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2K UV- and Sunlight-Curable Waterborne Polyurethane Coating Through Thiol-Ene Click Reaction

Zichen Ling, Haoran Wang and Qixin Zhou * 

Department of Chemical, Biomolecular, and Corrosion Engineering, The University of Akron,
Akron, OH 44325, USA; zl43@uakron.edu (Z.L.); 2023500023@mail.buct.edu.cn (H.W.)

* Correspondence: qzhou@uakron.edu

Abstract: Waterborne polyurethane (WPU) coatings have gained significant attention in the industry due to their low environmental impact and excellent properties. Furthermore, the UV-curing system reduces energy costs and enhances curing efficiency. Hence, exploring the UV-curable WPU system is essential for advancing the next generation of coatings. In this study, a 2K WPU system was developed by functionalizing isocyanate-terminated polyurethane with thiol and vinyl groups. The coating was cured under UV light through a thiol-ene click reaction, and the effects of photoinitiator content on the coating performance were investigated. The feasibility of sunlight curing for this WPU coating was also assessed. The results showed that while photoinitiator content had a slight impact on UV-cured WPU coatings, it significantly affected sunlight-cured WPU. Also, with the appropriate photoinitiator content, sunlight-cured WPU could achieve comparable performance to UV-curable ones.

Keywords: polyurethane; coating; UV curing; waterborne



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1. Introduction

Polyurethanes (PUs) are widely used in various industries, including footwear, automotive, furniture, and coatings, because of their excellent properties [1–5]. The global market size for PU was valued at USD 75 billion and is expected to continue growing [6]. PU is generally synthesized through the step-growth polymerization of polyisocyanates and polyols. In this process, the isocyanate groups typically contribute to the hard segments of PU, while polyols contribute to the soft segment. As a result, PU exhibits a combination of mechanical resistance and flexibility, which together determine its final properties [7,8].

Due to environmental concerns and stricter regulations regarding volatile organic compounds (VOCs) in coatings, the VOC content in PU coatings needs to be reduced. Waterborne polyurethane (WPU) has become a promising substitute for solvent-borne PU in industry because of its low levels of VOC emissions and isocyanate residues. WPU is generally achieved by incorporating hydrophilic groups into polymers, such as carboxyl groups, sulfonates, and tertiary amines; the compounds contain hydrophilic groups acting as internal emulsifiers. Depending on the type of internal emulsifier used, WPU can be classified as cationic, anionic, or nonionic [9,10]. Among these, anionic WPU is the most widely used in the coating industry. However, while the incorporation of hydrophilic groups enhances the stability of WPU particles in water, it can negatively impact coating properties, such as chemical resistance and durability; as a result, WPU generally does not have comparable properties to solvent-borne PU, which is the major challenge to be addressed [11,12].

Crosslinking can address the previously mentioned issues by incorporating epoxy groups and further reacting with amines to achieve high crosslinking or by obtaining isocyanate-terminated PU oligomers that can then react with polyol chain extenders [13,14]. However, these WPU usually require a long curing time and elevated temperature to complete crosslinking, which increases both time and energy consumption, thus hindering practical application. UV-cured coatings present efficient, energy-saving, and economical alternatives [15]. Commonly, UV curing is achieved through the reaction of methacrylate groups or thiol-ene click reaction. Thiol-ene click crosslinking offers several advantages including high reaction rate, high yield, high selectivity, low shrinkage, no byproducts, and insensitivity to oxygen and water [16,17]. Li et al. prepared a thiol-ene UV-curable WPU by introducing disulfide groups into the PU and then functionalizing the end chains with vinyl or thiol groups. The resulting product showed improved corrosion resistance. Yang et al. developed a UV-curable coating by mixing the thiol- and ene-terminated WPU dispersions, which demonstrated excellent physical properties [18,19]. However, no studies have investigated the curing of these coatings under sunlight, despite sunlight being a cost-free UV light source and a reliable curing option for outdoor applications.

In this study, a two-component (2K) thiol-ene UV-curable WPU coating system was developed. Thiol- and ene-terminated WPU dispersions were synthesized as the two components. Upon mixing, the samples under the UV light or sunlight cured through a thiol-ene click reaction, resulting in tack-free films. BAPO was selected as the photoinitiator due to its broad absorption range and high absorbance at 405 nm, which matches the wavelength of the UV curing box. The chemical structure of the WPU was confirmed by using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR). The morphology of the films, influenced by varying photoinitiator contents, was studied by scanning electron microscope (SEM), while thermal behavior was characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The mechanical and general coating properties of UV- and sunlight-cured WPU films were then compared.

2. Experimental Part

2.1. Materials

Isophorone diisocyanate (IPDI, 98%, 222.28 g mol⁻¹), polycaprolactone diol (PCL, average Mn ~2000 g mol⁻¹), dimethylolpropionic acid (DMPA, 134.13 g mol⁻¹), trimethylolpropane diallyl ether (TMPAE, 90%, 214.3 g mol⁻¹), pentaerythritol tetrakis (3-mercaptopropionate) (PETMP, >95%, 488.66 g mol⁻¹), triethylamine (TEA, ≥99.5%, 101.19 g mol⁻¹), dibutyltin dilaurate (DBTDL, 95%), phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide, (BAPO, 97%), tetrahydrofuran (THF, ≥99.0%), and methyl ethyl ketone (MEK, ≥9%) were purchased from Sigma-Aldrich (Burlington, MA, USA). MEK was dried by 3Å molecule sieves (Fisher Scientific, Waltham, MA, USA) before use. The other materials were used as received without further purification.

2.2. Synthesis of Thiol-Functionalized Waterborne Polyurethane (Thiol-WPU)

As shown in Figure 1, 35.57 g IPDI (0.16 mol), 80.00 g PCL (0.04 mol), 8.05 g DMPA (0.06 mol), and 0.21 g DBTDL (0.15 wt.%) were first dissolved in MEK. The temperature was then increased to 65 °C and the reaction proceeded for approximately 4 h, with the isocyanate group content monitored according to ASTM D2572. Afterward, 43.98 g PETMP (0.09 mol) was added to the mixture and reacted at room temperature for 6 h. Next, 6.07 g TEA (0.06 mol) was added to neutralize the product and stirred for 0.5 h. The product was then dissolved in water by a mechanical stirrer with a speed of 700 rpm for 1 h, after which

the MEK was evaporated using a rotary evaporator. The solid content of the Thiol-WPU dispersion was 35 wt.%.

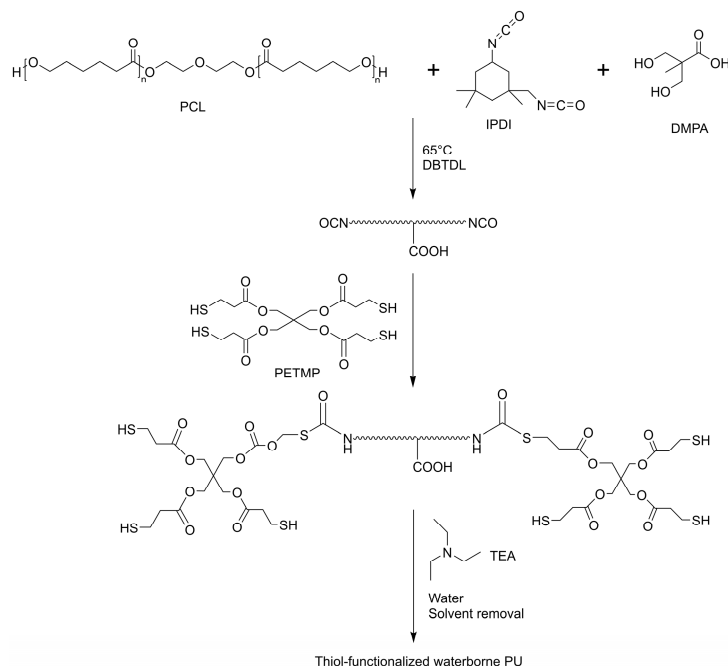


Figure 1. Synthesis of Thiol-WPU dispersion.

2.3. Synthesis of Ene-Functionalized Waterborne Polyurethane (Ene-WPU)

Similarly to the Thiol-WPU preparation, 35.57 g IPDI (0.16 mol), 80.00 g PCL (0.04 mol), 8.05 g DMPA (0.06 mol), and 0.19 g DBTDL (0.15 wt.%) were first dissolved in MEK and reacted at 65 °C for 4 h. Then, 25.72 g TMPAE (0.12 mol) was added and reacted for 70 h at room temperature, followed by the neutralization of 6.07 g TEA (0.06 mol), dispersion in water, and solvent removal (Figure 2). The solid content of Ene-WPU was 35 wt.%.

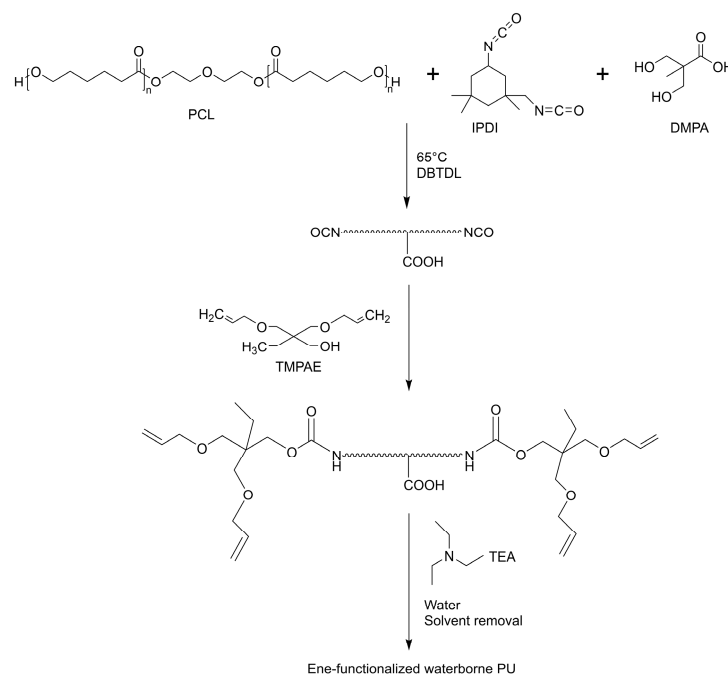


Figure 2. Synthesis of Ene-WPU dispersion.

2.4. Coating Preparation

Firstly, the Thiol-WPU and Ene-WPU were mixed in a molar ratio of 1:1 for the C=C to S=H. Then, 1 wt.%, 3 wt.%, and 5 wt.% BAPO as the photoinitiator was added to the mixture, respectively. The QD-36 standard test steel panels (Q-Lab Corporation, Westlake, OH, USA, W × L × H: 3 in × 5 in × 0.2 in) were cleaned with acetone, and the coating was applied to the panels with a 150 µm wet thickness using a drawdown bar. The coatings were left in a dark environment for 12 h to allow the water to evaporate and then cured either in the UV box (405 nm, 220 W/m², Geeetech, Shenzhen, China) for 5 min or under sunlight for 30 min. Under UV or sunlight exposure, the thiol and ene groups in the WPU underwent a reaction facilitated by the BAPO, resulting in the cured films. The crosslinked structures are illustrated in Figure 3. After curing, all coatings were left in an ambient environment for 7 days before testing. The dry film thickness of the cured coatings was around 40 µm, as measured by an Elcometer digital thickness gauge. The different samples were named based on the content of the photoinitiator, as WPU-1, WPU-3 and WPU-5.

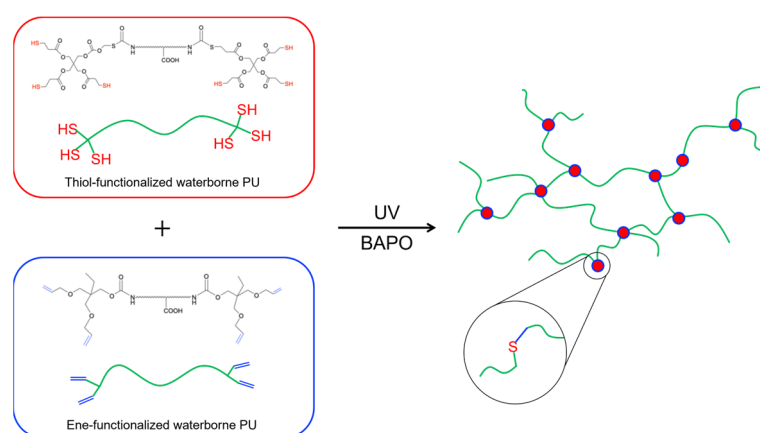


Figure 3. A schematic illustration of the thiol-ene reaction of Thiol-WPU and Ene-WPU.

2.5. Characterization

FTIR spectra were obtained by a Nicolet iS10 FTIR spectrometer (Fisher Scientific, Waltham, MA, USA) at room temperature with an attenuated total reflection mode of 64 scans and a resolution of 4 cm^{−1}. The ¹H NMR spectra were obtained by a Varian INOVA 300 spectrometer (Agilent, Santa Clara, CA, USA) using DMSO as the solvent. The solid-state ¹³C NMR spectra of cured and uncured films were obtained by a Varian VnmrS 500 spectrometer (Agilent, Santa Clara, CA, USA). All NMR measurements were conducted at 23 °C.

The molecular weight of WPU prepolymers was obtained by gel permeation chromatography (GPC; Tosoh HLC-8320GPC, Tosoh, Tokyo, Japan). Polystyrene was used as the standard, and the sample concentration was 5 mg/mL in THF.

The viscosity of WPU dispersions was measured using a rheometer (TA Instruments ARES-G2, New Castle, DE, USA) with a 25 mm cone-and-plate geometry. The measurement was carried out at room temperature, using a shear rate ranging from 1 to 100 s^{−1}.

The thermal stability of WPU coatings was characterized by thermogravimetric analysis (TGA; TA Instruments Q500, New Castle, DE, USA), where 10 mg samples were heated to 600 °C at a steady rate of 10 °C min^{−1} under a nitrogen atmosphere (10 mL min^{−1}) and maintained at 600 °C for 10 min.

The glass transition temperature (*T_g*) of WPU coating films was determined by differential scanning calorimetry (DSC; TA Instruments Q200, New Castle, DE, USA) under a nitrogen atmosphere (40 mL min^{−1}) and at a rate of 10 °C min^{−1}. The weight of the samples was around 5 mg. The temperature range was −70 °C to 80 °C.

The coating morphology images were captured by scanning electron microscope (SEM, FEI Quanta FEG 450, Hillsboro, OR, USA) at 5 kV.

Tensile testing was performed by an Instron 5567 testing machine (Instron Corp, Norwood, MA, USA) according to ASTM D882. Tests were conducted at room temperature, with a crosshead speed of 5 mm min⁻¹. Self-standing films were peeled from the substrates and cut to approximately 30 mm in length and 10 mm in width. Average results were obtained from five duplicable samples for each coating.

General coating properties that were investigated and the standards that were used included pendulum hardness (ASTM D4366), pencil hardness (ASTM D3363), solvent resistance (ASTM D4752), and reverse impact resistance (ISO 6272-2).

3. Results and Discussion

3.1. Analysis of Ene-WPU, Thiol-WPU, and Cured WPU Film

The molecular weights of Ene-WPU and Thiol-WPU were characterized using GPC, and the results are presented in Table 1. The viscosity as a function of shear rate is shown in Figure 4. As the shear rate increased, the viscosity decreased, demonstrating shear-thinning behavior for both Ene-WPU and Thiol-WPU.

Table 1. The molecular weight of WPU prepolymers.

Sample	M _n (g/mol)	M _w (g/mol)	PDI
Ene-WPU	7075	9635	1.36
Thiol-WPU	10,543	20,840	1.98

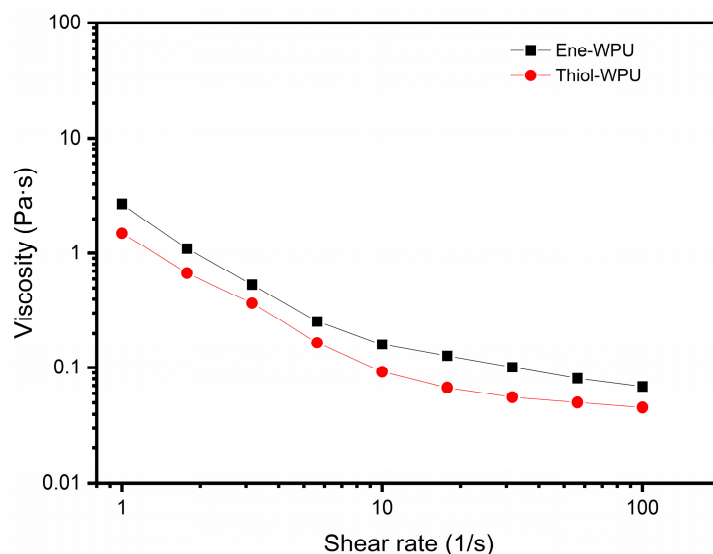


Figure 4. Viscosity of Ene-WPU and Thiol-WPU as the function of the shear rate.

The FTIR spectra of Ene-WPU and Thiol-WPU are shown in Figure 5. In the spectrum of Ene-WPU, the peaks at 1732 cm⁻¹ and 934 cm⁻¹ are attributed to the C=O stretching of the urethane group and the bending of the alkene, respectively [20]. For Thiol-WPU, the peaks at 1733 cm⁻¹ and 2568 cm⁻¹ represent the thiol and urethane groups. Additionally, no peak related to isocyanate groups was observed in both FTIR spectra, confirming that all isocyanate groups had fully reacted.

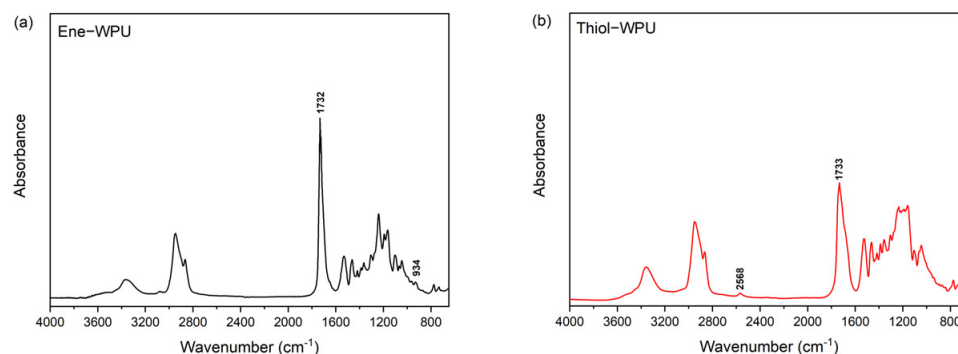


Figure 5. FTIR spectra of (a) Ene-WPU and (b) Thiol-WPU.

The ^1H NMR was used to further confirm the structures of the WPU prepolymers. As shown in Figure 6a, the peaks at 6.8–7.0 ppm correspond to the formation of urethane groups, while the peaks at 5.8 and 5.3 ppm are associated with the alkene groups. In Figure 6b, the peaks at 6.9–7.1 ppm are attributed to the urethane groups, and the peak at 2.4 ppm is linked to the thiol group while the peak at 8.1 ppm represents the formation of the thiourethane group [14,21–23]. For both spectra, the peaks at 0.8 ppm are attributed to $-\text{CH}_3$ from DMPA. Peaks at 0.8 ppm, 1.2 ppm, and 2.7–3 ppm are assigned to signals from IPDI. Additional peaks around 1.2–1.6 ppm, 2.5 ppm, 3.0 ppm, and 4.0 ppm correspond to $-\text{CH}_2$ originating from PCL, DMPA, PETMP, and TMPAE [24,25]. Overall, the FTIR and NMR results confirm the successful synthesis of Thiol- and Ene- WPU.

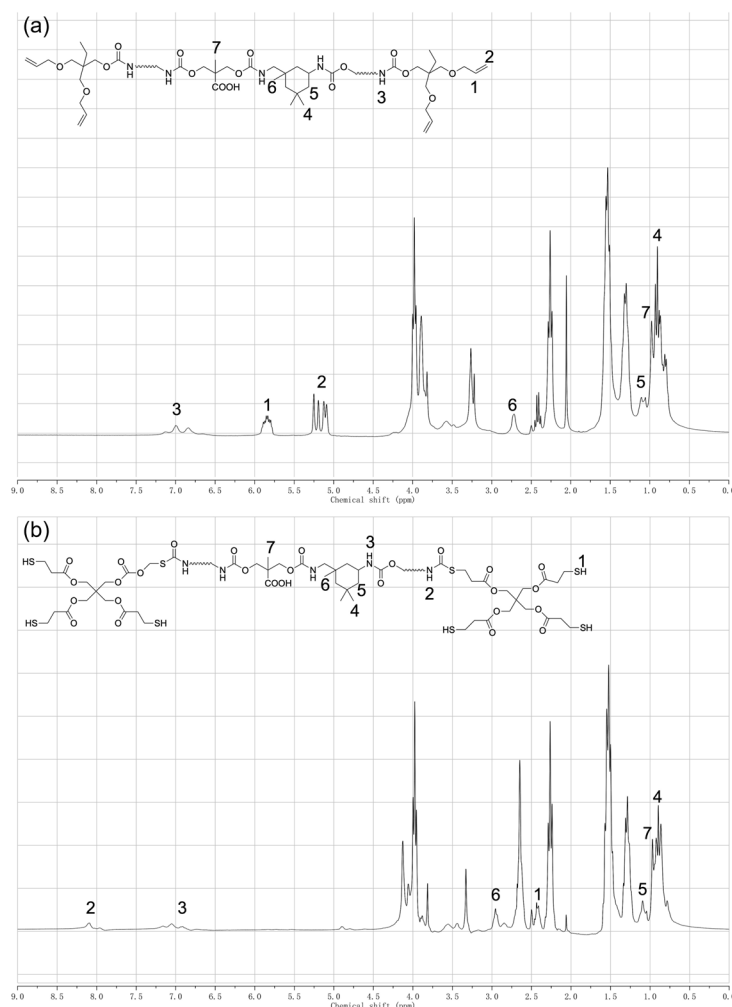


Figure 6. ^1H NMR spectra of (a) Ene-WPU and (b) Thiol-WPU.

The touch-free films could be obtained under UV exposure for 5 min. To further confirm the curing of the WPU film, solid-state NMR was utilized to characterize the WPU film before and after curing. As shown in Figure 7, the peaks at 117.0 and 136.2 ppm correspond to the alkene groups in the uncured WPU spectrum. In contrast, these characteristic peaks nearly disappeared in the cured WPU film, confirming the successful reaction of Thiol- and Ene-WPUs [26,27].

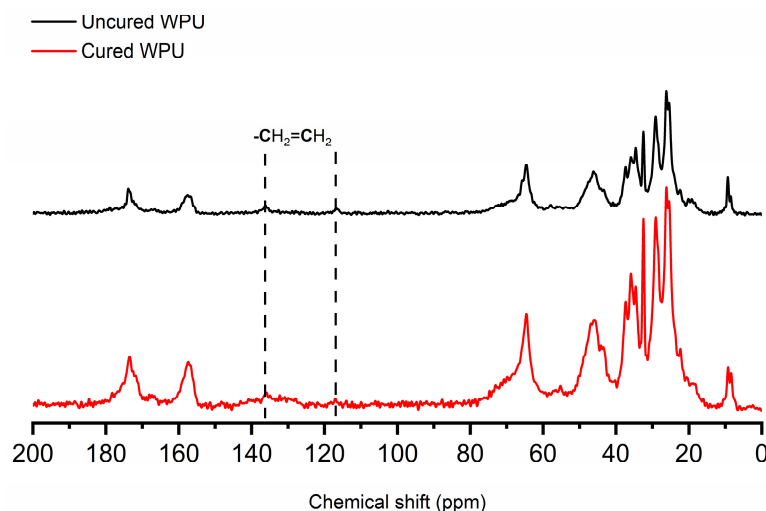


Figure 7. Solid-state ^{13}C NMR of WPU films before and after UV curing.

3.2. Thermal Behavior of WPU Coatings

Figure 8a presents the TGA curves of the WPU coatings. All samples show similar curves with two distinct stages. The first stage involves a gradual weight decrease occurring before 260 °C, attributed to the evaporation of moisture and the decomposition of small molecules within the samples. At this stage, the weight loss is around 5%, with a corresponding temperature (T_5) of 256, 241, and 227 °C for WPU-1, WPU-3, and WPU-5, respectively. The decrease in T_5 with increasing BAPO content may result from the decomposition of small molecules. A similar trend has been observed in other study with varying BAPO contents [28]. In the second stage, the weight percentage declines sharply, ending after 500 °C, which is attributed to the decomposition of the polymers. The increase in photoinitiator content leads to lower T_5 and higher residual mass, due to the decomposition of incompletely cured structures caused by excessive BAPO hindering light penetration [29].

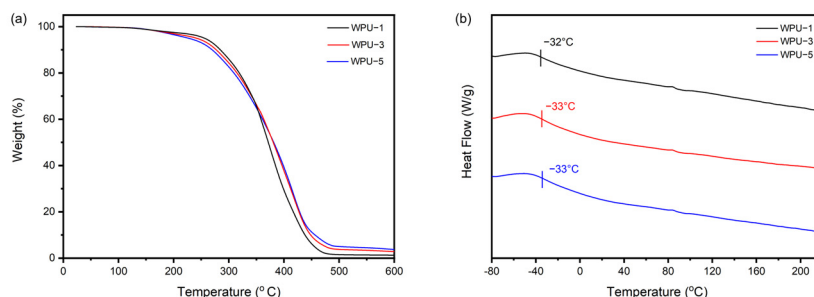


Figure 8. (a) TGA and (b) DSC curves of WPU coatings after UV curing.

The T_g of the WPU coatings was determined from the DSC curves, as shown in Figure 8b. Within the measured temperature range, no characteristic signals were observed, indicating that all functional groups had fully reacted. Additionally, all three samples exhibited a similar T_g between -32 °C and -33 °C, suggesting that the coatings were

homogeneous and that the variations in BAPO content did not significantly affect the T_g of the WPU coatings.

3.3. Surface Morphology of WPU Coatings

The surface morphology of the WPU coatings was evaluated by SEM. All coatings had spherical structures on their surfaces as shown in Figure 9. For WPU-1, the boundaries of the spherical structures were the most pronounced, resulting in the highest roughness of the surface. The formation of spherical structures is attributed to the heterogeneous drying process of the waterborne coating. The rapid drying of the top layer inhibits the evaporation of water from the inside of the wet film, leading to the formation of spherical structures [30,31]. As the BAPO content increased, the boundary became unclear, and the surface became smoother. Furthermore, no significant cracks were observed in any of the samples, indicating good film surface integrity.

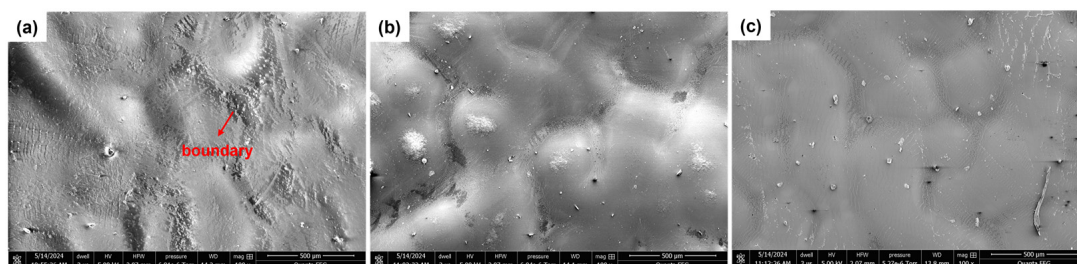


Figure 9. SEM images of (a) WPU-1, (b) WPU-3, and (c) WPU-5.

3.4. Mechanical and General Coatings Properties of WPU Coatings

To verify the feasibility of the WPU coating curing under sunlight, the samples with different BAPO contents were also prepared and cured under the winter sunlight (Akron, OH, USA, 1 °C) for 30 min. The mechanical properties of both UV-cured and sunlight-cured WPU coatings were tested, with results and strain–stress curves presented in Table 2 and Figure 10. In Table 2, the lowest elongation-at-break and tensile strength values are recorded at 149.94% and 3.06 MPa, respectively, for the UV-cured WPU-3; however, its Young's modulus is the highest at 3.95 MPa. Notably, the differences in tensile properties among the UV-cured films were minimal, with all samples showing similar values for elongation-at-break, tensile strength, and Young's modulus. In contrast, the impact of BAPO content on the sunlight-cured WPU coatings was more significant. Sunlight-cured WPU-1 exhibited the lowest tensile properties, indicating poor photoinitiation. Sunlight-cured WPU-5 also showed lower elongation-at-break (119.91%) and tensile strength (1.85 MPa) compared to the UV-cured films. Conversely, sunlight-cured WPU-3 demonstrated the highest elongation-at-break (204.38%), tensile strength (8.62 MPa), and Young's modulus (8.34 MPa) among other sunlight-cured samples, with its tensile strength and Young's modulus even exceeding those of the UV-cured samples. This suggests that 3 wt.% of BAPO is ideal for the WPU coatings cured under sunlight.

Table 2. Mechanical properties of WPU coatings from the tensile test.

	ϵ (%) ^a	σ (MPa) ^b	E (MPa) ^c
WPU-1 (UV)	184.20 ± 24.56	4.10 ± 0.65	3.46 ± 0.41
WPU-3 (UV)	149.94 ± 16.49	3.06 ± 0.89	3.95 ± 0.22
WPU-5 (UV)	195.07 ± 38.68	3.80 ± 1.19	3.43 ± 0.36
WPU-1 (Sun)	82.56 ± 9.95	1.68 ± 0.23	4.02 ± 0.25
WPU-3 (Sun)	204.38 ± 23.52	8.62 ± 1.88	8.34 ± 3.00
WPU-5 (Sun)	119.91 ± 22.07	1.85 ± 0.71	4.12 ± 0.34

^a Elongation-at-break, ^b tensile strength, ^c Young's modulus.

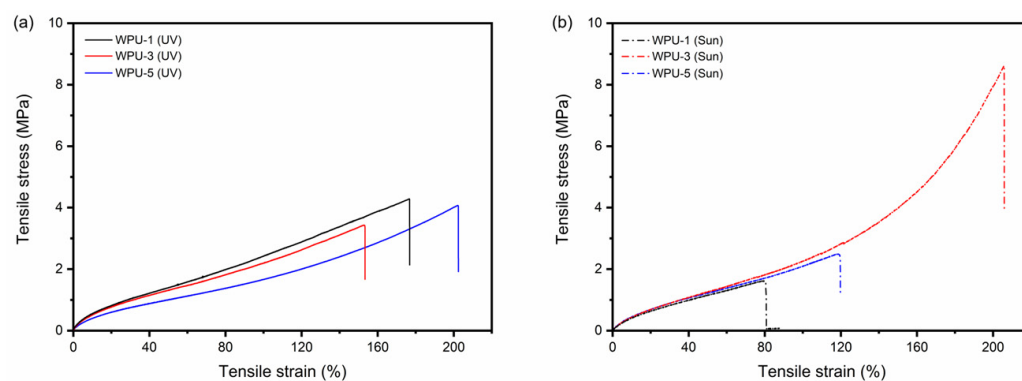


Figure 10. Strain–stress curves of (a) UV-cured WPU and (b) sunlight-cured WPU.

The general coating properties, including pendulum hardness, pencil hardness, solvent resistance, and impact resistance were tested and are summarized in Table 3. The WPU without UV or sunlight exposure was also listed as the control group and named WPU (uncured). These uncured coatings were left in a dark environment for 12 h to allow the water to evaporate. All cured samples showed comparable pendulum hardness, and all showed a pencil hardness of H, indicating good scratch resistance for the WPU coatings. Solvent resistance was evaluated using MEK double rubs. Generally, the UV-cured coatings demonstrated higher solvent resistance than the sunlight-cured WPU, although the difference was not significant. However, the uncured WPU had 3 s of pendulum hardness, less than 5B pencil hardness, and 26 MEK double rubs, which were significantly lower than those of cured films due to lacking crosslinking of uncured film. The result of the control group further proved the occurrence of cross-linking under UV and sunlight. Additionally, the impact resistance of all samples exceeded 200 kg·cm. In summary, while the BAPO content had a slight influence on mechanical properties, it significantly affected the performance of sunlight-cured coatings. Based on the tensile results, 3 wt.% of BAPO WPU is optimal for sunlight-cured WPU coatings. This suggests that the sunlight-cured WPU coatings can be effectively achieved with an appropriate choice of photoinitiator and its content.

Table 3. General coating properties of WPU coatings.

	Pendulum Hardness (s)	Pencil Hardness	Solvent Resistance	Impact Resistance (kg·cm)
WPU (uncured)	3	<5B	26	200 +
WPU-1 (UV)	17	H	42	200 +
WPU-3 (UV)	17	H	48	200 +
WPU-5 (UV)	17	H	45	200 +
WPU-1 (Sun)	17	H	40	200 +
WPU-3 (Sun)	16	H	37	200 +
WPU-5 (Sun)	16	H	41	200 +

4. Conclusions

In this study, Ene-WPU and Thiol-WPU dispersions were prepared by functionalizing isocyanate-terminated polyurethane derived from IPDI, DMPA, and PCL using thiol- and ene- agents. The successful synthesis was confirmed through FTIR and NMR analyses. Tac-free films were obtained via UV and sunlight curing methods through thiol-ene click reactions. The films exhibited low or no odor; solid-state NMR and results of general coating properties further validated the crosslinking of the WPU coatings. The completed films were observed with no visible cracks from SEM images. The thermal stability of

the WPU coatings decreased with the increase in BAPO content, while the DSC results indicated that the coatings were homogeneous with comparable T_g . Although the UV-cured coatings had similar mechanical properties, for sunlight-cured coatings, the WPU with 3 wt.% BAPO showed the best mechanical properties. All coatings showed similar hardness and impact resistance, proving that the WPU coatings can be effectively cured under both UV and sunlight. For sunlight curing, a BAPO content of 3 wt.% proved to be optimal. This research offers a novel method for acquiring WPU coatings by photoinitiation through a click reaction and paves the way for enhanced application in WPU coatings.

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