UV-Cured Transparent Flexible Silicone Materials with High Tensile Strength

Yufei Wu, Jiangling Liu, Xiaojiao Jiao, Fei Cheng, Guoqiao Lai, and Xiongfa Yang

ABSTRACT: Transparent flexible silicone materials are useful in electronics, sensors, coatings, and so forth. However, to the best of our knowledge, the tensile strength of unreinforced silicone rubber is lower than 0.4 MPa, and the highest tensile strength of highly transparent silicone-modified materials is no more than 1.5 MPa. The poor mechanical property limits their further application in electronic devices. Here, a kind of UV-cured transparent flexible silicone materials with tensile strength as high as 2.2 MPa were prepared by a UV-initiated thiol–ene reaction of a sulfur-containing hyperbranched polycarbosilane and a thiol silicone resin. Interestingly, their tensile strength can increase from 2.2 to 5.6 and 5.7 MPa after being immersed in an aqueous solution of 10 wt % hydrochloric acid and 10 wt % NaCl for 7 days, respectively. It is argued that the increase of the tensile strength of cured films may be attributed to the −SiOCH3 of the residual 3-trimethoxysilylpropanethiol in the sulfur-containing hyperbranched polycarbosilane. The performances of the cured materials were investigated in detail. These silicone materials exhibit transparency higher than 95% (wavenumber in the range of 400–800 nm), and the initial thermal decomposition temperatures of the cured materials are about 340 °C. These materials also show good anticorrosion property, and the mass loss of the materials immersed in the aqueous solution mediums is no more than 0.39 wt % even for 15 days.

1. INTRODUCTION

Transparent silicone materials have outstanding properties including good flexibility, ultraviolet (UV) resistance, thermal resistance, dimensional stability, a wide range of service temperatures, high transparency, and minimal moisture absorption.1−5 Therefore, they have been widely used in electronics,2 sensors,3 coatings,4,5 and so forth. However, to the best of our knowledge, the tensile strength of the unreinforced silicone with high transparency is no more than 0.4 MPa.6,7 Incorporation of various inorganic fillers such as nano-SiO28 and carbon nanotubes9 into a polysiloxane matrix has been shown to improve the mechanical properties, but at the expense of lower transparency. Even so far, the tensile strength of the chemical-modified transparent silicone materials is no more than 1.5 MPa.7,8,10−13 Seriously, the drawbacks of poor mechanical properties limit their further application in electronic devices,8,16 and efforts should be made to improve the tensile strength of transparent silicone materials.

On the other hand, it is noteworthy that corrosion is an obstacle for engineering applications.14−16 Silicone coatings have been reported to be anticorrosion layers because of the chemical inertness attributed by the Si–O–Si network.16−18 Nevertheless, these coatings possess a glassy-like behavior, which will be quite brittle.19 Polycarbosilanes are a class of polymers at the interface between organic and inorganic chemistry, whose Si–C bond is less susceptible to the nucleophilic attack than the Si–O bonds in siloxanes contributed to the relative stability of the carbosilane.20,21 The cross-linkable carbosilane polymers exhibit intriguing
physical and chemical properties, which could be used as anticorrosion coatings. A silicon-containing hyperbranched polycarbosilane, particularly phosphorus-hyperbranched carbosilanes, and a sulfur-containing hyperbranched polycarbosilane have emerged promising applications in polymer-derived ceramics, room-temperature-vulcanized silicone rubber, high-temperature-vulcanized silicone rubber, and coatings. Inspired by these efforts, the silicon-containing hyperbranched polycarbosilane may be used to improve the corrosion resistance of the materials.

Finally, as we know, transparent silicone materials prepared by traditional curing methods suffer from the disadvantages of long curing time and high energy consumption. The UV polycarbosilane may be used to improve the corrosion by traditional curing methods sufficiently curing method has drawn much attention in the under mild reaction conditions. The ene reaction has been utilized to prepare silicone elastomers because of their merits such as highly effective under mild reaction conditions, without a photoinitiator, extremely tolerant to a variety of functional groups, without oxygen inhibition, and lack of byproduct. Therefore, the thiol–ene reaction has been utilized to prepare silicone elastomers under mild reaction conditions.

To overcome the drawbacks mentioned above, attempts were made to prepare transparent flexible silicone materials through UV-initiated thiol–ene reaction with the sulfur-containing hyperbranched polycarbosilane. In this work, we are pleased to report the synthesis and properties of a kind of transparent flexible silicone materials with a tensile strength as high as 2.2 MPa prepared by the UV-initiated thiol–ene reaction. Interestingly, the materials show good anticorrosion property, and their tensile strength can increase from 2.2 to 5.6 and 5.7 MPa after being immersed in the aqueous solution of 10 wt % hydrochloric acid and 10 wt % NaCl for 7 days, respectively.

2. EXPERIMENTAL PROCEDURE

2.1. Materials. 3-Trimethoxysilylpropanethiol (A.R.) was purchased from Beijing HWRK Chem Co., Ltd. Dimethyl diethoxysilane (C.P.) and methyl trimethoxysilane (C.P.) were from Shanghai Jiancheng Industry and Trade Co., Ltd. Ether (A.R.) was bought from Beijing HWRK Chem Co., Ltd., and distilled over potassium before use. Hydrochloric acid (36.5%, A.R.), methanol (A.R.), and toluene (A.R.) were bought from Sinopharm Chemical Reagent Co., Ltd., China. Magnesium powder (A.R.) was bought from Shanghai Lingfeng Chemical Reagent Co., Ltd. 3-Bromopropene (A.R.) and iodine (A.R.) were purchased from Adams Reagent Co., Ltd. (Shanghai) and TCI (Shanghai) Chemical Industrial Development Co., Ltd., respectively.

2.2. Synthesis of the Sulphur-Containing Hyperbranched Polycarbosilane. The method of synthesis of sulphur-containing hyperbranched polycarbosilane is shown in Figure 1 according to ref 37. All the reactions were performed under argon atmosphere. Magnesium powder (180 g, 0.75 mol), 300 mL of ether, and a grain of iodine were placed in a clean and dry three-necked bottle. The mixture was maintained at 0–5 °C, and 120 mL of ether and 75.6 g (0.63 mol) of 3-bromopropene were added to the mixture for about 120 min. Then, 28.550 g (0.145 mol) of 3-trimethoxysilylpropanethiol and 250 mL of ether were added to the mixture and stirred at room temperature overnight. Later, the reaction was terminated by 200 mL of methanol and then filtered. After evaporating the solvent in vacuum, 27.8 g crude product of mercaptopropyl triaryl silane is obtained. The crude product was distilled by vacuum, and a 12.7 g colorless transparent liquid of the reaction at about 150 °C under 120 °C/20 mmHg was collected. Finally, the sulfur-containing hyperbranched polycarbosilane was prepared by a thiol-click reaction for 30 s initiated by UV (ZB1000, Changzhou Zibo Electron Technology Co. Ltd., laser wavelength 365 nm, laser power 1000 W).

2.3. Synthesis of the Thiol Silicone Resins. In a typical process of synthesizing the thiol silicone resin, 160.9 g (1.085 mol) of dimethyl diethoxysilane, 82.2 g (0.603 mol) of methyl trimethoxysilane, 196.4 g (1.000 mol) of 3-trimethoxysilylpropanethiol, and 220 g of toluene were added into a 1000 mL three-necked bottle, the mixture was stirred and heated to 50 °C, and then 8.80 g of hydrochloric acid and 150 g of deionized water were added to the mixture for about 60 min. Subsequently, the mixture was maintained at 60 °C for 3 h. The pH value of the organic phase was adjusted to 7 using deionized water. Later, the solvent and the low-boiling residues in the organic phase were removed under 120 °C/20 mmHg, and a transparent liquid was produced. H NMR (400 MHz, CDCl3, ppm): –0.36–0.18 (SiCH3), 0.37–0.76 (HSCH2CH2CH2Si–), 1.12–1.34 (HSCH2CH2CH2Si–), 1.43–1.74 (HSCH2CH2CH2Si–), 2.28–2.55 (HSCH2CH2CH2Si–), 1.02–1.14 (–OCH2CH3), 3.28–3.55 (–OCH2CH3), 3.50–3.78 (–OCH2CH3).

2.4. Preparation of Transparent Flexible Silicone Materials Based on the Sulfur-Containing Hyperbranched Polycarbosilane by UV. The mixtures of sulfur-containing hyperbranched polycarbosilane and thiol silicone resin were deposited on the slides with about 1 mm thickness by spin-coating under a rotation speed of 3000 r/s for 30 s and then cured by UV (ZB1000, Changzhou Zibo Electron Technology Co., Ltd., laser wavelength 365 nm, laser power 1000 W, and the distance of the slides to the light is 20 cm).

2.5. Characterization. The –H NMR spectrum was recorded on a Bruker AVANCE AV400 (400 MHz) spectrometer in CDCl3 at room temperature without tetramethylsilane as the internal reference. Fourier transform infrared (FT-IR) spectroscopy analysis was carried out using a Nicolet 700 spectrometer (Nicolet Co., Ltd., America) over the frequency range of 4000–650 cm⁻¹ with an attenuated total reflection appendix. Transmittance spectra (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, Jiaodu, China) according to GBT6739-2006. Thermogravimetric analysis (TGA) was carried out using a TG 209C apparatus (Germany), in which samples were heated from ambient temperature to 800 °C at a rate of 10 °C min⁻¹ in a nitrogen atmosphere. Differential scanning calorimetry (DSC) curves were recorded on a DSC Q100 apparatus under nitrogen atmosphere with a carrier gas flow rate of 20 mL min⁻¹. The samples were heated to 100 °C for 2 min to erase the thermal history, then cooled to −100 °C at a rate of 10 °C min⁻¹, and finally heated again to 100 °C at a heating rate of 10 °C min⁻¹. The degree of curing contents of the mixtures of sulfur-containing hyperbranched polycarbosilane and thiol silicone resins was measured by Soxhlet extraction with toluene at 150 °C for 4 h. The adhesion was measured with a BGD-502 paint film according to ISO 2409-2007. Water absorption was measured according to the “Determination of water absorption rate of insulac films” HGT 3856-2006. The surface water contact angle was measured according to the “Measurement of water-contact angle of plastic films” GB/T 30693-2014 on a KRUSS DSA30 water contact angle meter (KRÜSS, Germany). The tensile test was carried out according to GB/T 528-2009/ISO 37:2005 on an UH6503D electronic tensile testing machine (Optimal Hung Measurement & Control Technology) (Shanghai) Co. Ltd. The corrosion resistance to acid, alkali, and salt was carried out with a water solution of 10 wt % hydrochloric acid and 10 wt % sulfuric acid, 10 wt % sodium hydroxide, and 10 wt % sodium chloride, respectively, at room temperature.

3. RESULTS AND DISCUSSION

3.1. Analysis of Sulfur-Containing Hyperbranched Polycarbosilanes. Sulfur-containing hyperbranched polycarbosilane were prepared by the thiol-click reaction of mercaptopropyl triallyl silane by UV at various reaction times, and the ¹H NMR spectra are shown by Figures 2 and S1. The chemical shifts of the sulfur-containing hyperbranched polycarbosilanes can be assigned as follows: 0.47–0.97 (−SCH₂CH₂CH₂Si−), 1.24–1.40 (HSCH₂CH₂Si−), 1.41–1.73 (−CH₂CH==CH₂), 1.73–1.99 (−SCH₂CH₂−), 2.24–2.66 (−CH₃SCH₂−), 2.70–2.84 (HSCH₂CH₃CH₂Si−), 3.25–3.66 (−OCH₃), 4.68–5.01 (−CH₂CH==CH₂), and 5.60–5.95 (−CH₂CH==CH₂). The molar ratio of −CH₂CH==CH₂ to HSCH₂CH₃CH₂Si− and the content of −SiOCH₃ and −CH₂CH==CH₂ in the sulfur-containing hyperbranched polycarbosilanes prepared at various UV reaction times can be calculated by the ratio of the chemical shift integral area of −CH₂CH==CH₂ HSCH₂CH₃CH₂Si−, and −OCH₃ (Table 1). It can be seen from Table 1 that the molar ratio of −CH₂CH==CH₂ to HSCH₂CH₃CH₂Si− is about 3.0, and the content of −SiOCH₃ is about 0.00229 mol/g when the UV reaction time is 0, which means the Grignard reaction is not complete. The molar ratio of −CH₂CH==CH₂ to HSCH₂CH₃CH₂Si− (about 9.0:1) and the content of −CH₂CH==CH₂ almost remained unchanged when the UV reaction time prolongs from 30 to 90 s. Therefore, the sulfur-containing hyperbranched polycarbosilane prepared by UV for 30 s was used at the following investigation.

Table 1. Results for the Sulfur-Containing Hyperbranched Polycarbosilanes Calculated by ¹H NMR Analysis

| UV reaction time/s | 0  | 30 | 60 | 90 |
|-------------------|----|----|----|----|
| molar ratio of −CH₂CH==CH₂ to HSCH₂CH₃CH₂Si− in the product of hyperbranched polycarbosilane | 3.0:1 | 8.82:1 | 8.90:1 | 9.10:1 |
| content of −SiOCH₃ in the product/(mol/g) | 0.00229 | 0.00226 | 0.00236 | 0.00253 |
| content of −CH₂CH==CH₂ in the product/(mol/g) | 0.0113 | 0.00848 | 0.00842 | 0.00831 |

Table 2. Effect of Curing Time

| entry | curing time/s | pencil hardness | degree of curing content/% | surface water contact angle/° |
|-------|---------------|----------------|---------------------------|-----------------------------|
| 1     | 10            | 6B             | 84.3                      | 103.1                       |
| 2     | 20            | 2H             | 97.5                      | 103.4                       |
| 3     | 30            | 6H             | 97.1                      | 103.9                       |
| 4     | 40            | 6H             | 95.7                      | 104.4                       |
| 5     | 50            | 6H             | 97.7                      | 106.2                       |
| 6     | 60            | 6H             | 97.2                      | 105.9                       |

*Conditions: The sulfur-containing hyperbranched polycarbosilane was prepared by UV for 30 s. The thiol silicone resin is with R/Si = 1.4 and the thiol group content is 0.004 mol/g. The sulfur-containing hyperbranched polycarbosilane and the thiol silicone resin were mixed according to n(HSCH₂CH₃CH₂Si−)/n(−CH₂CH==CH₂) = 1:1.1.*

Figure 2. ¹H NMR spectra of sulfur-containing hyperbranched polycarbosilanes prepared by UV at various reaction times.
and the surface water contact angle of the films. These phenomena might be explained as the mixture was cured completely by UV for 30 s. The FT-IR spectra of the cured films shown in Figure 3 provide evidence for this opinion. The characteristic stretching vibration absorption peak of $\equiv C=H$ in the allyl group at 3074 cm$^{-1}$ disappeared quickly even when the mixture is only cured for 10 s. The characteristic vibration absorption peak of $C=C$ in the allyl group at 1627 cm$^{-1}$ and the weak characteristic absorption peak of HS at 2550 cm$^{-1}$ have become smaller and smaller with the prolongation of the curing time and almost vanished when the mixture is cured for 30 s by UV. The area of characteristic absorption peak of Si–O–Si at 1040 cm$^{-1}$ is unchanged.

3.3. Effect of R/Si Ratios for the Thiol Silicone Resins. The effect of R/Si ratios for the thiol silicone resin on the cured materials are summarized in Table 3. It can be seen that the pencil hardness of the cured materials is in the range of 6B and 9H, which can be tuned by adjustment of the molar ratios of SH to allyl when the molar ratios increase of the cross-linking density of the cured materials.

| Entry | R/Si ratio | Pencil hardness | Degree of curing content/% | Surface water contact angle/deg |
|-------|------------|----------------|-----------------------------|-------------------------------|
| 1     | 1.3        | 6H             | 90.7                        | 101.5                         |
| 2     | 1.4        | 6H             | 97.1                        | 103.9                         |
| 3     | 1.5        | 3H             | 91.5                        | 104.1                         |
| 4     | 1.6        | 2B             | 87.3                        | 104.4                         |

“Conditions: The sulfur-containing hyperbranched polycarbosilane was prepared by UV for 30 s. The thiol group content of the thiol silicone resin is 0.004 mol g$^{-1}$. The degree of curing content reaches the highest when the molar ratios of SH to allyl are in the range of 101.5–104.4$^3$.

DSC analysis is an effective method to measure the glass-transition temperature ($T_g$), and $T_g$ increases with the increase of cross-linking density because cross-linking makes the polymer molecules become continuously stacked to form polymer chains.$^8$ It can be seen from Figure 4 that the glass-transition temperature of the cured materials decreases from 4.83 to $-31.44 \, ^\circ C$ with the increase of the R/Si ratio. It can be concluded that the cured materials have good flexibility.$^{38}$

3.4. Effect of Various Thiol Contents of Thiol Silicone Resins. The effect of thiol content of the silicone resins was also investigated as given by Table 4. The pencil hardness of the cured materials increased obviously with the increase of the thiol content of the silicone resins, which may be due to the increase of the cross-linking density of the cured materials obtained. The degree of curing content reaches the highest when the thiol content of the silicone resin is 0.004 mol g$^{-1}$. There is an obvious decline for the surface water contact angle of the cured materials when the thiol content of the silicone resin is 0.006 mol g$^{-1}$, which may be due to the decline of the amount of thiol silicone resin caused by the high thiol content.

The molar ratios of SH to allyl have significant effect on the performance of the cured materials as given by Table 5. The pencil hardness of the cured materials increased with the increase of the molar ratios of SH to allyl when the molar ratios of SH to allyl are in the range of 0.4–1.3. A further increment of the molar ratios of SH to allyl will lead to the decline of the pencil hardness of the cured materials. In general, the pencil hardness of the cured materials is in the range of 6B and 9H, which can be tuned by adjustment of the molar ratios of SH to allyl. The degree of curing content of the cured materials is fairly high when the molar ratios of SH to allyl are in the range of 0.7–1.1, which means that the materials are cured more completely at this time.

3.5. Tensile Strength and the Corrosion Resistance Performance to Acid, Alkali, and Salt. As we know, the...
The tensile strength of unreinforced silicone with high transparency is no more than 0.4 MPa. The tensile strength of silicone can be improved by incorporation of various inorganic fillers such as nano-SiO₂ and carbon nanotubes into the polysiloxane matrix at the expense of lower transparency. So far, the tensile strength of chemical-modified transparent silicone materials is still no more than 1.5 MPa. The drawbacks of poor mechanical properties seriously limit the further application of transparent silicone materials in electronic devices. Interestingly, the tensile strength limit of the cured materials prepared is as high as 2.2 MPa (Table 6). It is obvious that the tensile strength of all the materials immersed in various corrosion solution mediums increased. Remarkably, the tensile strength can increase from 2.2 to 5.6 and 5.7 MPa after being immersed in the aqueous solutions of 10 wt % hydrochloric acid and 10 wt % NaCl for 7 days, respectively.

The increase of tensile strength after being immersed may be attributed to the residual alkoxy groups of 3-trimethoxysilylpropanethiol. As it can be seen from Figure 2 and Table 1, there is SiOCH₃ in the residual 3-trimethoxysilylpropanethiol. The residual 3-trimethoxysilylpropanethiol can react with −CH₂CH −OCH₃ in 3-trimethoxysilylpropanethiol. The residual −SiOCH₃, which will hydrolyze in the aqueous solution mediums and also reinforce the cured silicone materials. As discussed by the previous work, the alkoxy groups of the silicone coating can react with the hydroxyl counterparts on the activated metal substrates, which can improve the anticorrosion features of the materials. It is found that the transparent UV-cured silicone materials obtained are candidates of anticorrosion coating with good resistance to acid, alkali, and salt. It can be seen from Table 6 that the cured materials exhibit high transparency. The transparency of the films are all higher than 95% (wavenumber in the range of 400–800 nm) even being immersed for 15 days in various aqueous solution mediums.

The TGA curves of UV-cured materials before and after being immersed in various aqueous solution mediums are shown in Figure 7. The initial thermal decomposition temperature of the cured material before being immersed is about 340 °C, which is higher than those of the silicone resins (about 200 °C) reported by our group previously¹¹ and the alkyd-silicone hyperbranched resins (about 310 °C) reported by ref 29. Therefore, it can be concluded that the UV-cured silicone materials obtain are candidates of anticorrosion coating with good resistance to acid, alkali, and salt. It can be seen from Figures 5 and 6 that the cured materials exhibit high transparency. The transparency of the films are all higher than 95% (wavenumber in the range of 400–800 nm) even being immersed for 15 days in various aqueous solution mediums.

Table 6. Corrosion Resistance Performance to Acid, Alkali, Salt, and Water α

| corrosion media | immersed time/d | 10% HCl | 10% NaOH | 10% NaCl | deionized water | 10% H₂SO₄ | materials before being immersed |
|-----------------|----------------|---------|----------|----------|----------------|----------|----------------------------------|
| mass loss/%     | 3              | 0.05    | 0.11     | 0.07     | 0.04           | 0.04     | 103.9                            |
|                 | 15             | 0.12    | 0.39     | 0.14     | 0.12           | 0.08     |                                  |
| surface water contact angle/deg | 3           | 91.8    | 69.4     | 97.6     | 94.2           | 92.1     |                                  |
|                 | 15             | 84.0    | 76.5     | 98.2     | 86.6           | 76.7     |                                  |
| tensile strength/MPa | 3            | 4.5     | 2.6      | 4.7      | 4.9            | 1.6      | 2.2                             |
|                 | 15             | 4.4     | 2.6      | 5.7      | 4.9            | 3.9      |                                  |
| elongation at break/% | 3            | 14.0    | 8.8      | 16.2     | 17.0           | 14.4     | 21.4                            |
|                 | 15             | 16.8    | 17.1     | 19.2     | 17.8           | 17.8     |                                  |

αThe films were entry 3 in Table 2.
4. CONCLUSIONS

Silicone materials with high transparency, high tensile strength, and outstanding resistance to acid, alkali, and salt were prepared by the UV-initiated thiol–ene reaction of a sulfur-containing hyperbranched polycarbosilane and a thiol silicone resin. The tensile strength of the materials obtained can reach 2.2 MPa. Interestingly, their tensile strength can increase from 2.2 to 5.6 and 5.7 MPa after being immersed in an aqueous solution of 10 wt % hydrochloric acid and 10 wt % NaCl for 7 days, respectively. It is argued that the increase of the tensile strength of cured films may be attributed to the $\text{SiOCH}_3$ of the residual 3-trimethoxysilylpropanethiol in the sulfur-containing hyperbranched polycarbosilane. Whether being immersed or not, the materials obtained are with a transparency higher than 95% (wavenumber in the range of 400–800 nm), and the initial thermal decomposition temperature of the cured material is about 340 °C. The mass loss of the materials immersed in the aqueous solution mediums is no more than 0.39 wt % even for 15 days. It can be concluded that the UV-cured materials are with good resistance to acid, alkali, and salt.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00401.

$^1$H NMR spectra with integration for the different peaks of sulfur-containing hyperbranched polycarbosilanes prepared by UV for 0, 30, 60, and 90 s (PDF)
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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for financial support from the Zhejiang Provincial Natural Science Foundation of China (grant no. LY14E030008) and the Open Fund of the Collaborative Innovation Centre for Fluorosilicon Fine Chemicals and Materials Manufacturing of Zhejiang Province (FSI2019A007).

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