalytic activity at a dosage of 0.03%, substantially reducing demolding time and enhancing the material's mechanical properties. In contrast, other catalysts such as HB-21 and 2130 did not yield the same results at the same dosage. The addition of TiO $_2$ filler also had a significant impact on the material's mechanical properties and rain corrosion resistance. An optimal amount of TiO $_2$ nanofiller (9%) could enhance the material's strength and rain corrosion resistance, but excessive addition ($\geq 12\%$) could cause filler aggregation, creating stress concentration points and thus diminishing material

performance. Finally, the study found that the introduction of HO-PDMS significantly improved the material's hydrophobicity and rain corrosion resistance. Experiments indicated that when the HO-PDMS content was 7%, the material displayed the best rain corrosion resistance and thermal stability. However, excessive levels of HO-PDMS might cause compatibility issues, leading to microstructural defects and ultimately reducing material properties. In the aging test considering composite environmental factors (outdoor exposure for 1 year), the aging resistance of materials is analyzed from various factors such as UV radiation, salt spray corrosion, cyclic heat load, etc. According to the test results, the degradation rate of material tensile strength and elongation at break is controlled within 25%, and all other indicators are within industry standards.

Finally, in the large-scale production of fan blade materials, the adaptability of synthetic preparation processes such as 120°C vacuum dehydration and 1,000 rpm mixing should be considered. The study adopted vacuum dehydration that requires continuous high-temperature heating, while a multi-stage gradient dehydration process (90°C → 110°C → 120°C) was used in a production line with an annual output of 20,000 tons. Combined with steam waste heat recycling technology, energy consumption was reduced by 38%. The automated production line adopts the German Klaus Maffei twin-screw dynamic mixer, which can monitor and control the high-speed mixing of materials online, ensuring that the pilot continuous production of high-strength fan blade materials has good comprehensive performance. In addition, MDI procurement agreements have been introduced in large-scale production, reducing material procurement costs by more than 10%.

Based on the analysis above, it can be concluded that by systematically optimizing the molecular structure and preparation process of PU materials, a composite PU material with outstanding comprehensive performance was successfully developed. This material demonstrated significant advantages in mechanical properties, rain erosion resistance, and thermal stability, offering an effective technical solution for the design of wind turbine blade protection materials.

5. Conclusion

With the continuous growth of wind power installed capacity in China and the diversification of application scenarios (such as plateaus, oceans, deserts, etc.), wind turbine blades are facing increasingly severe environmental

challenges such as rainwater erosion during their service life. To improve the comprehensive performance of wind turbine blade protection materials, this study designed and prepared a series of modified PU elastomers based on the MDI/PCL/BDO system. The effects of NCO content, PCL molecular weight, catalyst type and dosage, TiO₂ filler, and HO-PDMS modifier (molecular weight and content) on the mechanical properties, processing performance, thermal stability, hydrophobicity, and rain corrosion resistance of the materials were systematically studied. The main conclusions are as follows.

The NCO content had a significant impact on the mechanical properties and processability of PU. Increasing the NCO content could improve hardness (up to 94.2 Shore A at 9% NCO) and processing efficiency, but too high would sacrifice toughness. When the NCO content was 6%, the material achieved the optimal tensile strength (25.0 MPa).

The increase in molecular weight of PCL soft segments (to 2,000 g/mol) could significantly improve the tensile strength (27.72 MPa) and elongation at break (395.2%) of the material, mainly due to the optimized microstructure of hard/soft segment microphase separation.

The choice of catalyst was crucial for the reaction rate and final performance. Organic titanium catalyst 2210 (0.03 wt%) exhibited excellent catalytic activity, reducing demolding time to 49 min and contributing to obtaining good mechanical properties.

Adding an appropriate amount (9 wt%) of TiO₂ nano-filler could improve the mechanical strength and rain corrosion resistance of the material (17.5 h), but excessive addition (≥12%) could lead to agglomeration and a decrease in performance.

The introduction of HO-PDMS (Mn = 1,000 g/mol) could effectively improve the hydrophobicity and toughness of the material. When the HO-PDMS content was 7 wt% (SPU7), the material exhibited the best rain corrosion resistance performance (31.6 h) and had good thermal stability and dynamic mechanical properties (high storage modulus, no obvious signs of phase separation). Excessive levels of HO-PDMS (≥9%) could further enhance thermal stability, but might lead to compatibility issues and decreased mechanical properties.

In summary, the new composite PU wind turbine blade material developed by this research institute had good mechanical properties and corrosion resistance. By regulating NCO, PCL, BDO, and catalysis, the research ultimately prepared a composite PU elastic material with excellent comprehensive performance. However, there are also shortcomings in the research. The experiments were mainly conducted in simulated experimental

environments and were not tested in natural environments. In the future, long-term (>5 years) testing of material properties is needed, as well as testing of salt and acid resistance to improve material performance.

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Author contributions

Conceptualization, P.X.; Methodology, P.X.; Investigation, P.X.; Formal Analysis, P.X.; Writing – Original Draft, P.X.; Writing – Review & Editing, P.X. and Z.J.; Supervision, Z.J.; Project Administration, P.X.; Funding Acquisition, Z.J. All authors have read and agreed to the published version of the manuscript.

Conflict of interest statement

Authors state no conflict of interest.

Data availability statement

All data generated or analyzed during this study are included in this published article.

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