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UV-Curable Optical-Silicone-Modified Coatings Prepared from CO_2-Based Non-Isocyanate Polyurethane Diol

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Abstract: Though polyurethanes (PUs) are widely used in people's daily lives, traditional PUs are generally fabricated from toxic (poly)isocyanates. Furthermore, (poly)isocyanates are commonly industrially prepared from a seriously toxic and injurious chemical compound named phosgene, which is a dangerous gas that can cause lung irritation and eventually death. As is known to all, the consumption of carbon dioxide (CO_2)-based raw materials in chemical reactions and productions will be conducive to reducing the greenhouse effect. In this paper, non-isocyanate polyurethane (NIPU) diol was fabricated through a polyaddition reaction from ethylenediamine and CO_2-based ethylene carbonate, and then NIPU-based silicone-containing thiol hyperbranched polymers (NIPU-SiHPs) were synthesized from the NIPU diol. Finally, UV-curable optical-silicone-modified CO_2-based coatings (UV-NIPUs) were fabricated from NIPU-SiHPs and pentaerythritol triacrylate by a UV-initiated thiol-ene click reaction without a UV initiator. The UV-NIPUs demonstrated high transparency over 90% (400–800 nm), good mechanical performance with tensile strength reaching 3.49 MPa, superior thermal stability with an initial decomposition temperature (T_{d5}) in the range of 239.7–265.6 °C, moderate hydrophilicity with a water contact angle in the range of 42.6–62.1°, a high pencil hardness in the range of 5–9H, and good adhesive performance of grade 0. The results indicate that it is a promising green chemical strategy to fabricate CO_2-based high-performance materials.

Keywords: UV-curable; silicone-modified coatings; non-isocyanate polyurethanes; carbon dioxide

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1. Introduction

Polyurethanes (PUs) are materials with urethane (carbamate) linkages possessing broad applications in fields such as coatings, adhesives, elastomers, flexible electronics, and wearable electronic devices [1–3]. According to previous reports, the global market of PUs was over USD 82 billion, and it is expected to reach USD 123 billion by 2030 [4]. However, traditional PUs are fabricated by a polyaddition process with (poly)isocyanates and (poly)alcohols [5,6]. As we know, isocyanates are severely toxic petrochemical substances with high risks, such as skin or eye irritation, asthma, and cancer [2,6,7]. Furthermore, isocyanates are commonly prepared from a seriously toxic and injurious chemical compound named phosgene, which is a highly toxic gas that can cause lung irritation and eventually death if inhaled at a concentration above 4 ppm [8]. Last but not least, dibutyltin dilaurate, a substance with toxicity at a low concentration, is most employed as a catalyst for the isocyanate/alcohol reaction to prepare traditional PUs [9].

Recently, non-isocyanate polyurethanes (NIPUs) were found to be a promising substitute to avoid the harmful chemical substances mentioned above [5] because they can be produced by four green chemical pathways, including the polyaddition of polyfunctional cyclic carbonates with polyamines, the copolymerization of carbon dioxide (CO_2) with aziridines, the polycondensation of bis-alkyl carbamates with diols, and the ring-opening polymerization of cyclic carbamates [10]. The synthesis of NIPU by the polyaddition of polyfunctional cyclic carbonates with polyamines is a very promising green chemical method because cyclic carbonates are raw materials synthesized from CO_2. As is known to all, CO_2 is a renewable, green, and abundant natural carbon building block and raw material in chemical synthesis, and the consumption of CO_2-based raw materials in the chemical industry will contribute to reducing the greenhouse effect [9–16]. Additionally, the preparation of NIPU by polyfunctional cyclic carbonates with polyamines will generate many hydroxyl groups on β-carbon atoms, which is beneficial for chemical modification and the formation of hydrogen bonds [13]. An aqueous NIPU reported by Liu shows good thermal resistance with a T_{d5} of 244.5 °C, and the hydroxyl group and tertiary amine of NIPU can enhance the polarity and wettability of carbon fiber [17]. Wang developed a linear NIPU containing polyitaconamide sequences with tensile strength of up to 27 MPa [18]. Clearly, the unique performance of NIPU prepared with this method can bring about new chemical pathways to develop high-performance polymers by chemical modification [19]. As reported, the application of PUs is greatly restricted by their poor thermal stability and low hardness [20–22]. Silicone materials composed of Si–O backbones demonstrate outstanding properties, such as excellent thermal stability, UV resistance, and minimal moisture absorption [23]. So, designing high-performance materials by virtue of polysiloxane and NIPU sequences is a promising strategy to overcome the shortcomings of PUs.

The UV curing method is a green technology widely studied due to its distinct advantages of low solvent emission (low VOC), high efficiency, and optimized energy consumption [21,22,24]. Commonly, a UV initiator is a quite important ingredient for UV-curable materials as it plays a key role in the curing speed and comprehensive performance of UV-curable materials [25]. However, the application of a UV initiator usually comes with serious drawbacks such as toxicity, yellowing, odor, migration, etc., which seriously limits the practical application of UV-curable materials in fields such as the biomedical field and food packaging [26,27]. In this paper, UV-curable optical-silicone-modified coatings (UV-NIPUs) were fabricated from CO_2-based NIPU diol by UV-initiated thiol-ene click reaction without a UV initiator. The UV-NIPUs exhibited high transparency, good mechanical performance, superior thermal stability, moderate hydrophilicity, good UV resistance, high pencil hardness, and good adhesive performance. This study presents a green strategy to design high-performance optical-silicone-modified materials made from CO_2-based raw materials.

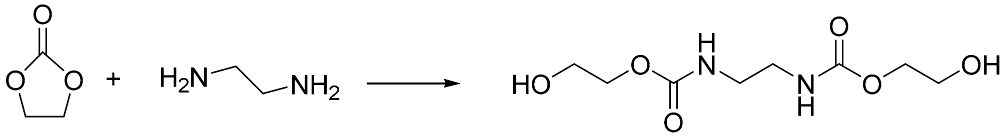
2. Materials and Methods

2.1. Materials and Reagents

Ethylene carbonate (EC, A. R.), mercaptopropyltrimethoxysilane (MPTES, A. R.), and ethylenediamine (EDA, A. R.) were purchased from Beijing HWRK Chem Co., Ltd. (Beijing, China). Pentaerythritol triacrylate (PETA, A. R.) was supplied by McLean Biochemical Technology Co., Ltd. (Shanghai, China). 2-Hydroxy-2-methyl-1- phenylacetone (HMPP, 99.0%, A. R.) was obtained from Shanghai Qitai Chemical Technology Co., Ltd. (Shanghai, China).

2.2. Synthesized CO_2-Based NIPU Diol

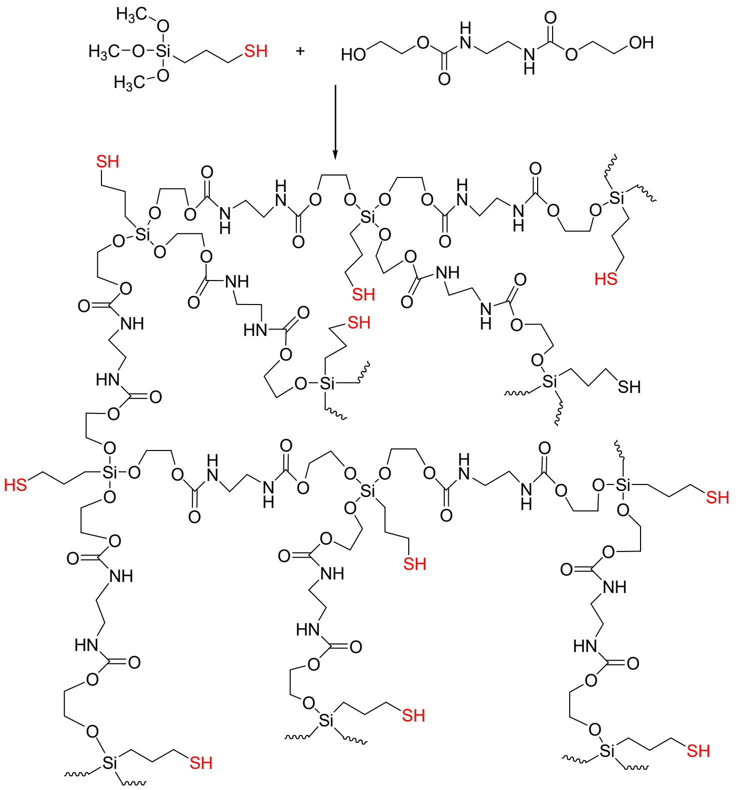
Synthesis of NIPU by polyaddition of CO_2-based raw material polyfunctional cyclic carbonates with polyamines is one of promising green chemical methods [6]. According to the route shown in Scheme 1, like in reference [28], 92.4630 g (1.05 mol) EC was added into a 250 mL three-necked flask and heated to 60 °C, then 30.0500 g (0.5 mol) EDA was dropped into it with a funnel for about 2 h. Thereafter, the reaction was conducted at 100 °C for 8 h followed by removing the residual raw materials and by-products by vacuum distillation at 110 °C for about 3 h. Finally, 107.8344 g white solid product of CO_2-based NIPU diol with yield of 91.3% was obtained after a further treatment in a vacuum oven for 24 h at 60 °C. The NIPU diol prepared was characterized by FT-IR and ^{1}H-NMR, as shown in Figures S1 and S2.



Scheme 1. Route for synthesis of CO_2-based NIPU diol.

2.3. Synthesized NIPU-Based Silicone-Containing Thiol Hyperbranched Polymers (NIPU-SiHPs)

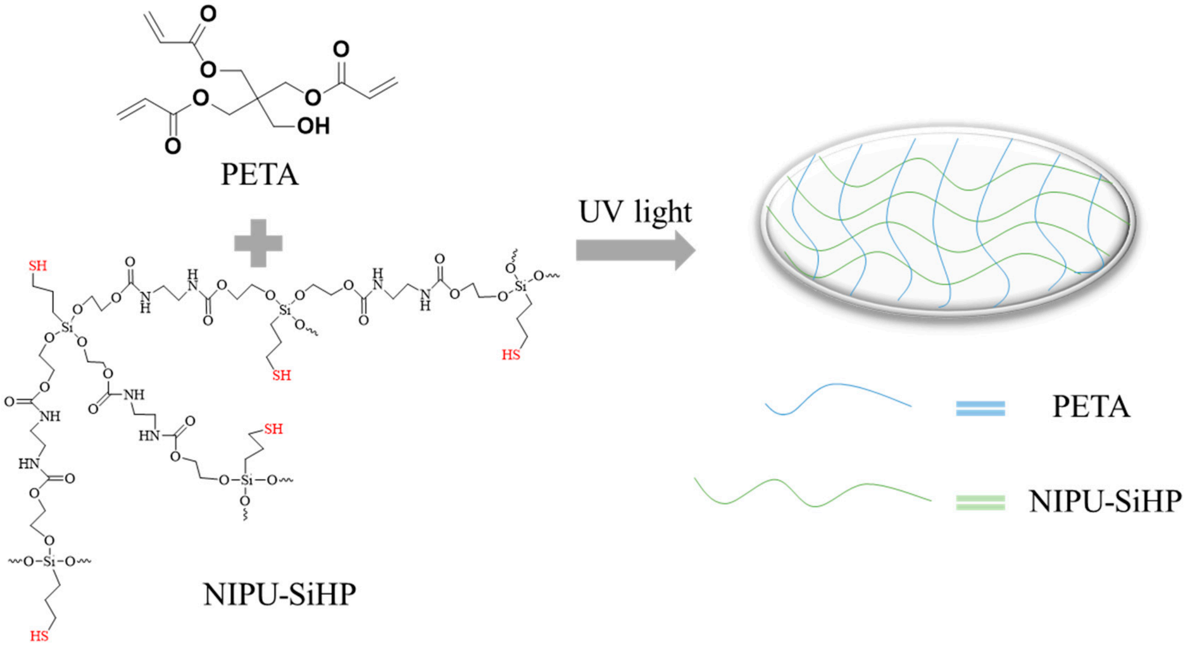
According to the formula collected in Table S1 and the route shown in Scheme 2, NIPU-SiHPs were synthesized by condensation reaction between the hydroxyl group of NIPU diol and the Si–OCH_3 group according to [29]. Taking the fabrication of NIPU-SiHP-3 for example, 19.6340 g (0.1 mol) MPTES and 23.7088 g NIPU diol (0.16 mol) were added into a 100 mL three-necked flask and reacted at 100 °C for 2 h. Later, the temperature was elevated from 100 °C to 160 °C gradually for 3 h and the reaction was conducted for another 1 h. Finally, about 22.6428 g light yellow liquid of NIPU-SiHP-3 was obtained after the mixture was cooled to about 80 °C. The raw materials and by-products were removed by vacuum distillation for about 2 h. The NIPU-SiHP-3 prepared was characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR and ^{29}Si-NMR, as shown in Figures S3–S6.



Scheme 2. Route for synthesis of NIPU-SiHPs.

2.4. Fabrication of UV-Curable Optical Silicone-Modified Coatings (UV-NIPUs) from CO_2-Based NIPU

According to the procedure shown in Scheme 3, the UV-NIPUs were fabricated. As is typical, the molar ratio of thiol groups to acrylate groups (n_{thiol}:$n_{acrylate}$) was 2:1, and about 0.5 g mixture of NIPU-SiHP-3 and PETA were coated on half of the glass slides with thickness of about 0.3 mm. After the slides were kept in a vacuum oven to remove bubbles and make the uncured coatings as smooth as possible for about 0.5 h at 25 °C, they were cured by UV-initiated thiol-ene reaction using a UV apparatus (ZB1000, Changzhou Zibo Electron Technology Co., Ltd. (Changzhou, China), 365 nm, 10.6 mW·cm^{-2}, the distance of the slides to the light is 20 cm).



Scheme 3. Route for synthesis of UV-NIPUs.

2.5. Characterization

^{1}H-NMR spectra were record on a Bruker AVANCE AV400 (400 MHz) spectrometer (Bruker Corporation, Karlsruher, Germany). ^{13}C-NMR and ^{29}Si-NMR spectra were record on a Bruker AVANCE AV600 (600 MHz) spectrometer (Bruker Corporation, Karlsruher, Germany). All the NMR analyses were conducted in $CDCl_3$ without tetramethylsilane (TMS) as internal reference. FT-IR spectra were record on a Nicolet 700 spectrometer (Nicolet Co., Ltd., Madison, WI, USA) with an ATR. Transmittance over 400–800 nm of UV-NIPUs was measured by a UH5300 double-beam UV/Vis spectrophotometer (Hitachi Instrument Co., Ltd., Tokyo, Japan). Gelation rate (GR) were calculated by the equation GR = $\frac{M_0-M}{M_0} \times 100\%$, where M_0 and M were the original and residual mass of UV-NIPUs before and after washing with toluene by Soxhlet extraction at 150 °C for 4 h. The pencil hardness of UV-NIPUs was evaluated according to GBT6739-2006 using a BGD-562 pencil hardness meter (Zhenwei Testing Machinery Co., Ltd., Jiangdu, China). Adhesion performance was examined with a BGD-502 paint film according to ISO 2409-2007 by cross-cut test. Surface water contact angle was evaluated by a KRUSS DSA30 water contact angle meter (KRÜSS, Hamburg, Germany) according to "Measurement of water-contact angle of plastic films", GB/T 30693-2014. Differential scanning calorimetry (DSC) of UV-NIPUs was analyzed with a DSC Q100 apparatus (TA Instruments, New Castle, DE, USA) under N_2 atmosphere according to the following procedure. UV-NIPUs were heated to 80 °C, kept for 2 min to eliminate the thermal history, then cooled to −60 °C, and finally heated again to

80 °C with a speed of 10 $^{\circ}C \cdot min^{-1}$. Thermogravimetric analysis (TGA) was conducted on a TG 209C apparatus (NETZSCH–Gerätebau GmbH, Selb, Germany) under N_2 atmosphere from room temperature to 800 °C at a rate of 10 $^{\circ}C\ min^{-1}$. Tensile testing of UV-NIPUs (60 mm × 8 mm × 0.7 mm) was conducted according to GB/T 528-2009/ISO 37:2005 on a XLW-500 electronic tensile testing machine (Sanquan Zhongshi Experimental Instruments Co., Ltd., Jinan, China) with a load of 100 N at a loading rate of 60 mm/min. The cross-linking density was assessed by swelling experiment according to reference [30]. The samples were immersed in toluene for 72 h and cross-linking density (SD) was described as $SD = [m_0/\rho_e + (m - m_0)/\rho_s]/(m_0/\rho_e)$, where m_0 and m are the weight of the unswollen and swollen material (in g), respectively, and ρ_e and ρ_s are the density of UV-NIPUs and toluene (in g cm^{-3}), respectively.

3. Results and Discussion

3.1. Comparison Between the UV-NIPUs Prepared with and Without UV Initiator HMPP

Generally, UV initiator and UV curing time both significantly impact the curing degree, so as to play an important role in the comprehensive performance of UV-curable materials. Firstly, the UV-NIPU prepared from NIPU-SiHP-3 and PETA was cured with UV initiator HMPP. It can be seen from Figure 1 and Table 1 that when UV curing time is only 10 s, the GR and pencil hardness are as high as 92.7% and 9H, respectively, which demonstrated that the UV-NIPUs can be cured quite quickly. It is in favor of improving the production efficiency and reducing energy consumption. As mentioned above, a UV initiator is an essential ingredient for traditional UV-curable materials, significantly influencing the curing speed and comprehensive performance [25]. However, the application of a UV initiator usually causes drawbacks such as toxicity, yellowing, odor, migration, etc., which seriously restricts the practical application in the biomedical field and food packaging [26,27]. Since a UV initiator usually causes significant drawbacks and this UV-curable system can be cured so quickly, it is very worthwhile to try the UV-curing reaction without a UV initiator. Encouragingly, it can be seen from Figure 1 and Table 1 that the UV-NIPUs can also be cured quickly without HMPP. If the UV-curing time is only 5 s, the cured materials have GR and pencil hardness as high as 79.1% and 5H, respectively. As shown by Figure 1, the cross-linking density of the UV-NIPUs prepared with HMPP ranges from 0.9821 $g \cdot mL^{-1}$ to 1.4.56 $g \cdot mL^{-1}$, while that of UV-NIPUs prepared without HMPP ranges from 0.6791 $g \cdot mL^{-1}$ to 1.2837 $g \cdot mL^{-1}$. Though both the GR and cross-linking density of the UV-NIPUs prepared without a UV initiator are lower than those of the UV-NIPUs initiated by HMPP at the same curing time, the pencil hardness of the UV-NIPUs without HMPP can also reach 5H when the curing time is as short as 5 s (Table 1). If the curing time is longer than 10 s, the pencil hardness of UV-NIPUs prepared without a UV initiator also can reach 9H. It can be seen that the favorable UV-curing time is 40 s.

From the results mentioned above, it is evident that this method possesses three prominent advantages. (1) The process of fabrication of UV-NIPUs avoids the application of highly toxic raw materials such as phosgene and (poly)isocyanates; (2) CO_2-based raw materials can be utilized to develop silicone-modified NIPUs with high performance, which will contribute to reducing the greenhouse effect; (3) the UV-NIPUs were prepared without a UV initiator, which will be helpful to expand the practical application of UV-curable materials in fields such as the biomedical field and food packaging.

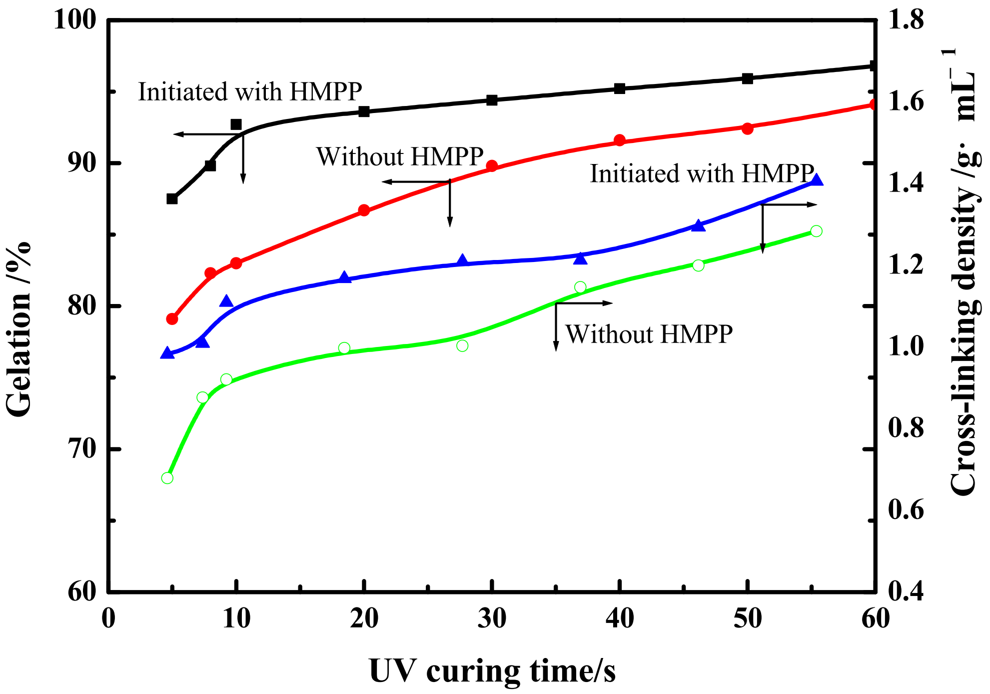


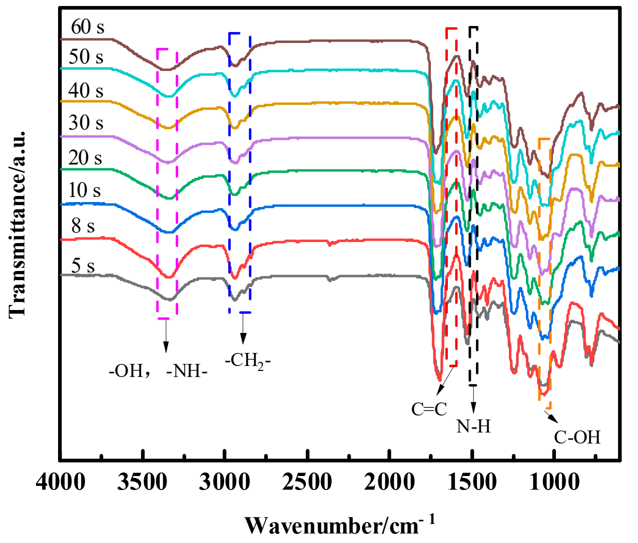
Figure 1. Comparison between the gelatin ratios of UV-NIPUs prepared with and without HMPP.

Table 1. Comparison of pencil hardness between UV-NIPUs prepared with and without HMPP.

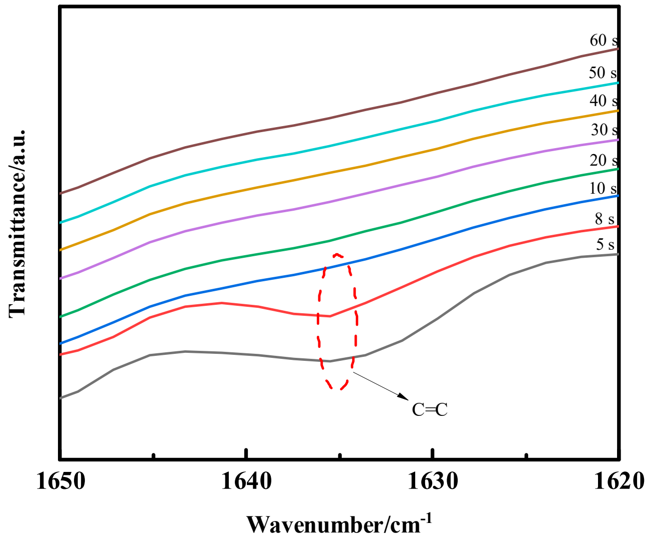
UV Curing Time/s	Pencil Hardness	
	Initiated by HMPP	Without HMPP
5	8H	5H
8	9H	8H
10	9H	9H
20	9H	9H
30	9H	9H
40	9H	9H
50	9H	9H
60	9H	9H

Conditions: NIPU-SiHP is NIPU-SiHP-3 and n_{thiol}:$n_{acrylate}$ = 2:1.

FT-IR spectra of UV-NIPUs cured without HMPP for different amounts of time are shown in Figure 2. The characteristic absorption peaks are as follows: –OH (v, 3400 cm^{-1}), –NH– (v, 3300 cm^{-1}), 2942 cm^{-1} (vas, $–CH_2–$), 2836 cm^{-1} (v, $–CH_2–$), 1540 cm^{-1} (δ, N–H), 1043 cm^{-1} (v, C–OH) [28]. Clearly, there is an obvious absorption peak at 1635 cm^{-1} attributed to the characteristic absorption of C=C in acrylate groups of PETA when the UV-curing time is about 5–8 s, while with the prolongation of UV-curing time, the intensity of the absorption peak gradually became weaker and weaker until it vanished completely when the UV-curing time reached 40 s.



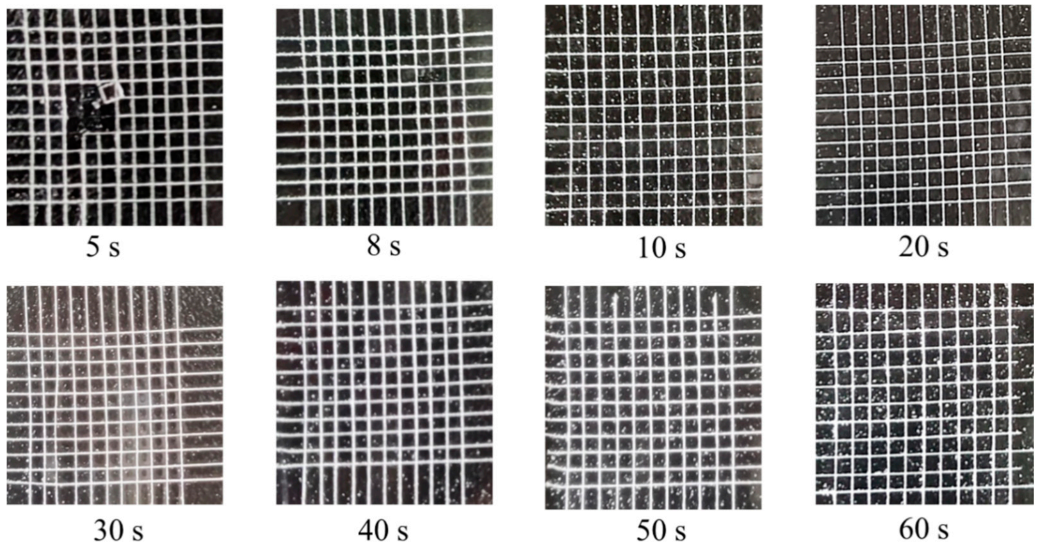
(**a**) The spectra over 4000–600 cm^{-1}



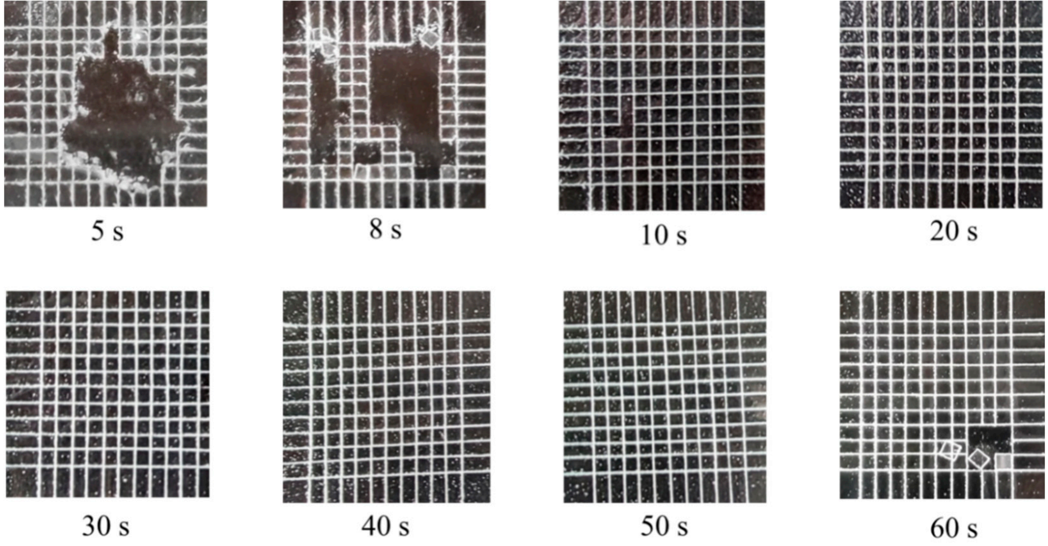
(**b**) The spectra over 1620–1650 cm^{-1}

Figure 2. FT-IR spectra of UV-NIPUs cured for different amounts of time.

The adhesive performance of the UV-NIPUs on glass slides was studied as shown in Figure 3. In both the UV-NIPUs cured with and without HMPP, the adhesive performance can reach grade 0 when the UV-curing time is in the range of 20–60 s. Clearly, if the UV-curing time is shorter than 20 s, the UV-NIPUs prepared without HMPP exhibit relatively worse adhesive property than those prepared with HMPP. So, a conclusion can be drawn that a higher cross-linking density of the UV-NIPUs obtained will result in a better adhesive property. Above all, UV-NIPUs with GR about 94.1%, pencil hardness as high as 9H, and good adhesive performance of grade 0 can be developed by the UV-curing method for 20–60 s without a UV initiator, which may meet the requirements of 3D printing and overcome the drawbacks of the UV-curable materials prepared with photo-initiators.



(**a**) Adhesive performance of materials cured for different time with HMPP



(**b**) Adhesive performance of materials cured for different amounts of time without HMPP.

Figure 3. Adhesive performance of materials cured for different time.

3.2. Performance of UV-NIPUs Prepared Without HMPP

3.2.1. Coating Performance of Different NIPU-SiHPs on the Properties of UV-NIPUs

The molar ratio of MPTES to NIPU will affect the chemical structure of NIPU-SiHPs, so a series of UV-NIPUs were fabricated from NIPU-SiHPs synthesized by adjusting the molar ratio of MPTES to NIPU, as shown in Table S1, and the coating performance of them is shown in Table 2. As reported, the pencil hardness of UV-curable traditional PUs mainly ranges from 2B to HB, and not more than 2H, while that of the transparent silicone-modified PUs ranges from 3H to 9H [21]. Obviously, one can see from Table 2 that the UV-NIPUs exhibit very high pencil hardness of 9H, which will contribute to the anti-scratch properties in the course of storage and transportation [21]. It also can be seen in Table 2 that the UV-NIPUs demonstrated a fairly low water absorption rate ranging from 2.1% to 2.9%, which increased with the reduction in the cross-linking density from 1.3156 g·mL^{-1} to 1.1985 g·mL^{-1}. The nonpolar Si−O chain and special self-helical molecular structure give the surfaces of silicone materials strong hydrophobicity [31]. As reported, hydrophilicity will contribute to the sense of texture and touch of materials, which can be used as a moisturizing material for wound dressings, toiletries, etc. [32]. Water contact angle is an impact factor to evaluate the hydrophilicity of the materials. As shown in Table 2, the water contact angle of UV-NIPUs reduced from 62.1° to 42.6° with the decrement in the molar ratio of MPTES to NIPU from 1:1.4 to 1:1.8. It implies that a lower molar ratio of MPTES to NIPU will result in a higher content of NIPU, which is responsible for the improvement of hydrophilicity thanks to a higher content of secondary amine and hydroxyl groups in NIPU-SiHPs.

Table 2. Coating performance of UV-NIPUs prepared with different NIPU-SiHPs.

UV-NIPUs	GR/%	Pencil Hardness	Water Absorption Rate/%	Water Contact Angle/°	Cross-Linking Density/g·mL^{-1}
UV-NIPU-1	94.5	9H	2.1	62.1	1.3156
UV-NIPU-2	94.8	9H	2.5	55.1	1.3328
UV-NIPU-3	93.0	9H	2.6	53.4	1.2461
UV-NIPU-4	92.2	9H	2.7	45.6	1.2097
UV-NIPU-5	91.7	9H	2.9	42.6	1.1985

Conditions: n_{thiol}:$n_{acrylate}$ = 2:1. The UV-curing time is 40 s.

3.2.2. Transmittance

Highly transparent materials are sought for package materials of optical devices, and the transparency of UV-NIPUs was evaluated, as shown in Figure 4. The transmittance is in the order of UV-NIPU-5 < UV-NIPU-2 < UV-NIPU-1 < UV-NIPU-3 < UV-NIPU-4, which means the compatibility of NIPU-SiHPs with PETA is in the order of NIPU-SiHP-5 < NIPU-SiHP-2 < NIPU-SiHP-1 < NIPU-SiHP-3 < NIPU-SiHP-4. It can be seen that UV-NIPUs obtained from different NIPU-SiHPs show a fairly high transmittance in the range of 88.3%–99.0% at 400–800 nm, and in particular, the transmittance of UV-NIPUs is in the range of 93.1%–99.0% at 800 nm, which means they can meet the demand of optical devices [21,22].

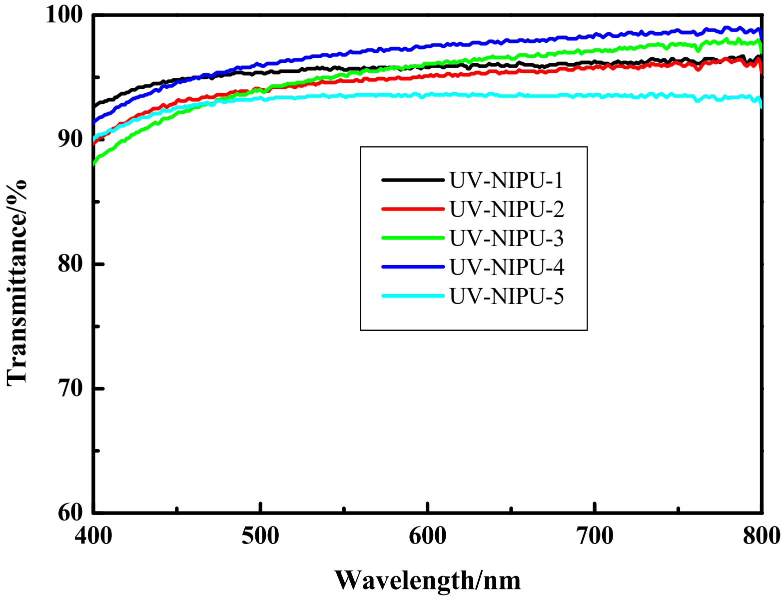
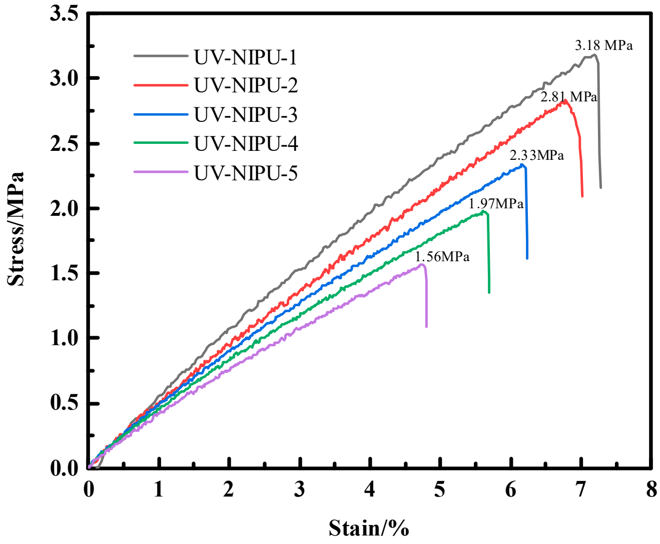


Figure 4. Transmittance of UV-NIPUs.

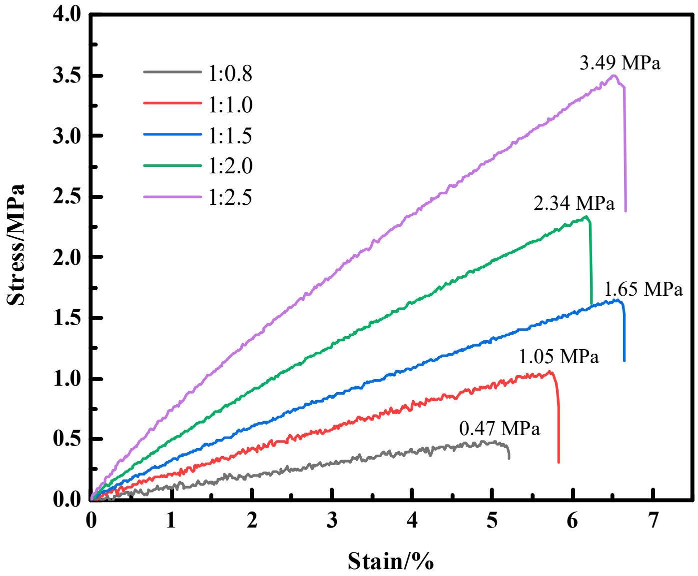
3.2.3. Mechanical Performance

As shown Figure 5a, the tensile strength of UV-NIPUs increased from 1.6 MPa to 3.2 MPa with NIPU-SiHPs synthesized by varying the molar ratio of MPTES to NIPU from 1:1.8 to 1:1.4, which is attributed to the cross-linking density increasing from 1.1985 g·mL^{-1}

to 1.3156 g·mL^{-1} (Table 2). A higher content of NIPU will lead to a lower cross-linking density, resulting in a lower tensile strength of UV-NIPUs.



(**a**) UV-NIPUs prepared with different NIPU-SiHPs



(**b**) UV-NIPUs prepared with different n_{thiol}:$n_{acrylate}$

Figure 5. Stress–strain curves of UV-NIPUs.

The n_{thiol}:$n_{acrylate}$ ratio also plays an important role in the mechanical performance because it will greatly affect the cross-linking density of UV-NIPUs. As shown in Figure 5b, when n_{thiol}:$n_{acrylate}$ decreases from 1:0.8 from 1:2.5, the UV-NIPUs have an enhancement of tensile strength from 0.47 MPa to 3.49 MPa accompanied by an increment in gelatin ratio from 81.0% to 93.5% (Table S2). It revealed that a higher n_{thiol}:$n_{acrylate}$ ratio will result in a poorer mechanical performance due to the lower gelatin ratio.

As reported, unreinforced transparent pure silicone elastomers have tensile strength not higher than 0.4 MPa, and that of UV-curable transparent silicone-modified materials prepared from hyperbranched silicon-containing polymers and polyurethane-acrylates can reach 3.40 MPa [29]. The tensile strength of transparent and mechanically high-performance soft materials reported by Y. Takeoka et al. is no more than 1.5 MPa [33]. All in all, the UV-NIPUs can achieve fairly high tensile strength of 3.49 MPa, attributed to the hydrogen bonds formed by hydroxyl groups on β-carbon atoms generated during the course of preparation of NIPU by polyfunctional cyclic carbonates with polyamines [13,34].

3.2.4. Solvent/Water Resistant Performance

To evaluate the UV-NIPUs in a variety of environmental conditions, the solvent/water resistant performance was further assessed by immersing the intact UV-NIPU-3 samples into deionized water, N,N-dimethylformamide (DMF), n-hexane, toluene and tetrahydrofuran (THF), respectively. As shown in Figure 6, after being immersed for about 24 h, except the samples in DMF, toluene and THF, which became brittle and easily broke, the samples in deionized water and n-hexane were still in good condition. Therefore, the UV-NIPUs exhibited good resistance to water and n-hexane but poor resistance to solvents such as DMF, toluene and THF.

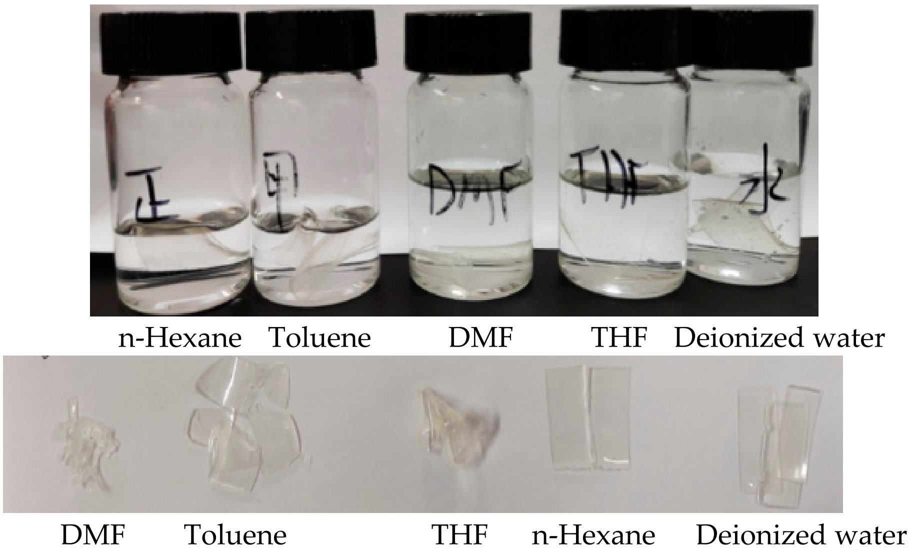


Figure 6. Images of UV-NIPUs immersed in solvent/water for 24 h.

3.2.5. Thermal Stability

TGA analysis was adopted to evaluate the thermal stability of UV-NIPUs. As exhibited by Figure 7 and Table 3, when the NIPU-SiHPs were synthesized by changing the molar ratio of MPTES to NIPU from 1:1.4 to 1:1.8, the thermal decomposition temperature T_{d5}, T_{d10} and T_{d50} of UV-NIPUs reduced from 265.6, 286.6 and 428.6 °C to 239.7, 257.7 and 411.7 °C, respectively. As we know, the silicone segment exhibited good thermal stability, attributed to a high Si–O bond energy [35]. So, the decrement in thermal stability may be attributed to the decease in the cross-linking density from 1.3156 g·mL^{-1} to 1.1985 g·mL^{-1} and the reduction in the amount of silicone segments in the UV-NIPUs. Clearly, T_{d5} of UV-NIPUs is in the range of 239.7–265.6 °C, which is higher than the T_{d5} of the UV-curable silicone-modified traditional PUs reported by reference [29] (203.4–281.0 °C). So, the UV-NIPUs demonstrated outstanding thermal stability.

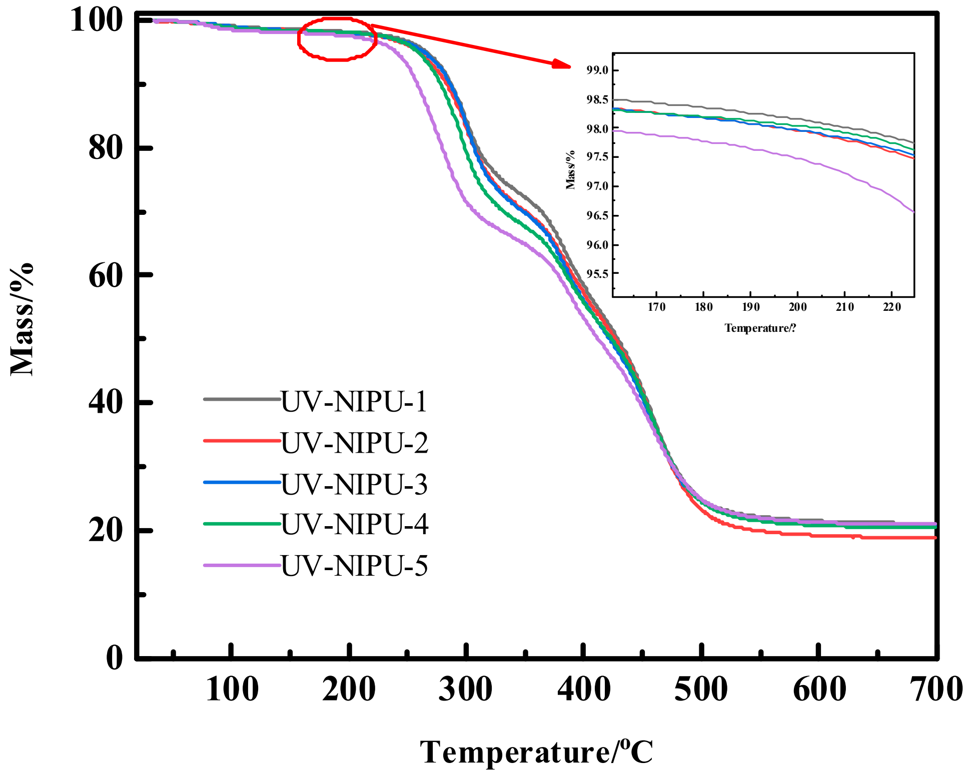


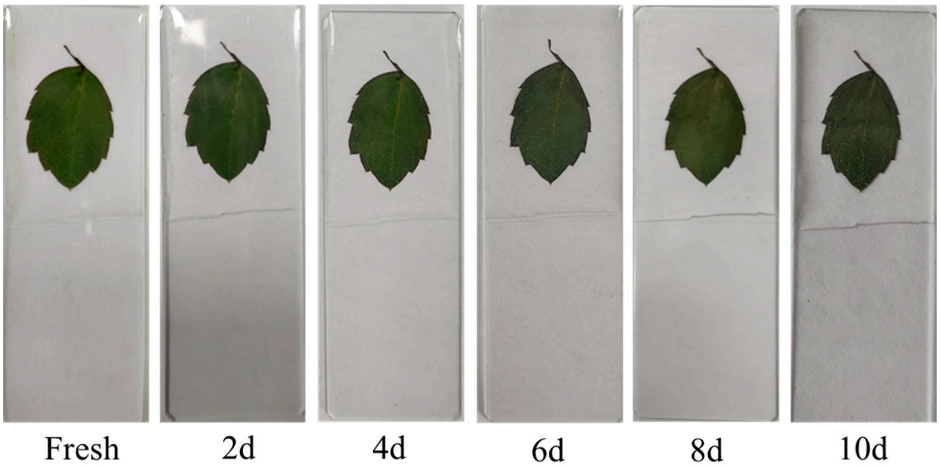
Figure 7. TGA curves of UV-NIPUs.

Table 3. The data of TGA analysis of UV-NIPUs.

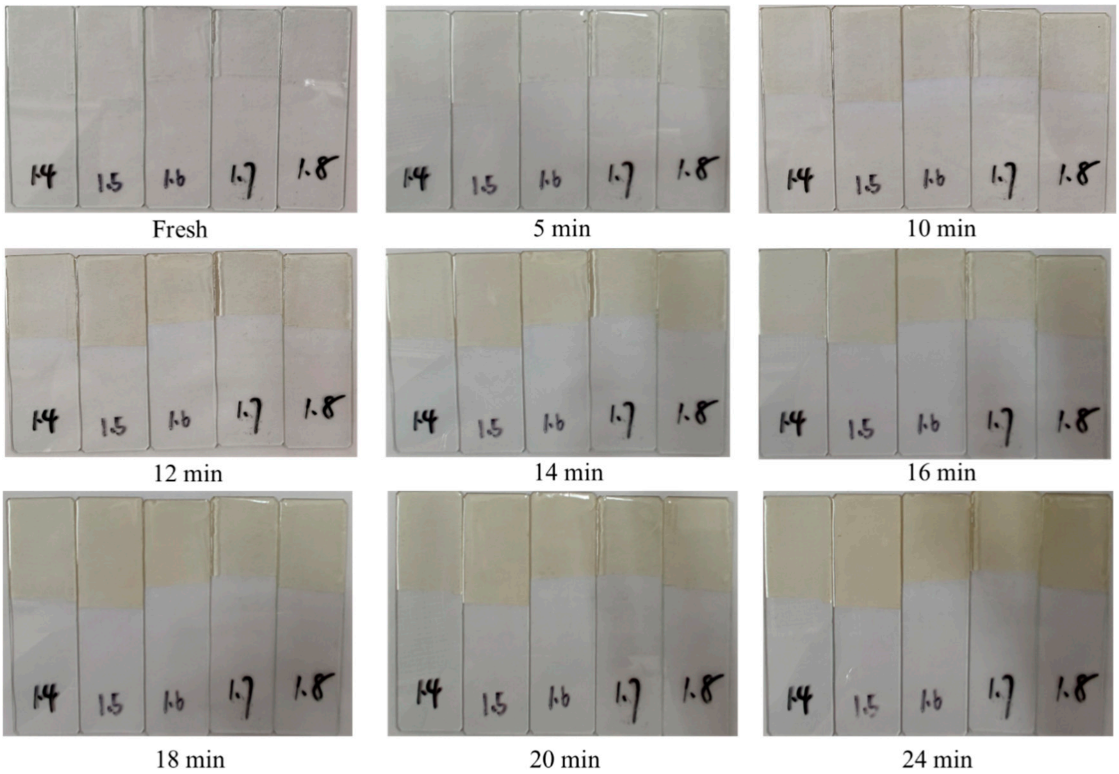
Samples	T_{d5}/°C	T_{d10}/°C	T_{d50}/°C
NIPU-SiHP-1	265.6	286.6	428.6
NIPU-SiHP-2	262.6	285.6	426.6
NIPU-SiHP-3	258.6	282.6	421.6
NIPU-SiHP-4	257.7	277.7	423.7
NIPU-SiHP-5	239.7	257.7	411.7

3.2.6. UV Resistance

To evaluate the UV resistance performance, firstly, slides coated with UV-NIPUs-3 were exposed to UV under 6.5 mW·cm^{-2} (JC2-UV400,120 w, 365 nm, the distance of the slides to the light is 38 cm) with rotation rate of 6 r/min. As shown in Figure 8a, even after being exposed to UV for 10 days, the UV-NIPUs-3 samples remain almost the same as the fresh samples. Later, to investigate the accelerated UV aging performance, slides coated with UV-NIPUs prepared with different n_{thiol}:$n_{acrylate}$ were exposed to UV under 10.6 mW·cm^{-2} (ZB1000, Changzhou Zibo Electron Technology Co., Ltd. (Changzhou, China), 365 nm, the distance of the slides to the light is 20 cm). It can be seen from Figure 8b that the sample began to turn slightly yellow after 10 min exposure and turned obviously yellow after 24 min exposure. Compared with the UV-curable silicone-modified materials reported previously [21], the UV-NIPUs possess fairly good UV resistance ability.



(**a**) Exposed to UV under *6.5* mW·cm^{-2}



(**b**) Exposed to UV under 10.6 m*W*·cm^{-2}

Figure 8. Images of UV resistance performance investigation.

4. Conclusions

To overcome the serious shortcomings of traditional PUs fabricated from toxic raw materials, UV-curable optical silicone-modified coatings were developed from CO_2-based NIPU diol by UV-initiated thiol-ene click reaction without a UV initiator. The UV-curable CO_2-based silicone-modified coatings demonstrated transparency over 90% (400–800 nm), tensile strength reaching 3.49 MPa, T_{d5} in the range of 239.7–265.6 °C, water contact angle of 42.6–62.1°, pencil hardness of 5–9H, and good adhesive performance of grade 0. It provides a promising green chemical ideal for developing high-performance silicone-modified materials from CO_2-based raw materials.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings15020165/s1, Figure S1: FT-IR spectrum of NIPU diol with the integral ratios. Figure S2: ^{1}H-NMR spectrum of NIPU. Figures S3–S6: FT-IR, ^{1}H-NMR, ^{13}C-NMR and ^{29}Si-NMR spectra of NIPU-SiHP-3. Table S1: The formula for fabrication NIPU-SiHPs. Table S2: Impact of different molar ratio of acrylate to thiol group on the UV-NIPUs. Refs. [28,36] are cited in the Supplementary Materials file.

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Conflicts of Interest: Author Junyi Li was employed by Sunliky New Material Technology Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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