

A Fast and Room-temperature Self-healing Thermal Conductive Polymer Composite

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 Electronic Supplementary Information

Abstract Thermal conducting materials may be damaged during long-term use, resulting in the increase of thermal resistance and therefore inefficient heat dissipation. The introduction of self-healing ability may solve this problem, but the realization of fast and room-temperature self-healing in thermal conducting composites is quite challenging. Herein, we choose a flexible poly(dimethylsiloxane) polymer material (PDMS-COOH) as the matrix and graphene nanosheets as the thermal conductive filler to prepare a new kind of thermal conductive polymer composite (PDMS-COOH-CG) that can quickly self-heal at room temperature. The thermal conductivity of PDMS-COOH-CG₁₀ with 10% of graphene content is 0.48 W·m⁻¹·K⁻¹, which is 16 times that of PDMS-COOH (0.03 W·m⁻¹·K⁻¹). At room temperature, self-healing efficiency of PDMS-COOH-CG₁₀ based on tensile strength can be 53.8% for 30 s and 84.6% for 24 h. Dynamic infrared thermal imaging depicted that after 2 min of self-healing at room temperature, the thermal conduction temperature near the damage was basically restored to the level of the pristine sample.

Keywords Self-healing; Thermal conductive; Infrared thermal imaging

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INTRODUCTION

Thermal conductive materials are of vital importance in electrical and electronic applications. In the past several decades, the density of transistors on components doubled approximately every two years, as predicted by Moore's law.^[1] While computers' processing performance increased, there is also an unwanted but unavoidable side effect, that is, the emission of a considerable amount of heat towards their surroundings.^[2,3] If the heat generated cannot be dissipated efficiently, it will concentrate in a small space and result in high temperature, which may lower the stability of devices, or even fail.^[4,5] Therefore, the efficient heat dissipation becomes more and more important.

It is known that when two solid surfaces contact, imperfect joints with many voids are formed.^[6,7] The air with poor thermal conducting property will enter the voids, making the thermal conduction between the heat producing and heat sink insufficient. Thermal interface materials (TIMs) are thus introduced to fill the gap between them, reducing the solid contact resistance and improving heat transfer properties.^[8–10] Compared with metal-based TIMs,^[11] polymer-based

TIMs are advantageous due to their low cost, convenient processability, adjustable modulus, light weight and free design.^[12–15] However, bulk polymers possess relatively low thermal conductivity (0.2–0.4 W·m⁻¹·K⁻¹)^[16] due to photon scattering in entangled chain of amorphous polymer materials.^[4] Therefore, high thermal conductivity fillers, such as boron nitride, silicon carbide, metallic gold, silver, copper, aluminium, graphene, carbon nanotubes, or graphite, have been introduced into the polymer matrix to obtain thermal conducting composite.^[17–19]

Despite the significant improvement of thermal conducting composite after the addition of fillers with high thermal conductivity, polymer-based TIMs still face some challenges for practical applications. One of them is that the thermal conducting composite will be inevitably subjected to various temperatures during long-term storage. The change in temperature will alter the interfacial adhesion behavior between two solid surfaces, which results in cracking formation and permeation of air. The presence of cracks and air will lead to the increase of thermal resistance, resulting in inefficient heat dissipation. Therefore, the thermal conducting composite should be improved in terms of crack resistance to guarantee stability and safety.

An effective approach to obtaining a durable thermal conducting composite is to introduce the concept of self-healing.^[20–22] Generally, synthetic self-healing materials can be readily obtained by either encapsulating healing reagents

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or incorporating various dynamic bonds into polymer matrices.^[23] There are two main types of dynamic bonds for constructing self-healing materials: (i) dynamic reversible covalent bonds, such as Diels-Alder reaction,^[24–26] disulfide bonds,^[27–29] boron-based bonds,^[30–32] transesterification reactions,^[33,34] and imine bonds^[35,36] and (ii) dynamic reversible non-covalent bonds, such as metal-ligand coordination,^[37–40] hydrogen bonds,^[41–46] and ionic interactions.^[28,47,48] Self-healing thermal conductive polymer composites have been reported in previous work.^[33,49,50] However, there are few room-temperature self-healing thermal conductive polymers which have been obtained. It is evident that healing under external stimuli is not favorable for electronic applications. Moreover, the healing speed is crucial for practical application as the electronic devices might be rapidly lose efficacy if the local defects cannot be fixed without delay.

Herein, we choose a flexible polymer backbone, poly[(2-carboxylethyl-2-methyl)methylsiloxane-co-dimethylsiloxane] denoted as **PDMS-COOH**, for our investigation as silicone-based polymers have been widely used as TIMs and electronic packaging materials due to their transparency, weatherability, chemical and thermal stability.^[51] By simply mixing with graphene nanosheet through ultrasonication, we successfully prepared a series of thermally conductive composites, denoted as **PDMS-COOH-CG**. We optimized the mass percentage of graphene filler to 10 wt%, and obtained a fast room-temperature self-healing thermally conductive film **PDMS-COOH-CG₁₀**. The thermal conductivity is $0.48 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is 16 times as much as that of **PDMS-COOH** bulk polymer. The optimized sample manifests tensile strength of 0.5 MPa, toughness of $1.98 \text{ MJ}\cdot\text{m}^{-3}$, tensile strain of 550% and high tensile strength self-healing efficiency of 53.8% after healing at room temperature for only 30 s by simply contacting without any external stimuli. Such a new thermal conducting composite might have potential application in the field of TIMs which needs long-term use.

EXPERIMENTAL

Materials

Poly(methylhydrosiloxane) and trimethylsilyl terminated (PHMS, $M_w=2000$, molar ratio of $\text{MeHSiO}=50\%$) were purchased from Zhejiang JOTEC New Material Technology Co., Ltd., China. Karstedt catalyst solution (Pt, 2% in xylene) was purchased from Dongguan Dongsheng Synthetic Material Co., Ltd., China. Graphene (with a diameter of 5–10 μm and thickness of 3–10 nm) was purchased from Nanjing XFANO Materials Tech Co., Ltd., China. Methyl methacrylate (MMA) and other chemicals and solvents were purchased from Aladdin Chemical Reagent Co., Ltd. All reagents were used without further purified.

Synthesis of PDMS-COOH

The **PDMS-COOH** was synthesized according to our previous work with slight modification.^[38] (Fig. S1 in the electronic supplementary information, ESI) PHMS (25 g, 0.2 mol Si—H), MMA (22 g, 0.22 mol) and toluene (50 mL) were added in a 250 mL round flask, then 10 μL of Karstedt catalyst was added via a syringe. The mixture was stirred for 30 min under room temperature and then heated to 80 °C and refluxed for 12 h under inert atmosphere. After reaction, toluene was removed by

rotary evaporator, resulting in a brown viscous liquid. The viscous liquid (PDMS-MMA) was purified by adding 80 mL of ether, followed by centrifugation to remove the PMMA solid and rotary evaporation to remove the ether. The PDMS-MMA was then dissolved with 150 mL of tetrahydrofuran in a 500 mL two-necked flask and 330 mL of 1 mol/L aqueous LiOH solution was added. The mixture was stirred at room temperature for 15 min, then heated to 85 °C and reacted for another 1.5 h. After cooling down, 150 mL of ether was added. The pH of the mixture was adjusted to 2–3 with hydrochloric acid (6 mol/L). The ether phase was collected and dried with anhydrous MgSO_4 . **PDMS-COOH** was obtained as a transparent film (Fig. S2 in ESI) after rotary evaporation to remove the residual solvent and heating for 24 h in an air oven (30 g, yield 72.4%).

Preparation of PDMS-COOH/Graphene Composite Film (PDMS-COOH-CG₁₀)

The as-prepared **PDMS-COOH** (5.0 g) was dissolved in 20 mL of tetrahydrofuran in beaker. Graphene was then added to the solution with a weight percentage of 10% **PDMS-COOH**, followed by ultrasonication for 1 h. The mixture was then loaded into a Teflon mold. The mold was placed under ambient condition and dried over 24 h, then transferred to an air oven and heated at 70 °C for 12 h. The residual solvent was removed by vacuum dryer at 70 °C for 24 h, resulting in a black solid elastomer. A thin film (thickness 1.0 mm) could be obtained after plate hot-pressing for 1 h at 70 °C, denoted as **PDMS-COOH-CG₁₀**.

General Characterizations

Thermogravimetric analysis (TGA) was performed on a simultaneous SDT2960 thermal analyser from 30 °C to 600 °C under N_2 atmosphere with a heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Differential scanning calorimeter (DSC) experiments were performed using a Mettler-Toledo DSC1 STAR^e differential scanning calorimeter under a dry nitrogen atmosphere ($20 \text{ mL}\cdot\text{min}^{-1}$) with a rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from $-60 \text{ }^\circ\text{C}$ to $100 \text{ }^\circ\text{C}$ to measure the glass transition temperature (T_g). The scanning electron microscopy (SEM) images were obtained on an S-4800 SEM (Hitachi, Japan) at 10 kV. XRD measurements were carried out on a Bruker D8 ADVANCE powder X-ray diffractometer (40 kV) with Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) between 5° and 50° at a scanning rate of $5 \text{ (}^\circ\text{)}\cdot\text{min}^{-1}$.

Rheological Test

The rheological behaviors were evaluated on a TA Instruments DHR-2 system (New Castle, DE, USA). All tests were performed on a 20 mm parallel plates with circular samples with diameter of 20 mm. Temperature sweeps run from 0 °C to 105 °C at a rate of $2 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and a frequency of 1 Hz, and the auto-compression feature was set to $0.50\pm0.2 \text{ N}$. Frequency sweeps were performed from $0.01 \text{ rad}\cdot\text{s}^{-1}$ to $100 \text{ rad}\cdot\text{s}^{-1}$ with a constant strain of 0.1% at 25 °C. Oscillatory strain sweeps were carried out ranging from 0.01% to 1000% strain at 1 Hz at 25 °C. Oscillation frequency of continuous step strain measurement was fixed to 1 Hz and the small and large strain amplitudes are 0.1% and 300%, respectively. Each scan lasted 60 s.

Mechanical Test

The mechanical properties were measured on an Instron (Boston, MA, USA) instrument with a maximum load cell of 500 N at 25 °C, and the tensile speed of $10 \text{ mm}\cdot\text{min}^{-1}$. Each experiment was performed for three times. Cyclic tensile test

was also performed by conducting successive of loaded-unloaded 9 cycles with a maximum strain of 500%. Wise-step cyclic tensile test was performed in an increasing strain from 500% to 800% without relaxation. All test samples were adopted with the size of 40 mm length $\times$ 5 mm width $\times$ 1 mm height.

Self-healing Test

For the self-healing tests, the sample was cut into two pieces and then put together and healed at room temperature without applying any pressure. The healed samples were performed in the same procedure as the original samples and obtained strain-stress curves. The scratch recovery was observed *via* optical microscope (MT 1100T, YSC Technologies, USA) equipped with a DLC300-L camera and a hot pad at different time.

Thermal Conductivity Test

Thermal conductivity experiments were performed *via* DECCA-III plate heat flow conductometer (Shenzhen Decca Precision Instrument Co., Ltd.). The samples were cut into discs with a diameter of 50 mm. And the temperatures of hot plate and cold plate were set to 50 and 25 $^{\circ}\text{C}$, respectively.

Infrared Thermal Imaging

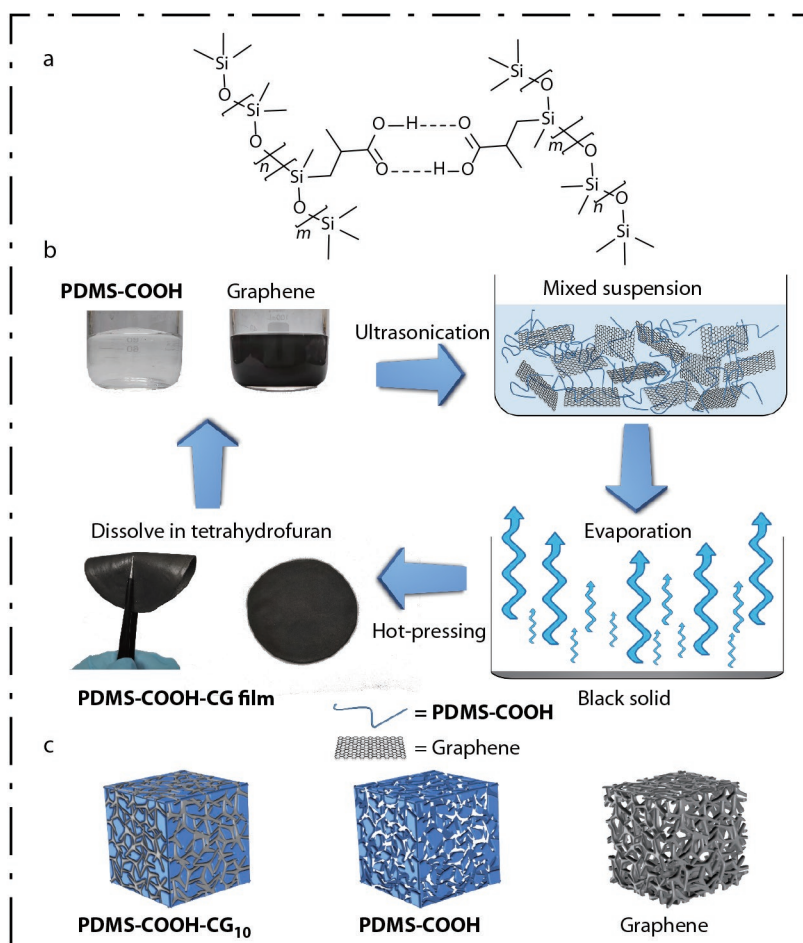
Infrared thermal imaging was carried out to evaluate self-healing of thermal conductivity of the **PDMS-COOH-CG₁₀**.

Infrared photos were taken *via* Fotric 227 infrared camera. First of all, in a room with constant temperature and humidity, we prepared a silicone electric heating film with adhesive on both sides. The film (20 mm $\times$ 10 mm $\times$ 2 mm) was stuck to an upright thermal isolation board and heated with a voltage of 6 V until the temperature was stabilized around 80 $^{\circ}\text{C}$. It was then adjusted and fixed to the position of the camera so that the camera frame was perpendicular to the spline. Then we stuck one end of the original sample on the silicone heater, and recorded the maximum temperature change on the selected upper and lower sides at 1/2 of the film length at the same time. Stop recording when the recording area is heated to 38 $^{\circ}\text{C}$.

RESULTS AND DISCUSSION

Preparation and Characterization of the PDMS-COOH-CG Film

Scheme 1 depicts the fabrication process of **PDMS-COOH-CG** film. A black elastic film was obtained simply by ultrasonication. Interestingly, the **PDMS-COOH-CG** films are dissolvable in tetrahydrofuran, ester or methanol, and therefore, graphene and bulk polymer **PDMS-COOH** can be recycled after filtration and evaporation. To optimize the composites' filler proportion, we prepared a series of composites in different



Scheme 1 Preparations of **PDMS-COOH-CG₁₀**. (a) Structure of **PDMS-COOH** polymer. (b) Preparation and recycling of **PDMS-COOH-CG₁₀** and (c) simulation diagram of composites.

percentages of 5 wt%, 10 wt% and 20 wt% [$m_{\text{graphene}}/m_{\text{(PDMS-COOH+graphene)}}$], respectively. Fig. 1(a) illustrates the effect of different percentages of graphene on the thermal conductivity of composites. Although the thermal conductivity of **PDMS-COOH** is only $0.03 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, it was increased to $0.07 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (233% of the intrinsic value) when the content of graphene is 2.5 wt%. Such enhancement is due to the high intrinsic thermal conductivity of graphene nanosheet, which improves the phonon transmission channel of the amorphous chain-entangled polymer. As graphene filler content increases, the thermal conductivity of the composite increases rapidly when the filler percentages is in the range of 2.5 wt%–10 wt%. The thermal percolation threshold can be considered as 2.5 wt%. When the percentages of graphene are 10 wt% and 20 wt%, the thermal conductivities further increased to 0.48 and $0.67 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, respectively, corresponding to 1600% and 2233% enhancement. Although the thermal conductivity has been improved from 10 wt% to 20 wt%, the increase rate has been reduced which may possibly due to the voids formed in the composites.^[52–54] Besides, there is a trade-off between the thermal conductivity and the self-healing properties of the composites. Too much graphene will slow down the mobility of the polymer chain, thereby reducing the reversibility of hydrogen bond, resulting in a poor self-healing ability. Therefore, we choose 10 wt% as the best filler ratio. The as-prepared film was denoted as **PDMS-COOH-CG₁₀**. The X-ray diffraction (XRD) patterns of **PDMS-COOH** and **PDMS-COOH-**

CG₁₀ are very similar except that there is an additional sharp peak at 26.8° which is attributed to graphene (Fig. 1b). The thermal properties of **PDMS-COOH** and **PDMS-COOH-CG₁₀** were investigated through differential scanning calorimetry (DSC) tests (Fig. 1c). The glass transition temperatures (T_g) of **PDMS-COOH** and **PDMS-COOH-CG₁₀** are -15.65°C and 12.05°C , respectively. It demonstrated that the addition of graphene slightly increased the T_g point of the composites, but the sample is still in soft state at room temperature (higher than T_g) with high chain mobility. In the DSC curve of **PDMS-COOH-CG₁₀**, the endothermic peak near 0°C on the **PDMS-COOH-CG₁₀** curve is probably caused by entrance of water vapor. The thermal stability of **PDMS-COOH** and **PDMS-COOH-CG₁₀** composite was characterized via thermal gravimetric analysis (TGA) instrument in a nitrogen atmosphere (Fig. 1d). As it is shown, the **PDMS-COOH** and **PDMS-COOH-CG₁₀** is thermal stable under 200°C . Moreover, the **PDMS-CG** film is non-absorbent. As shown in Fig. S3 (in ESI), we cut a sample with a mass of 0.1730 g, after soaking in water for 7 days, the final mass of the sample is 0.1737 g, indicating that the mass of the sample remains almost unchanged. Although there are so many water-absorbing hydrogen bonds on the polymer side chain, the hydrophobic PDMS chain especially dimethyl siloxane segments prevent the polymer from forming hydrogen bonds with water molecules.

Fig. S4 (in ESI) shows the SEM images of the **PDMS-COOH-CG₁₀**. Figs. S4(a)–S4(c) (in ESI) show the surface morphologies of **PDMS-COOH-CG₁₀** after hot pressing, which indicate

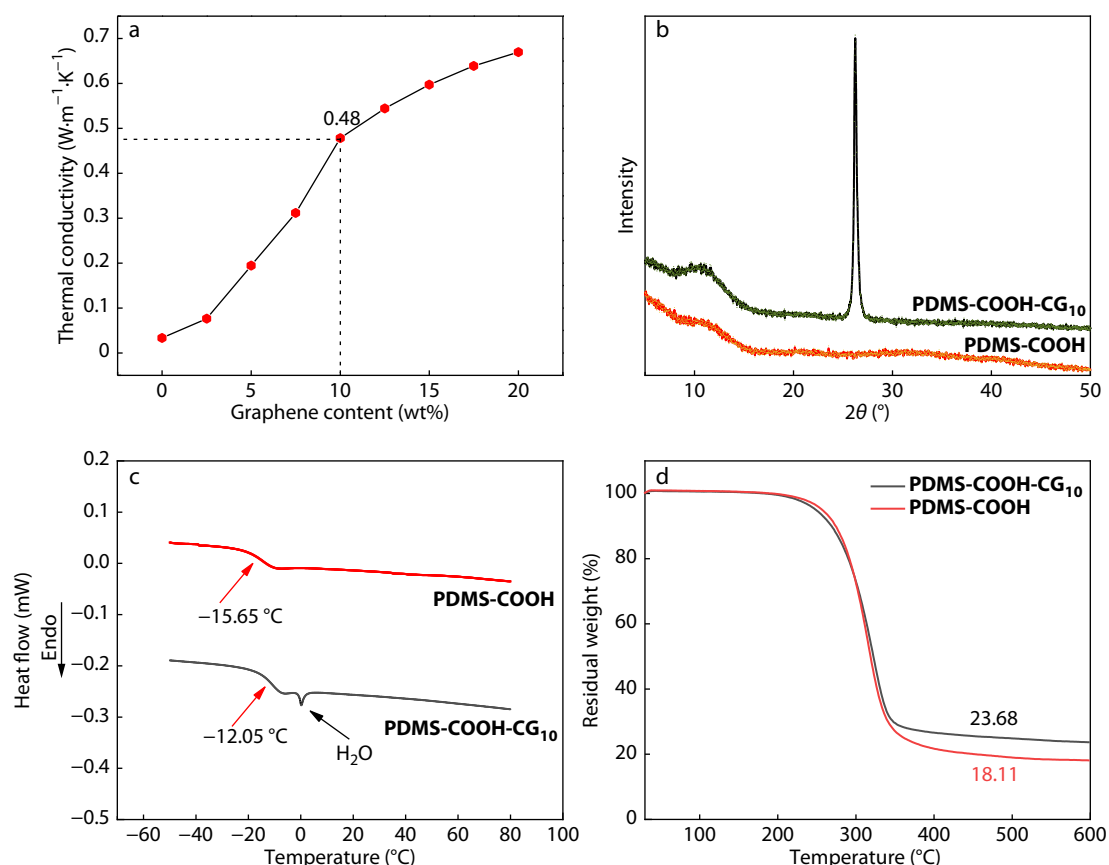


Fig. 1 Characterizations of **PDMS-COOH-CG₁₀**. (a) Thermal conductivity of **PDMS-COOH-CG₁₀**; (b) XRD patterns of **PDMS-COOH** and **PDMS-COOH-CG₁₀**; (c) DSC curves of **PDMS-COOH** and **PDMS-COOH-CG₁₀**; (d) TGA curves of **PDMS-COOH** and **PDMS-COOH-CG₁₀**.

the homodisperse of graphene in the PDMS polymer in different scales. Figs. S4(d)–S4(f) (in ESI) show the fracture section of **PDMS-COOH-CG₁₀** composites, which exhibit non-smooth surface due to the exist of graphene.

Rheology Study

Rotational test was performed to systematically study the rheological behaviors of **PDMS-COOH-CG₁₀** composite. Dynamic temperature-dependent mechanical properties of **PDMS-COOH-CG₁₀** composite were illustrated in Fig. 2(a). The temperature of dynamic oscillatory sweep ranges from 0 °C to 100 °C while the frequency is fixed to 1 Hz. As shown in Fig. 2(a), the storage modulus G' is 4.652 MPa at 0 °C and decreases upon decreasing the temperature. The loss modulus G'' is also decreasing but it decreases faster. Therefore, G' is lower than G'' at lower temperatures but higher upon heating. A crossing point was found at 13.02 °C. The rheological properties of **PDMS-COOH-CG₁₀** were further investigated by frequency sweeping from 0.01 rad·s⁻¹ to 100 rad·s⁻¹ at 25 °C. G' is higher than G'' at low frequencies but lower at high frequency. Thus, at lower angular frequencies, the material behaves more elastic-like, storing more energy; while at higher frequencies the material exhibits viscous-like behavior, dissipating more energy. The reciprocal of the crossover angular frequency (ω_c), where

$G'(\omega) = G''(\omega)$, can be taken as a characteristic relaxation time of the network (denoted as τ_c). As shown in Fig. 2(b), the ω_c of **PDMS-COOH-CG₁₀** is 2.88 rad·s⁻¹, correspondingly, $\tau_c = 1/\omega_c = 0.347$ s, indicating fast dynamic exchange of hydrogen bonds in the **PDMS-COOH-CG₁₀**.

According to the results of the strain sweep experiments in Fig. 2(c), G' is higher than G'' when the strain is less than 55% at 120 °C and less than 11% at 50 °C, indicating that the composite is primarily elastic at comparatively small strains. When the strain increases (>55% at 120 °C and >11% at 50 °C), G' and G'' decrease suddenly, implying that the sample has been destroyed due to partial broken of the supramolecular network. Besides, G' is almost equal to G'' when the strain is less than 5% at 13 °C, indicating that the viscous-elastic transition temperature of sample is 13 °C.

Continuous oscillation step strain experiments were conducted to simulate the recovery after mechanical breakdown. Each oscillation time sweep was performed for 60 s. As depicted in Fig. 2(d), a small strain (0.1%) and a larger strain (300%) were carried out alternatively. The initial G' and G'' were measured under small strain (0.1%) in the first 60 s. In the next 60 s, G' decreased by almost 2 orders of magnitude when the strain increased from 0.1% to 300%, indicating partially

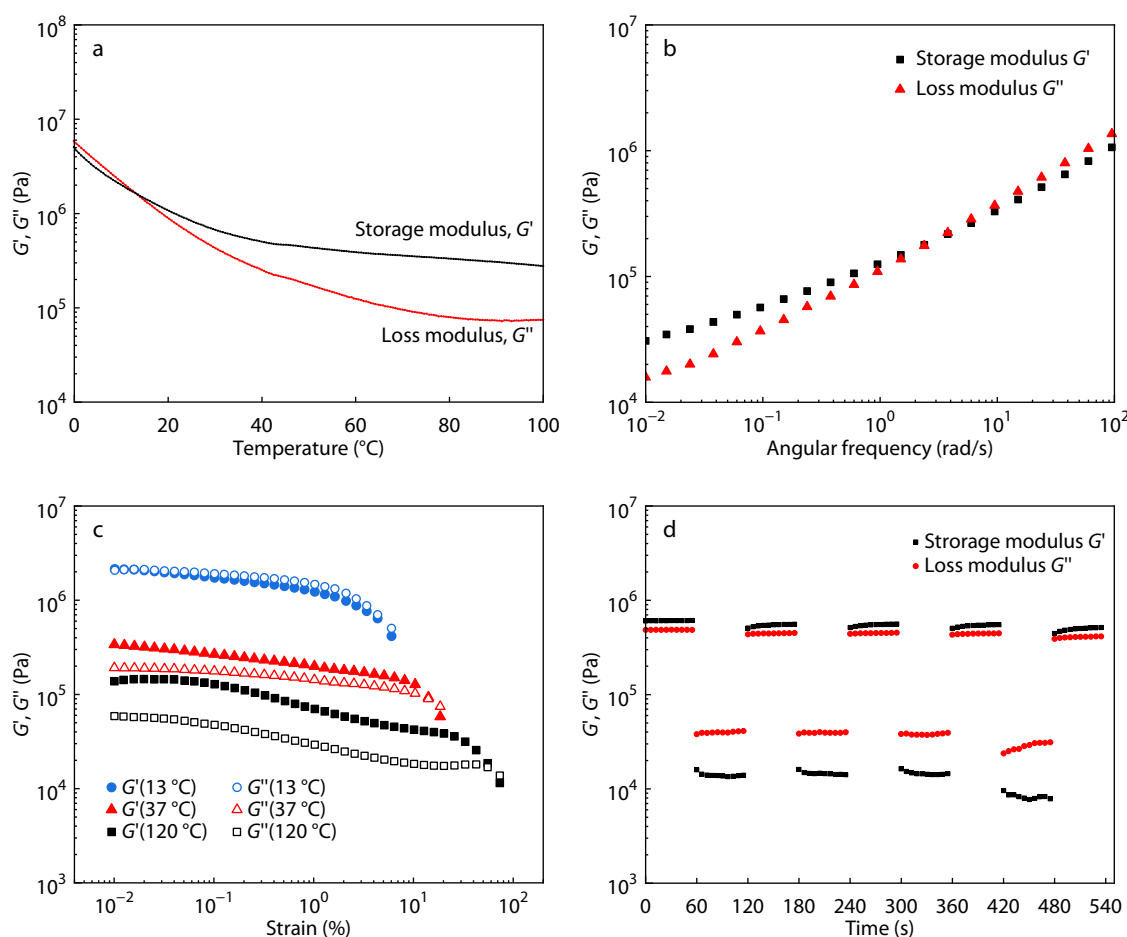


Fig. 2 Rheological properties of **PDMS-COOH-CG₁₀**. (a) Dynamic oscillatory temperature sweeps of **PDMS-COOH-CG₁₀** ranging from 0 °C to 100 °C at 1 Hz; (b) Frequency sweeps of **PDMS-COOH-CG₁₀** in the range of 0.01–100 rad/s with 0.1% strain amplitude at 25 °C; (c) Oscillatory strain sweeps of **PDMS-COOH-CG₁₀** at different temperatures; (d) Continuous step strain measurements of **PDMS-COOH-CG₁₀** at 25 °C.

broken of the hydrogen bond. When strain amplitude was brought back to 0.1% in the next 60 s, G' and G'' recovered to their original state immediately. The followed three cycles were conducted to confirmed the repeatability of the damage-recovery process. Such a rapid recovery of modulus can be ascribed to the dissociation and recombination of dynamic hydrogen bonding interactions.

Mechanical Properties

The mechanical properties of **PDMS-COOH-CG₁₀** composites under different conditions were investigated through uniaxial tensile test. Figs. 3(a) and 3(b) show the tested sample in relaxed (0%) and stretched states respectively. As illustrated in Fig. 3(c), when increasing the strain speed from 10 mm·min⁻¹ to 100 mm·min⁻¹, the breaking elongations decreased because of the less time for breaking the hydrogen bonds. On the contrary, tensile strength increased because the tangled polymer chains are not easy to untie in a short time. To reveal the energy dissipation caused by the dynamic bonds, the loading-unloading test under 500% and 800% strain was performed. As presented in Fig. 3(d), hysteresis was observed, which verifies an efficient energy dissipation from dynamic hydrogen bond breakage. However, if the sample was stretched successively in a higher strain without relaxation, the hysteresis loop of the second stretch would be lower than those of the original cycles, because the sacrificed hydrogen bonds need time to recover. Furthermore, polymer composites require fast recovery to its mechanical properties in some situations. Thus, multiple cycle loaded-unloaded test was performed to investigate the self-recovery properties of the **PDMS-COOH-CG₁₀**. As depicted in Fig. 3(e), the composites were successively loaded-unloaded

at a strain of 500% for nine continuous cycles. After nine circulations, **PDMS-COOH-CG₁₀** shows good self-recovery properties within its elastic range.

Self-healing/Recovery Properties

Besides the good mechanical properties, self-healing ability is also important in prolonging the lifetime of materials. The dynamic hydrogen bonds provide admirable self-healing ability of **PDMS-COOH-CG₁₀** composite. The self-healing ability of **PDMS-COOH-CG₁₀** composite film was tested at room temperature. Figs. 4(a) and 4(b) depict the optical microscope images of the scratched **PDMS-COOH-CG₁₀** film, showing a gradual disappearance of the scratch after healing for 6 h at room temperature. Typically, as Fig. 4(c) depicts, the film (25 mm × 5 mm × 1 mm) was cut into two completely separated parts using a fresh razor blade, and then two half-plates were brought back into contact, gently pressed for 10 s and then heated at 25 °C. Fig. 4(d) depicts the representative stress-strain curves for the cut **PDMS-COOH-CG₁₀** films that were healed for different lengths of time. The mechanical self-healing efficiency (η) was defined as the proportion of the restored tensile strength (stress at fracture). The **PDMS-COOH-CG₁₀** film can be held and stretched after 30 s with 53.8% self-healing efficiency. After healing for 24 h, self-healing efficiency was as high as 84.6%.

Infrared Thermal Imaging

We investigated the thermal conductivity changes of **PDMS-COOH-CG₁₀** film in the original, cut and healed state through infrared thermal imaging camera. Due to the uniform heat transfer, the temperature on the upper and lower sides of the

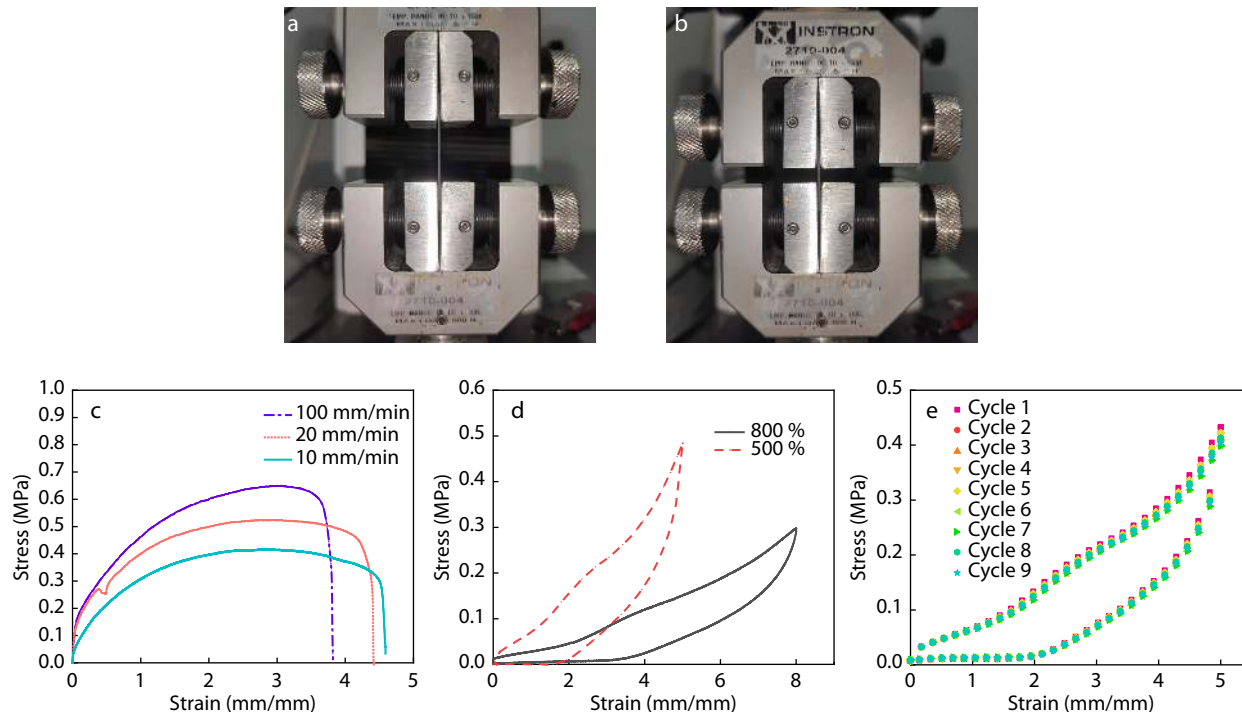


Fig. 3 Mechanical properties of the **PDMS-COOH-CG₁₀**. Optical images showing the **PDMS-COOH-CG₁₀** polymer films at 0% (a) and 500% (b) strains, respectively; (c) Stress-strain curves of the **PDMS-COOH-CG₁₀** samples with different stretch speeds ranging from 10 mm·min⁻¹ to 100 mm·min⁻¹ at 25 °C; (d) Cyclic tensile curves of **PDMS-COOH-CG₁₀** from 500% to 800% strains without relaxing time; (e) Nine successive loaded-unloaded cycles of **PDMS-COOH-CG₁₀** with a maximum strain of 500%.

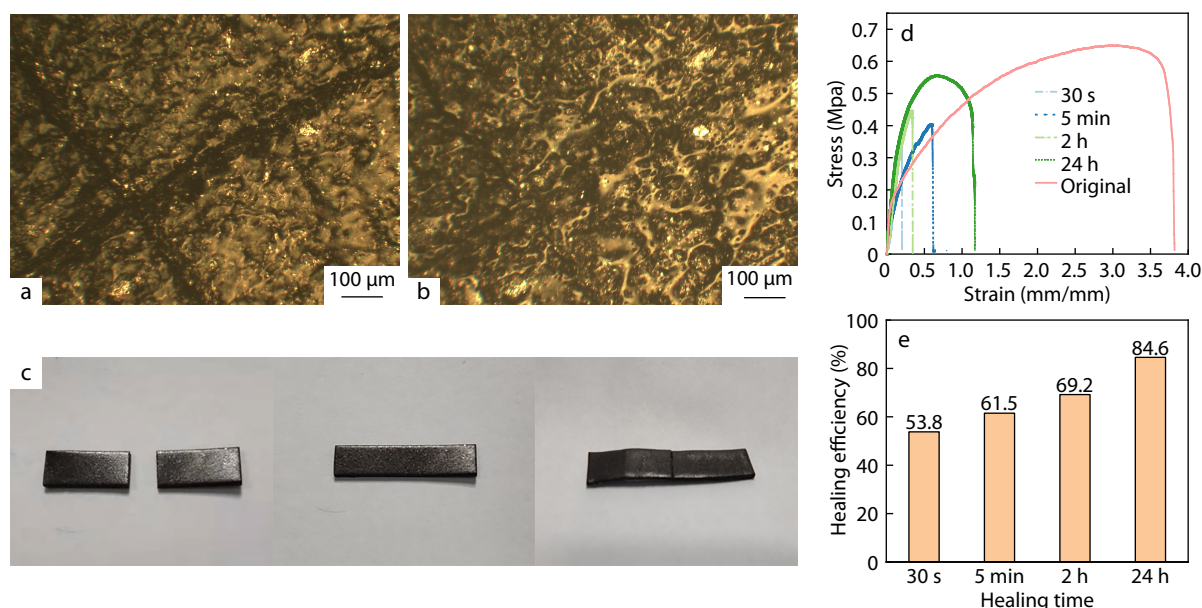


Fig. 4 Optical microscopy images of the scratched PDMS-COOH-CG₁₀ film before (a) and after (b) self-healing at room temperature; (c) Photographs depicting the macroscopic cutting-healing-stretching procedure of PDMS-COOH-CG₁₀ samples at room temperature; (d) Self-healing tensile experiments at original and after healing at 25 °C for different time; (e) Self-healing efficiency of PDMS-COOH-CG₁₀ healed for different time at 25 °C.

film reached 38 °C at the same time. Then the film was half cut-off at 1/2 of the film length. After cooling down, the half cut-off film was stuck in the same position. As shown in Fig. 5(b), the

upper side was cut while the lower side was complete. When the temperature of lower side reached 38 °C, the temperature on the upper side is only 37 °C due to the presence of air at the fracture. After healing at room temperature for 2 min, we tested the temperature changes on the upper and lower sides of the sample again, and it could be found that the temperature on the upper and lower sides reached 38 °C almost simultaneously, indicating the self-healing of thermal conductivity.

CONCLUSIONS

In summary, we prepared a thermally conductive composites with autonomous self-healing at room temperature due to the hydrogen bonds between carboxylic groups in the side chain of PDMS-COOH. We optimized the percentage of graphene filler, which balances both thermal conductivity and self-healing properties of the composites. Furthermore, the rheological study showed that the composites possessed good dynamic adaptability, that is, when temperature of system rises, the modulus of composites decreases, and enables better fill the interface, improve thermal efficiency. And the composites are expected to be used in intelligent thermal interface management materials, such as the microelectronics industry and LED lighting.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-021-2620-1>.

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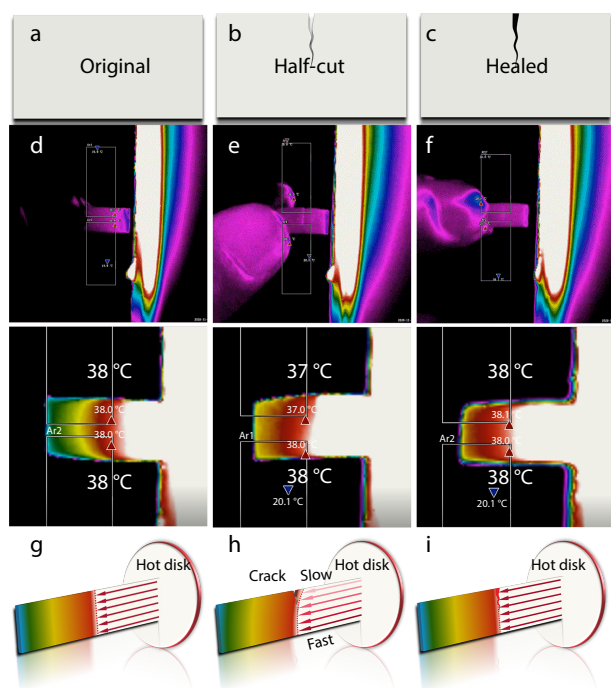


Fig. 5 Thermal conductivity recovery of PDMS-COOH-CG₁₀ film via infrared thermal imaging camera. The figure of original (a), half-cut (b), and healed sample (c). Infrared thermal conductive image of original (d), half-cut (e), and the sample healed for 2 min (f). (g, h, i) The heat transfer simulation of (g) original (h) half-cut and (i) healed sample.

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