Investigation on Self-healing Property of Epoxy Resins Based on Disulfide Dynamic Links

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Abstract  Self-healing polymers based on dynamic crosslinkers have drawn rapidly increasing interest over the last decade. Here, a self-healable epoxy network with exchangeable disulfide bonds was synthesized by polymerizing two epoxies with an aromatic amine containing a disulfide bond. The bisphenol A diglycidyl ether (DGEBA) and poly(ethylene glycol) diglycidyl ether (DER736) were used as rigid and soft components, respectively. The crosslinking densities of studied polymers decreased with the increasing amount of DER736, resulting in the lower glassy temperature and weaker mechanical strength. The dynamic covalent network character of disulfide bond and its low active energy were also investigated through stress relaxation experiments at various temperatures. The self-healing performance of healable epoxy resins with varied flexibility was measured by tensile tests. The tensile strength of a full-cut sample was restored to 84% (13 MPa) of the initial values (16 MPa) at moderate temperature. Its healed fracture strain was up to 505%. Moreover, the effect of healing time and temperature on the self-healing properties was also studied. A model was proposed to investigate the self-repairing efficiency evolution with healing time, suggesting that hydrogen bonds mainly contributed to the initial sticking or interfacial adhesion while disulfide links and chain interdiffusion assisted time dependent reformation of networks to restore the original mechanical strength.

Keywords Self-healing; Epoxy resin; Disulfide bond

INTRODUCTION

The epoxy resin with excellent mechanical properties, thermal stability, and chemical resistance has been widely applied in coatings, adhesives, insulation and packaging materials for electrical appliances, etc.[1,2] These application products are inevitably subject to various injuries in service. The evolution of injuries will overwhelmingly shorten the service life of the polymers. In recent years, synthetic smart self-healable epoxy materials inspired biologically have attracted great attention, which can improve their reliability and prolong the lifetime. Various self-healing epoxy resins with different healing mechanisms including extrinsic healing[3–5] and intrinsic healing[6–8] have been developed. The extrinsic self-healing epoxy systems often employ incorporation of capsules or vessel containing repair agents into the matrix.[9] The external force generates injuries and simultaneously breaks the microcontainers, resulting in the release of healing agents and following reaction at the injuries sites to repair the cracks. The healing time of the extrinsic self-healing materials is limited as the repair agents will be eventually consumed, while the intrinsic self-healing polymer does not have such problem. Recently, a lot of dynamic bonds or structures have been introduced into epoxy resins to construct self-healing materials, including hydrogen bonds,[10,11] Diels–Alder reaction,[12–14] transesterification reaction[15–17] and disulfide bonds,[18–20] etc.

Among them, disulfide bonds have attracted many researchers because of their exchange reaction at moderate temperature. The incorporation of exchangeable disulfide bonds into epoxy network can rearrange with heat (or ultraviolet, etc.) and preserve the integrity of network, which contribute the unprecedented capability of thermosetting epoxy networks, such as self-repairing, reprocessing, and thermforming. Canadell et al. studied the effect of disulfide concentration on the self-healing performance of epoxy rubber by controlling the different ratio of polyglycol diglycidyl ether (DER732) and polysulfide diglycidyl ether (EPS25).[20] Their epoxy materials showed high self-healing properties but poor tensile strength. In order to improve the chain rigidity, Lafont et al. used epoxidized polysulfides thioplastic (EPS70) in the

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polysulfide-containing epoxy matrix.\textsuperscript{[21]} Unfortunately, the strength of their studied samples was still less than 0.6 MPa. Luzuriaga et al. reported a dynamic epoxy resin with high tensile strength, while its repairing temperature was as high as 200 °C, and the elongation at break was only 8%.\textsuperscript{[19]}

On the one hand, many researchers have made great efforts to prepare self-healing polymer materials with good mechanical properties.\textsuperscript{[6],[22]} On the other hand, some researchers have also studied the self-healing mechanism of healable polymers. Wool et al. pointed out that the self-healing process of a crack involves five stages: segmental surface rearrangements, surface approach, wetting, diffusion, and randomization.\textsuperscript{[23]}

The latter stages of diffusion and randomization were considered to be the most important ones to control the final self-healing performance.\textsuperscript{[24]} Urban et al. discussed the thermodynamic requirements for self-healing networks in terms of conformation changes that contributed to the Gibbs free energy.\textsuperscript{[25]} The chain flexibility tremendously facilitates the entropy changes, while the external energy input and the heat of reaction are mainly conductive to the enthalpy changes. Luo et al. studied the self-healing mechanism of microcracks on waterborne polyurethane with different disulfide contents.\textsuperscript{[26]} In their opinions, the whole self-healing process could be simplified to cohesive movements, diffusion, and randomization.

Herein, we prepared self-healing epoxy resins with commercial crosslinker (2-aminophenyl disulfide) through disulfide exchange reactions. By tuning the content of soft segments in the resins, the self-healing materials with varied flexibility were obtained. The more flexible polymer had lower glass transition temperature, activation energy and weaker mechanical strength, but better self-healing performance. The optimal specimen exhibited a high mechanical strength in combination with a good self-healing efficiency. The effect of healing time and temperature on self-healing property was also discussed. In particular, a model has been proposed to describe the effect of healing time on self-healing performance.

**EXPERIMENTAL**

**Materials**
Bisphenol A diglycidyl ether (DGEBA), 2-aminophenyl disulfide (AFD), \( p \)-phenylenediamine, and \( N,N \)-dimethylformamide (DMF) were purchased from Aladdin Bio-Chem Technology Co., Ltd. Poly(ethylene glycol) diglycidyl ether (DER736) was supplied by Macklin Biochemical Co., Ltd. All chemicals were of analytical grade and used as received.

**Synthesis of Reversible Cross-linking Epoxy Resin**
The cross-linked epoxy resin was synthesized as follows (Scheme 1). The different molar ratios of two epoxy resins (DGEBA and DER736) were firstly dissolved in DMF at room temperature according to Table 1. The weighted AFD as a reversible covalent crosslinker was then added into the mixed solution under stirring. In order to study the effect of segment flexibility on self-healing properties, the amount of cross-linking agent and the equivalent ratio of epoxy to amine were fixed. The resulting viscous homogeneous liquid was poured into a polystyrenefluorethylene (PTFE) mold for curing at 120 °C for 2.5 h and following post curing at 150 °C for 2 h. The final products were obtained by cooling to room temperature. An epoxy resin cured with \( p \)-phenylenediamine (EDBP) was also prepared. The formulation of EDBP was similar to that of EDBS-2 (Table 1). The dry film thickness was around 0.5 mm.

**Characterization**
Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vertex 70 spectrometer in attenuated total reflection mode. Dynamic mechanical thermal analysis (DMA) measurement on the sample with 6 mm × 3 mm × 1 mm (length × width × thickness) was carried out using a TA Instruments Q800 with film tension clamps from −50 °C to 130 °C at a heating rate of 5 °C/min under nitrogen atmosphere. The DMA experiments were strain-controlled with a constant amplitude of 10 μm. A preload force of 0.01 N, a frequency of 1 Hz, and a force track factor of 125% were used. For the stress relaxation, samples with 6 mm × 3 mm × 1 mm (length × width × thickness) were initially preloaded at a force of 0.001 N to maintain straightness. After thermal equilibrium at testing temperature, a strain of 3% was applied within the linear region of the material and the relaxation modulus was collected as a function of time. Thermogravimetric analysis (TGA) was performed with a TA Instruments Q500 equipment at a heating rate of 10 °C/min from 25 °C to 750 °C. Differential scanning calorimetry (DSC) measurements were conducted using a Perkin Elmer Diamond DSC from −70 °C to 150 °C at a scan rate of 20 °C/min under nitrogen flow. Tensile tests were carried out on a SANS CMT 6000 universal testing machine at a cross-head speed of 50 mm/min. The optical

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microscopy images were achieved using a Meiji optical microscope equipped with a digital camera.

RESULTS AND DISCUSSION

The FTIR spectra were used to identify the chemical structure of EDBS-1, EDBS-2 and EDBS-3, as shown in Fig. 1. The band located at 1098 cm\(^{-1}\) was attributed to the stretching vibration of the C—O—C segment from aliphatic ether in DER736.\(^{[27]}\) The bands at 1588 and 1505 cm\(^{-1}\) corresponded to the skeletal vibrations of the aromatic rings.\(^{[28]}\) The band at 3409 cm\(^{-1}\) was due to the hydroxyl group generated in ring opening reaction (Fig. 1b).\(^{[29]}\) The hydroxyl groups would generate hydrogen bonding sites, which might favor the contact of polymer chains to provide initial repair behavior.\(^{[30]}\) Meanwhile, the characteristic vibration bands of epoxide group at 910 and 854 cm\(^{-1}\) also disappeared from the studied samples (Fig. 1c).\(^{[31]}\) These results demonstrated the completion of the curing process of epoxy resins.

Fig. 2 shows the DSC curves of our cured epoxy resins. The glass transition temperature values, \(T_g\), of different EDBS samples were determined by the inflection point of the heat flow step. The \(T_g\) values gradually decreased from 40.6 and 29.9 °C to 10.2 °C for EDBS-1, EDBS-2, and EDBS-3, respectively, resulting from the incremental concentration of DER736 epoxy units as soft-segments. Moreover, there were no exothermic signs in the DSC curves from room temperature to 130 °C, confirming again the complete curing of epoxy resins EDBS.\(^{[31,32]}\)

The investigated samples were further characterized by DMA and the results are shown in Fig. 3 and Table 2. Fig. 3(a) shows the storage modulus (\(E\)) and loss modulus (\(E''\)) as a function of temperature for different resins. All samples exhibited relatively stable storage modulus in the glassy and rubbery domains. From 2 to 3 orders of magnitude decrease in storage modulus was observed between the glassy modulus and rubbery modulus. The value of \(E\) for EDBS-3 was lower than those of EDBS-1 and EDBS-2 in both glassy and rubbery states due to its higher content of soft segments. The rubbery plateau of the studied samples demonstrated the presence of crosslinked networks.\(^{[31,32]}\) According to previous reports,\(^{[33,34]}\) the crosslinking density (\(\nu_e\)) could be calculated by the following equation:

\[
\nu_e = \frac{E'}{3kT} \left( \frac{T}{T_g} \right)
\]

where \(E'\) is the storage modulus, \(R\) is the universal gas constant, and \(T\) is the temperature. The relationship is effective when \(T\) is more than 50 K greater than \(T_g\).\(^{[35]}\) The crosslinking density was decreased from 669 and 281 mol/m\(^3\) to 161 mol/m\(^3\) for EDBS-1, EDBS-2, and EDBS-3, respectively. \(T_g\) could also be obtained by the value of tan\(\delta\) peak maximum in Fig. 3(b).\(^{[36]}\) \(T_g\) decayed with increasing DER736 content, which accorded with those values achieved from DSC. It was attributed to higher flexibility of DER736 and less rigid content of DGEBA in epoxy resin.\(^{[36]}\) Generally, \(T_g\) measured by DSC is lower than that determined by DMA as a result of different measurement methods.\(^{[37]}\) In addition, the peak value of tan\(\delta\) for EDBS-3 was much higher than that of EDBS-1, indicating more viscous behavior of EDBS-3, probably because of the occurrence of more segments motion.\(^{[31]}\) The thermal stabilities of the epoxy resins were characterized by TGA experiments, as shown in Fig. 4. All measured samples displayed a similar thermal decomposition behavior. The temperatures for a mass loss of 5 wt% (\(T_5\)) were around 250 °C. The EDBS-3 resin exhibited a lower value of \(T_5\) compared with EDBS-1 and EDBS-2 due to more components of DER736, as shown in Table 2. The TGA curves could be divided into the following phases. Firstly, the moderate weight loss between 150 and 210 °C arose from the decomposition of oxygen-containing and heat labile groups.\(^{[38]}\) Then, a degra-

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**Table 1** Formulations of self-healing epoxy resins.

| Sample | DGEBA (mmol) | DER736 (mmol) | AFD (mmol) | Content of S-S (wt%) |
|--------|--------------|---------------|------------|---------------------|
| EDBS-1 | 11.2         | 7.5           | 10.0       | 35                  |
| EDBS-2 | 9.8          | 8.9           | 10.0       | 35                  |
| EDBS-3 | 7.7          | 11.0          | 10.0       | 35                  |

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The exchange rate of disulfide bonds increased with stretched state owing to disulfide metathesis, as we expected. The thermal stabilities of our samples were analogous to those of reported disulfide bond.

The stress relaxation behaviors of studied samples as a function of time and temperature were investigated to characterize the dynamic properties of EDBS, as shown in Fig. 5. For the stress relaxation measurements, a fixed strain of 3% was applied and the relaxation modulus was followed with the variation of time at different temperatures. From Figs. 5(a)–5(c), there was no obvious stress relaxation phenomenon below the glassy temperature. As the temperature was further increased above 110 °C, the relaxation modulus of the three epoxy networks was decreased briskly in the initial stage, and then continually relaxed to zero. It indicated that the internal cross-linked network was not persistently bonded any more, and allowed for rearrangement to attain less stretched state owing to disulfide metathesis, as we expected. The exchange rate of disulfide bonds increased with temperature, resulting in the increase in relaxation rate. Based on the Maxwell model for viscoelastic fluids, relaxation time was defined as the time required to obtain $E/E_0 = 1/e$. The achieved relaxation times ranged from 645.65 min to 19.50 and 4.79 min at 130 °C for EDBS-1, EDBS-2, and EDBS-3, respectively, which indicated that the increase of dynamic reversible property decreased the relaxation time of the labile network. Fig. 5(d) shows the dependence of the relaxation time on temperature that could be described by the Arrhenius equation:

$$\tau(T) = \tau_0 \exp \left( \frac{E_a}{RT} \right)$$  \hspace{1cm} (2)

where $\tau_0$ is the relaxation time at infinite $T$, $E_a$ represents the activation energy of the dynamic epoxy network, and $R$ is the universal gas constant. It could be observed that the relaxation time of the reversible crosslinking networks fitted well with the Arrhenius law. The calculated activation energies ($E_a$) of epoxy networks from the slope were 91.7, 82.1, and 67.8 kJ/mol for EDBS-1, EDBS-2, and EDBS-3, respectively. The lower the activation energy, the more flexible the motion of segment in crosslinked network.

To verify the full-cut self-healing performance, tensile stress-strain testing was carried out to quantify the recovery of strength. The samples (EDBS-1, EDBS-2, and EDBS-3) were completely cut in half and then joined at 80 °C for 24 h. The healing efficiency ($\eta$) was defined as the ratio of tensile...
strength of the healed sample ($\sigma_{\text{healed}}$) to the original ($\sigma_{\text{original}}$), according to the following equation:

$$\eta = \frac{\sigma_{\text{healed}}}{\sigma_{\text{original}}}$$

(3)

where $\sigma_{\text{healed}}$ and $\sigma_{\text{original}}$ were the average tensile strengths of the healed samples and the pristine samples, respectively. The representative tensile curves of EDBS are shown in Fig. 6, and the mechanical properties are tabulated in Table 3. It was obvious that the original tensile strength and Young’s modulus were decreased with increase of DER736 concentration. An increase in the DER736 content resulted in more soft segments and an enhanced chain mobility due to decreased cross-linking density and lower activation energy. The self-healing efficiency, however, was increased with increase of chain flexibility. The healing process required the chain ends continuously expanded into open voids driven by the entropy changes when two surfaces were at favorable distances. The entropy changes of polymeric chains were determined by the

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**Fig. 5** Normalized stress-relaxation curves at different temperatures for (a) EDBS-1, (b) EDBS-2, and (c) EDBS-3; (d) linear fitting of the relaxation times by Arrhenius equation.

**Fig. 6** (a) Stress-strain curves of different EDBS samples (solid lines and corresponding dashed lines represent the original samples and the cracked sample healing 24 h at 80 °C, respectively); (b) Self-healing properties of different specimens.
flexibility of the chains. Consequently, the higher the flexibility, the higher the self-healing efficiency.

Although EDBS-2 showed a lower self-repairing efficiency (84%) compared to EDBS-3 sample, it had a relatively high recovered mechanical strength (13.4 MPa). Taken together, EDBS-2 would be a more practical specimen due to its relatively good comprehensive performance. This dynamic reversible crosslinked material pleasingly provided a new pattern for repairing injuries. The conventional thermosetting materials were quite difficult to repair owing to cross-linking curing reaction. However, the deconstruction of the reversible crosslinking network was potential to diffuse and entangle between the polymer chains, resulting in the interpenetration of molecular chains at the fractured interface under heating, and reformation of network structure with the assist of the disulfide exchange reaction and the hydrogen bond.

Plotting the data collected from the related references of self-healing epoxy systems showed that our EDBS-2 sample possessed good mechanical performance and healing efficiency at moderate temperature among other dynamic bonds systems (Fig. 7).

In order to further study the self-healing process, the EDBS-2 samples were completely cut in half and then joined at different temperatures for different time. Fig. 8 shows the effect of healing time and temperature on the self-healing properties of cured EDBS-2 samples. From Fig. 8(a), the stress-strain curves with different healing time at 80 °C displayed that the

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**Table 3** Tensile properties of EDBS samples.

| Sample  | $\sigma_{\text{original}}$ (MPa) | $\sigma_{\text{healed}}$ (MPa) | $\varepsilon_{\text{original}}$ (%) | $\varepsilon_{\text{healed}}$ (%) | $E_{\text{original}}$ (MPa) | $E_{\text{healed}}$ (MPa) |
|---------|-------------------------------|-------------------------------|-----------------------------------|-----------------------------------|--------------------------|--------------------------|
| EDBS-1  | 23.7                          | 15.5                          | 19.4                              | 9.3                               | 281.2                    | 231.3                    |
| EDBS-2  | 15.9                          | 13.4                          | 556.5                             | 504.8                             | 29.2                     | 25.8                     |
| EDBS-3  | 3.7                           | 3.7                           | 481.5                             | 490.0                             | 8.1                      | 7.9                      |

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Fig. 7 Comparisons of initial strength and healed strength with epoxy resins in the related references [20,30,36,39,44−47].

Fig. 8 Stress-strain curves of EDBS-2 (a) healed at 80 °C for different healing time and (b) healed for 3 h at different temperatures; (c) The healing efficiency as a function of healing time; (d) Stress-strain curves of EDBP healed at 80 °C for different healing time.
healing efficiency of the polymer was enhanced by prolonging healing time. The detailed values of original and healed tensile stress, fracture strain, and Young’s modulus are shown in Table S1 (in the electronic supplementary information, ESI). Typically, after healing for 24 h, the repaired sample exhibited a tensile strength of 13.3 MPa and an elongation at break of 504.9%. The parallel healing efficiencies of stress, strain, and Young’s modulus were 84%, 91%, and 88%, respectively, which suggested a relatively impressive result for an effectively crosslinking material.

Furthermore, according to the reports,[48] a simple healing model could be used to describe the healing efficiency evolution of EDBS system over a broad time range:

$$\eta = \eta_0 + \eta_s \left(1 - e^{-\frac{t}{\tau_s}}\right)$$  \hspace{1cm} (4)

where $\eta_0$ is the healing efficiency mainly influenced by hydrogen bonding, $\eta_s$ is the contribution to dominant healing process of disulfide bonds for EDBS, $\tau_s$ represents the characteristic time constant of the main process, and $t$ is the healing time. This theoretical equation agreed well the experimental data as shown in Fig. 8(c). To our knowledge, this is the first time that a physical model was proposed to characterize the relationship between self-healing efficiency and healing time in the self-healing epoxy system based on dynamic disulfide links. The fitted results were $\eta_0 = 18.36$, $\eta_s = 81.64$, and $\tau_s = 5.46 \times 10^5$ s, respectively, which suggested that the dynamic disulfide bonds predominated in the investigated healable EDBS polymer, and the reversible hydrogen bonds played a secondary role in the restoration process. It could also be inferred from the fitted equation that the self-healing provided by hydrogen bond was completed in short time, and the main recovery of mechanical strength depended on the time-related dynamic disulfide bonds. The self-healing process of epoxy resin cured with p-phenylenediamine (EDBP) confirmed the above results. The formulation of EDBP was similar to that of EDBS-2. Fig. 8(d) shows that the self-healing efficiency of EDBP was about 20%, and changed a little in its prolonging healing time, which was in agreement with other’s results.[48–50]

According to the above results, the self-healing performance caused by the disulfide exchange for EDBS was time-dependent. This healing process, thus, should also be related to temperature based on the time-temperature superposition principle. Fig. 8(b) and Table S2 (in ESI) show the healing properties of cracked samples after healing for 3 h at different temperatures. It was evident that the healing efficiency of resin increased with the increase of temperature. The accelerated metathesis reaction of disulfide bonds and faster chain mobility promoted the healing process at raised temperatures.[48] The healing efficiency, therefore, was noticeably improved by elevating temperature. However, the inevitable thermo-oxidative aging of the material would be induced, and high temperature was not an energy-saving choice.[50] In this respect, the 24 h healing time at 80 °C was considered to be the reasonable choice.

To reveal the recovery more intuitively, two dumbbell EDBS-2 samples with 50 mm in length and thickness of 0.5 mm were fully cut into pieces, and healed for 3 h at 80 °C. One of them was stained with red dye to make the cut region more distinguishable. The self-healing specimen was able to lift 500 g of weight without tearing (Fig. 9), indicating its excellent self-healable property. In order to further observe the self-healing behavior of reversible crosslinked epoxy resins, the optical microscopic images of EDBS-2 were recorded in the healing process. The fresh crack was made on the surface of EDBS-2 resin. The cracked EDBS-2 was healing at 120 °C. The optical photos after healing for 0, 1.5, and 3 h are shown in Fig. 10. Initially, the crack around 50 μm was clearly observed on the surface of the injured specimen (Fig. 10a), but it kept only a slight trace after repairing for 1.5 h (Fig. 10b). After healing for 3 h, the cut on the surface was healed completely (Fig. 10c).

Fig. 11 shows the schematic illustration of the self-healing.

![Fig. 9](https://doi.org/10.1007/s10118-020-2406-x)

**Fig. 9** Images of EDBS-2 sample and the colored one that was cut into two pieces, respectively, and healed for 4 h at 80 °C, and then subjected to a 500 g weight lifting test.

![Fig. 10](https://doi.org/10.1007/s10118-020-2406-x)

**Fig. 10** Optical microscopic images of cracked EDBS-2 sample healing for various time: (a) 0 h, (b) 1.5 h, and (c) 3 h.
mechanism of epoxy dynamic networks. The self-healing EDBS consisted of soft segments, hard segments, and active crosslinkers featuring dynamic aromatic disulfides and reversible hydrogen bonding interactions (Fig. 11i). The external injuries fractured the connection of molecular chains (Fig. 11ii). Prior to the self-healing process, the cracked samples were heated above $T_g$ to thaw segmental motion for cohesive movements of polymer chains in the interface. The hydrogen bonds contributed to the initial sticking or interfacial adhesion (Fig. 11iii), and the disulfide exchange reaction facilitated chain interdiffusion to reform the crosslinking networks of epoxy (Fig. 11iv), endowing polymers with good mechanical properties and intrinsic self-healable performance.

CONCLUSIONS

In conclusion, the thermosetting epoxy resins with aromatic disulfide crosslinks were prepared by a simple method. The fitted results of stress relaxation indicated the relatively low activation energies of our epoxy networks. Benefitting from disulfide exchange reaction and hydrogen bonding, the studied samples in this work not only exhibited good mechanical property, but also had a self-healable ability at moderate temperature. Experimental results revealed that the flexible chains promoted the conformational change and facilitated the chain ends expansion into open voids at fractured interfaces, which led to the enhanced self-healing efficiency. A model was proposed to simulate the self-healing process with the variation of healing time. It was found that the hydrogen bonds were quickly reconstructed to provide initial adhesion, and the dynamic exchanges of disulfide bonds were time dependent.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2406-x.

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