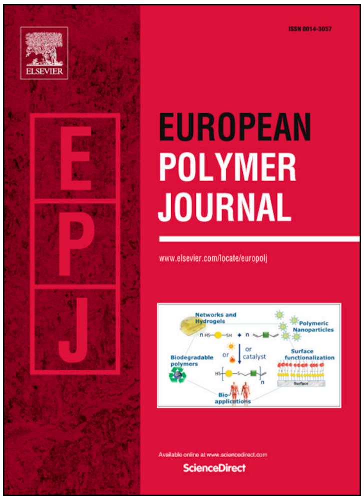

Effect of the stoichiometric ratio on the crosslinked network structure and cryogenic properties of epoxy resins cured at low temperature

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Effect of the stoichiometric ratio on the crosslinked network structure and cryogenic properties of epoxy resins cured at low temperature

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Abstract: Recently, epoxy resins with outstanding cryogenic performance have attracted much attention for low-cost space exploration. Since the structure-property relationship is the foundation of materials design, the present study investigates the effect of the stoichiometric ratio of active-hydrogen to epoxy-group ([H]/[E]) on the crosslinked network structure and cryogenic properties of a polyurethane modified epoxy resin (PUE). The average molecular weight (*M*c) and integrity of the crosslinked network structure in PUE thermosets are studied by dynamic mechanical analysis and FTIR. Cryogenic properties including the coefficient of thermal expansion (CTE) and tensile properties of all PUE thermosets are determined. The results show that increasing the [H]/[E] stoichiometric ratio from 0.7 to 1.3 can decrease the *M*c of PUE thermosets cured at low temperature. The crosslinked network structure of PUE thermosets with lower *M*c possesses smaller CTE. The tensile strength of the thermosets at 77 K is increased to about 105 MPa when the

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[H]/[E] stoichiometric ratio reaches 1.3. And appropriately excessive content of curing agent is necessary to get optimum mechanical properties at RT and 77 K for these low-temperature cured PUE thermosets. Finally, the influence of the [H]/[E] stoichiometric ratio on the fracture mechanism of PUE thermosets is discussed in terms of the morphological characteristic of the propagation zones on the fracture surface of the tensile samples as well.

Key words: Epoxy resin; Crosslinked network structure; Cryogenic temperature; Thermal expansion; Mechanical properties

1. Introduction

As the continuous development of deep space exploration technology, epoxy resins with excellent mechanical properties at cryogenic temperature arouse intensive interest [1,2]. To date, considerable work has been done to gain a better understanding on the relationship between the structure and properties at room or elevated temperature [3-5], while the impact of cryogenic temperature on the properties of the matrix with different network structures still remains an open issue [6]. Since the relationship between the structure and properties is the foundation of materials design, researches about cryogenic properties of epoxy resins with tailored crosslinked network structure in the thermosets are desired.

On the one hand, the crosslinked network structure of epoxy resins can be tuned via different approaches, e.g. controlling the curing process [7], changing the chemical structures of epoxy resins and curing agents, and so on [8,9]. For an epoxy-amine system with the specific curing process, design of the crosslinking network structure of the thermosets can be obtained by changing the stoichiometric ratio of active-hydrogen to epoxy-group ([H]/[E]) [10,11]. Fred et al. [12] studied the effect of [H]/[E] stoichiometry on the network structure and dynamic mechanical properties of a DGEBA/DDS system, and reported that the highest Tg and rubbery state modulus were observed at the equivalent [H]/[E] stoichiometric ratio with the curing process of 160 ℃/1.5 h+180 ℃/4 h+220 ℃/2 h. Additionally, the influence of the [H]/[E] stoichiometry on other properties including curing behavior and mechanical properties was also reported for other high temperature curing systems [13-15]. However, most efforts were focused on their properties at room or elevated temperature, while the impact of the [H]/[E] stoichiometry on the properties of the matrix at cryogenic temperature has been rarely reported.

On the other hand, epoxy resin system with high temperature curing process usually exhibits superiority in mechanical and thermal properties at elevated temperature [16-18]. However, materials served at cryogenic engineering always suffer from low temperature or alternating hot and cold temperature [19,20]. Compared with the high-temperature curing process, low-temperature curing process will significantly decrease the large temperature gradient from the curing temperature to the operating temperature. Therefore, the internal stress caused by the contraction during the decrease of temperature is likely to be reduced [21-23]. This unique advantage endows low temperature curing system with possible applications in cryogenic engineering [24,25]. Additionally, as the properties of the thermosets are deeply affected by curing temperature [26,27], it is desirable to investigate the effects of the stoichiometric ratio on curing characteristic, cryogenic properties and morphology of low-temperature cured epoxy resins.

In this respect, the main objective of this research is to illuminate the effect of [H]/[E] stoichiometric ratio on the cryogenic properties of polyurethane modified epoxy thermosets which were cured at low temperature. Dynamic mechanical analysis was used to study the characteristic of the crosslinked network structure in the thermosets. FTIR spectrum was used to evaluate the extent of reaction as well as the integrity of the crosslinked network structure. The thermal expansion behavior and tensile properties both at room temperature and cryogenic temperature, and morphological properties of all thermosets were investigated in detail. Relationships between the crosslinked network structures and the cryogenic properties of resulting epoxy thermosets were obtained.

2. Experimental section

2.1. Materials

The epoxy resin used in this work was a polyurethane modified epoxy resin (PUE; supplied by Hengchuang Insulating Material Co., China) with an epoxide equivalent weight (EEW) of 270.3 g/eq. The aliphatic amine curing agent (B1; supplied by Changsha Research Institute of Chemical Industry) with an active hydrogen equivalent weight (AHEW) of 56.8 g/eq, and a phenolic modified amine curing agent (B2; supplied by Tianjin Yanhai Chemical Co., China) with an AHEW of 147.6 g/eq, were used to achieve a low temperature curing system which has a mean AHEW of 91.9 g/eq. All the materials were used without further purification. The chemical structures of the epoxy resin PUE and the curing agents B1 and B2 are shown in Fig.1.

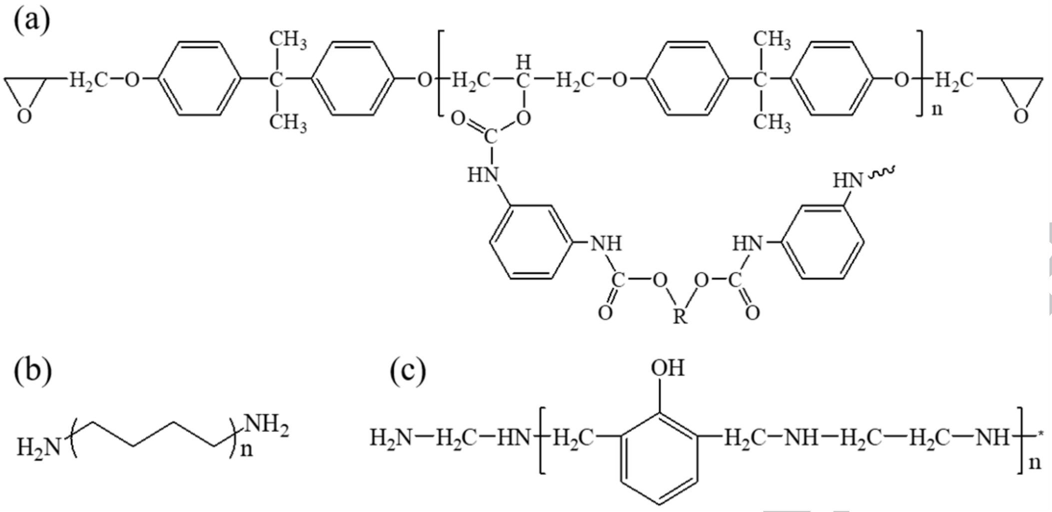

Fig.1. Chemical structures of the epoxy resin and curing agents: (a) polyurethane modified epoxy resin; (b) Flexible diamine; and (c) Phenolic modified diamine.

2.2. Sample preparation

Prior to curing, B1 and B2 were mixed at a certain proportion by Planetary Mixer (ZYMC-200V; supplied by Shenzhen ZYE Science & Technology Co., Ltd) with a speed of 1800 RPM for approximately 60 s to ensure a homogeneous mixture B12. Then the blend of B12 and PUE with a series of stoichiometric ratio of hydrogen /epoxy ([H]/[E]), i.e. [H]/[E]=0.7, 0.85, 1.0, 1.15, 1.3, was mixed for about 60 s, where [H] and [E] correspond to the amount of the active H and epoxy-group in B12 and PUE, respectively. The curing procedure was carried out at ambient temperature for 24 h and a post-cure at 80℃ for 1 h to make sure a fully curing.

2.3. Characterization

2.3.1. Dynamic mechanical analysis

The thermomechanical properties of the cured resins were determined by a dynamic mechanical analysis (DMA) instrument (METTLER, Switzerland) at the rate of 3 K/min, frequency of 1 Hz. The temperature ranged from -125 to 100 ℃. Thermosets with a dimension of 10 mm × 3 mm ×40 mm were clamped in the medium frame in three-point bending mode.

The rubbery equilibrium tensile modulus, *E*r, obtained at the rubber platform was used to determine the crosslinking density of the thermosets with all stoichiometric ratios. The average molecular weight between crosslinks, *M*c, was calculated according to Nielsen's semi-empirical equation (1)-(2) [28]:

$$\log G\mathrm{r} = 6.0 + \frac{293\rho}{M\mathrm{c}} \qquad (1)$$

$$E\mathrm{r} = 2G\mathrm{r}(1+\nu) \qquad (2)$$

Where, ρ is the density of the specimen in g/cm^3, *E*r denotes the elastic modulus at rubbery state in Pa, *G*r is the shear modulus in Pa. ν is the Poisson's ratio and is assumed to be 0.5, which is typical for a rubber material.

2.3.2. FTIR spectra

The FTIR spectra were collected with a Nicolet IS50 FIRT spectrometer. The liquid sample was tested by the coating film of the neat epoxy on the KBr wafer and the thermosets were tested by ATR mode.

2.3.3. Thermal expansion behavior

The length variation (Δl) of the epoxy films with different stoichiometric ratios was measured by DMA in tension-creep mode with the force set at 0.02 N. The temperature ranged from -125℃ to 100 ℃ at a rate of 3 K/min. The dimension of the testing films is 10 mm × 10 mm × 0.6 mm. The coefficient of thermal expansion (CTE), α, and its mean value, $\overline{\alpha}$, were obtained by the following equation (3)-(4).

$$\alpha = \frac{1}{l_0}\frac{dl}{dT} \qquad (3)$$

$$\overline{\alpha} = \frac{\Delta l}{l_0}\frac{1}{\Delta T} \qquad (4)$$

Where, l_0 is the length of the sample, which is 10 mm. ΔT is the temperature gradient.

2.3.4. Tensile properties

Tensile specimens of the epoxy thermosets were prepared according to ASTM D638-14. The tensile properties of the sample at room temperature and 77 K were evaluated by a SANS tensile tester with a cross head of 5 mm/min. The tensile specimens are 6 mm × 4 mm in the working section, and 115 mm long in the tensile direction. The cryogenic temperature condition was achieved by immersing the samples fixed on the clamps in a liquid nitrogen cryostat. The tensile samples and the cryogenic fixture are shown in Fig.2. No less than five specimens were tested for each set of conditions and the mean value and their standard deviation were calculated for the mechanical tests.

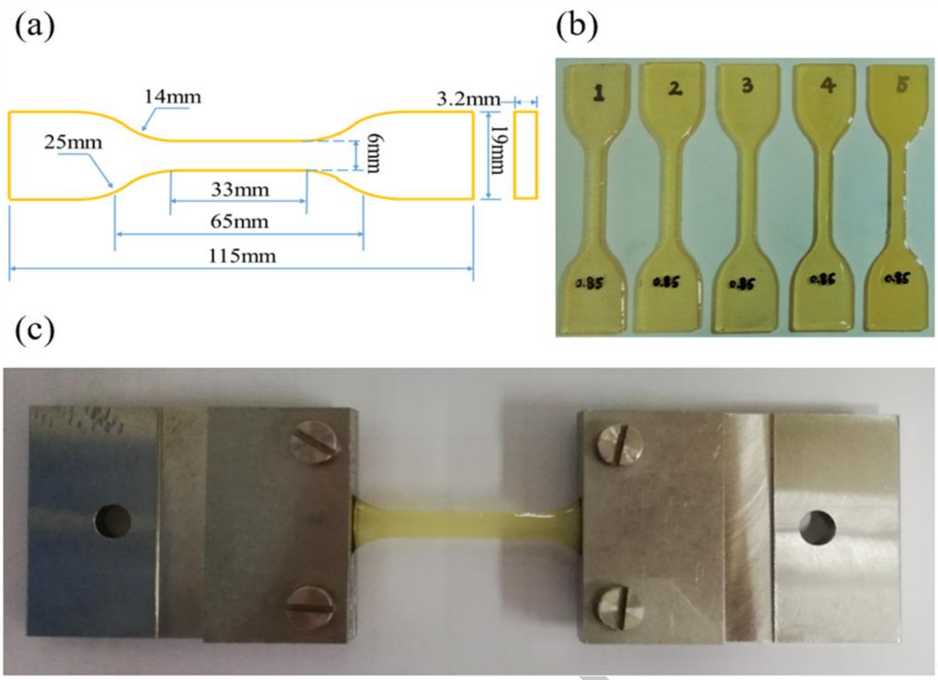

Fig.2. (a) Form and dimensions of dogbone test specimens; (b) the test specimens; and (c) self-designed tensile testing jag at 77 K.

2.3.5. Fracture surface characterization

Fracture surfaces of the tensile specimens with different stoichiometric ratios were examined by scanning electron microscopy (SEM; JSM-6010LA, Japan) at an accelerating voltage of 15.0 kV. Before examination, the fracture surface was coated with a thin evaporated layer of gold to improve the conductivity.

3. Results and discussion

3.1. Effect of the [H]/[E] stoichiometric ratio on the crosslinked network structure of PUE epoxy thermosets

Designing the crosslinked network structure of epoxy resins can be achieved not only by choosing different chemical structures of epoxy and hardener, but also by changing the content of hardener. Therefore, the network structure of polyurethane modified epoxy resin (PUE) with different [H]/[E] stoichiometric ratio was studied by the dynamic mechanical analysis (DMA) and presented in Fig. 3(a), which could reveal the information about the crosslinking density and molecular motion in thermosets [29].

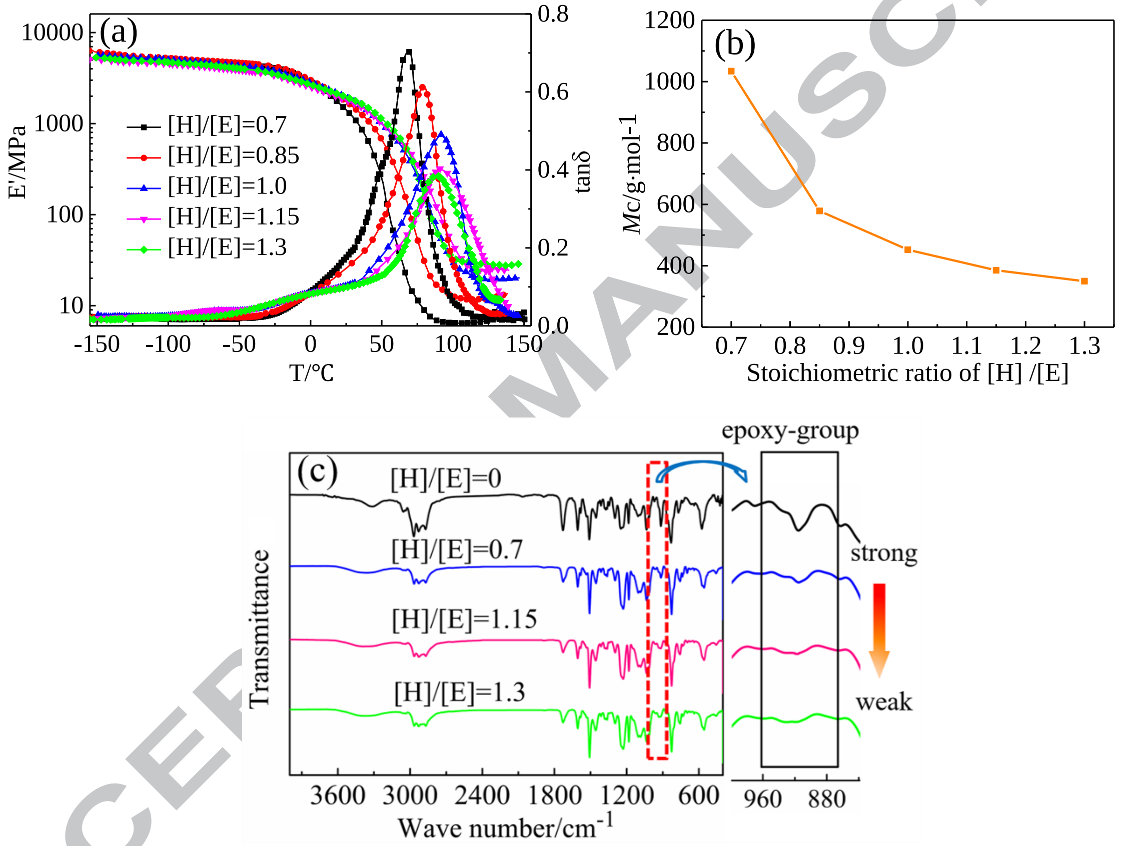

Fig.3. The influence of different [H]/[E] stoichiometric ratio on the PUE network structure based on: (a) DMA results; (b) calculated *M*c results; (c) FTIR spectra.

The storage modulus *E* ' at -150℃, and Tg values measured by the peak of tanδ in Fig. 3(a) are listed in Table 1. It is clear that *E* ' at -150℃ is within the range of 4~6 GPa for PUEs with various [H]/[E] stoichiometric ratio, which is agreed with the low-temperature modulus of epoxy resins reported in literatures [30]. In the meantime, *T*g value is increased to the maximum then decreased slightly when the [H]/[E] stoichiometric ratio is more than 1.0. This is ascribed to the plasticizing effect of the free chain ending or the excessive amount of curing agent, which can be confirmed by the broader peak width of tanδ with higher stoichiometric ratios as shown in Fig. 3(a).

Table 1. DMA results and calculated molecular weight between crosslinks (*M*c).

[H]/[E] stoichiometric ratio	*E*' at -150℃ [MPa]	*T*g [a] [℃]	*E*r [MPa]	ρ [b] [$g\cdot cm^{-3}$]	*M*c [$g\cdot mol^{-1}$]
0.70	5640	69	6.4	1.1685	1034
0.85	6063	78	12.8	1.1636	541
1.00	5578	91	17.0	1.1620	452
1.15	5094	91	23.0	1.1614	385
1.30	4328	90	27.6	1.1608	353

Note: [a] measured by the peak of tanδ in DMA, [b] measured by pycnometer.

On the other hand, rubbery modulus, *E*r, shown in Table 1, is increased with increased [H]/[E] ratio. As a result, the average molecular weight between crosslinks of the thermosets, *M*c, calculated by the *E*r and density ρ according to equations (1)-(2), is decreased from 1034 to 353 g/mol (Fig. 3(b) and Table 1), suggesting that the crosslinking network density of the thermosets is improved with increased [H]/[E] stoichiometric ratio. Interestingly, ρ of the thermoset is negatively correlated with the [H]/[E] ratio, which is consistent with the result reported by Gupta et al. [31].

In order to further investigate the integrity of the crosslinked network structure, FTIR was used to evaluate the reaction degree of epoxy-groups in the thermosets after post-curing at 80℃ for 1 h. For the sake of comparison and simplification, the FTIR transmittance spectra of uncured PUE ([H]/[E]=0) and the thermosets cured at the [H]/[E] stoichiometric ratio of 0.7, 1.15 and 1.3, respectively, are shown in Fig. 3(c).

The vibration absorption peak of epoxy band in PUE is located at 915 cm^{-1} (in the rectangle), which is in accord with the fact that the typical epoxy absorption is 910~916 cm $^{-1}$ [32,33]. The declined vibration absorption of the epoxy-groups with the increased stoichiometric ratio confirms the reaction between epoxy-groups and active-hydrogens. The downward trend of epoxy vibration absorption in FTIR is in good agreement with the Mc data, implying the continuous improvement of crosslinked network structure when the [H]/[E] stoichiometric ratio is beyond 1.0. This could be attributed to the entrapment of the reactive-hydrogen in the rigid 3-dimensional network because the vitrification of the thermosets hindered the further reaction of epoxy and hardener molecules, demonstrated by Fernandez el al. as well [34]. The result also suggests that the excessive content of curing agent is necessary to make full reaction of the epoxy-group for room temperature curing systems.

3.2. Effect of the [H]/[E] stoichiometric ratio on the thermal expansion behavior of PUE epoxy thermosets

Because the mechanical properties of materials applied to cryogenic engineering are considered to be influenced by the internal stress of the contraction which is attributed to the larger coefficient of thermal expansion (CTE) of polymer matrix, the effect of [H]/[E] stoichiometric ratio on the thermal expansion behavior of PUE epoxy thermosets is illuminated and plotted in Fig. 4.

It is clear that the CTE of all PUE thermosets, calculated by equation (3) and presented in Fig. 4(a), tends to be constant despite some fluctuation when temperature is below -100 ℃. At -125 ℃, the PUE thermoset with [H]/[E]=0.7 possesses the largest CTE which is about 62 $\times 10^{-6}$ K^{-1}. With the increase of the stoichiometric ratio in PUE, the CTE of the PUE thermosets reduces to 39 $\times 10^{-6}$ K^{-1}. However, when the temperature rises to about -25 ℃, the CTE of the PUE thermosets begins to increase, implying the initial movement of small molecular segments in the local area. This result is in keeping with the change of tanδ versus temperature as shown in Fig. 3(a) and Table 1. In addition, the cured PUE exhibits large thermal expansion behavior at room temperature, and the CTE of all PUE thermosets is in the range of 100~160 $\times 10^{-6}$ K^{-1} at 25 ℃.

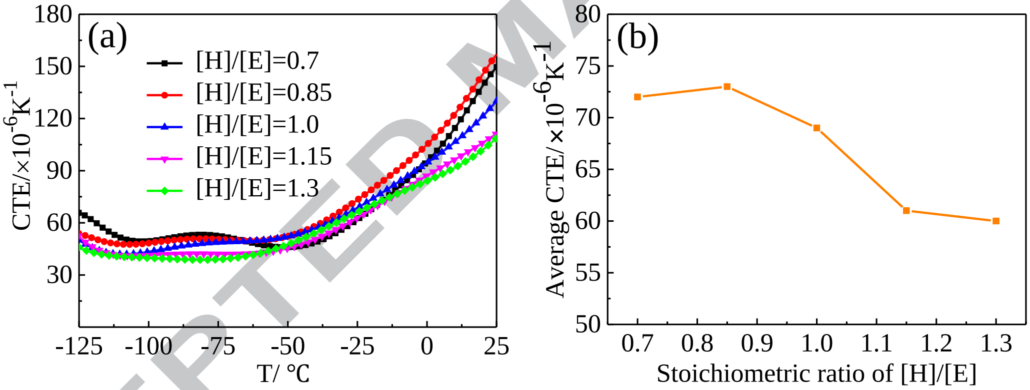

Fig.4. Thermal expansion behavior of PUE thermosets: (a) CTE from -125℃ to 25℃; (b) Average CTE between -125 and 25℃ for the thermosets with different stoichiometry ratio.

The average value of the CTE between -125 ℃ and 25 ℃ for PUE thermosets with different stoichiometry ratio was calculated by equation (4) and shown in Fig. 4(b). The average CTE of the thermosets is about 60~75 $\times 10^{-6}$ K^{-1}, which is inversely correlated to the [H]/[E] stoichiometric ratio, and changes a little when the stoichiometric ratio is 1.15 and more. This suggests that higher [H]/[E] stoichiometric ratio contributes to lower CTE in PUE thermosets. The result in our work is aligned with previous studies which reported the average CTE of epoxy resins below the glass state was about 40~100 × 10^{-6} K^{-1} [35-37].

3.3. Effect of the [H]/[E] stoichiometric ratio on the tensile properties of PUE epoxy thermosets at room temperature and 77 K

Tensile properties of all PUE epoxy thermosets at RT and 77 K versus the [H]/[E] stoichiometric ratio is presented in Fig. 5. By comparing their performance at RT and 77 K, we can study the influence of temperature on the properties of the PUE thermosets.

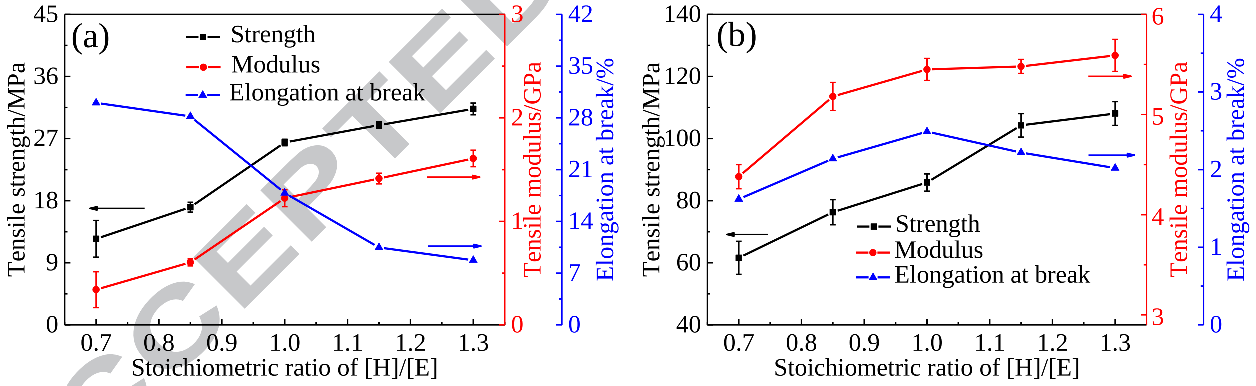

Fig.5. The influence of [H]/[E] stoichiometric ratio on the tensile properties of the PUE epoxy thermosets at: (a) RT; (b) 77 K.

It is obvious that both tensile strength and modulus of PUE thermosets at RT are enhanced with increased [H]/[E] ratio, corresponding to the decreased *M*c and CTE. And the maximum tensile strength and modulus are 32 MPa and 1.6 GPa, respectively, companying with an excellent toughness, that is, more than 7% of elongation at break. By contrast, their elongation at break drops sharply from 28% to 10% then slows down to about 7% because of the increased [H]/[E] stoichiometric ratio in PUE thermosets, indicating an improved rigidity in the thermosets with smaller *M*c and CTE.

Interestingly, Fig. 5(b) shows that the effect of the [H]/[E] stoichiometric ratio in PUE thermosets on their tensile strength and modulus at 77 K is identical to those at RT, suggesting that decreasing their *M*c and CTE by increasing the [H]/[E] ratio has positive influence on the tensile properties of PUE thermosets at RT and 77 K. It is remarkable that 105 MPa of tensile strength for PUE thermoset with [H]/[E]=1.30 at 77 K is nearly three times higher than that at RT. And this excellent tensile strength at 77 K is even comparable to some systems of nanomaterial reinforced epoxy composites [38].

Most studies have suggested that the tensile strength of epoxy resins at 77 K is higher than that at RT [39, 40]. This is because that the shrinkage of chemical bonds and molecules induced by the decline of temperature contributes to the enhancement in cohesive energy of the thermosets. Thus, larger external load will be needed to break the matrix at 77 K. However, the larger error bar values of tensile strengths at 77 K demonstrate that the cryogenic properties of PUE thermosets are more sensitive to the structural defects. Local uneven contraction and drawbacks in the matrix could have an adverse impact on the performance of the thermosets. Therefore, the thermosets present a large fluctuation in cryogenic properties.

On the other hand, the elongation at break of the cured PUEs is between 1.5~2.5% at 77 K, which is much lower than that at RT. This can be explained by the freezing of motion units in PUEs, indicating the brittle feature for PUE thermosets at 77 K in contrast to their toughness characteristic at RT. It is worth noting that their elongation at break at 77 K is gradually raised when the [H]/[E] stoichiometric ratio is below 1.0, and followed by a small fall from 2.5% to 2.0% (Fig. 5(b)) after that. As a result, optimum mechanical properties both at RT and 77 K are observed in PUE thermosets with an appropriately excessive content of curing agent.

To further explore the fracture mechanism of the PUE thermosets with different [H]/[E] ratios and network structures, morphological characteristics of the tensile specimens are discussed in detail. The crack propagation zones on the fracture surfaces of PUE thermosets with different stoichiometric ratios after tensile test at RT are shown in Fig.6. Ductile deformation of matrix and crack pining [41,42] can be seen on the surfaces of PUE thermosets with [H]/[E]=0.7 and 0.85, respectively (Fig. 6(a) and (b)). The fracture sections of thermosets with lower stoichiometric ratios are rougher than those with higher ratios, which explains the higher elongation at break of the thermosets at RT. With the increase of the [H]/[E] stoichiometric ratio, the fracture surface becomes more and more smooth. Although some deflections of the cracks can be seen in PUE surface with [H]/[E]=1.15 (Fig. 6(d)), generally main-cracks appear on the smooth surface with [H]/[E]=1.30 (Fig. 6(e)).

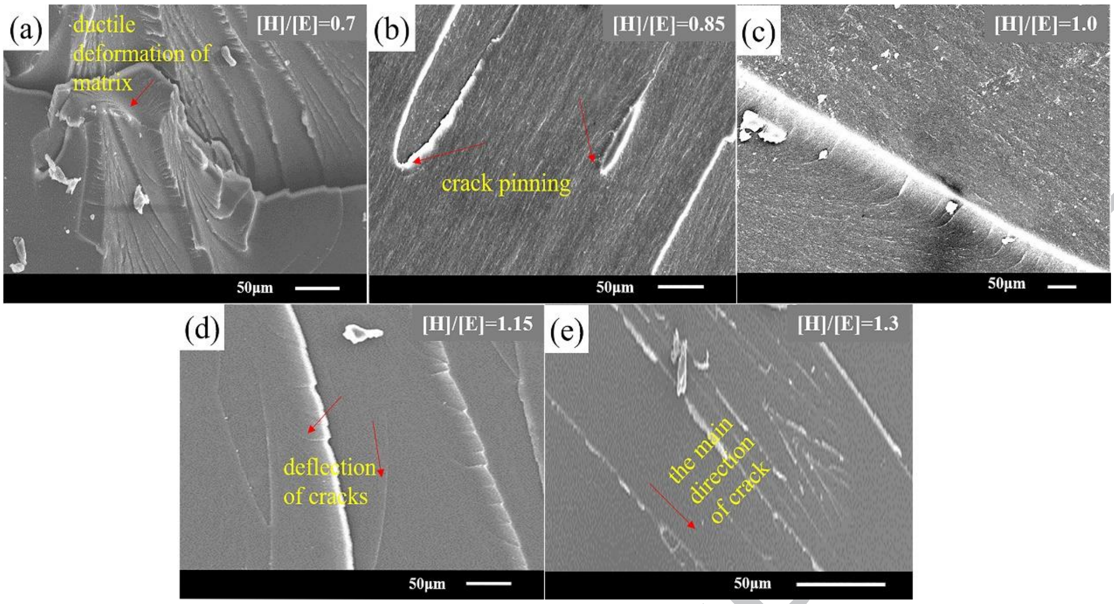

Fig.6. The propagation zones on the fracture surfaces of PUE thermosets after tensile test at RT with different [H]/[E] stoichiometric ratio=: (a) 0.7; (b) 0.85; (c) 1.0; (d) 1.15; (e) 1.3.

In contrast, Fig.7 shows the propagation zones on the fracture surfaces of the PUE thermosets with different stoichiometric ratios after tensile test at 77 K. Compared with Fig. 6(a)-(c), rougher fracture surfaces of the cryogenic specimens shown in Fig. 7(a)-(c) seem to be uncommon when the stoichiometric ratio is less than 1.0. However, this can be ascribed to the imperfect crosslinked network structure of the thermosets with the lower stoichiometric ratio. Because the cohesive energy of the thermoset at the condition is weaker than the internal stress arisen from the large contraction of the matrix and the freezing of macromolecular segments, microcracks generate in different parts of the matrix and then propagate toward various direction in the matrix under the external force [43]. With increasing the stoichiometric ratio, the crack density gradually decreases (Fig. 7(d) and (e)).

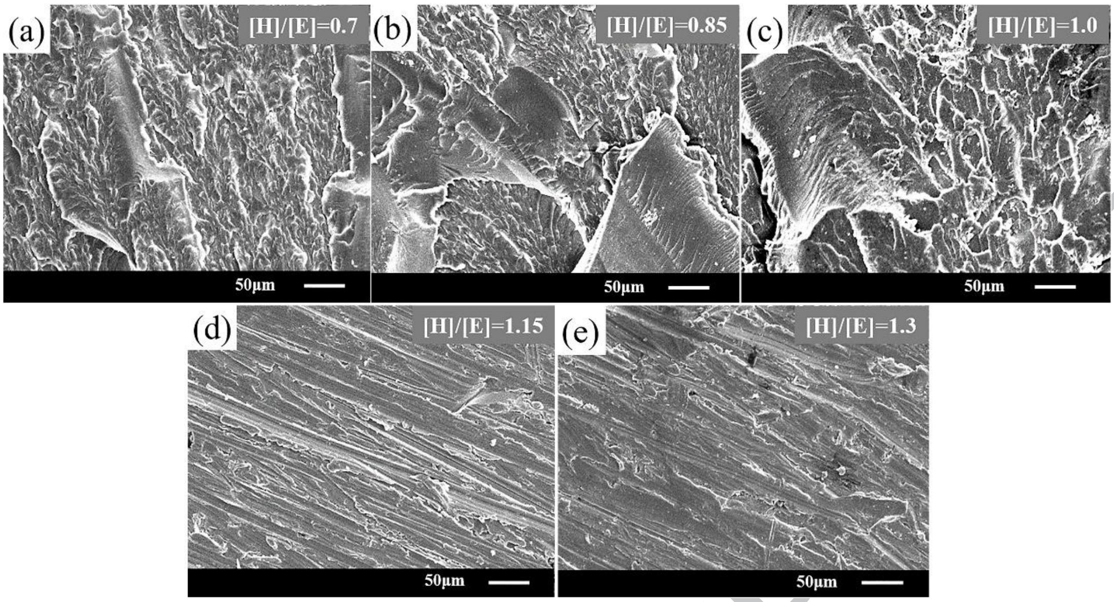

Fig.7. The crack propagation zones on the fracture surfaces of PUE thermosets after tensile test at 77 K with different [H]/[E] stoichiometric ratio=: (a) 0.7; (b) 0.85; (c) 1.0; (d) 1.15; (e) 1.3.

According to the increase of elongation at break in Fig. 5(b), the micro-crack mechanism contributes to the toughness of the thermosets. Further improvement of the crosslinked network structure is obtained with increased stoichiometric ratio in PUE thermosets, leading to the higher cohesive energy of the thermosets. And fracture occurs along the direction of the main-crack when the stoichiometric ratio reaches 1.15 (Fig. 7(d)-(e)), which is consistent with the decline of the elongation at break in Fig. 5(b). However, the tensile strength at 77 K of the thermosets with the stoichiometric ratio higher than 1.15 is not deteriorated by the increased brittleness of the matrix, which would benefit from their low CTE reduced by the higher stoichiometric ratio in PUE thermosets.

4. Conclusion

A polyurethane modified epoxy resin was cured at low temperature. Dynamic mechanical analysis and FTIR results suggested that there was a notable increase in the crosslinked network density accompanying decreased *M*c and reduced thermal expansion coefficient (CTE) when the [H]/[E] stoichiometric ratio in thermosets was increased from 0.7 and 1.3.

Meanwhile, the tensile strength and modulus of all thermosets both at room temperature (RT) and 77 K were enhanced with increased stoichiometric ratio as well, while their elongations at break decreased gradually at RT, but rised and then declined a little at 77 K. And optimum mechanical properties at RT and 77 K were observed in the low-temperature cured PUE thermosets with an appropriately excessive content of curing agent.

Further analyses of crack propagation zones on the fracture surface of PUE thermosets confirmed that, the tensile strength of the thermosets at RT was benefit from the gradually improved crosslinked network structure, while the lower CTE played a leading role in increasing the tensile strength of the thermosets with higher stoichiometric ratio at 77 K.

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Data Availability Statement

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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Highlights:

1. The relationship between the network structure and cryogenic properties is determined for a low-temperature cured polyurethane modified epoxy resin.

2. Increasing the [H]/[E] stoichiometric ratio results in decreased average molecular weight between cross-linked points, indicating an improved crosslink network structure in PUE thermosets.

3. Improved network structure of the matrix results in decreased CTE and enhanced tensile strength and modulus of the thermosets at RT and 77 K.

4. The appropriately excessive content of curing agent is necessary to get optimum mechanical properties both at RT and 77 K for low-temperature cured PUE thermosets.

Graphic Abstract: