

Article ID: 1674-8085 (2023) 01-0018-07

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A FAST SELF-HEALING MAGNETIC POLYMER

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Abstract: In this work, a room temperature self-healing magnetic polymer which possesses excellent flexibility and stretchability was synthesized through a facile pathway. Based on the hydrogen bondings between single molecule magnet (SMM) $\text{Mn}_{12}\text{-Ac}$ and polymer matrix poly(dimethylsiloxane) (PDMS) containing urea groups, the resultant composite exhibits superior magnetic and fast room temperature self-healing abilities (healing time = 60 s, healing efficiency = 99.5%). This study will provide more opportunities of self-healing magnetic polymers for future applications in intelligent devices, responsive robots and other fields.

Key words: polymer; magnetic; self-healing; composite

CLC number: O631.1

Document Code: A

DOI: 10.3969/j.issn.1674-8085.2023.01.004

一种快速自修复磁性聚合物高分子

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摘要: 通过简单的方法合成了一种兼具柔韧性和拉伸性的室温快速自修复磁性聚合物高分子。基于单分子磁体 $\text{Mn}_{12}\text{-Ac}$ 和含有脲键的聚二甲基硅氧烷高分子基底之间的氢键作用, 该复合物材料展现了出色的磁性和室温快速自修复性质 (修复时间为 60 s, 修复效率为 99.5%)。这项工作将为磁性自修复材料在未来智能器件、响应型机器人等领域的应用提供更多的机会。

关键词: 聚合物; 磁性; 自修复; 复合物

中图分类号: O631.1

文献标识码: A

DOI: 10.3969/j.issn.1674-8085.2023.01.004

1 INTRODUCTION

Magnetic polymer materials, which are generally obtained via using a variety of magnetic particle fillers (such as iron oxide nanoparticles, single-molecule magnets (SMMs)) to composite with polymer

matrices, possess essential application value in the areas of electrical equipment, soft robots, and medical instruments^[1-7]. Particularly, SMMs are nanoscale magnetic clusters with large spin ground states and stepwise magnetization hysteresis loops, providing potential access to realize high-density information storage^[8-9]. The Mn_{12} complexes are the typical SMM

Received date: 2022-11-22; Modified date: 2022-12-24

Foundation item: the National Natural Science Foundation of China (Grant No. 22271139) and the Fundamental Research Funds for the Central Universities (020514380281).

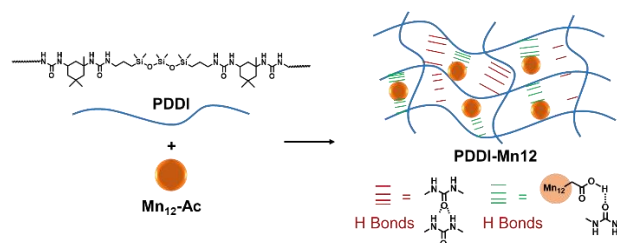
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systems which have been widely investigated for a long time^[10-11]. Casting Mn_{12} clusters into various polymer matrices is the main strategy to construct magnetic molecular devices of SMMs^[12-13]. However, most reported magnetic materials based on Mn_{12} SMMs are still difficult to restore their original nanostructures and functions after the inevitable mechanical fracture or scratches, resulting in the deterioration of magnetism response. Therefore, endowing magnetic polymers with self-healing ability is highly desirable but remains a great challenge to overcome.

Self-healing polymers have attracted large amounts of attention in the past decades because of the excellent ability of intrinsically healing the damages which can significantly prolong the lifetime of materials in various applications^[14-16]. Until now, lots of synthetic self-healing polymers which can repair the internal or external damages have been developed^[17-18]. The pristine strategy to develop self-healing materials usually depends on the assistance of microencapsulated healing reagents^[19-21]. Owing to the consumption of encapsulated reagents, the number of healing procedures is limited. To solve this conundrum, dynamic non-covalent and covalent bonds have been introduced into polymers as crosslinking sites because they can reversibly break and re-form, leading to repetitive self-healing^[22-25]. Self-healing polymers with multifunctionalities such as conductive adhesive, hydrophobic, fluorescent and other properties have been widely reported in recent years^[26-28]. But self-healing polymers with magnetism which can efficiently broaden their service life are rarely constructed. Thus, developing a novel strategy to produce versatile self-healing magnetic polymers is an urgent mission.

Herein, we developed a facile strategy for fabricating the magnetic polymer with flexible mechanical property and superior self-healing ability at room temperature (Scheme. 1). Through the reaction between isophorone diisocyanate and amine-terminated poly(dimethylsiloxane) (PDMS), a fast

self-healing polymer PDDI was successfully synthesized. After incorporating the SMM Mn_{12} -Ac into PDDI substrate, the magnetic self-healing polymer PDDI-Mn12 containing abundant hydrogen bonds was obtained. The resultant composite displays enhanced mechanical properties, obvious magnetism as well as ultrafast room temperature self-healing capacity. We believe this novel magnetic self-healing polymer system, which can be produced in a large scale, will offer new development guidelines for functional self-healing materials in the applications of information storage, intelligent robots and responsive actuators.



Scheme.1 Design concept of self-healing magnetic PDDI-Mn12 polymer network.

2 EXPERIMENTAL SECTION

2.1 Materials and general measurements

$Mn(OAc)_2 \cdot 4H_2O$, $KMnO_4$, acetic acid and isophorone diisocyanate (IPDI) were purchased from Sigma Aldrich. Bis(3-aminopropyl)-terminated PDMS ($M_n = 25000 \text{ g} \cdot \text{mol}^{-1}$, and $5000 \text{ g} \cdot \text{mol}^{-1}$ noted as A31 and A21, respectively) were purchased from Gelest. All solvents used in the experiment, such as dichloromethane (DCM), and tetrahydrofuran (THF) were purchased from Nanjing Reagents Co. Ltd (AR grade). The experimental powder X-ray diffraction (PXRD) patterns were obtained in 2θ range of $3 \sim 50^\circ$ on a D8 ADVANCE X-ray powder diffractometer using $Cu K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The simulated PXRD spectra were obtained from the single crystal data using the program Mercury 3.8. FT-IR spectra were recorded on a Bruker Tensor 27 Fourier transform infrared spectrometer by 64 scans from 4000 to 400 cm^{-1} . Tensile tests were performed on an Instron 3365 machine. The rheological measurements

were studied through a TA DHR-2 Rheometer. Thermal gravimetric analysis (TGA) curves were measured on a PerkinElmer TA 2100-SDT 2960 ranging from 30 to 800 °C with a heating rate of 20 °C min⁻¹ under a dry nitrogen atmosphere. Differential scanning calorimetry (DSC) data were measured with DSC apparatus of Mettler-Toledo under a dry nitrogen atmosphere (50 mL min⁻¹). The temperature range is from -100 to 50 °C, with a ramp rate of 10 °C min⁻¹. Variable-temperature magnetic susceptibilities of polycrystalline samples were measured on a Quantum Design SQUID vibrating sample magnetometer (VSM). All magnetic data were corrected for the sample holder and the diamagnetic contribution of the sample using Pascal's constants.

2.2 Synthesis and characteristics of Mn₁₂-Ac

[Mn₁₂O₁₂(CH₃COO)₁₆(H₂O)₄] (**Mn₁₂-Ac**) was prepared as described in previous work^[29]. The experimental PXRD diffraction pattern (Fig. 1) of it is consistent with the simulated result from single-crystal X-ray diffraction data, showing the structural stability and purity of the SMMs **Mn₁₂-Ac** under ambient temperature.

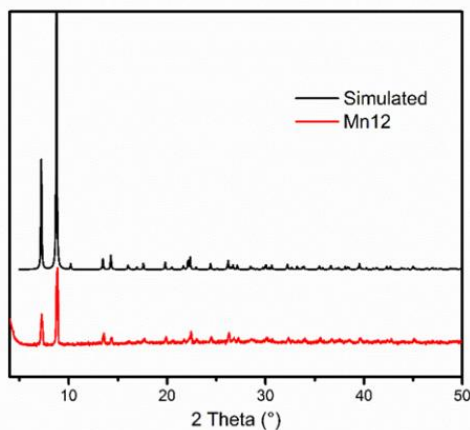


Fig. 1 The experimental (red) and simulated (black) PXRD patterns for prepared **Mn₁₂-Ac** at room temperature

2.3 Preparation of self-healing polymer PDDI

The self-healing polymer PDDI was synthesized through 1.0 g A21 and 5.0 g A31 reacting with 89.0 mg IPDI in 150 mL THF under a nitrogen atmosphere. After stirring at room temperature for 16 h, the resulting solution was evaporated to obtain colorless and transparent viscous liquid. Then, the liquid was

poured into a poly tetrafluoroethylene (PTFE) mold and dried at 60 °C for 12 h, giving a transparent polymer film for further testing. FTIR spectra (Fig. 2) show that the obvious -NCO stretch absorption bands at about 2250 cm⁻¹ of IPDI disappeared basically, illustrating the polymer formed successfully.

2.4 Preparation of magnetic self-healing material PDDI-Mn₁₂

The functional material PDDI-Mn₁₂ was fabricated by mixing 5.0 g PDDI and 1.0 g **Mn₁₂-Ac** in 50 mL DCM. The mixture was stirred at room temperature for 4 h and ultrasound for ten minutes. Then, the solvent was evaporated and the black product was obtained after being dried in a 40 °C oven for 8 h. As shown in Fig. 2, the characteristic peaks at 500 ~ 700 cm⁻¹ of **Mn₁₂-Ac** also appeared in the FTIR spectrum of PDDI-Mn₁₂, indicating the successful preparation of the magnetic polymer.

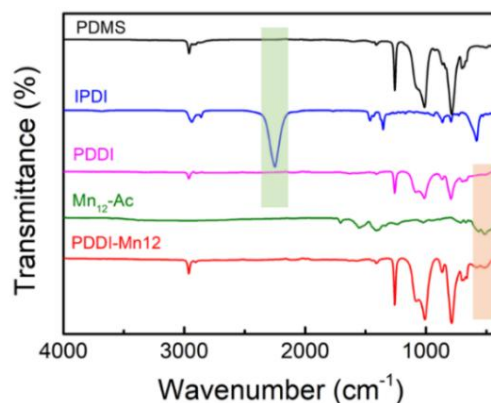


Fig. 2 FTIR spectra of reactants and products

3 RESULTS AND DISCUSSION

The thermodynamic properties of the prepared materials were investigated by Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) measurements. As demonstrated in Fig. 3a, the SMMs **Mn₁₂-Ac** started to decompose from only 80 °C, demonstrating instability at high temperatures. However, PDDI and PDDI-Mn₁₂ polymers showed no decomposition below 300 °C because of the siloxane backbone with excellent thermal stability in polymeric networks. Moreover, the glass transition temperatures (*T_g*s) of PDDI and PDDI-Mn₁₂ are equal

to $-46\text{ }^{\circ}\text{C}$ and $-42\text{ }^{\circ}\text{C}$, respectively (Fig. 3b). The incorporation of small amount of **Mn₁₂-Ac** can restrain the mobility of polymer chains, resulting in the slight increase of T_g of the magnetic polymer.

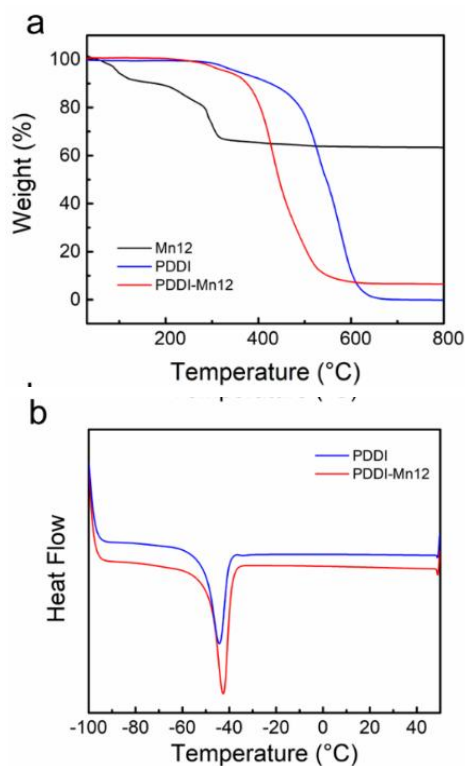


Fig. 3 TGA (a) and DSC (b) curves of polymers

Furthermore, PDDI and PDDI-Mn12 exhibit superior flexibility and stretchability. The mechanical properties of polymers were characterized under ambient conditions via static uniaxial tensile measurements and dynamic rheological tests. The stress-strain curves of these two materials with different tensile rates are presented in Fig. 4. The tensile stress increased, whereas the fracture strain decreased with increasing the extension speed from 20 to 100 mm min^{-1} , indicating a typical stretching speed dependence of obtained polymers. The Young's modulus of PDDI and PDDI-Mn12 are determined to be 0.35 MPa and 0.56 MPa from the initial stiffening area ($<10\%$ strain) according to the tensile plots. Meanwhile, the tensile strengths of PDDI-Mn12 under different stretching rates are higher than those of PDDI, demonstrating that the doping of **Mn₁₂-Ac** particles into soft PDDI substrate can significantly reinforce the chain winding and enhance the

mechanical property. Additionally, the rheological performances of PDDI-Mn12 polymer films were studied with a rotational rheometer. Briefly, the oscillatory strain sweep of PDDI-Mn12 was performed as presented in Fig. 5a, the storage moduli (G') is much higher than the loss moduli (G'') when the applied strain is less than 90%, indicating that the sample is predominantly elastic at relatively small strains. Nevertheless, G' has a tendency of falling behind G'' under a larger strain ($>90\%$), suggesting that the sample turns into a viscous state due to the partial broken of the polymeric network. Besides, the dynamic oscillatory temperature sweep of the composite was measured as shown in Fig. 5b. The transition temperature from the elastic state to the viscous state of PDDI-Mn12 is calculated to be $80\text{ }^{\circ}\text{C}$, illustrating that PDDI-Mn12 can maintain its elastic property at a wide range of temperatures. Moreover, dynamic frequency sweeps ranging from 0.01 to 100 rad/s at different temperatures were conducted in the linear viscoelastic region of strains (Fig. 6a). The spectra appeared to follow the time-temperature superposition shifts (TTS) principle, resulting in the TTS master curve of PDDI-Mn12 at a reference temperature (Fig. 6b). In hydrogen bonding networks, 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)^[30]. Therefore, at $\omega > 1/\tau_c$, the material behaves more elastic-like, storing more energy than it dissipates, while at $\omega < 1/\tau_c$, the material exhibits viscous-like behavior, dissipating more energy than it can store. As shown in Fig. 6b, the ω_c of PDDI-Mn12 is 0.1 rad/s . According to the observed ω_c , the calculated relaxation time τ_c of PDDI-Mn12 is equal to 10 s. Meanwhile, the apparent activation energy E_a (81.57 kJ mol^{-1}) of PDDI-Mn12 polymer was calculated from the Arrhenius fitting plot for the temperature-dependent shift factors, indicating the ultrafast chain mobility and sufficient dynamic exchange of hydrogen bonds in PDDI-Mn12 polymeric network.

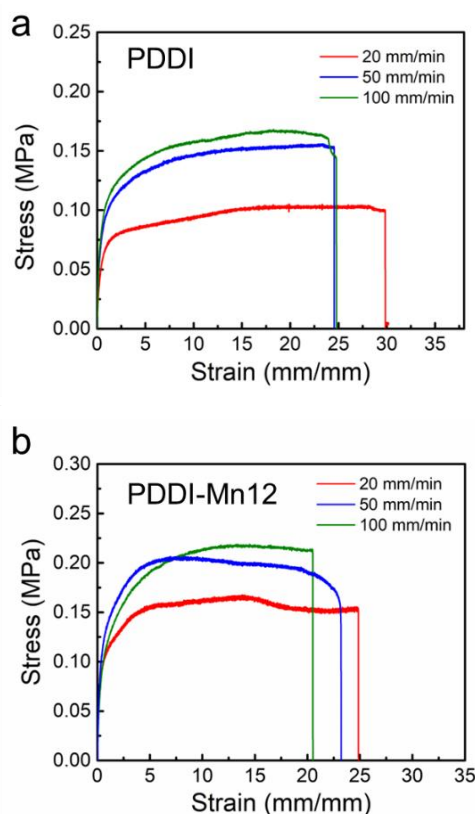


Fig.4 Stress-strain curves of PDDI (a) and PDDI-Mn₁₂ (b) under different tensile rates

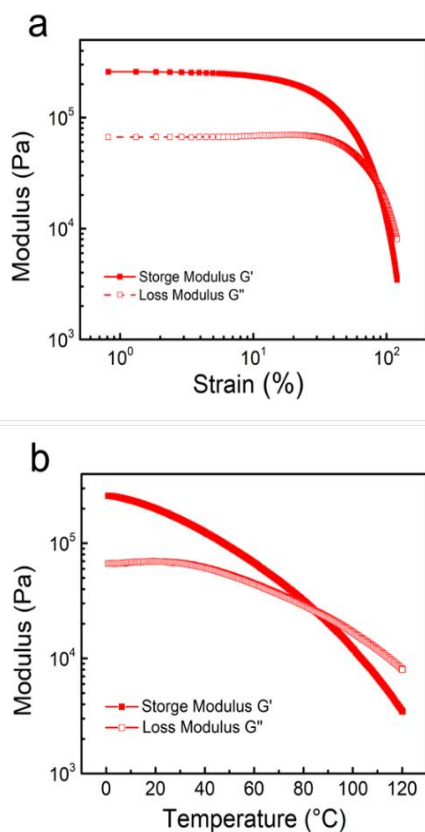
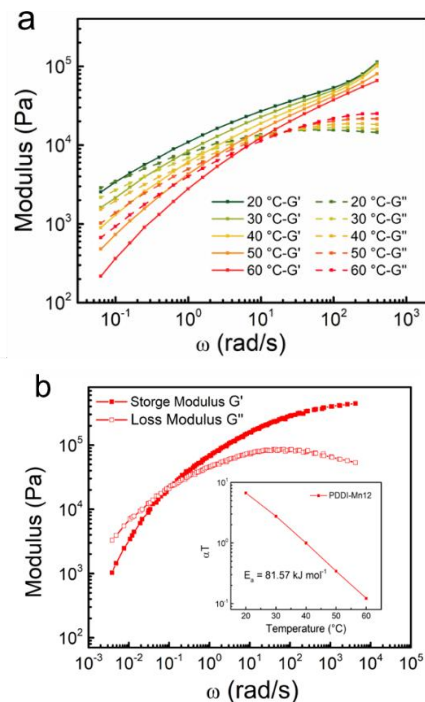


Fig.5 Dynamic oscillatory strain (a) and temperature (b) sweeps of PDDI-Mn₁₂



(a) Dynamic frequency sweeps at different temperatures with 1% strain amplitude. (b) TTS master curve obtained at a reference temperature. Inset: Arrhenius fitting plot for the temperature-dependent shift factors

Fig. 6 Time-temperature superposition rheological property of PDDI-Mn₁₂

Owing to the characteristic magnetic behavior of SMMs, the polymer doped with **Mn₁₂-Ac** exhibits obvious magnetism. The magnetic property of **Mn₁₂-Ac** and PDDI-Mn₁₂ were studied with a SQUID magnetometer. The hysteresis loops at 1.8, 2.2, 2.6 and 3.0 K were measured and presented in Fig. 7, which illustrated that the loops closed gradually as the temperature increased. The coercivity fields of the prepared **Mn₁₂-Ac** are $H_c = 16.85, 12.05, 11.68$ and 8.36 kOe at 1.8, 2.2, 2.6 and 3.0 K, respectively, whereas the coercivities for the PDDI-Mn₁₂ polymer are larger ($H_c = 24.50, 19.71, 14.08$ and 8.56 kOe at 1.8, 2.2, 2.6 and 3.0 K). This phenomenon may be attributed to the minor doping of **Mn₁₂-Ac** and the resistive components in the polymer matrix. However, it is worth mentioning that the incorporation of **Mn₁₂-Ac** endows the dynamic polymer with excellent magnetic properties, leading to the potential applications of PDDI-Mn₁₂ in stimuli-responsive materials, information storage, soft robotics, actuators and biomaterials.

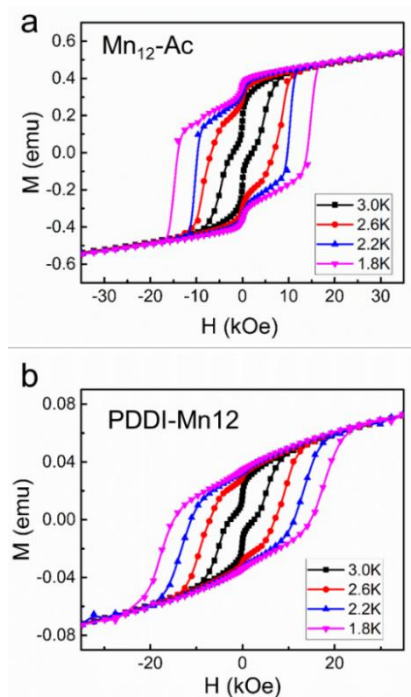
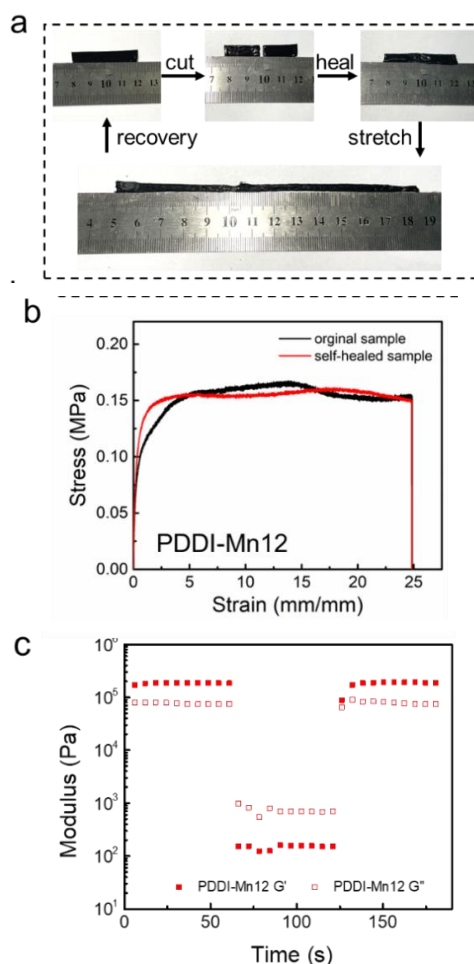


Fig.7 Hysteresis loops of the prepared $\text{Mn}_{12}\text{-Ac}$ and PDDI-Mn12 at different temperatures

To directly observe the self-healing performance of PDDI-Mn12 magnetic polymer film at room temperature, the sample was initially cut into halves and then brought into contact at the fracture surface for further self-healing within 60 s. Such a cutting-touching-healing process was recorded as illustrated in Fig. 8a, the healed PDDI-Mn12 film can be stretched to a strain more than three times the original length. Upon loosening the hands, the stretched sample can gradually recover to the original length owing to its natural elasticity, demonstrating the recyclable and repetitive self-healing capacity. The mechanical property of the healed polymer sample fully recovered to the original state with a healing efficiency of 99.5% (Fig. 8b). In addition, the autonomously self-healing property of PDDI-Mn12 can also be observed in rheological oscillation step strain tests (Fig. 8c). Firstly, the sample underwent the typical oscillation time sweep for 60 s at a relatively low strain amplitude of 1% to determine the original storage modulus G' of PDDI-Mn12. Subsequently, by transferring the applied strain from 1% to 500%, G' rapidly dropped by three orders of magnitude to below the level of the loss modulus G'' , indicating the elastic

sample had been broken completely. Upon switching to the low strain amplitude (1%) again, the PDDI-Mn12 specimen immediately recovered its natural elasticity with 98.3% of the original G' regained within 5 s. The reason for the fantastic self-healing performance of PDDI-Mn12 is attributed to our polymer design. On one hand, the PDMS matrix has extremely long and flexible polymer backbones, which can facilitate the rapid slippage and interpenetration of polymer chains at the damaged surface. On the other hand, abundant hydrogen bonds within PDDI-Mn12 polymeric network can dynamically break and reform to dissipate the strain energy as well as restore the initial mechanical properties.



(a) Optical photographs giving the cutting-healing-stretching procedure of PDDI-Mn12. (b) Stress-strain curves of the polymers before and after the healing process. (c) Continuous rheological recovery tests of PDDI-Mn12 polymer film at $f=1$ Hz

Fig. 8 Self-healing performance of PDDI-Mn12 at room temperature

4 CONCLUSION

In summary, we have successfully synthesized a fast self-healing magnetic polymer through introducing the SMM $\text{Mn}_{12}\text{-Ac}$ particles into a flexible self-healing polymer matrix containing sufficient hydrogen bonds. The obtained composite demonstrates excellent mechanical stretchability and magnetism. Benefiting from the mobility of polymer chains and the various hydrogen bonds in the networks, the magnetic polymer exhibits fast self-healing performance at room temperature (healing time = 60 s, healing efficiency = 99.5%). This novel magnetic material with room temperature self-healing ability ideally overcomes the problem of the limited service lifetime of existing magnetic devices and provides promising applications in many fields such as data storage, responsive materials and functional robots.

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