High Tensile Strength UV-Cured Castor Oil-Based Silicone-Modified Polyurethane Acrylates

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Procedure for preparation of UV cured materials

Tensile−strain curves of UV cured materials prepared with different molar ratios of acrylate to mercapto groups
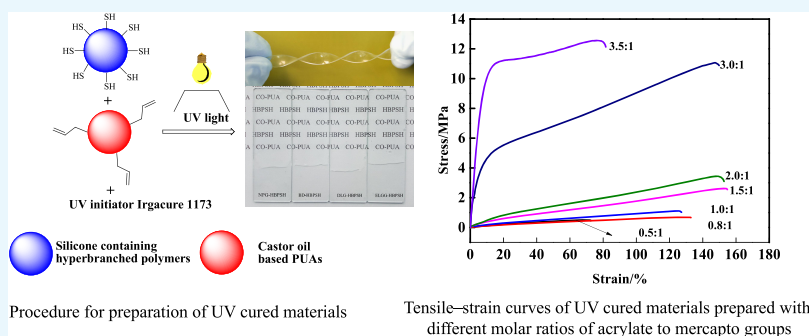
ABSTRACT: High tensile strength UV-cured transparent materials are highly desired in optical devices. In this paper, high tensile strength UV-cured transparent castor oil-based polyurethane acrylates (PUAs) with a very high transmittance over 95% (400−800 nm) were prepared from UV-curable castor oil-based polyurethane acrylates (CO-PUAs) and mercapto silicone-containing hyperbranched polymers (HBPSHs) under UV irradiation. The tensile strengths of UV-cured transparent castor oil-based PUAs can reach 12.49 MPa, which is obviously higher than that of UV-cured CO-PUAs reported previously (0.7−10.20 MPa). The chemical structure of HBPSHs will play an important role in the mechanical performance of UV-cured silicone-modified materials, and it can be concluded that the more rigid the units of α,β-dihydroxyl derivatives used in the fabrication of HBPSHs are, the higher the mechanical strength and pencil hardness of the UV-cured materials will be.

1. INTRODUCTION

As reported, the global market of UV-curable materials stood at about $4.6 billion in 2020,[1] which is attributed to their broad applications in fields such as coatings,[2−4] packaging materials,[5,6] electronics,[7,8] 3D printing,[9,10] and adhesives owing to their fast curing speed at ambient temperature, low energy consumption, low volatile organic chemical (VOC) emissions, etc. As a kind of important UV-curable material, UV-cured polyurethane acrylates (PUAs) have outstanding performances, including excellent adhesion to substrates, extraordinary flexibility, and excellent abrasion resistance.[2,11] However, the mechanical performance and chemical resistance of UV-cured PUAs are limited by the low density and inadequate photosensitive groups of the linear PUA oligomers.[12] Because high tensile strength transparent materials are highly desired in optical devices,[7,13,14] efforts should be devoted to develop high tensile strength transparent PUAs.

On the other hand, UV-curable materials are mostly composites of derivatives of petroleum-based raw materials, including reactive diluents, prepolymers, and photoinitiators.[15] However, due to the energy shortage crisis throughout the world due to the depletion of fossil resources and environmental pollution resulting from the petrochemical industry,

great efforts have been devoted to substituting petroleum-based materials with renewable materials in the development of UV-curable materials.[1,16,17] As a kind of important renewable resource, plant oils have become a preferred selection for the fabrication of UV-curable materials due to their distinguish merits such as low cost, high availability, low toxicity, low viscosity at room temperature, unique triglyceride structure, and ease of modification.[17−19] As one of the most widely available vegetable oils, castor oil has attracted increasingly more attention in the fabrication of green and eco-friendly UV-cured materials to improve the mechanical properties, hardness, and water resistance of cured materials because of its unique molecular structure containing unsaturated alkene bonds and hydroxyl groups.[20−22]
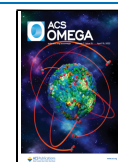
Table 1. Effect of UV Curing Time on the Performance of UV-Cured Materials[a]

entry	time (s)	gel content (%)	hardness	water absorption (wt %)	water contact angle (deg)
1	10	76.8	2H	1.5 ± 0.2	89.1 ± 2.5
2	20	84.4	3H	1.0 ± 0.2	89.6 ± 2.5
3	30	89.2	5H	0.9 ± 0.2	90.2 ± 2.0
4	40	92.3	6H	0.7 ± 0.2	90.5 ± 2.0
5	50	95.4	8H	0.6 ± 0.2	91.1 ± 2.5
6	60	97.2	9H	0.3 ± 0.2	90.3 ± 1.8
7	70	98.0	9H	0.4 ± 0.2	94.3 ± 2.0

[a]Conditions: HBPSH is NPG-HBPSH; CO-PUA is CO-PUA-3; the molar ratio of acrylate to mercapto groups is 3:1; the amount of Irgacure 1173 is 1 wt % CO-PUA.

For example, UV-curable CO-PUAs can be prepared from castor oil, diisocyanates, and hydroxy acrylic acid, which can overcome these shortcomings by taking advantage of three long-chain fatty acids of castor oil.[23] UV-cured CO-PUAs prepared by Hu et al.[24] had a tensile strength of 0.7−3.3 MPa, glass-transition temperature (T_g) of 32−48 °C, and thermal initial decomposition temperatures above 344.5 °C. Castor oil-based UV-cured hyperbranched PUAs prepared by Wei et al.[22] showed quite high transparency over 90% (400−800 nm), a Td5 of 159−179 °C, pencil hardness of 4 H−7 H, and tensile strength of 4.6 ± 0.4−17.3 ± 0.9 MPa. Recently, Wei et al.[25] developed UV-cured CO-PUAs by a castor oil-based hyperbranched polyol with acrylic acid, which was employed as a crosslinking agent of a commercialized linear PUA oligomer. The coatings exhibited high transparency over 90% (400−800 nm) and a tensile strength in the range of 1.7−6.1 MPa. UV-cured CO-PUA with 1,4-butane diol as the chain extender and poly(ε-caprolactone) diol as a macroglycol reported by Thakur and Karak.[26] exhibited a tensile strength of 7 MPa. Li et al.[27] synthesized CO-PUA using a one-pot method, which exhibited an excellent tensile strength of 9.87 MPa. These good works confirmed that it is a proven strategy to prepare UV-cured PUAs with good properties using castor oil.

Furthermore, the density and content of UV-sensitive groups of the existing UV-curable PUAs are not abundant, which will result in a poor hardness of coatings and a fairly low curing speed. These drawbacks will limit the practical applications of UV-cured PUAs[11] Hyperbranched polymers exhibit high solubility, low solution viscosity, densely branched structure, and a large number of reactive end groups,[28] which will increase the UV curing speed[29] and the hardness of cured materials[30] and reduce the VOC emission of UV-cured coatings for reduction the content of reactive diluents and solvents.[1−3] So, hyperbranched polymers are widely used in the preparation of UV-cured PUA coatings.

Recently, our group prepared UV-cured transparent silicone-modified PUAs with a fairly high tensile strength of 3.40 MPa from hyperbranched silicon-containing polymers and petroleum-based PUAs[7] and castor oil-based highly transparent UV-cured silicone-modified PUAs by silicon resins with tensile strength as high as 10.20 MPa.[31] Although highly transparent UV-cured silicone-containing PUAs with fairly high tensile strength were reported by our group previously, the development of new biomass-based silicone-modified UV-cured PUAs with outstanding mechanical performance is still worthy of pursuit. Inspired by these works,[7,31] high tensile strength, transparent, UV-cured, castor oil-based silicone-modified PUAs were prepared by a UV-initiated thiol-ene click reaction of castor oil-based UV-cured PUAs and HBPSHs. The fabrication and performance of these UV-cured PUAs were investigated in detail. It revealed that the tensile strength of UV-cured castor oil-based PUAs can reach 12.49 MPa, which is obviously higher than those UV-cured silicone-modified PUAs reported previously.

2. RESULTS AND DISCUSSION

**2.1. Features of Prepared UV-Cured Materials.**
2.1.1. Effect of UV Curing Time. The effect of UV time is shown in Table 1. If there were no UV initiators, the UV-curable system could not be cured even for 5 min. However, when the UV-curable system was initiated by 1 wt % Irgacure 1173 for only 10 s, the gel content and pencil hardness of the UV-cured materials could reach 76.8% and 2 H, respectively. The pencil hardness of UV-cured materials increased from 2 to 9 H, while water absorption decreased from 1.5 to 0.5 wt % when the UV curing time was prolonged from 10 to 60 s, which implies that the curing degree and cross-link density increased with the prolongation of time.[7] An UV curing time longer than 60 s will almost have no effect on the materials obtained.

The FTIR spectra of UV-cured materials prepared at different times are shown in Figure 1. The characteristic absorption peak of mercapto groups at about 2570 cm^{-1} and acrylate groups at 1635 and 813 cm^{-1} almost disappeared when the UV-curable system was cured for 60 s, which indicated that the suitable curing time is 60 s.

2.1.2. Effect of the Molar Ratio of Acrylate to Mercapto Groups. The molar ratio of acrylate to mercapto groups will affect the cross-link density of UV-cured materials; therefore, the effect of the molar ratio of acrylate to mercapto groups was studied, as shown in Table 2. If the molar ratio of acrylate to mercapto groups increased from 0.5:1 to 3.5:1, the gel content increased from 77.8 to 97.5% and pencil hardness increased from 2 B to 9 H, while the water absorption decreased from 4.1 to 0.3 wt %.

High-transparency UV-cured silicone-modified PUAs are highly desired in optical devices.[2,3,15] The transparency of UV-cured materials prepared with different molar ratios of acrylate to mercapto groups was studied, as shown in Figure 2. It can be obviously seen that the UV-cured materials obtained are with a very high transmittance over 95% (400−800 nm), which attributed to the good miscibility of HBPSHs and CO-PUAs just as reported by our group previously.[31]

The thermal stability of UV-cured materials was investigated, as shown in Figure 3. The initial decomposition temperature (Td5) of these UV-cured materials increased from 170 to 275 °C when the molar ratio of acrylate to mercapto groups increased from 0.5:1 to 3.5:1, which is ascribed to the increase of the cross-link density of UV-curable systems. As reported previously, the traditional PUAs will decompose
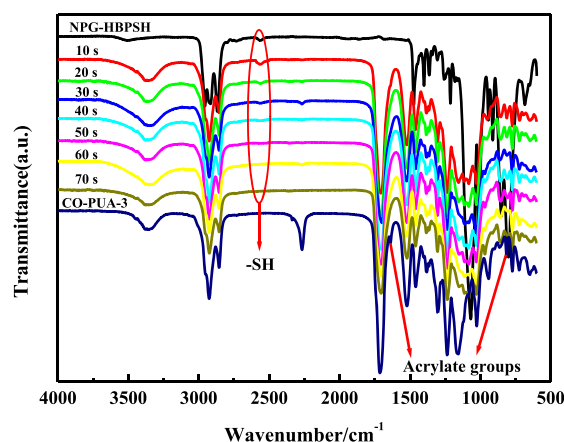
a FT−IR spectra of UV cured materials prepared with different time
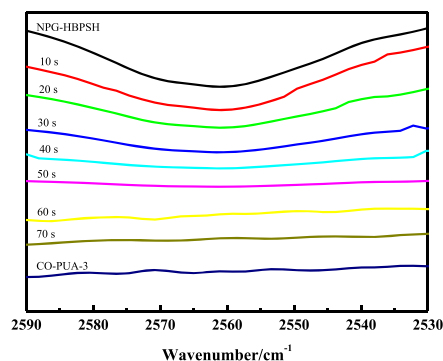
b Characteristic absorption peak of mercapto groups in FT−IR spectra of UV cured materials prepared with different time

Figure 1. FTIR measurement of UV-cured materials prepared at different times.

Figure 2. Transparency of UV-cured materials prepared with different molar ratios of acrylate to mercapto groups.

Figure 3. Thermogravimetric analysis (TGA) curves of UV-cured materials prepared with different molar ratios of acrylate to mercapto groups.

severely over 200 °C.[32,33] Therefore, compared with traditional PUAs, the thermal stability of UV-cured materials prepared is obviously improved.

The mechanical performance of UV-cured materials prepared with different molar ratios of acrylate to mercapto groups was measured by tensile test (Figure 4) because the tensile strength and elongation at break are very important mechanical performance of materials. As seen in Figure 4, the tensile strength significantly increased from 0.46 to 11.06 MPa and elongation at break also increased from 68.7 to 150.2% when the molar ratio of acrylate to mercapto groups increased from 0.5:1 to 3.0:1. It can be said that the mechanical properties of materials have undergone a qualitative leap from soft and weak to tough and strong. When the molar ratio of acrylate to mercapto groups continues to increase to be 3.5:1, the tensile strength will increase to be as high as 12.49 MPa,
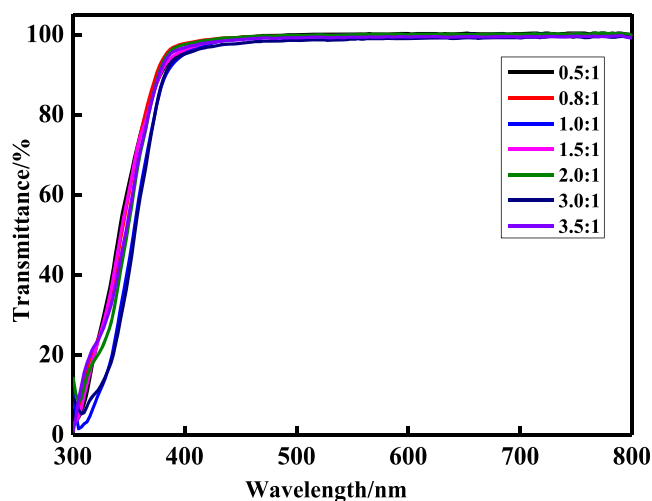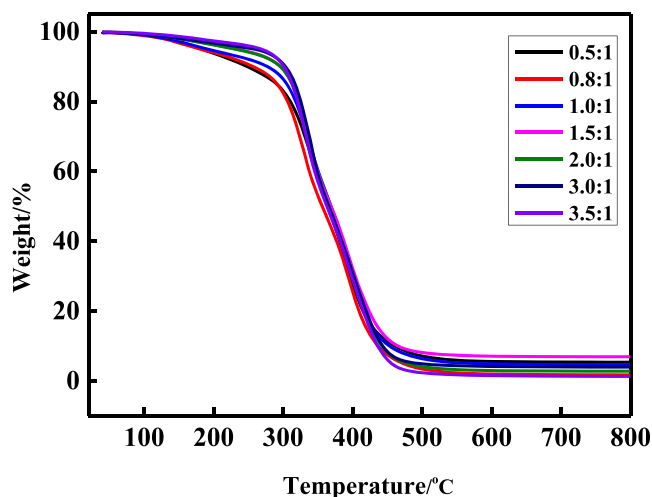
but elongation at break is not higher than 80%, which is ascribed to the brittleness caused by the high cross-link density.

As discussed above, UV-cured CO-PUAs prepared by Hu et al.[24] had a tensile strength of 0.7−3.3 MPa. Castor oil-based UV-cured hyperbranched PUAs prepared by Wei et al.[22] exhibited a tensile strength of 4.6 ± 0.4−17.3 ± 0.9 MPa. The tensile strength of UV-cured coatings prepared from CO-PUAs by a castor oil-based hyperbranched polyol with acrylic acid

Table 2. Effect of the Molar Ratio of Acrylate to Mercapto Groups on the Properties of UV-Cured Materials[a]

entry	molar ratio of acrylate to mercapto groups	gel content (%)	hardness	water absorption (wt %)	water contact angle (deg)
1	0.5:1	77.8	2B	4.1 ± 0.2	95.1 ± 2.0
2	0.8:1	84.8	2H	1.5 ± 0.3	97.6 ± 1.5
3	1.0:1	87.1	5H	0.8 ± 0.2	93.7 ± 2.0
4	1.5:1	95.6	7H	0.5 ± 0.2	93.4 ± 2.0
5	2.0:1	96.0	8H	0.4 ± 0.2	92.0 ± 2.5
6	3.0:1	97.2	9H	0.3 ± 0.2	90.3 ± 1.8
7	3.5:1	97.5	9H	0.3 ± 0.2	89.6 ± 1.5

[a]Conditions: The UV-curable systems were cured for 60 s, and the other conditions were the same as in Table 1.
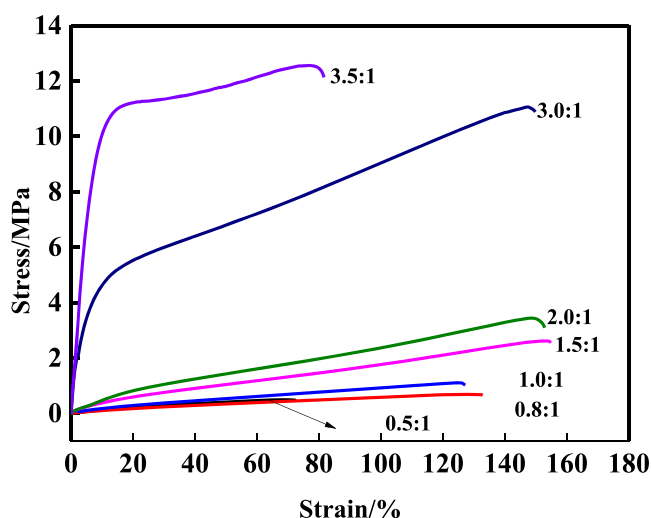
Figure 4. Tensile—strain curves of UV-cured materials prepared with different molar ratios of acrylate to mercapto groups.

and a commercialized linear PUA oligomer is in the range of 1.7—6.1 MPa.[25] UV-cured CO-PUAs with 1,4-butane diol as the chain extender and poly(ε-caprolactone) diol as a macroglycol reported by Thakur and Karak.[26] exhibited a tensile strength of 7 MPa. The tensile strength of CO-PUAs synthesized by Li et al.[27] through a one-pot method was 9.87 MPa. UV-cured transparent silicone-modified PUAs exhibited a tensile strength of 3.40 MPa,[7] and castor oil-based transparent UV-cured silicone-modified PUAs exhibited tensile strength as high as 10.20 MPa.[31] So, it can be concluded that the UV-cured silicone-modified PUAs obtained possess very high tensile strength.

2.2. Chemical Structure Effect of CO-PUAs and HBPSHs. *2.2.1. Effect of the Chemical Structure of CO-PUAs.* The chemical structure of CO-PUAs will have a significant effect on the cross-link density and cross-link network, and so it will inevitably have a great impact on the performance of UV-cured materials. The chemical structure can be manipulated by adjusting the molar ratio of NCO to OH. So, to explore the effect of the chemical structure of CO-PUAs on UV-cured materials obtained, the effect of the molar ratio of NCO to OH for the feed ratio of IPDI and castor oil should be studied. Therefore, the CO-PUAs investigated were prepared with the molar ratio of NCO to OH in the range of 1.5:1—3.0:1 (Table 3). It can be seen from Table 3 that the pencil hardness of materials obtained increased from 4 H to 9 H when the molar ratio of NCO to OH increased from 1.5:1 to 2.0:1 because of the increase of the cross-link density. From the appearance, the viscosity of CO-PUAs increased continuously with the increase of the molar ratio of NCO to OH. If the molar ratio of NCO to OH was higher than 2.0:1,

the CO-PUAs often crosslinked during the course of preparation. Even if the CO-PUAs with the molar ratio of NCO to OH higher than 2.0:1 were prepared, they will be too viscous to be coated on the substrates smoothly without air bubbles. Moreover, there is nearly no change in the comprehensive performance for the materials prepared from CO-PUAs with the molar ratio of NCO to OH being higher than 2.0:1, and so the optimum molar ratio of NCO to OH is 2.0:1.

2.2.2. Effect of the Chemical Structure of HBPSHs. HBPSHs serve as a crosslinking agent in the fabrication of UV-curable materials, and the chemical structure of HBPSHs also plays an important role in affecting the cross-link density and cross-link network of UV-cured materials. To clarify how the chemical structure of HBPSHs affects the performance of UV-cured materials, four HBPSHs were synthesized with different α,β-dihydroxyl derivatives such as NPG, butane-1,4-diol, diethylene glycol, and ethylene glycol, and the performances of the materials prepared from them were discussed in detail.

First, the effect of the chemical structure of HBPSHs on the material property is summarized in Table 4. It can be seen from Table 4 that the pencil hardness of the materials is in the order of DLG-HBPSH < BD-HBPSH = ELG-HBPSH < NPG-HBPSH, which is just the opposite order of the flexibility of diethylene glycol, butane-1,4-diol, ethylene glycol, and NPG. So, it can be said that the more rigid the units of α,β-dihydroxyl derivatives are, the more hard the materials will be.

Second, the effect of the chemical structure of HBPSHs on the thermal stability of materials is shown in Figure 5. The thermal stability of these materials is quite high because their Td5 is in the range of 240—269 °C. The molecular structure of HBPSHs had almost no effect on the thermal stability of UV-cured materials. As reported previously, the traditional PUAs will decompose severely over 200 °C.[31,32] Therefore, compared with traditional PUAs, the thermal stability of UV-cured materials prepared is obviously improved.

The chemical structure of HBPSHs will have a significant impact on the mechanical performance of UV-cured materials because the molecular chain length and steric hindrance of α,β-dihydroxyl derivatives will affect the cross-link density and cross-link network; therefore, the tensile test of UV-cured materials was carried out. As shown in Figure 6, the tensile strength and elongation at break of these UV-cured materials were in the range of 5.38—11.08 MPa and 84.9—146.9%, respectively. It also can be seen that the tensile strength and elongation at break of the material prepared with NPG-HBPSH were both the best among these materials prepared. The tensile strength of the materials is in order of DLG-HBPSH < BD-HBPSH < ELG-HBPSH < NPG-HBPSH, which is also the opposite order of the molecular chain length and the flexibility of diethylene glycol, butane-1,4-diol,

Table 3. Effect of the Chemical Structure of CO-PUAs on the Properties of UV-Cured Materials[a]

entry	name of CO-PUAs	molar ratio of NCO to OH	gel content (%)	hardness	water absorption (wt %)	water contact angle (deg)
1	CO-UA-1	1.5:1	89.7	4H	1.1 ± 0.2	90.9 ± 2.0
2	CO-PUA-2	1.8:1	92.6	7H	0.8 ± 0.2	92.2 ± 2.0
3	CO-PUA-3	2.0:1	97.2	9H	0.3 ± 0.2	90.3 ± 1.8
4	CO-PUA-4	2.5:1	96.5	9H	0.4 ± 0.2	91.6 ± 1.5
5	CO-PUA-5	3.0:1	97.6	9H	0.4 ± 0.2	91.4 ± 2.0

[a]Conditions: The conditions were the same as in Table 2.

Table 4. Effect of the Chemical Structure of HBPSHs on the Properties of UV-Cured Materials[a]

entry[a]	different HBPSHs	gel content (%)	hardness	water absorption (wt %)	water contact angle (deg)
1	NPG-HBPSH	97.2	9H	0.3 ± 0.2	90.3 ± 1.8
2	BD-HBPSH	93.1	8H	1.1 ± 0.2	90.2 ± 2.0
3	DLG-HBPSH	92.5	6H	0.7 ± 0.2	87.4 ± 2.5
4	ELG-HBPSH	94.1	8H	0.9 ± 0.2	85.6 ± 2.5

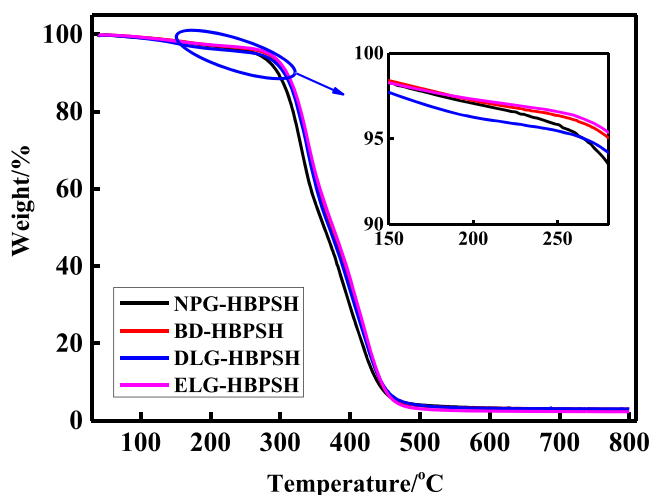[a]Conditions: The conditions were the same as in Table 2.

Figure 5. TGA curves of materials prepared with different HBPSHs.
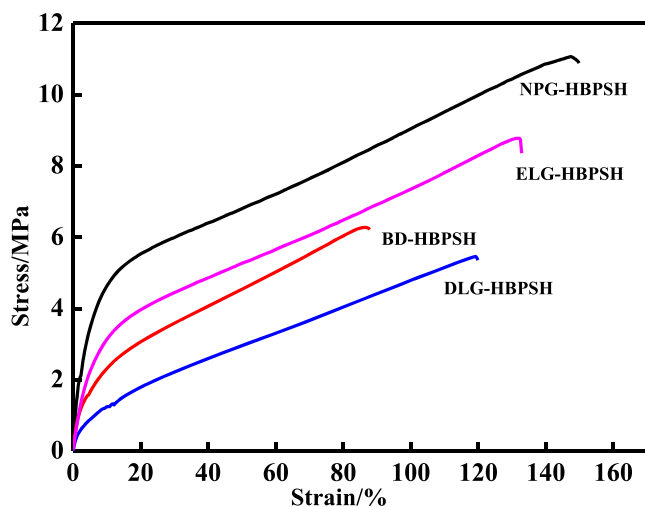

Figure 6. Tensile−strain curves of UV-cured materials prepared with different HBPSHs.

ethylene glycol, and NPG. From the results above, it can be said that the flexibility and the molecular chain length of α,β-dihydroxyl derivatives will play an important role in the mechanical performance of UV-cured materials. The more rigid the units of α,β-dihydroxyl derivatives used in the fabrication of HBPSHs are, the higher the mechanical strength and pencil hardness of the UV-cured materials will be.

2.3. Coating Performance of UV-Cured Materials.
2.3.1. UV Resistance Ability. UV resistance ability is essential for coatings exposed to the outdoors for a long time; therefore, the UV resistance ability of UV-cured materials was studied by exposing them to a 365 nm UV box with a radiation intensity of 10.6 mW·cm^{-2} at 60 °C. It can be seen from Figure 7 that

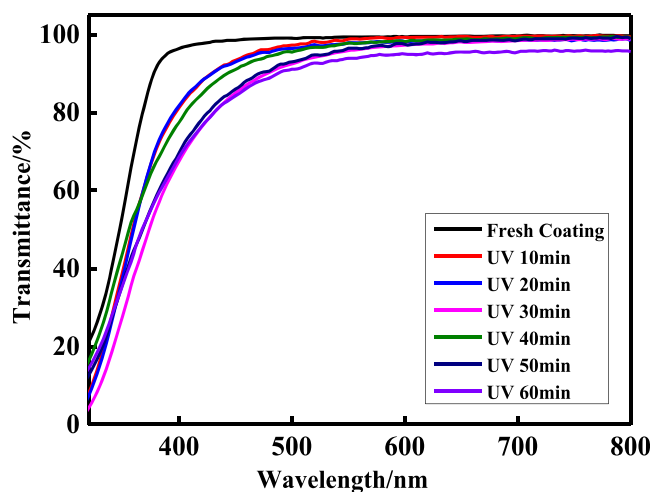the transmittance of the materials is still above 96% even after being exposed to UV for 60 min.

Figure 7. Transmittance of UV-cured material (entry 6 in Table 2) exposed to UV for different times.

As seen in Figure 8, the material exposed to UV for 10 min remained colorless and transparent just like a fresh one. The material started to turn slightly yellow when it was exposed to UV for 20−30 min. The material did not turn severely yellow until it was exposed to UV for 40 min. On exposure to the same UV aging conditions, UV-cured silicone-modified PUA materials[2] and UV-cured castor oil-based PUAs[31] turned slightly yellow after 8−12 min and 30 min, respectively. Compared with these UV-cured materials, the castor oil-based UV-cured silicone-modified PUA materials in this paper exhibit moderate UV resistance ability.

2.3.2. Adhesion Property. To investigate the adhesion property of UV-cured materials on different substrates, including aluminum plate, tinplate, wood, and glass slide, the material sample of entry 6 in Table 2 was studied by the cross-cut method, as shown in Figure 9. The adhesion property of the material on the aluminum plate and tinplate was of grade 1 because the shedding area of the material on the aluminum plate and tinplate was lower than 5%. The adhesion of the material to the wood and glass slides was too good to be grade 0 that there was no shedding area at all. So, it revealed that the material exhibits quite good adhesion property to these substrates.

Furthermore, the adhesion property of UV-cured materials prepared with different molar ratios of acrylate to mercapto groups was measured by the cross-cut method on a glass slide (Figure 10). When the molar ratio of acrylate to mercapto groups was 0.5:1−0.8:1, the adhesion property was of grade 2 because the shedding area was about 9%. When the molar ratios of acrylate to mercapto groups increased from 1.0:1−1.5:1, the adhesion property changed from grade 1 to grade 0,
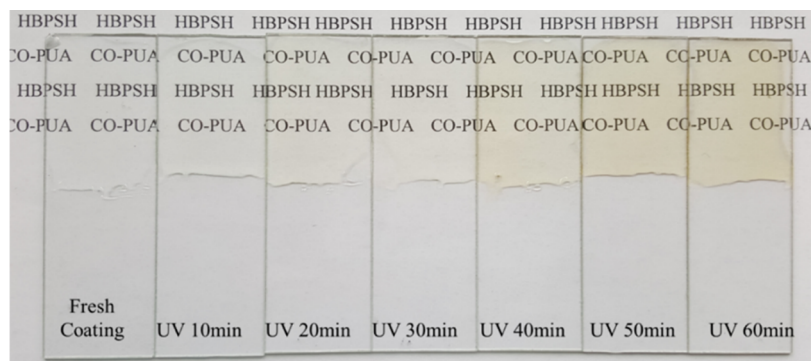
Figure 8. Photos of the UV-cured material (entry 6 in Table 2) exposed to UV for different times.
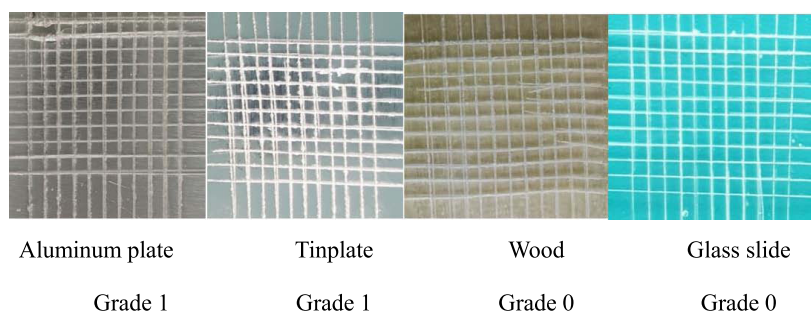

| Aluminum plate | Tinplate | Wood | Glass slide |
| Grade 1 | Grade 1 | Grade 0 | Grade 0 |

Figure 9. Photos for the adhesion property of materials (entry 6 in Table 2) measured by the cross-cut method on different substrates.

| 0.5:1 | 0.8:1 | 1.0:1 | 1.5:1 |
| Grade 2 | Grade 2 | Grade 1 | Grade 0 |

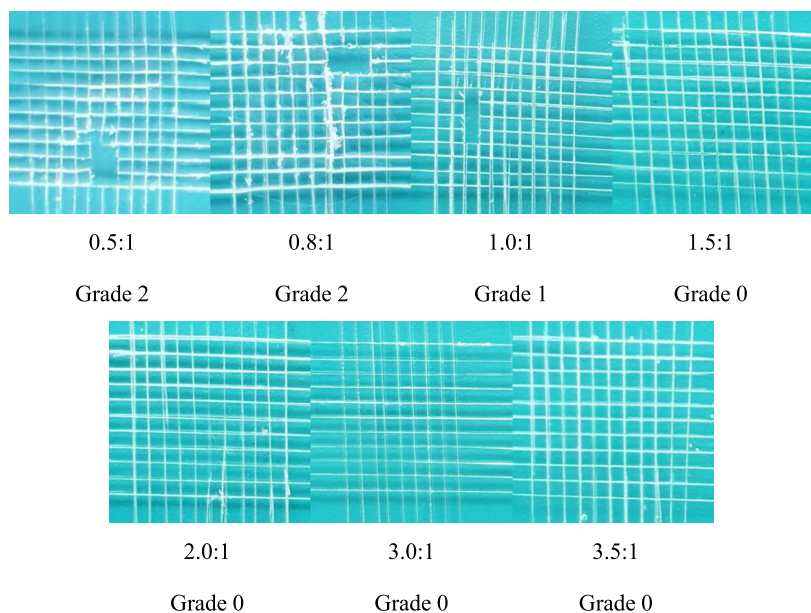| 2.0:1 | 3.0:1 | 3.5:1 |
| Grade 0 | Grade 0 | Grade 0 |

Figure 10. Photos for the adhesion property of UV-cured materials prepared with different molar ratios of acrylate to mercapto groups on a glass slide.

which means that the higher molar ratios of acrylate to mercapto groups will be beneficial to increase the adhesive force of the materials on glass slide due to the increase of the cross-link density.

2.3.3. Corrosion Resistance Property. To study the corrosion resistance property of UV-cured materials prepared, the tinplate coated with samples of entry 6 in Table 2 was immersed in 3.5 wt % hydrochloric acid, 3.5 wt % NaCl, 3.5 wt % KOH, and deionized water separately at room temperature for 7 days (Figure 11). After being immersed for 7 days, the degree of the materials on the tinplate turned white and brittle
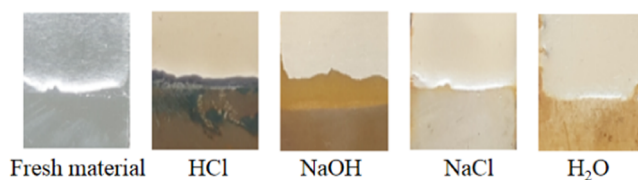

| Fresh material | HCl | NaOH | NaCl | H_2O |

Figure 11. Corrosion resistance property of materials in different media.

in the order of NaCl < H_2O < NaOH < HCl. Even so, the materials still had good adhesion to the tinplate and maintained a good appearance without cracking and pulverization. Therefore, it can be inferred that the UV-cured materials can serve as a protective coating for metals operated in acidic, high salt, or humid environments.

3. CONCLUSIONS

High tensile strength UV-cured castor oil-based PUAs were prepared by a UV-initiated thiol-ene click reaction of castor oil-based UV-curable PUAs and HBPSHs. When HBPSHs were prepared with (3-mercaptopropyl)-trimethoxysilane and neopentyl glycol according to the molar ratio of 1.7:1 and castor oil-based PUAs were prepared with IPDI and castor oil according to the molar ratio of 3:1, the tensile strength of UV-cured castor oil-based silicone-modified PUAs prepared with them can reach 12.49 MPa. The flexibility and the molecular chain length of α,β-dihydroxyl derivatives will play an important role in the mechanical performance of UV-cured materials, and it can be concluded that the more rigid the units of α,β-dihydroxyl derivatives used in the fabrication of HBPSHs are, the higher the mechanical strength and the pencil hardness of the UV-cured materials will be. The UV-cured materials obtained possess very high transmittance over 95% (400−800 nm), attributed to the good miscibility of mercapto-containing HBPSHs and castor oil-based PUAs. The UV-cured materials obtained also show a good UV resistance property because they still remain colorless and transparent, just like a fresh material even after being exposed to UV for 10 min.

4. EXPERIMENTAL PROCEDURE

4.1. Materials. 2-Hydroxy-2-methyl-1-phenyl propanone (Irgacure 1173, 99.0%, AR) was purchased from Chitec Technology Co., Ltd. (Shanghai, China). Castor oil, neopentyl glycol (NPG, AR), and isophorone diisocyanate (IPDI, AR) were purchased from Beijing HWRK Chem Co., Ltd. (Beijing, China). Dibutyltin dilaurate (DBTDL, AR), ethylene glycol (AR), diethylene glycol (AR), butane-1,4-diol (AR), and 2-hydroxypropyl methacrylate (AR) were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acetone (AR) was supplied by Shuangling Chemical Factory, (Hangzhou, China). (3-Mercaptopropyl)-trimethoxysilane (MPTS, AR) was supplied by Beijing Hehuang Chemical Factory (Beijing, China). Castor oil-based polyurethane acrylates (CO-PUAs) were prepared by our group according to ref 31, as shown in Table S1.

4.2. Preparation of HBPSHs. Similar to ref 7, HBPSHs shown in Table 5 were prepared with different α,β-dihydroxyl derivatives, including NPG, butane-1,4-diol, diethylene glycol, and ethylene glycol according to the procedure in Scheme 1. Typically, taking the preparation of NPG-HBPSH, for example, 19.634 g of MPTS (0.1 mol) and 17.706 g of NPG (0.17 mol)

were added to a 50 mL three-necked bottle; thereafter, the reaction system was heated from room temperature to 100 °C for 1 h and then from 100 to 160 °C slowly for about 4 h. Finally, the residue of raw materials and byproducts were removed by distillation under vacuum for about 0.5 h, and a transparent light yellow liquid of NPG-HBPSH was prepared. The ^{1}H-NMR spectra of these HBPSHs are shown in Figure S1.
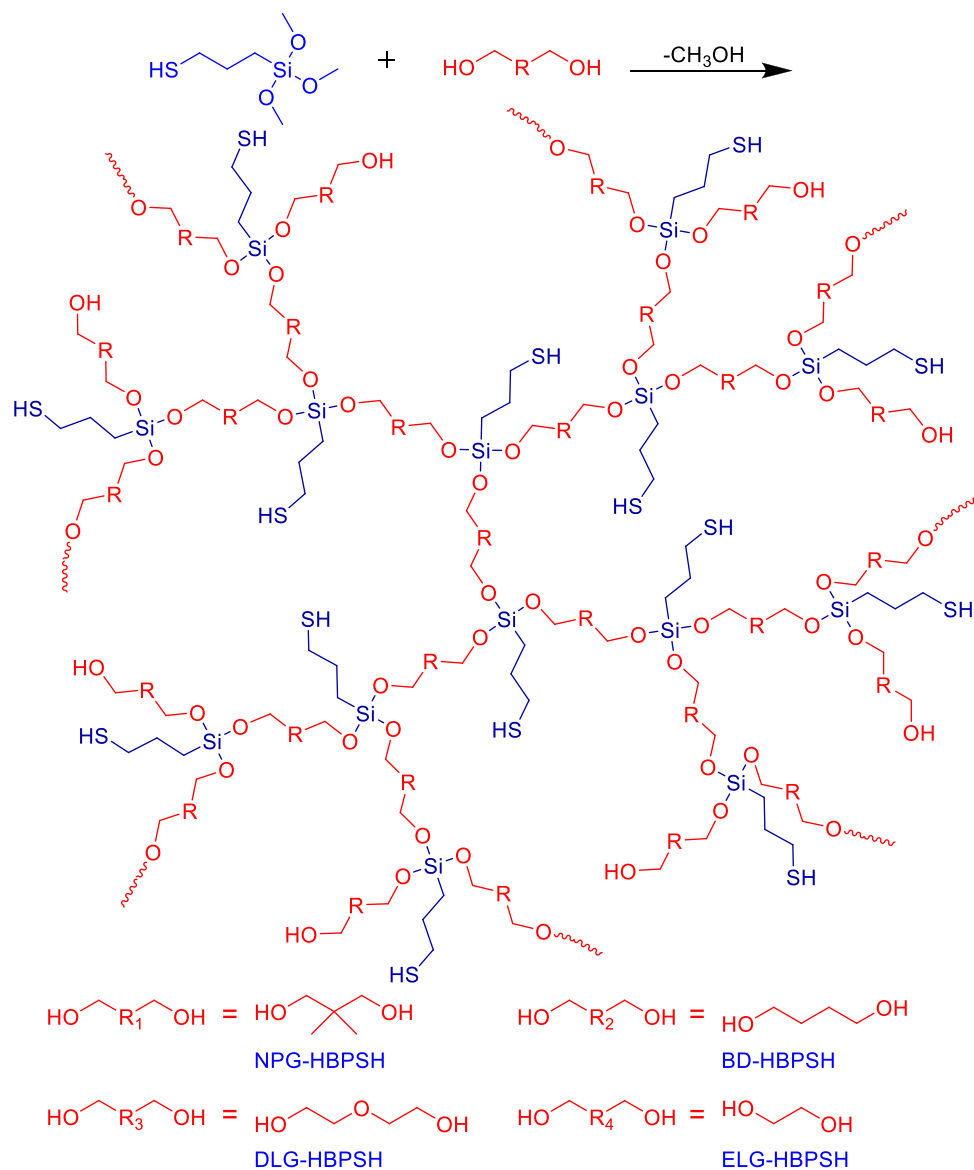
4.3. Preparation of UV-Cured Materials. The fabrication procedure for UV-cured materials is shown in Scheme 2. CO-PUAs, HBPSHs, and UV initiator Irgacure 1173 were mixed for about 5 min and deposited on glass slides. About 24 h later, the materials were cured by UV (ZB1000, Changzhou Zibo Electron Technology Co., Ltd.; laser wavelength, 365 nm; radiation intensity, 10.6 mW·cm^{-2}; the distance of the slides to the light, 20 cm). The thicknesses of films for transmittance measurement and mechanical experiments were 0.5 and 0.7 mm, respectively.

4.4. Characterization. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AVANCE AV400 (400 MHz) spectrometer in CDCl$_3$ with tetramethylsilane (TMS) as the internal reference. Fourier transform infrared (FTIR) spectroscopic analysis was performed on a Nicolet 700 spectrometer (Nicolet Co., Ltd.) over the frequency range of 4000−650 cm^{-1}. The gel content, transmittance, pencil hardness, surface water contact angle, water absorption, adhesion properties, tensile testing, and UV resistance property were measured as described in refs 2 and 7. The cured samples were washed with toluene by Soxhlet extraction at 150 °C for 4 h, and then the gel content was calculated as a percentage of the residual mass in the original mass of the cured coatings. Transmittance spectra of coatings obtained (placed in a 10 mm thick quartz absorption cell) were measured on a Unico UV-4802 UV/Vis spectrophotometer (Unico Instrument Co., Ltd., Shanghai) in the range of 400−800 nm. The pencil hardness of the cured samples was measured with a BGD-562 pencil hardness meter (Zhenwei Testing Machinery Co., Ltd., Jiangdu, China) according to GBT6739-2006. The water absorption was measured according to "Determination of water absorption rate of insullac films" HGT 3856-2006. The surface water contact angle was measured according to "Measurement of water contact angle of plastic films", GB/T 30693−2014, on a KRUSS DSA30 water contact angle meter (KRÜSS, Germany). The adhesion was measured with a BGD-502 paint film according to ISO 2409-2007 by the cross-cut test. The tensile test of the films (6 mm × 0.7 mm × 8 mm strips) scraped from the slides was carried out according to GB/T 528-2009/ISO 37:2005 on a UH6503D electronic tensile testing machine (Optimal Hung Measurement & Control Technology, Shanghai) Co., Ltd. The load was 100 N at a loading rate of 60 mm/min. UV resistance measurement of UV-cured materials was conducted in a UV test chamber of 10.6 mW·cm^{-2}. The thermal stability of the samples was measured by thermogravimetric analysis (TGA) using a TG 209C apparatus (NETZSCH-Gerätebau GmbH, Germany), in which samples were heated from ambient temperature to 800 °C at a rate of 10 °C min^{-1} in a nitrogen atmosphere. The corrosion resistance property was determined by immersing the tinplate coated with UV-cured materials in 3.5 wt % hydrochloric acid, 3.5 wt % NaCl, 3.5 wt % KOH, and deionized water separately at room temperature according to ISO-2812-1-2017.

Table 5. HBPSHs Prepared with Different α,β-Dihydroxyl Derivatives

HBPSHs	trimethoxysilane	α,β-dihydroxyl derivatives
NPG-HBPSH	MPTS	NPG
BD-HBPSH		butane-1,4-diol
DLG-HBPSH		diethylene glycol
ELG-HBPSH		ethylene glycol

Scheme 1. Procedure for Fabrication of HBPSHs

Scheme 2. Procedure for Preparation of UV-Cured Materials
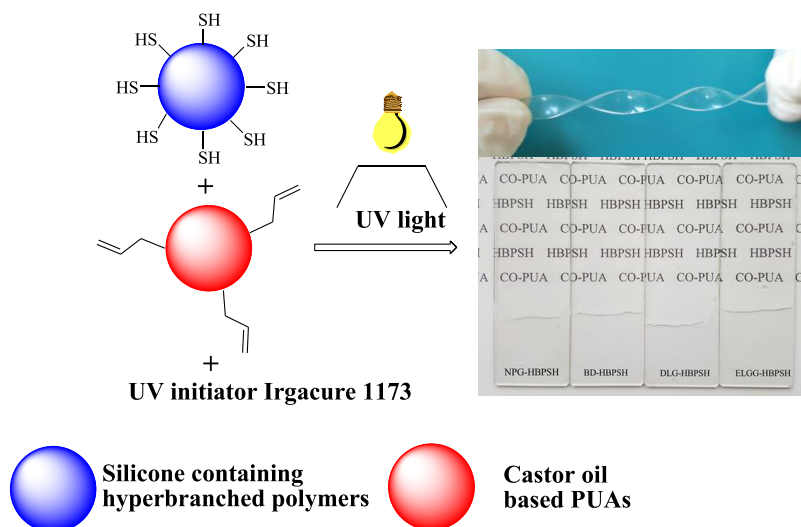
■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06959.

The ^{1}H-NMR and ^{13}C-NMR spectra of castor oil-based polyurethane acrylate (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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