

Unraveling the Heterogeneity of Epoxy-amine Networks by Introducing Dynamic Covalent Bonds

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 Electronic Supplementary Information

Abstract Epoxy resins are a kind of universal thermosetting plastics, which are widely used as structural materials in various applications. Thus, it is necessary to understand the network structure of epoxy resins. However, it is challenging to reveal the network heterogeneity of epoxy resins due to the permanent covalent crosslinking. Here, we provide a novel strategy to characterize the network heterogeneity of epoxy resins by using the dynamic covalent bonds to replace the conventional covalent bonds. The dynamic covalent bonds can reorganize under heat stimulus and the network keeps a constant crosslinking density during topological rearrangement, making it convenient to study the heterogeneity of epoxy resins. Kohlrausch-Williams-Watts (KWW) stretched exponential function is used to fit the stress relaxation data, and the parameters β and σ_{perm}/σ_0 extracted from KWW equation indicate the network becomes more homogenous with the stoichiometric ratio of epoxy groups and amines decreases from 1/1 to 1/1.5. This method proves that the side reaction between epoxy and hydroxyl is the main origin of the structural heterogeneity in epoxy resins compared to the secondary amines network.

Keywords Epoxy resins; Heterogeneity; Dynamic covalent bonds

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INTRODUCTION

Epoxy resins as an important member of the thermosetting resin family are widely used in many fields, such as encapsulants, airplanes, automobiles and adhesives, due to their high mechanical properties and excellent environmental resistance.^[1–7] Such properties are attributed to the high crosslinking density of networks formed by the curing reaction between epoxy and amines, acids, phenols, alcohols and thiols.^[8–10] Meanwhile, the heterogeneity of the three-dimensional spatial network also has significant influence on the macroscopic mechanical properties.^[11–13] Especially for epoxy resins with complicated curing mechanism, the crosslinking caused by some side reactions may affect the continuity of the network structure and lead to the deterioration of the mechanical properties of the cured resins. Thus, it is vital to understand the network heterogeneity of epoxy resins.

To date, only a few potential approaches could be used to indirectly characterize the network heterogeneity of thermosetting resins because of their irreversible covalent networks, such as scanning electron microscopy (SEM), atomic force microscopy (AFM), small-angle neutron scattering (SANS) and

small-angle X-ray scattering (SAXS).^[14–17] However, these methods always require the thermosetting resins to be fractured or swollen with a good solvent. Moreover, there are some inconsistencies between these results, as they cannot accurately reflect the heterogeneity of the thermosetting resins in the non-destructive state. Therefore, it still remains a big challenge to examine the microscopic network heterogeneity.

In 2011, Leibler and coworkers proposed the concept of vitrimer based on associative covalent adaptable networks (CANs).^[18] The dynamic chemically cross-linked networks are different from traditional covalent crosslinked networks, which shows the Arrhenius temperature dependence behavior like silica through bonds exchange at temperatures higher than the glass transition temperature. In this process, the crosslinking density, one of the major molecular variables to control physical properties, will not change. Thus, by taking the advantage of dynamic exchange behavior, it is possible to evaluate the network heterogeneity of highly crosslinked thermosetting polymers.

Here, we propose a new strategy by introducing dynamic covalent bonds for studying the network heterogeneity of an epoxy resin at the microscopic scale. In this strategy, 4-aminophenyl disulfide (AD) is used as a crosslinking agent to cure diglycidyl ether of bisphenol F (DGEF) with different stoichiometric ratios (Fig. 1). The stoichiometric ratio will in-

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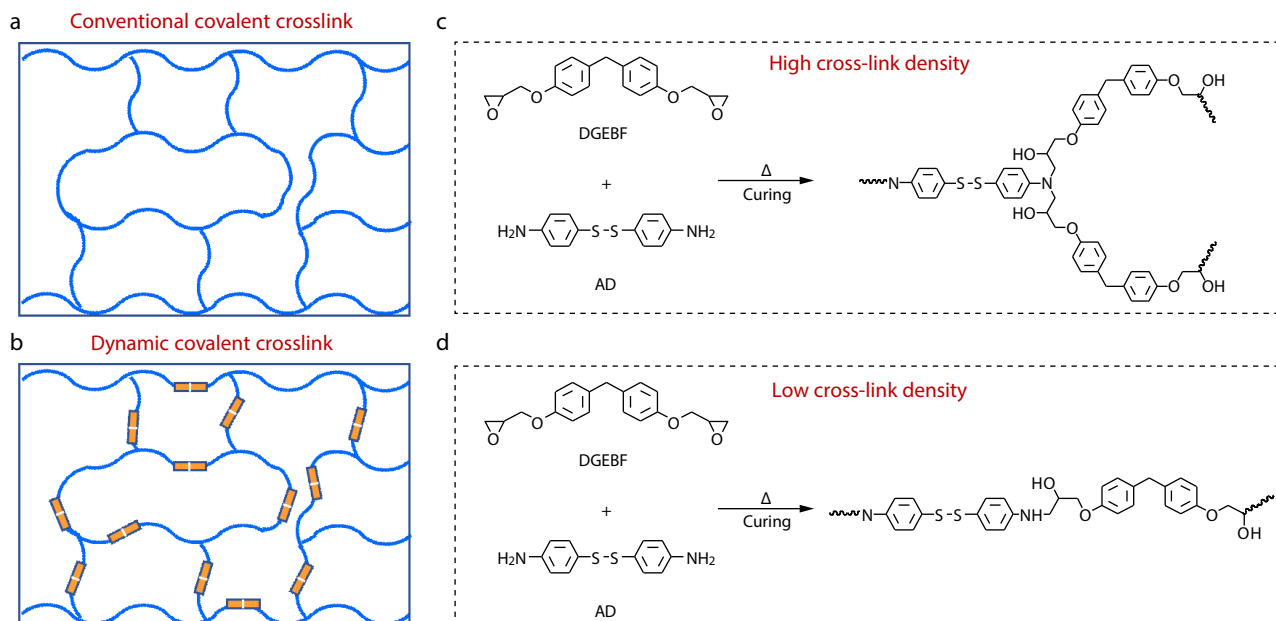


Fig. 1 Design concept and synthesis of EP-AD-*m*. Schematic illustration for the difference between (a) conventional covalent crosslinked network and (b) dynamic covalent crosslinked network. Chemical route to the synthesis of EP-AD-*m* when the ratio of epoxy groups and amines is changed to make the network from (c) high crosslinking density to (d) low crosslinking density.

fluence the crosslinking density and heterogeneity of epoxy resins. Firstly, we investigate the effect of stoichiometric ratio on crosslinking density through DMA measurement. Next, we study the stress relaxation times of all samples and calculate the activation energy. Finally, we use the stretched exponential function to fit the stress relaxation data to derive the influence of stoichiometric ratio on the network heterogeneity. This work provides a simple method to study the microscopic heterogeneity of epoxy resins, which can be easily extended to other thermosetting resins.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol F (DGEBF, EEW=170) was obtained from Luohe Chemistry Co., Ltd. 4-Aminophenyl disulfide (AD) was purchased from Adamas. Acetone was purchased from Chengdu Kelong Chemical Reagent Factory. All the chemicals were used as received without further purification.

Preparation of Epoxy Resins

A certain stoichiometric amount of AD was solved in acetone and then mixed with DGEBF. The solvent was evaporated and the mixture was mechanically stirred for 15 min before it was degassed in a vacuum to remove air bubbles. Afterward, the degassed mixture was poured into a preheated PTFE mold, and curing was performed at 75 °C for 2 h, 125 °C for 2 h and 165 °C for 3 h. Samples are denoted as EP-AD-*m*, where *m* refers to the stoichiometric ratio of the hydrogen on the amine group to the epoxy group on DGEBF.

Characterization

Fourier transformation infrared spectroscopy (FTIR)

FTIR spectra were recorded on Nicolet iS10 (Nicolet, America) in the range of 4000–400 cm^{-1} at room temperature.

Differential scanning calorimeter (DSC)

DSC tests were performed on Q2000 (TA instrument) with the mass of all samples ranging from 3 mg to 8 mg. Samples were heated from 0 °C to 200 °C at a heating rate of 10 °C/min and then cooling to 0 °C at 10 °C/min. The heating and cooling processes were performed for twice.

Dynamic mechanical analysis (DMA)

DMA tests were measured on Q800 (TA Instrument) in a three-point bending mode with the sample dimension about 20 mm $\times$ 5 mm $\times$ 1 mm. Tests were performed in temperature scanning mode in the range of –20 °C to 150 °C at a ramping rate of 3 °C/min and a frequency of 1 Hz with a strain amplitude of 30 μm . Stress relaxation tests were conducted with the same instrument in a tensile mode. During the test, a sample was first equilibrated at a certain temperature for 15 min. Then an instantaneous 0.5% strain was applied to the sample within 2 s.

Gel fraction

EP-AD-*m* is immersed in DMF at 30 °C for 48 h, the solvent is removed after dried in vacuum oven at 100 °C for 24 h.

RESULTS AND DISCUSSION

Fabrication and Crosslinking Density

We use AD to cure DGEBF with different stoichiometric ratios, resulting in epoxy resin vitrimers containing dynamic disulfide bonds. FTIR results demonstrate the successful crosslinking reaction to form the network of EP-AD-*m* (Fig. S1 in the electronic supplementary information, ESI). When the stoichiometric ratio of epoxy groups on DGEBF and hydrogen on the amine groups is 1/1, the primary amine groups react with epoxy groups to produce secondary amino groups. The secondary amino groups will continue to react with other epoxy groups to form tertiary amine groups, yielding a high

crosslinking density network (Fig. 1c). With the stoichiometric ratio decreasing from 1/1 to 1/1.5, the epoxy groups tend to react with primary amines and the crosslinking density of the network gradually decreases (Fig. 1d). That is to say, the number of tertiary amines is reduced due to the excess primary amines consuming epoxy groups to form secondary amines. These results will influence the microscopic heterogeneity of epoxy resins, which will be discussed in the later section. We can envision that the network formed by AD is similar to that formed by conventional amine crosslinker. Due to the associative nature of dynamic rearrangement at high temperature, the network keeps a constant crosslinking density. Therefore, the network heterogeneity of EP-AD-*m* should be consistent with that of conventional epoxy resins (Fig. 1a).

To better understand the relationship between stoichiometric ratio and crosslinking density of EP-AD-*m*, the classical theory of rubber elasticity is used to calculate the crosslinking density (ρ).^[19–21] The crosslinking density could be calculated using the following equations:

$$V_c = \frac{E_r}{3RT} \quad (1)$$

$$M_c = \frac{\rho}{V_c} \quad (2)$$

where V_c represents the crosslinking density per unit volume (mol/m^3), M_c represents the molecular weight between the crosslinkers, ρ is the density of the thermoset ($0.984 \text{ g}/\text{cm}^3$), E_r is the rubbery modulus (MPa), R is the gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), and T is the absolute temperature at $T_g + 30^\circ\text{C}$. Fig. 2(a) shows the DMA curves of EP-AD-1, EP-AD-1.25 and EP-AD-1.5.

We can see that the T_g values of EP-AD-*m* decrease with increasing AD content, which is consistent with DSC data (Figs. 2b and 2c). The decrease in T_g with the decreasing stoichiometric ratio between epoxy and hydrogen can be attributed to the decreasing crosslinking density. Indeed, the crosslinking density calculated by Eqs. (1) and (2) decreases from $1700 \text{ mol}/\text{m}^3$ of EP-AD-1 to $1088 \text{ mol}/\text{m}^3$ of EP-AD-1.5, and the calculated values of the gel fraction also prove this (Fig. 2c).

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Dynamic Property of the EP-AD-*m* Crosslinking Network

To study the dynamic properties of the EP-AD-*m* networks, stress relaxation tests are performed. We can obviously observe that the EP-AD-*m* shows stress relaxation behavior at 200°C (Fig. 3a). Among them, EP-AD-1 shows faster relaxation than EP-AD-1.25, which is related to the fact that EP-AD-1 has more dynamic disulfide bonds.^[22] Moreover, as the stoichiometric ratio of $-\text{NH}-$ to epoxy group increases from 1/1 to 1.5/1, the equilibrium value ($\sigma(t)/\sigma_0$) of EP-AD-*m* gradually decreases due to the decreased crosslinking density. Then we further used the 1/e method to determine the relaxation time ($\tau_{1/e}$) of EP-AD-*m*, which follows Arrhenius' law (Figs. 3b and 3c, Figs. S2 and S3 in ESI);^[23]

$$\tau = \tau_0 \exp \frac{E_a}{RT} \quad (3)$$

where E_a is the activation energy and τ_0 is a proportionality constant. The calculated activation energies of EP-AD-1, EP-AD-1.25 and EP-AD-1.5 are 101.1, 175.8 and $186.9 \text{ kJ}/\text{mol}$, respectively (Fig. 3d). The exchange reaction is related to the topology freezing transition temperature (T_v), corresponding to transition from the solid to the liquid state.^[18,24] This transition temperature is as the viscosity reaches $10^{12} \text{ Pa}\cdot\text{s}$.^[25–27] Thus, we used the Maxwell relation to study the T_v :

$$\eta = G\tau^* \quad (4)$$

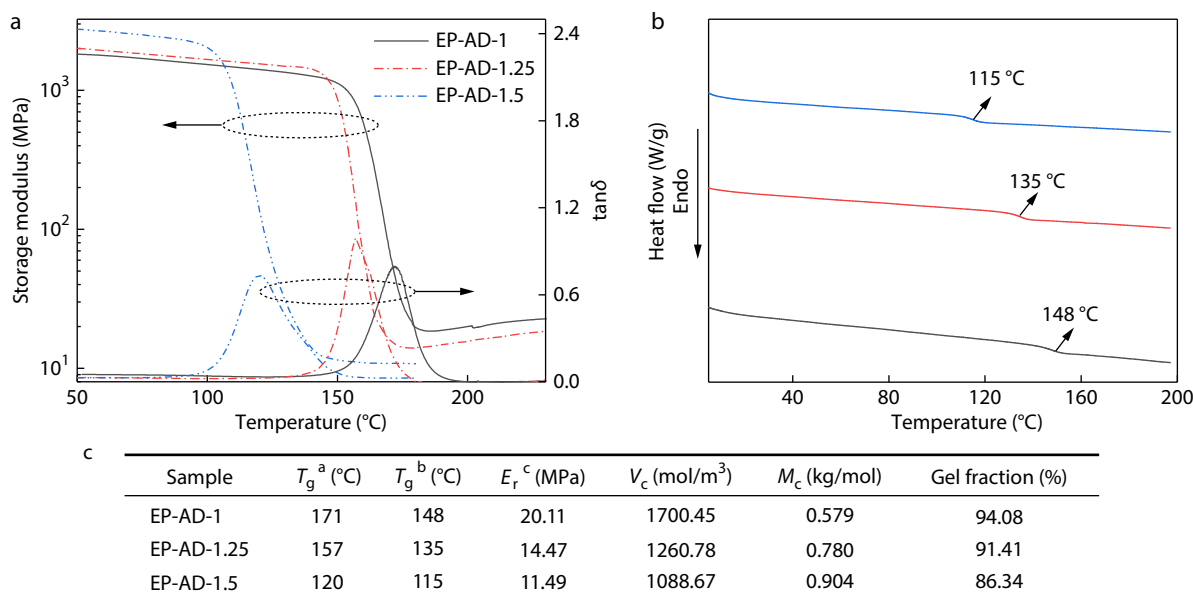


Fig. 2 Thermomechanical properties of EP-AD-*m*. (a) Storage modulus and $\tan\delta$ of EP-AD-*m* system; (b) DSC thermograms for EP-AD-*m* on the second heating from 0°C to 200°C at a rate of $10^\circ\text{C}/\text{min}$. From down to up, the samples are EP-AD-1, EP-AD-1.25 and EP-AD-1.5, respectively; (c) Thermomechanical Properties of EP-AD-*m*. ^a Determined by DMA; ^b Determined by DSC at a heating rate of $10^\circ\text{C}/\text{min}$; ^c E_r is the plateau modulus obtained from the DMA curves at the temperature $T_g + 30^\circ\text{C}$.

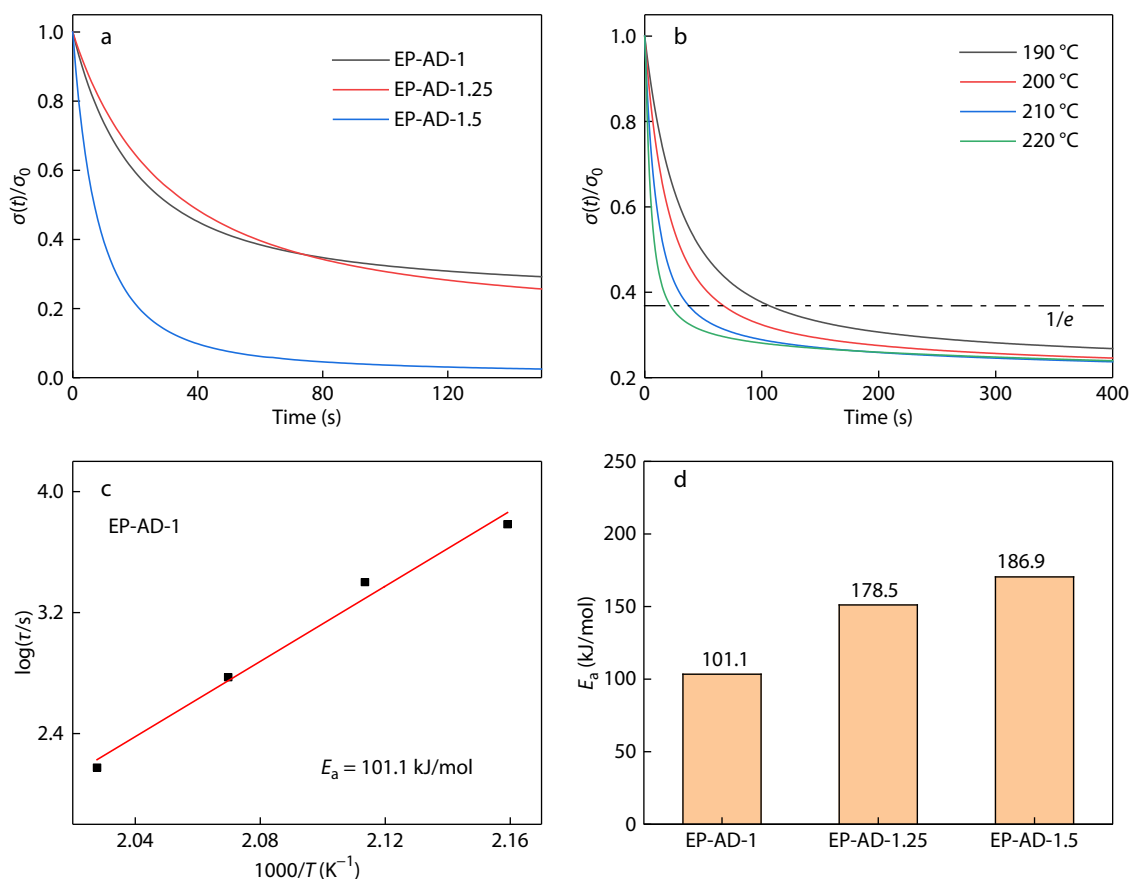


Fig. 3 Dynamic properties of EP-AD-*m*. (a) Normalized stress-relaxation curves of EP-AD-*m* samples at 200 °C; (b) Normalized stress-relaxation curves of EP-AD-1 at different temperatures; (c) Arrhenius fitting for relaxation time; (d) Activation energies (E_a) of EP-AD-*m* samples.

$$G = \frac{E_r}{2(1 + \nu)} \quad (5)$$

where E_r is the rubbery modulus (MPa) and ν is the Poisson's ratio (0.5, usually used for rubbery materials). It is revealed that the hypothetical T_v values of EP-AD-1, EP-AD-1.25 and EP-AD-1.5 are 90, 129 and 117 °C, respectively, which are below their T_g (*vide supra*). However, when the temperature is below T_g , the EP-AD-*m* network is frozen and the segmental motions are arrested. Thus, the topology network can hardly change at such state. After the temperature rises, the faster exchange of dynamic disulfide bonds of EP-AD-1 leads to the faster stress relaxation of the dynamic network (Fig. 3a).^[28]

Heterogeneity Study of EP-AD-*m* Network

To study the heterogeneity of EP-AD-*m* network, Kohlrausch-Williams-Watts (KWW) stretched exponential function is used to fit the stress relaxation data.^[29–33]

$$\frac{\sigma(t)}{\sigma_0} = \frac{\sigma_{perm}}{\sigma_0} + \left(1 - \frac{\sigma_{perm}}{\sigma_0}\right) \exp\left\{-\left(t/t^*\right)^\beta\right\} \quad (6)$$

where t is the relaxation time, t^* is a characteristic relaxation time, β ($0 < \beta \leq 1$) is the heterogeneity parameter of the sample that controls the shape of the stretched exponential decay. $\beta=1$ means a homogeneous network and the stress relaxation is a single exponential relaxation process, while the more it deviates from 1, the more complex relaxation is, which means the network is the more heterogeneous. σ_{perm}/σ_0 is the normalized

$\sigma(t)/\sigma_0$ as time approaches infinity and the materials with percolated permanent networks show positive values of σ_{perm}/σ_0 . As mentioned above, the network heterogeneity of EP-AD-*m* is consistent with that of conventional epoxy resins. Due to the incorporation of dynamic disulfide bonds, the topological rearrangement of EP-AD-*m* could take place at high temperature and the permanent covalent bonds in network are still inert at the same time, which means the heterogeneity of network will not be affected by exchange reaction. Based on this, we apply KWW equation to the stress relaxation data for the EP-AD-*m* samples at different temperatures, which shows excellent fits to data with adjusted $R^2 > 0.96$ (Fig. 4, Figs. S4 and S5 in ESI).

Furtherly, we extract the heterogeneity parameter β and σ_{perm}/σ_0 from the KWW equation and plot it as a function of EP-AD-*m*, as shown in Fig. 5. We can obviously see that the EP-AD-1.5 has maximum β values and minimum σ_{perm}/σ_0 , followed by EP-AD-1.25 and EP-AD-1 (details shown in Tables S1–S3 in ESI). These results indicate that the network structure of EP-AD-1.5 is the most homogeneous, while the network structure of EP-AD-1 is the most heterogeneous. In the first discussion session, we have mentioned that with the stoichiometric ratio decreasing from 1/1 to 1/1.5, the tertiary amines network will gradually transform into secondary amines network. Thus, the network of EP-AD-1 is dominated

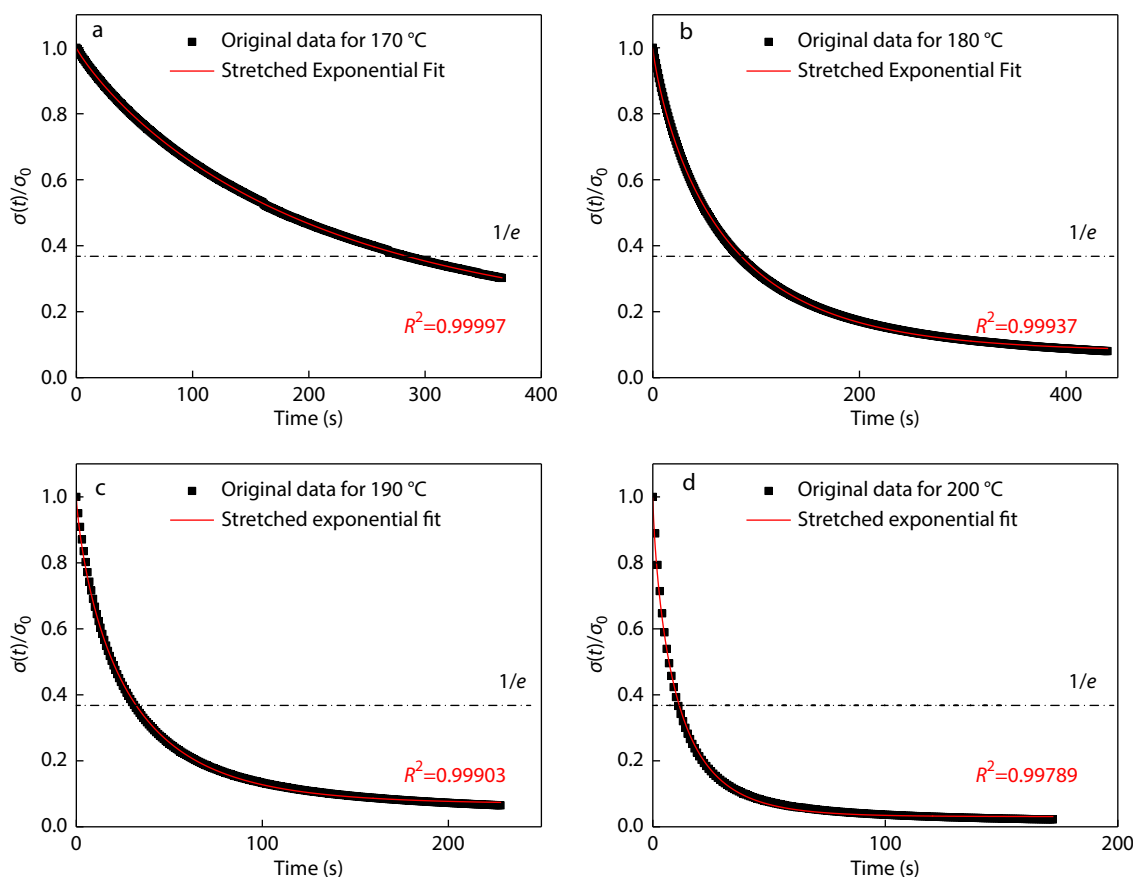


Fig. 4 Stretched exponential fits to stress relaxation data for EP-AD-1.5 at different temperatures.

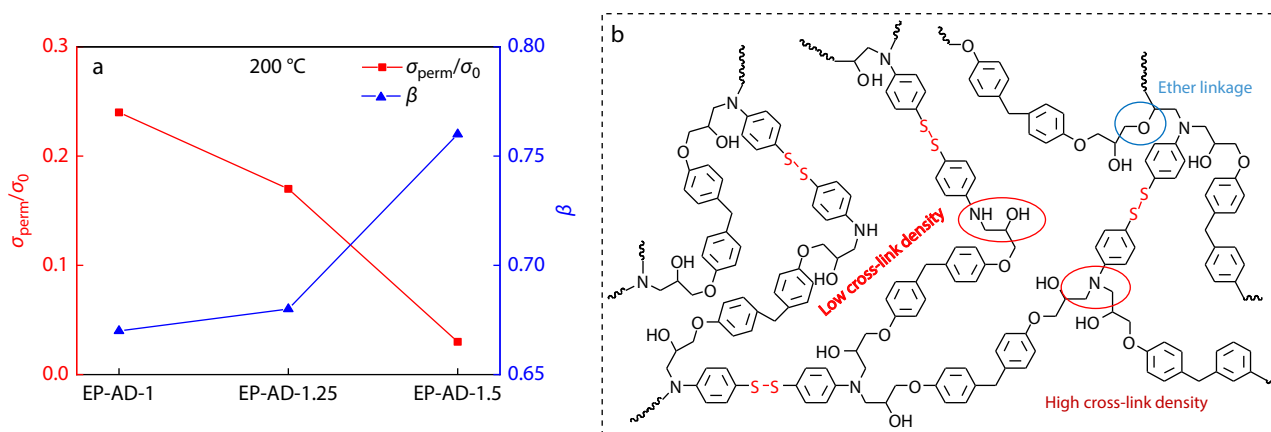


Fig. 5 (a) The heterogeneity parameter β and $\sigma_{\text{perm}}/\sigma_0$ of EP-AD- m at 200 °C; (b) Network structures of EP-AD- m .

by tertiary amines, while the networks of EP-AD-1.25 and EP-AD-1.5 show coexistence of tertiary amines and secondary amines. Actually, the cross-links between epoxy and AD are dynamic and the rearrangement of disulfide bonds does not change the crosslinking density. If time approaches infinity, $\sigma_{\text{perm}}/\sigma_0$ would be close to 0. However, we can see that all samples have positive values of $\sigma_{\text{perm}}/\sigma_0$. In fact, in epoxy-amine system, the curing reactions take place mainly between epoxy groups and amine groups. There are also side reactions between epoxy groups and hydroxyl groups at high temperature.^[34] This will form ether linkage crosslinking net-

work and the resulted percolated network will lead to residual stress in EP-AD- m , so the data from stress relaxation shows a positive value of $\sigma_{\text{perm}}/\sigma_0$ instead of 0. This permanent covalent crosslinking causes EP-AD- m heterogeneous. It is obvious that when the stoichiometric ratio of epoxy/amine decreases, the values of β increase the values of $\sigma_{\text{perm}}/\sigma_0$ decrease. This is because the excess number of amino groups will suppress the reaction of the epoxy groups with the hydroxyl groups, thereby avoiding the formation of ether linkage and causing the homogeneous network of EP-AD-1.25 and EP-AD-1.5.

CONCLUSIONS

In summary, this work provides a new strategy to study the heterogeneity of the thermosetting epoxy resins. This strategy is enabled by using dynamic covalent bonds to replace covalent bonds to indirectly study the heterogeneity of epoxy resins. The heterogeneity parameter β and $\sigma_{\text{perm}}/\sigma_0$ extracted from the KWW equation reveal the relationship between the heterogeneous structure and epoxy/amine stoichiometric ratio, *i.e.*, as epoxy/amine stoichiometric ratio decreases, the network structure of epoxy resins gradually becomes homogeneous. This is because that there is a competitive process between epoxy/hydroxyl reaction and epoxy/amine reaction. The ether linkage will cause the heterogeneous network of epoxy resins. The knowledge obtained herein should be useful for understanding the heterogeneity of epoxy resins, which will be applicable to other thermosetting polymers. Hence, we believe that this study will contribute to the development of fundamental research of thermosetting polymer materials.

NOTES

The authors declare no competing financial interest.

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/s10118-022-2881-3>.

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