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A Self-Healing, Re-moldable and Biocompatible Crosslinked Polysiloxane Elastomer

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The thermally healable polysiloxane elastomers were successfully prepared by cross-linking polydimethylsiloxane bearing maleimide pendants with furan-end functionalized siloxane via Diels-Alder (DA) reaction. The elastomers with good mechanical properties show excellent self-healing and remoldability functions due to the thermally reversible feature of DA reaction. The molecular mechanism of self-healing was confirmed by in-situ structure characterization. Moreover, the biocompatibility of the polysiloxane elastomer containing DA bonds is fairly good by cytotoxicity evaluation and animal subcutaneous experiments, suggesting a potential application in biomedical field such as artificial skin and scaffold for tissue engineering.

1. Introduction

Self-healing polymer materials represent the forefront of recent developments in materials chemistry and engineering. They can recover their properties after damages such as impact, wear or fatigue to improve their durability and safety, thereby reducing resource demand and environmental impact.[1-3] Self-healing polymers can be classified into extrinsic and intrinsic types according to the way of healing. For the extrinsic ones, a healing agent has to be embedded into the matrix in the form of microcapsule structures.[4,5] When microcracks propagate through the matrix, the healing agent is released from ruptured microcapsules and polymerizes with the released catalyst to repair the damaged region. For the intrinsic ones, the materials can heal the damage by themselves based on reversible dynamic covalent or non-covalent bonds without adding healing agents and catalysts. Reversible dynamic bonds can be introduced by chemical reactions such as the Diels–Alder reaction, trans-esterification or photodimerization or by noncovalent interactions such as hydrogen bonding, metal–ligand bonding or π–π stacking.[6-19]

Self-healing polysiloxane elastomers have attracted increasingly attentions recently because polysiloxane are widely used in biomedical devices, seals, damping etc, but often fail in the long-term service life.[20-25] In 2007, Sottos et al. introduced the self-healing functionality into a poly(dimethyl siloxane) elastomer for the first time by embedding the microencapsulated PDMS resin and crosslinker into the PDMS matrix.[21] The specimens could recover 70–100 % of the original tear strength at room temperature for 48 h. However, this system was limited to repair a given location for only one time. In order to overcome this problem, other approaches have been developed.[22-25] McCarthy et al. discovered a self-healing silicone rubber based on a patent from 1950s.[22] The rubber was healed through anionic siloxane equilibration at 90 °C for 24 h. The multiple times healing was possible with almost 100 % recovery, however, the Young's modulus of this rubber was relatively low. Li et al. incorporated a cobalt (II) triazole complex into the PDMS matrix.[23] The Young's modulus for the resulting polymers was improved but self-healing efficiency was not ideal, just ~52 % after being heated at 140 °C for 24 h. Therefore, it is necessary to develop the self-healing polysiloxane elastomers with high healing efficiency and good mechanical property.

The Diels–Alder reaction is a [4+2] cycloaddition involving a diene and a dienophile as precursors. The "click" characteristic of the DA reaction provides some convenience for polymer design and synthesis.[26-30] More importantly, the Diels–Alder (DA) reaction is thermally reversible: when a DA adduct is heated to an appropriate temperature, the retro-DA reaction takes place and once cooled down to lower temperature, the DA reaction occurs and the covalent DA bonds re-form again. This important feature may endow the crosslinked polymer containing DA bonds with remoldability and remendability.[31] However, the self-healing polysiloxane elastomers based on DA reactions are rarely reported, possibly because it is difficult to find the proper precursors for the synthesis of self-healing PDMS. To prepare an excellent self-healing PDMS, the compatibility of two main precursors, reactivity of DA bond moieties (maleimide or furan) in the precursor, as well as the crosslink network parameters such as molecule chain mobility and the crosslink degree must be considered.

Herein we reported a facile route to prepare a thermally healable polysiloxane elastomer by directly cross-linking a polydimethyl-siloxane bearing maleimide pendants (PM) with a furan-end

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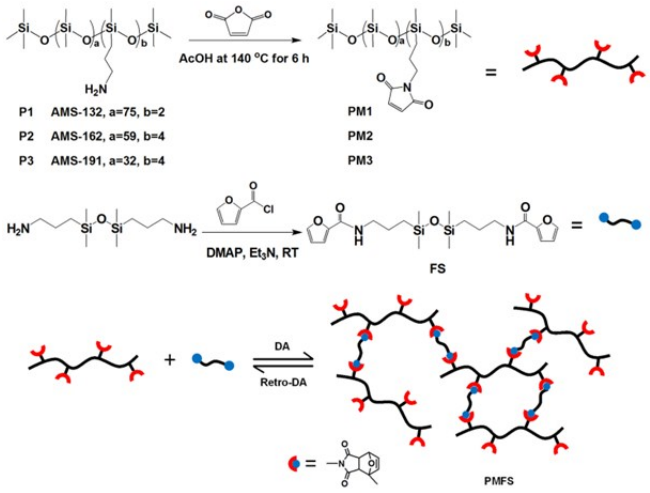
functionalized siloxane (FS) via DA reaction (Scheme 1). The precursors containing maleimide and furan are used, because the C=O groups in the maleimide make the C=C group more electron-insufficient and more reactive in the DA reaction and furan derivatives are produced from renewable resources, which provides sustainable approaches to materials.[32,33] Also the hydrogen-bonding between C=O in maleimide and N-H in the vicinity of furan contributes to the promotion of mechanical property, and also makes the dissociative maleimide and furan to reconnect easily.[34] The structure and composition of the precursor containing maleimide groups was optimized with regard to the materials properties. The obtained cross-linked polysiloxane materials show excellent self-healing and remoldability functions. Moreover, the biocompatibility of the novel materials was characterized by the cytotoxicity evaluation and animal subcutaneous embedding experiments.



Scheme 1 Preparation of polysiloxane elastomer PMFS containing DA bonds.

2. Experimental

2.1. Materials

Three aminopropylmethylsiloxane(AMS)-dimethylsiloxane copolymers with different AMS content and different molecular weight (AMS-132: Mw~6000, AMS content: 2~3%; AMS-162: Mw~5000, AMS content: 6~7%; AMS-191: Mw~3000, AMS content: 9~11%), polymethylhydrosiloxane (HMS-991, Mw~1800), vinyl terminated polydimethylsiloxane (DMS-V03, Mw~500), 1,3-bis(3-aminoproyl) tetrametyldisiloxane, and Pt-divinyltetramethyldi-siloxane complex (Karstedt's catalyst) were purchased from Gelest (U.S.A.). 2-Furoyl chloride (98 %) and 4-dimethylaminopyridine (DMAP) were from Maya Reagent (China). Cell Counting Kit-8 was from Dojindo (Japan). Dulbecco's Modified Eagle's Medium culture medium (DMEM) was from Gibco (USA). Dichloromethane was dried and distilled before use. All other solvents and reagents were purchased from Aldrich and used without any further purification. BALB/c mice (male, 18-20 g) were purchased from the Experimental Animal Department of the Third Military Medical University. The animals were individually raised in plastic cages under standardized conditions (room temperature: 25 °C; relative humidity: 50 %; and circadian rhythm: 12 h). The animals were fed autoclaved standard rodent chow and water ad libitum and were adaptively bred for 1 week in the facility before the experiments.

2.2. Characterizations

The ^{1}H NMR spectra were recorded on a Bruker 400 (400 MHz) spectrometer with tetramethylsilane as the internal reference. The time dependence of the DA and retro-DA reactions were monitored using NMR spectroscopy. A UV2300 UV-Visible spectrometer with heating platform was used to monitor the DA and retro-DA reactions. Firstly the PM and FS were dissolved in dichloromethane. After being mixed, coated on a quartz slide and dried with nitrogen gas flow, the UV-visible spectra were recorded at 80 °C for 6 hours. When it referred to retro-DA reactions, a very thin PMFS film was covered on a quartz slide, the spectra were recorded at 140 °C. FTIR spectra were measured with a Nicolet 560 FTIR, the solution of PM and FS in dichloromethane was coated on a KBr plate and dried with nitrogen gas flow. The KBr plate was stored in 80 °C oven and the FTIR spectra were recorded every 6 hours. DSC experiments were carried out under nitrogen atmosphere on TA Instruments DSC Q2000 at a heating rate of 10 °C min^{-1}. Mechanical properties were measured with an Instron Machine (Model 5567) at room temperature. The elongation rate was 20 mm min^{-1}. The fracture surface was observed by an optical microscope (VHX-1000, KEYENCE, Japan).

2.3. Synthesis of the polydimethylsiloxane bearing maleimide pendants (PM)

According to the general procedure, a solution of AMS-191 (50 g, 16.67 mmol) and maleic anhydride (32.67 g, 333.33 mmol) in glacial AcOH (300 mL) was heated under 140 °C for 6 h with magnetic stirring.[35] After the solution was cooled to room temperature, AcOH was removed on a rotary evaporation. The crude product was redissolved in 300 mL CH_2Cl_2 and washed with saturated sodium chloride aqueous solution (150 mL, three times). The organic layer was dried over anhydrous magnesium sulfate, filtered, and the solvent was removed to give the desired product as brown viscous oil (yield: 48.69 g, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ [ppm]): 0.04 (180H, Si-CH_3), 0.41 (8H, Si-CH_2), 1.54 (8H, Si-CH_2-CH_2), 3.41 (8H, Si-CH_2-CH_2-CH_2), 6.61 (8H, -CH=CH- in maleimide); IR (KBr, cm^{-1}): ν = 2962 (ν(CH)), 1712 (νas(C=O)), 1442 (δ(CH)), 1407 (δ(CH_2)), 1260 (δ(CH_3)), 1027, 1093 (νs(Si-O-Si)), 800 (δ(C-Si-C)). The corresponding copolymers from AMS-132 and AMS-162 were prepared likewise.

In order to determine the complete conversion of –NH_2 to maleimide groups was achieved, the polydimethylsiloxane bearing maleamic acid pendants (PMA) was also synthesized (see details in the ESI). The differences among the copolymers AMS-191 (1), PMA (2), and PM (3) were characterized by ^{1}H NMR (Fig. S1) and FTIR (Fig. S2) spectroscopy. The proton peaks at 6.2-6.3 ppm belong to the maleamic acid structure in the sample PMA, while only a single signal at 6.6 ppm can be observed for the maleimide structure in the sample PM. In FTIR spectra, there were also no characteristic peaks of -OH and –NH– for the maleamic acid structure in the sample PM. The above results confirmed that the conversion is complete and there is no maleamic acid structure in the PM.

2.4. Synthesis of the furan-end functionalized siloxane (FS)

All glassware were dried before use. 1,3-bis(3-aminoproyl) tetra-metyldisiloxane (10.00 g, 40.3 mmol), triethylamine (8.14 g, 80.6 mmol), DMAP (0.10 g, 0.8 mmol), and anhydrous CH_2Cl_2 (100 mL) were added to a 250 mL round bottom flask fitted with an addition funnel. The whole system was placed in an ice bath. Then, 2-Furoyl chloride (10.48 g, 80.6 mmol) and anhydrous CH_2Cl_2 (70 mL) were added to the addition funnel, and added drop-wise to the flask with stirring. A white precipitate was formed gradually, and the reaction was left for 24 h at ambient temperature. The precipitate was removed by filtration and the solution was washed with saturated sodium hydrogen carbonate aqueous solution (100 mL, twice) and deionized water (100 mL, twice) successively. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed to give the desired product as light brown waxy solid (yield: 15.8g, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ [ppm]): 0.01 (12H, Si-CH_3), 0.50 (4H, Si-CH_2), 1.56 (4H, Si-CH_2-CH_2), 3.34 (4H, Si-CH_2-CH_2-CH_2), 6.42 (2H, furan), 7.03 (2H, furan), 7.35 (2H, furan). IR (KBr, cm^{-1}): ν = 3304 (ν(NH)), 3120 (ν(CH), furan), 2964 (ν(CH)), 1648 (νas(C=O)), 1533 (δ(NH)), 1260 (δ(CH_3)), 1015, 1054 (νs(Si-O-Si)), 800 (δ(C-Si-C)).

2.5. Cross-Linking of PM with FS (PMFS)

The PM and FS mixed solutions in dichloromethane (M/F molar ratio = 1/1) were prepared, then the solutions were cast into an open PTFE mold. The homogeneous mixtures of PM and FS were obtained after the solvent evaporated at room temperature. Hereafter the cross-linking reactions were allowed to proceed for 4-10 days at 80 °C. Polysiloxane cross-linked by DA bonds (PMFS) were formed as a yellowish transparent elastomeric materials.

2.6. Preparation of the control polysilxoane sample without DA bonds (PHPV)

Mixture of polymethylhydrosiloxane (PH), vinyl terminated poly-dimethylsiloxane (PV), and Karstedt's catalyst (100 ppm) (Si-H/C=C molar ratio = 1/1) was prepared. The mixture was degassed under vacuum for 10 minutes and was placed into the open PTFE mold. The curing was allowed to proceed for 2 h at 80 °C. Polysiloxane cross-linked by hydrosilylation (PHPV) was obtained as a colorless transparent elastomer.

2.7. The biocompatibility characterization of PM3FS

The surgical glove is common used in clinic, its biocompatibility is relative good and it is used as control material in the following experiment. The PM3FS and surgical glove samples were sterilized by irradiation with a ^{60}Co source and then washed with phosphate-buffered saline (PBS; pH 7.4) three times before experiments.

2.7.1. Cytotoxicity evaluation. The fibroblasts were isolated from neonatal mice as previously described.[36] The 3rd-passage sub-cultured fibroblasts were used for the following experiment. The PM3FS sample was cut into a disc with a diameter of 0.4 cm by using a punch. Fibroblast suspension was adjusted to 1×10^4 cells mL^{-1} and 100 μL of the cell suspension was seeded in a 96-well plate, with three replicates for each group, then samples were added to the well and the cells cultured in the well without sample are served as control. Cell numbers on the samples were counted with CCK8. After incubation for 1, 3, 5 and 7 days, samples and wells were washed with PBS and then 100 μL fresh DMEM culture medium was added to each well. Then 10 μL of CCK8 was added to each well. After incubation at 37 °C for 2 h, the absorbance was measured at 450 nm using an enzyme-linked immunosorbent assay reader (Thermo Varioskan Flash, USA).

2.7.2. Animal subcutaneous embedding experiment. Five mice were implanted with each of PM3FS and surgical glove. Each mouse was initially anesthetized and then the longitudinal incision was made along the dorsum. Blunt dissection was carried out to make a subcutaneous pocket with the size of 1.5 × 1.5 cm^2. With a single implant allotted to a single pocket, standardized 1 × 1 cm^2 implants of PM3FS and surgical glove were then placed subcutaneously. Each implant was anchored to underlying fascia with a single 6-0 rapid-absorbing catgut suture. Each pocket was then irrigated with sterile saline and closed with a continuous resorbable suture. Following carbon dioxide euthanasia of the animals after 30 days, great care was taken to complete the excision with all implanted materials and surrounding tissues intact. Extracted specimens were evaluated for their gross appearance, including shape, texture, rigidity, and signs of implant migration or extrusion. The tissues were carefully biopsied, fixed with 4 % formaldehyde, embedded in paraffin, sectioned at a thickness of 5 μm and stained with H&E (hematoxylin and eosin) for histological analysis, the surrounding capsule thickness were examined.

2.7.3. Statistical analysis. All data were presented as the mean ± standard deviation (SD). One-way ANOVA was used to evaluate statistical significance, followed by post-hoc LSD test and Bonferroni's test. p values less than 0.05 were considered significant.

3. Results and discussion

3.1. Preparation and Characterization of PMFS

Three PMs containing different contents of maleimide (PM1, PM2 and PM3) were firstly synthesized. PMs were cross-linked with FS by DA reaction between the stoichiometric amount of furan and maleimide. ^{1}H NMR spectra of PM and FS mixture before crosslinking was shown in Fig. 1a. The chemical shifts at 6.42, 7.03, 7.35, and 6.61 ppm are assigned to the furan and maleimide groups. The polymerization time for PM1FS, PM2FS, and PM3FS were 10, 6, 4 days, respectively. The mechanical properties for three materials were shown in Table 1. The crosslinked samples PM2FS and PM3FS are elastomers while the PM1FS is not solid but a low consistency fluids or ''slimes'' even after reacted for 10 days. For the sample PM3FS, the Young's modulus and tensile strength are 2.27 ± 0.29 MPa and 0.61 ± 0.05 Mpa, respectively, which is suitable for some biomedical use such as artificial skin. The significant difference in mechanical properties derived from three different precursors suggests that the structure and composition of the precursors is very important to obtain a good PDMS elastomer. PM3FS needs a short reaction time as it possesses a relatively high content of maleimide groups and lower molecular weight. It should be pointed

Table 1 Mechanical properties for the samples PM1FS, PM2FS, and PM3FS.

Samples	Reaction time [days]	Appearance	Tensile strength [MPa]	Elongation at break [%]	Young's modulus [MPa]
PM1FS	10	Slime-like	-	-	-
PM2FS	6	elastomer	0.13 ± 0.01	35.5 ± 2.3	0.61 ± 0.07
PM3FS	4	elastomer	0.61 ± 0.05	50.9 ± 2.3	2.27 ± 0.29

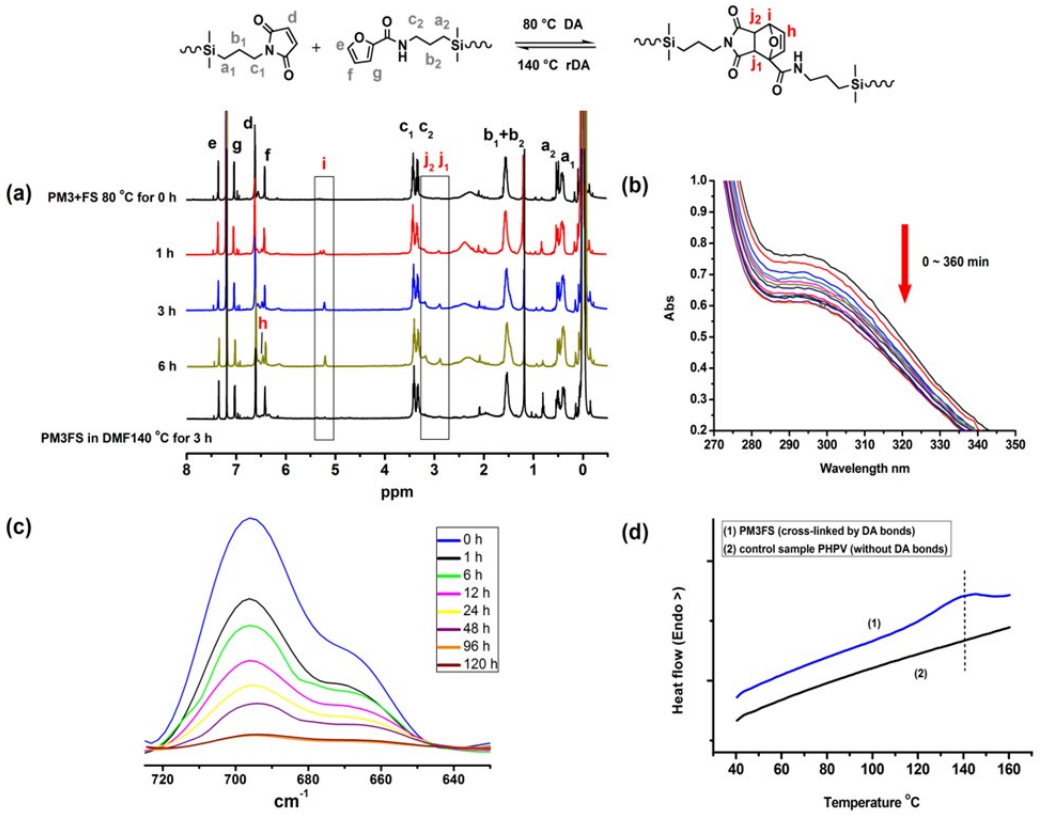


Fig. 1 (a) [1] H NMR spectra of the mixture of PM3 and FS during the DA crosslinking reaction at different times, and [1]H NMR spectrum of the viscous liquid retro-DA product of the cross-linked polymer PM3FS after being heated at 140 °C for 3 h in DMF. (b) Time-dependent UV-vis curves and (c) FTIR spectra of the adduct of PM3 and FS with the reaction time. (d) The DSC thermograms of cross-linked polymers PM3FS with DA bonds and the control sample PHPV without DA bonds.

out that the compatibility of the precursors is also important for the crosslinked PDMS elastomer. In our case, the compatibility of PM and FS is very good because of the similar molecular structure, they can keep good contact without phase separation and react with each other even after the solvent evaporation.

The in-situ monitoring of the DA reaction between PM3 and FS was conducted by [1]H NMR, and the results were shown in Fig. 1a. During the cross-linking process of PM3 and FS at 80 °C, a few milligrams of the reacting mixture were withdrawn at 0, 1, 3 and 6 hours for NMR test, respectively. It can be found that the intensities of the proton peaks at 6.42 (f), 7.03 (g), 7.35 (e) ppm belonged to furan and the proton peaks at 6.61 (d) ppm belonged to maleimide decrease, and new peaks appear at 2.89 (j_1), 3.18 (j_2), 5.21 (i), and 6.47 (h) ppm, which correspond to the characteristic peaks of the DA adduct. Also the intensities of these new peaks increase with the reaction time. The result confirms that the DA reaction between maleimide and furan groups occurs.

The DA reaction was also verified by UV-vis and FTIR. The maleimide group displays the characteristic absorption at 293 nm arising from the conjugated effect of its π-π* (C=C) and n-π* (C=O) chromophore excitation.[37] The formation of the DA adduct from maleimide and furan breaks the conjugation between the two chromophores of maleimide. So the decrease in the absorption at 293 nm during the DA reaction due to the conversion of maleimide to the DA adduct was observed as shown in Fig. 1b. Fig. 1c shows that the imide peak near 700 cm^{-1} in the FTIR spectra of PM3FS which is assigned to the maleimide in PM3 diminishes over the reaction time,[29] indicating the formation of DA bonds between

furan and maleimide groups. The DA reaction will reach an equilibrium state after ~96 h.

3.2. Thermally reversible cross-linking behavior of PM3FS

The DA reaction is thermally reversible, and the retro-DA for furan-maleimide DA-adducts can occur at above 100 °C.[38-40] Thermal properties of PM3FS cross-linked with DA bonds and the control sample PHPV without DA bonds were analyzed by DSC. The samples were heated from 40 to 160 °C with a heating rate of 10 °C min^{-1}. As shown in the DSC thermograms (Fig. 1d), a broad endothermic peak was observed at ca. 140 °C for PM3FS due to the retro-DA reaction, while for PHPV no any endothermic peak was observed.

Fig. 2 shows the photographs of dissolution behavior of PM3FS and PHPV. When the specimen sheets were immersed in DMF, both of the samples could not dissolve at room temperature in 12 h. However, the PM3FS began to dissolve slowly under heating at 140 °C, and was converted to clear solution after 3 h. While the control sample PHPV without DA bonds could only swell slightly in DMF at 140 °C. After removing DMF from PM3FS solution, the dissolved PM3FS sample was viscous liquid, which was characterized by ^{1}H NMR. As shown in Fig. 1a, ^{1}H NMR spectrum for PM3FS after being heated at 140 °C for 3 h in DMF is nearly the same as the original mixture of PM3 and FS. The results indicate that PM3FS could convert to clear and fluid solution under heating due to the occurrence of retro-DA reactions. Through retro-DA reaction the cross-linked PM3FS disconnected back to the original PM3 and FS, which dissolve in DMF again to form clear solution. When the viscous liquid product was heated at 80 °C, the DA reactions occurred and a monolithic PM3FS elastomer was formed again (Fig. 2).

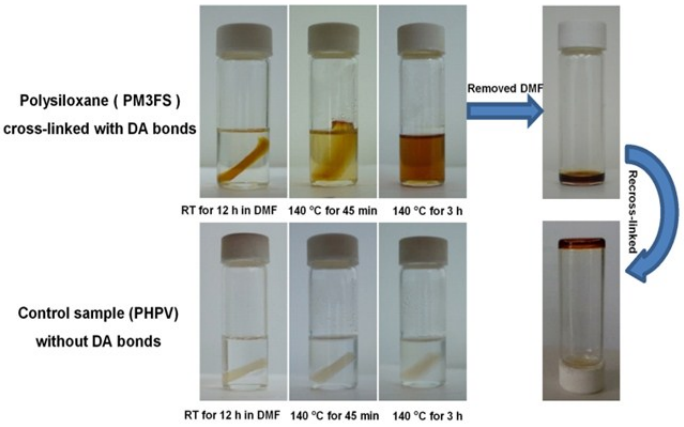


Fig. 2 The dissolution behavior of the DA cross-linked polymers PM3FS and PHPV in DMF.

The DA crosslinked PDMS elastomer has another advantage, i.e. thermal reprocessing, like thermoplastic polymer, which endows the crosslinked polymer for recycling. Fig. 3 shows the reprocessing performance of PM3FS. A rectangle PM3FS sample was cut into small fragments and remolded into the shape of a triangle through hot compression at 140 °C for 1.5 h under a pressure of 20 MPa. Sample was then cooled to 80 °C, held at this temperature for 24 h. It was found that the small fragments of PM3FS could form a monolithic triangle sample. However, for the control sample PHPV without DA bonds, it cannot be reshaped, and just be crashed into powders during the same procedure. The cross-linked PM3FS possesses good remoldability owing to the thermally reversible DA bonds.

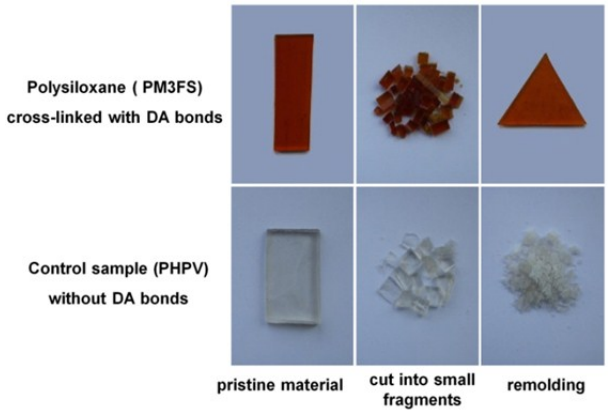


Fig. 3 The remoldability of the cross-linked polymers PM3FS and PHPV.

3.3. Self-healing properties

The self-healing properties of polysiloxane elastomers cross-linked by DA bonds were examined. The rectangular sample was first cut into two pieces and was then brought into contact immediately at room temperature, following by thermally treatment successively at 140 °C for 3 h and at 80 °C for different times. Fig. 4 shows the self-healing properties of PMFS polymers. The healed PM3FS sample could be bent and stretched without breaking at the cutting location (Fig. 4a). Additionally, the self-healing properties of the PM3FS and PM2FS were evaluated by tensile–stress curves in a more quantitative way (Fig. 4b, c), and the healing efficiencies were calculated from the ratio of tensile strength of healed and original samples. It can be seen from Table 2 that healing efficiency is a function of healing time. The healing efficiency of PM3FS increases from 29 % to 95 % with the healing time from 1 h to 24 h at 80 °C (Fig. 4b, solid lines). The healing efficiency of PM2FS is lower than PM3FS under the same healing condition (Fig. 4c). This is because that the content of DA bonds in PM2FS is low and the mobility of molecular chain is relative poor because of its high molecule weight. Moreover, the remolded PM3FS sample through hot compression showed the same healing efficiency as the original PM3FS prepared through casting method (Fig. 4b, dotted line), the reprocessing did not change the self-healing property of PM3FS. The control sample PHPV without DA bonds showed no self-healing ability under the same heating program, suggesting that the DA bonds in the materials play a significant role in their self-healing performance.

3.4. Mechanism

When the sample is cut off, the molecular chains and DA bonds could be ruptured, because the bond strength between diene and dienophile of the DA adduct is much lower than all the other covalent bonds.[6] The fracture surface was observed by the optical microscope (Fig. 5a), it was smooth with patterns along the cutting

Table 2 Self-healing efficiencies of the PMFS polymers at different conditions.

Samples	Healing time [h]	Tensile strength [MPa]	Elongation at break [%]	Young' s modulus [MPa]	Self-healing efficiency [%][a)]
PM2FS	12	0.09 ± 0.01	26.4 ± 3.1	0.51 ± 0.07	69
	24	0.11 ± 0.01	31.1 ± 6.3	0.52 ± 0.06	85
PM3FS	1	0.17 ± 0.01	30.6 ± 2.8	0.89 ± 0.04	29
	6	0.36 ± 0.02	40.9 ± 0.1	1.62 ± 0.09	59
	12	0.59 ± 0.01	38.6 ± 4.6	2.22 ± 0.34	89
	24	0.58 ± 0.01	44.7 ± 1.4	2.34 ± 0.09	95
PM3FS-remolded	12	0.56 ± 0.01	35.6 ± 1.5	2.80 ± 0.08	89

a) The self-healing efficiencies were calculated from the ratio of tensile strength of healed and original

direction. The surface after being heated was also observed, it could be clearly seen in Fig. 5a that the surface morphology turned rough and random, indicating the occurrence of the molecular chains diffusion at the surface. After the two fracture surfaces were contacted, the sample was stored at 140 °C for 3 hours. During this heating procedure, the retro-DA reactions were characterized by UV-Vis (Fig. 5b). The increase of the absorption at 293 nm can be observed, indicating the conversion of the DA adduct to maleimide and furan. However, it was worth noting that not all the DA bonds were decomposed, because the material was not depolymerized into viscous liquid. This phenomenon is different from the thermally decrosslinking process in DMF solvent (Fig. 2), in that case the existence of solvent promotes the depolymerization. Once the sample was heated at 80 °C again, the dissociative maleimide and furan moieties rebonded, and thus the fracture was healed. The hydrogen-bonding between C=O in maleimide and N-H in the vicinity of furan makes the dissociative maleimide and furan to reconnect easily. The self-healing process of the PMFS elastomers includes the following three steps: (1) contacting two fracture surfaces, (2) retro-DA reactions and molecular diffusion, and (3) DA bonds regeneration (Fig. 5c). If comparing the self-healing behavior of PM3FS with PM2FS, it can be concluded that the healing efficiency of the material containing reversible dynamic bonds depends on the mobility of molecular chain, reactivity of DA bonds, and the content of DA bonds or crosslink density. When the molecule weight of precursor bearing maleimide pendants is too

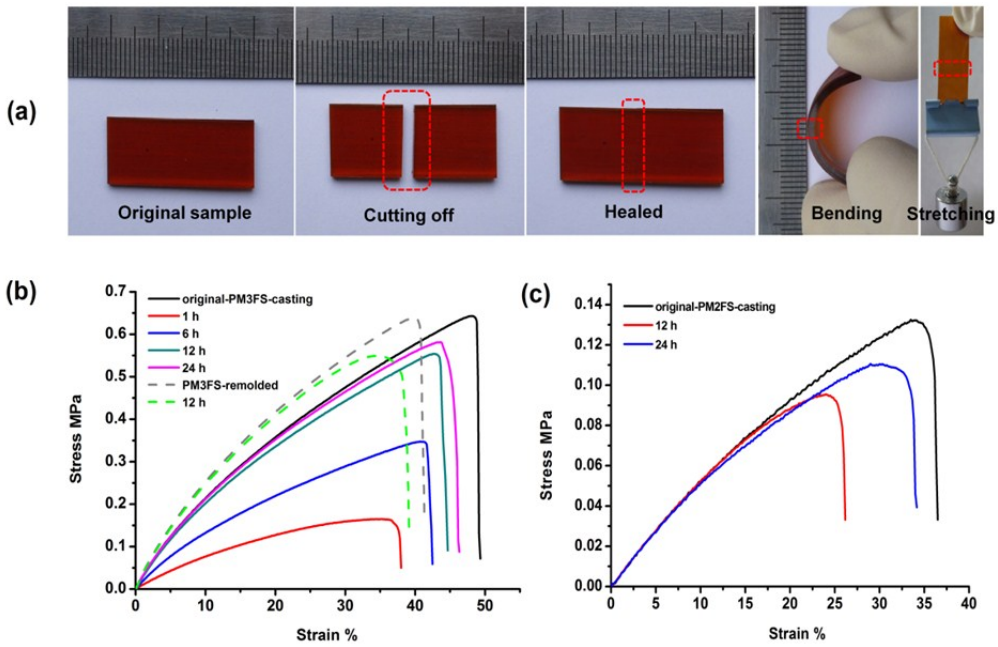


Fig. 4 The self-healing properties of the PMFS polymers: (a) the healed PM3FS sample can be bent or stretched, (b) stress–strain curves of the PM3FS prepared through casting method (solid lines) and compression molding method (dotted lines) healed for different times, (c) stress–strain curves of the PM2FS prepared through casting method healed for 12 and 24 h.

high, the mobility of molecular chains reduces, the molecular diffusion and DA bond re-formation at the fracture interface are limited, which will decrease the self-healing efficiency. However, if molecule weight of precursor is too low or DA bonds content is too high, the obtained cross-linked polymers will be very brittle and no useful. In order to develop the self-healing polysiloxane elastomers with good properties, a proper precursor with appropriate molecule weight and maleimide content must be considered.

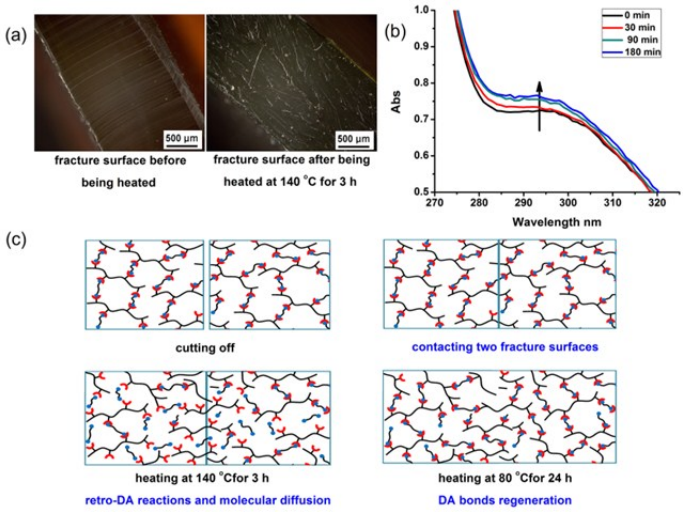


Fig. 5 (a) The optical microscopy photos of the cut surface before and after being heated at 140 °C for 3 h, (b) time-dependent UV spectra of the retro-DA depolymerization of PM3FS at 140 °C, (c) schematic illustration of self-healing process of PM3FS.

3.5. Biocompatibility Characterization

The selection of a material to be employed as a biomaterial must meet several criteria such as physicochemical and physiological properties, desired functions, durability, adverse effects in the case of failure. However, the biocompatibility is the foremost requirement for all biomaterials. In the present study, the biocompatibility of the material was characterized by the cytotoxicity evaluation and animal subcutaneous embedding experiments.

Cell numbers on the samples were counted by means of CCK8 at the time points: 1, 3, 5 and 7 days after the fibroblasts were seeded. The cell numbers on the PM3FS increased with the time, and there was no significant difference between the PM3FS and blank control (Fig. 6a). The prepared self-healing polysiloxane elastomer PM3FS does not inhibit the cell growth.

In animal subcutaneous embedding experiment (Fig. 6b), all implants retained approximately the same dimensions as upon implantation. Neighboring dermal, subcutaneous, and muscular tissues were not affected by implant materials, and no signs of infection or allergic reaction were present. There was no incidence of graft migration or extrusion. The tissues around the implants were also characterized through histological analysis. As shown in Fig. 6c, a thin fibrous capsule (between arrows) surrounding the implant due to minimal chronic inflammation could be observed in both of two implants. In addition, it was found that the fibrous capsule in PM3FS was much thin than the fibrous capsule in surgical glove (Fig. 6d). It demonstrates that the inflammatory reaction caused by PM3FS in 30 days is very weak.

The above results suggest that the biocompatibility of PM3FS is good and it could be a candidate for artificial skin, artificial prosthesis, artificial blood vessel, scaffold for tissue engineering, as PDMS is widely used in the field of biomedical materials.

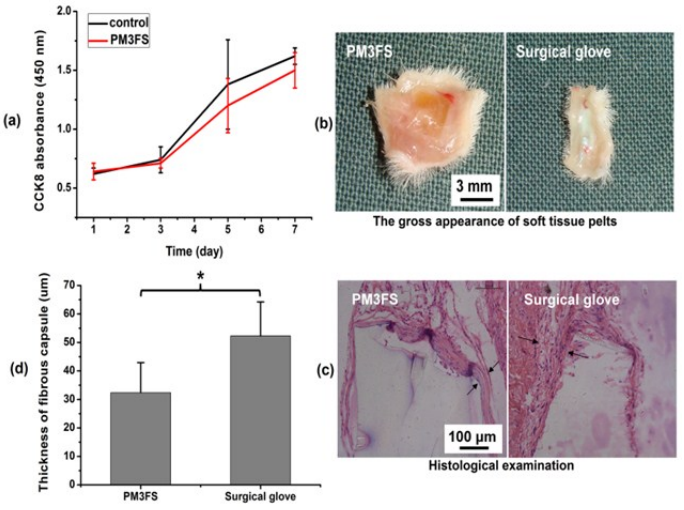


Fig. 6 (a) Cell number on the samples at different times, (b) the photos and (c) histological examination of dorsal soft tissue pelts from the mice implanted different materials, (d) thickness of fibrous capsule in dorsal soft tissue from the mice implanted different materials.

4. Conclusions

The thermally healable polysiloxane elastomers were prepared by cross-linking polydimethylsiloxane bearing maleimide pendants with furan-end functionalized siloxane via Diels-Alder reaction. A proper precursor with appropriate molecular weight and maleimide content is the key to obtain a self-healing polysiloxane elastomer with good mechanical properties. The thermally reversible cross-linked polysiloxane elastomers show good self-healing and reprocessing behaviors via DA and retro-DA reactions, which were confirmed by in-situ structure characterization. The prepared polysiloxane elastomer is nontoxic and has a potential application in biomedical field such as artificial skin and scaffold for tissue engineering.

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The self-healable polysiloxane elastomers cross-linked with DA bonds show high healing efficiency, good mechanical property and good biocompatibility.