

Effect of free volume on cryogenic mechanical properties of epoxy resin reinforced by hyperbranched polymers

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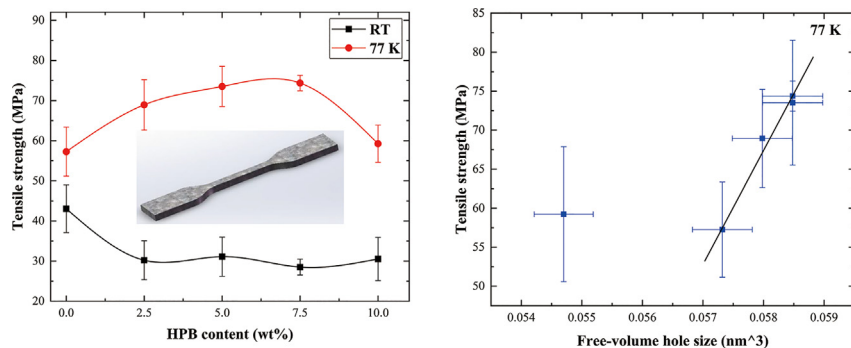
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HIGHLIGHTS

- One type of high strength hyperbranched epoxy composite was successfully fabricated.
- The positron annihilation lifetime (PAL) measurements were carried out to detect the microstructure of hyperbranched epoxy composite.
- The effect of free volume holes on mechanical properties provide valuable information for improving the cryogenic mechanical properties of epoxy resins in future.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermosetting polymer materials with excellent mechanical properties are highly promising in cryogenic engineering applications. However, the research on the toughening mechanism of thermosetting materials at cryogenic temperatures is always difficult. Herein, one type of high strength hyperbranched epoxy composite was successfully fabricated, and the correlation between microstructure (free volume) and mechanical properties of the HPB/epoxy composites was studied. To disclose the correlations between mechanical properties and microstructures for these composites, positron annihilation lifetime (PAL) measurements were carried out. Thereafter, better impact and compression properties were observed for composites with smaller free volume holes. Meanwhile, the impact and tensile properties of the composites are positively correlated with the free volume holes fraction at 77 K. The correlation between microstructure and mechanical properties provide valuable information for regulating the cryogenic mechanical properties of thermosetting materials in the future.

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1. Introduction

Epoxy resins have been widely used in many applications, owing to their good electrical insulation properties, great thermal properties, low

shrinkage during curing, and excellent processability [1–8]. In the cryogenic engineering fields, with the rapid development of aerospace, superconducting technology, and large cryogenic engineering projects, epoxy resins, and their composite materials are also increasingly used as impregnating materials or adhesives [9,10]. However, the engineering application of epoxy resins is generally limited by their poor fracture toughness and brittleness problem at cryogenic temperatures [11–15]. Therefore, the improvement of cryogenic mechanical properties of epoxy resin is desirable for its application in cryogenic engineering.

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The introduction of toughening agents into epoxy networks is the most common and effective method for toughening brittle epoxy resins. Toughening agents, such as rigid inorganic particles [16–18], rubber elastomers [19,20], and polyetherimide [21], etc., have been reported to improve the mechanical properties of epoxy resins. However, most investigations have focused on the properties of epoxy resins at room temperature (RT), and few studies have been done at cryogenic temperatures. Moreover, the toughening mechanism of epoxy resin at RT is different from that at low temperature, so the toughening method of epoxy resin at RT cannot be simply transferred to the cryogenic condition. For example, the method of rubber toughening can enhance the mechanical properties of epoxy resin at RT, but it caused a significant decrease in modulus and tensile properties at cryogenic temperatures [22]. For low-temperature systems, Ueki et al. found that priority should be given to network structure to improve cryogenic mechanical properties [23]. For the crosslinking network of epoxy resins, Nishijima et al. explained the cryogenic toughening mechanism by using the concept of free volume (intramolecular hole) in epoxy resin network. At cryogenic temperatures, the free volume still exists, which relaxes the internal stress of epoxy resin, consequently lead to an increase in the mechanical properties of epoxy resin [24,25]. In addition, flexible groups are also considered to contribute to improving mechanical properties at low temperatures. Guo et al. used flexible polymers (D-230 and D-400) to modify the impact properties of the brittle resins at cryogenic temperatures [26].

Hyperbranched polymer (HPB), a novel and interesting polymer with both network structure and flexible chains, has been explored [27–29]. Firstly, it has a unique structure and exhibits lower viscosities than the linear polymer of the same molar mass and non-entangled architecture. Secondly, a significant advantage of hyperbranched polymers is the high-density terminal groups. A large number of terminal groups can promote further modification and enhance the interaction with the target polymer through hydrogen or covalent bonds. For example, the hydroxyl groups can react with curing agents, so the cured epoxy system can be adjusted by adding hydroxy-terminated hyperbranched polymers [30]. Previous studies have been shown that hyperbranched polymers can effectively improve the mechanical properties of epoxy resins at RT. To our best knowledge, the research on the cryogenic mechanical properties and the exploration of the molecular internal microstructure of the hyperbranched polymer-modified epoxy resin is rarely reported.

Herein, we present an effective route to hydroxy-terminated hyperbranched polyester HPB modified epoxy resin at both RT and cryogenic temperatures. An effective mechanical properties enhancement is achieved. The tensile strength, impact strength, and compression strength of the HPB/epoxy composites at RT and 77 K were studied. The fracture morphology of the HPB/epoxy composites was observed by scanning electron microscopy (SEM). Moreover, the positron annihilation lifetime (PAL) spectroscopy was carried out to study the microstructural properties of the HPB/epoxy composites, reveal the correlations between the free volume holes in the HPB/epoxy composites and mechanical parameters at both RT and 77 K.

2. Materials and methods

2.1. Materials

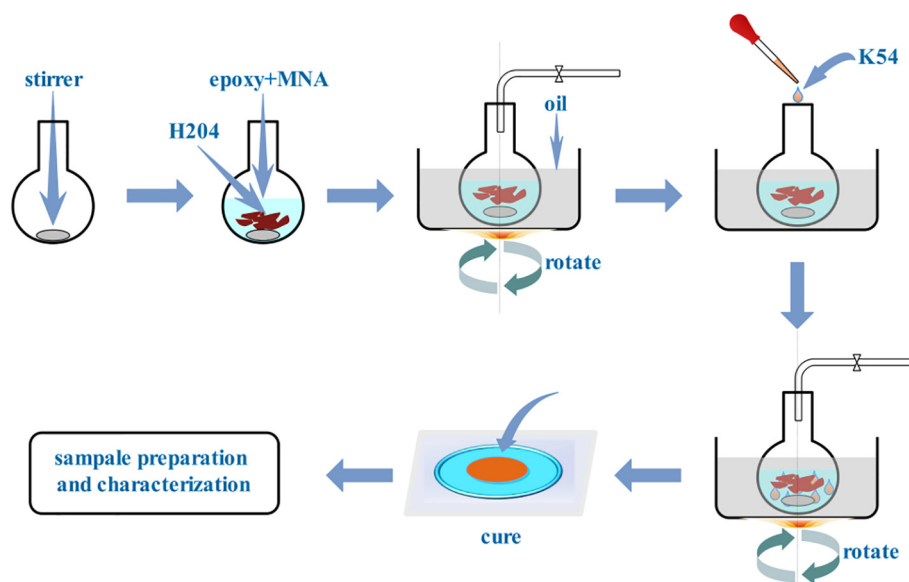
The epoxy resin was DGEBA (DER332) from Shanghai King Chemical, China. The curing agent was methyl nadic anhydride MNA from Shanghai Macklin Biochemical Co., Ltd., China. The accelerator was K54 from Changzhou Mingyao Chemical New Material Co. Ltd., China. The hyperbranched polymer was polyester H204 from Wuhan Hyperbranched Polymers Science & Technology Co. Ltd., China. HPB is a fourth-generation hydroxy-terminated hyperbranched polyester with a hydroxyl number of 40–45 /mol, a molecular weight of 5400 g/mol.

2.2. Preparation of samples

Scheme 1 indicates the preparation process of HPB/epoxy composites. Firstly, the H204 was added to the DER332/MNA mixture. The mixture was stirred at 120 °C for 2 h. The content of H204 in the mixture varied from zero to 10% in weight. The accelerator K54 (1 wt%) was added to the H204/epoxy mixtures. After the bubbles are completely removed by vacuum rotary pump, the mixture was poured into the preheated mold at 85 °C, and then cured at 80 °C for 16 h, 100 °C for 4 h, and post-cured at 125 °C for 6 h.

2.3. Mechanical properties characterizations

The mechanical measurements of the HPB/epoxy composites at RT (25 °C) and 77 K were taken on an RGT-20A Reger Mechanical Tester



Scheme 1. The preparation process of HPB/epoxy composites.

with a 2 mm/min crosshead speed. Tensile samples are dumbbell-shaped samples, and the test section size is 4 mm × 10 mm × 50 mm. The size of the impact sample and compression sample are 4 mm × 10 mm × 80 mm, 10 mm × 10 mm × 20 mm, respectively. Schematic diagram of the sample is shown in Fig. S1. During the temperature tensile test of liquid nitrogen, the material low-temperature mechanical testing device designed by our research group was used to completely immerse the sample and low-temperature tensile fixture in liquid nitrogen for 20 min for testing, and the sample was kept completely immersed in liquid nitrogen during the whole testing process. At least five samples of each component were measured.

The fracture morphology of the HPB/epoxy composites was taken by S-4800 Scanning electron microscopy (SEM) of HITACHI (Japan), with samples prepared by spraying coated with a gold layer. Fourier transforms infrared (FTIR) spectroscopy was carried out on HPB/epoxy composites.

2.4. Positron annihilation lifetime measurements

The positron annihilation lifetime (PAL) spectra of samples were collected at both RT and 77 ± 0.1 K by a fast-fast coincidence PAL spectrometer (time resolution in FWHM of ~210 ps, determined by analyzing the PAL spectra of some reference samples including yttria-stabilized ZrO (YSZ) and GaN) at USTC. The positron source (²²NaCl, 30 μCi, sealed between two polyimide Kapton foils in the size of 10 × 10 × 0.0075 mm) was sandwiched between two identical samples (10 × 10 × 1 mm). The sample-source-sample set was placed in a vacuum chamber (vacuum better than 10⁻³ Pa) which was evacuated by a turbo molecular pump and a scroll pump. For the low temperature measurements, the samples were cooled down from RT to 77 K in 30 min by a closed-cycle helium cryostat (cooling head model DE-204S, temperature controller model Lakeshore 335, Advanced Research Systems Inc.). The two PAL detectors were perpendicularly placed to reduce the backscattering of γ-rays. The distance between the sample-source-sample set and each lifetime detector was around 20 mm. The PAL spectrum was collected for 8192 channels with a channel width of 6.58 ps/channel. Each PAL spectrum was collected to the total counts of 4 × 10⁶ in less than 2 h at a counting rate of around 600 counts/s. The source correction (positron annihilation in ²²NaCl and two polyimide Kapton supporting foils) was determined by the measurement of two identical YSZ samples in the size of 10 × 10 × 1 mm.

3. Results and discussion

3.1. Mechanical properties

The mechanical properties of the HPB/epoxy composites with different HPB contents were measured as shown in Fig. 1. In Fig. 1a, the results show that the tensile strength at 77 K is higher than that at RT. Moreover, the dependence of tensile strength on HPB content is completely different at RT and 77 K. At RT, the tensile strength decreased from 43.04 MPa to 30.21 MPa at the addition of 2.5 wt% HPB. And when the content of HPB exceeds 2.5 wt%, the tensile strength at RT remains unchanged. This might mainly due to the following factors. The hydrogen bonds would improve the tensile strength at RT of the HPB/epoxy composites, and the introduction of flexible ester groups of HPB in the brittle epoxy resin can reduce the residual internal stress would enhance the tensile strength [26]. However, too many flexible polymer chains in the molecular structure of HPB would reduce the rigidity of the polymer, which reduces the tensile strength. This is consistent with previous studies [31,32].

In addition, the free volume introduction of HPB would reduce the crosslinking density of HPB/epoxy composites [33,34], which reduces the tensile strength at RT [35]. As a result, the positive contribution of positive factors to tensile strength is greater than that of negative factors. Therefore, when 2.5 wt% HPB is introduced, the tensile strength

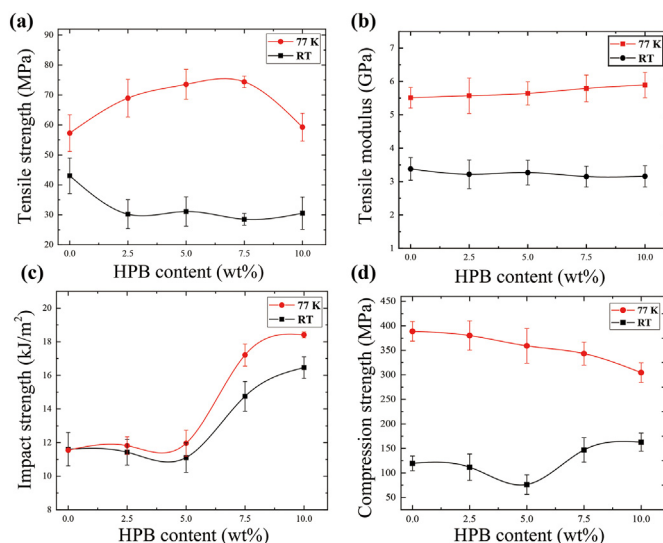


Fig. 1. Variation of (a) tensile strength, (b) tensile modulus, (c) impact strength, and (d) compression strength of HPB/epoxy composites at RT and 77 K.

decreases, which is consistent with the previous report [35]. As the HPB continued to increase to more than 2.5 wt%, the positive contribution to tensile strength just offsets the negative contribution.

At 77 K, the tensile strength increases with the increase of HPB content. When the content of HPB is 7.5 wt%, the tensile strength of the modified system reaches the maximum value of 74.37 MPa, which is 29.9% higher than that of pure epoxy resin. At 77 K, the free volume of hyperbranched HPB in the composite decreases due to thermal shrinkage, but it still exists (Fig. 2) [24,25], making the intermolecular force stronger and the tensile strength higher than that of RT. And the bond length is shorter and the hydrogen bond becomes stronger due to thermal contraction shrinkage [36], which would enhance the tensile strength. Moreover, the residual stress of high temperature cured epoxy resin is caused by the volume shrinkage from curing temperature to RT [37]. At cryogenic temperatures, because of thermal shrinkage, the internal stress becomes more severe [23,38]. The internal stress in epoxy resin will produce microcracks and holes, which greatly influence the properties of epoxy resin. But, the introduction of flexible sections to epoxy resin can obviously reduce the internal stress [26,37,39]. Therefore, the addition of an appropriate amount of HPB can improve the tensile strength at cryogenic temperatures. A similar observation has been reported in previous studies [26]. When the content of HPB increased more, the tensile strength at 77 K decreased, which is similar to the situation at RT.

Fig. 1b presents the tensile modulus of the HPB/epoxy composites. The tensile modulus does not change with concentration apparently at RT. However, the cryogenic modulus is higher than that at RT. This might be due to the increase of the tensile modulus due to the higher intermolecular adhesion at 77 K than that at RT. It is similar to previous studies [40].

Fig. 1c plots the impact strength of the HPB/epoxy composites. It can be seen that the content of HPB has different effects on the impact strength of HPB/epoxy composites at RT and 77 K. Comparing with pure epoxy resin, the impact strength at RT and 77 K increased by 41.8% and 59.4%, respectively.

Moreover, the cryogenic impact strength of epoxy resin is generally lower than that at RT, because epoxy resin usually becomes more brittle at low temperature [26]. However, the higher cryogenic impact strength has been observed for HPB/epoxy composites. At RT, the flexible group (ester group) of HPB dissipates the impact energy through the segment movement on the molecular chain, improving the impact strength at RT [26,41]. The free volume can also dissipate energy through its deformation and provide space for the molecular chain to move in the process of

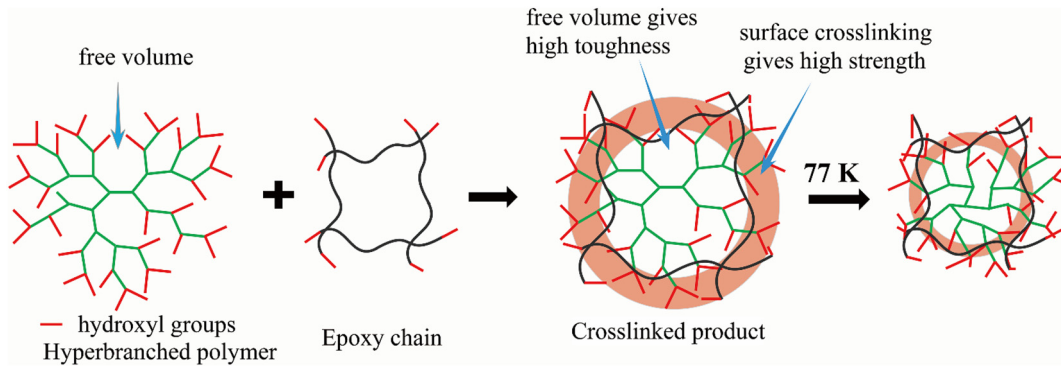


Fig. 2. Schematic of hyperbranched polymer toughened epoxy at cryogenic temperatures.

impact [24,25]. Thus, as the content of HPB reaches a certain level, the impact strength of cured epoxy resin increases at RT.

At 77 K, the flexible ester group in HPB is not frozen completely [24,25], the impact energy can still be consumed by segmental movement, and the smaller free volume still exists at 77 K [24,25], which can still absorb much energy. Both of these factors will increase the cryogenic impact strength of the HPB/epoxy composites. The free volume still exists at 77 K, only became smaller (in Fig. 2). Hence the cohesive strength of the molecule does not increase too much, and the out-of-plane vibration of the chemical bond still exists, not completely frozen. Then the hydrogen bonds and chemical-bonds would become shorter and stronger [36]. The glass transition temperature (T_g) (Fig. S2) of the HPB/epoxy composites increases with the increase of HPB content. Moreover, through the infrared spectrum analysis (Fig. S3), with the increase of the amount of hyperbranched polymer added, the infrared characteristic absorption peak strength of hydrogen bond at 3500 cm^{-1} increased. Further elucidated with the addition of hyperbranched polymers, the free volume in the hyperbranched structure will replace the original free volume in the epoxy resin network, resulting in a decline in the cross-linking density.

As shown in Fig. 1d, when the content of HPB increased to 2.5 wt%, the compression strength at RT does not change much. With the increase of HPB content to 5 wt%, the compression strength decreased obviously. At the addition of 7.5 wt% and 10 wt% HPB, the compression strength gradually increased. It is striking to note that, the compression strength at 77 K is a completely different change from that at RT. The compression strength decreased gradually with the addition of HPB. In addition, it can be found in Fig. 1d that the compression strength of HPB/epoxy composites at 77 K is higher than that at RT.

The compression strength of HPB/epoxy composites is mainly affected by the free volume inside the molecules. At RT, the addition of 5 wt% HPB resulted in the introduction of free volume into the epoxy resins (in Fig. 4d), thus increasing the range of motion of the molecular chains. When the sample is compressed, it is more likely to break, which leads to the reduction of compression strength. As the content of HPB

increased to 7.5 wt% and 10 wt%, the crosslinking density of the molecular chains increases, and then intermolecular distance decreased, the size of free volume in the system decreased (in Fig. 4c), leading to the enhancement of compression strength.

At 77 K, on the one hand, as the temperature decreases, the free volume don't disappear, but became smaller (in Fig. 2), which is consistent with Fig. 4c, lead to the increase of compression strength. However, the cryogenic temperatures would also freeze the molecular chains, and the activity of the molecular chains would be greatly reduced. At this time, the existence of free volume would have a negative impact on compression strength. Also, like impact strength and tensile strength, the intermolecular forces of epoxy resins are enhanced at cryogenic temperatures, so they have higher compression strength at 77 K than at RT.

To better understand the role of HPB modification, the scanning electron micrograph of fracture surface at RT and 77 K is shown in Fig. 3. Overall, the fracture surface of the sample reinforced with HPB is rougher than that of pure epoxy resin, which is due to the increase of toughness of the sample. The smooth and glassy surfaces as shown in Fig. 3a and b, and the crack is single and grows in a straight line, which is substantial evidence of brittle failure.

In comparison, the fracture surfaces for the HPB/epoxy composites with 2.5–10 wt% of HPB from Fig. 3c to 3j were different from the pure epoxy. The fracture surface of HPB/epoxy composite presents multi-plane characteristics and bending cracks appear. This indicates that the deflection of the crack front edge is caused by the addition of HPB. The process of crack deformation will cause out of plane load, produce a new fracture surface, and increase the strain energy required for crack propagation. Moreover, no second phase was observed from Fig. 3, which indicates that HPB/epoxy composites are homogeneous.

3.2. PAL measurements

The nano-scaled free volume holes are difficult to characterize with traditional experimental techniques, and positron annihilation spectroscopy has been regarded as an effective method for studying free

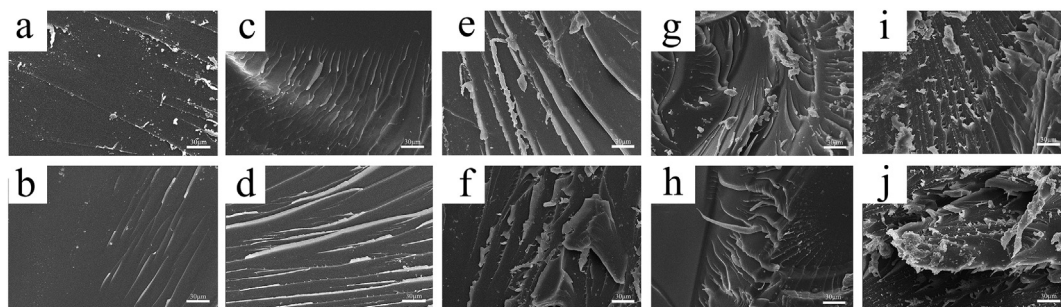


Fig. 3. SEM micrographs of fracture surfaces after impact testing with different HPB contents of (a) 0 wt%, RT. (b) 0 wt%, 77 K. (c) 2.5 wt%, RT. (d) 2.5 wt%, 77 K. (e) 5 wt%, RT. (f) 5 wt%, 77 K. (g) 7.5 wt%, RT. (h) 7.5 wt%, 77 K. (i) 10 wt%, RT. (j) 10 wt%, 77 K.

volume holes in polymers [42,43]. In polymers, positrons can capture electrons before electron annihilation, forming a hydrogen-like bound state, positronium (Ps). A Ps atom can only exist in the spin state p-Ps or o-Ps. The size and proportion of the free volume (the holes between polymer chains) determine the formation and annihilation of o-Ps atoms [43].

In this study, all the PAL spectra at both RT and 77 K were resolved into three components by the PATFIT-88 program [44]. The longest lifetime (τ_3) among the three-lifetime components corresponds to the pick-off annihilation of o-Ps in the free volume holes [43,45,46]. Using the Tao-Eldrup model [45,47], the average radius (R) of free-volume holes could be calculated:

$$\tau_3^{-1} = 2 \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \left(2\pi \frac{R}{R + \Delta R} \right) \right] \quad (1)$$

where ΔR is the thickness (empirical value of 0.1656 nm) of the electron layer, which is on the surface of free volume. The average size (V_f) of free-volume holes could be calculated from

$$V_f = 4\pi R^3 / 3 \quad (2)$$

The relative fractional free volume f_r (in %) is defined as:

$$f_r = V_f I_3 \quad (3)$$

where I_3 is o-Ps intensity (in %).

Fig. 4 presents the PAL measured results for the o-Ps lifetime τ_3 , o-Ps intensity I_3 , free volume hole size, and relative fractional free volume as a function of HPB content. It can be seen from Fig. 4c that the free volume hole size of pure epoxy resin is higher than those of the HPB/epoxy composites at RT. With the addition of HPB, the hole size of free volume decreases gradually (in Fig. 4c), but the relative fractional free volume increases (in Fig. 4d). But at 77 K, it can be seen from Fig. 4 that the free volume hole size, o-Ps lifetime τ_3 , o-Ps intensity, and relative fractional free volume all show a trend of first increasing and then decreasing, and they all reached their maximum values at the HPB content of 7.5 wt%. When the temperature is lowered, part of the free volume originally present in the pure epoxy resin will disappear due to thermal expansion. With the addition of hyperbranched polymer HPB to 10 wt%, the size of free volume decreases, and the distribution concentration of free volume increases instead, indicating that the free volume is introduced by HPB into epoxy resin does not disappear with the decrease of temperature. Moreover, through the infrared spectrum

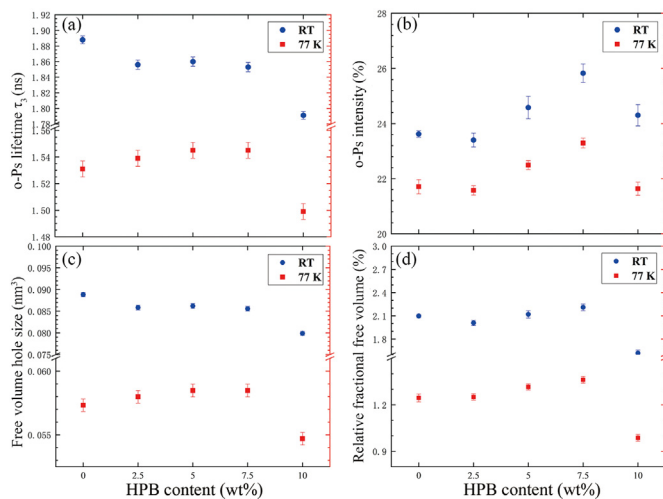


Fig. 4. HPB content dependences of (a) o-Ps lifetime τ_3 , (b) o-Ps intensity, (c) free volume hole size, and (d) relative fractional free volume.

analysis (Fig. S3), with the increase of the amount of HPB added, the infrared characteristic absorption peak strength of hydrogen bond at 3500 cm^{-1} increased. Further elucidated with the addition of HPB, the free volume in the hyperbranched structure will replace the original free volume in the epoxy resin network, resulting in a decline in the cross-linking density. Comparing RT and 77 K, it is obvious that the free volume hole becomes smaller at 77 K. Meanwhile, in Fig. 4b, o-Ps intensity (I_3) gradually increases with the increase of HPB content, and begins to decrease with the addition of HPB reaching 10 wt%. This may be due to the increase in the concentration of free volume due to the introduction of HPB in the epoxy resin, resulting in an increase in I_3 . However, when the content of HPB is 10 wt%, part of the free volume may disappear due to the introduction of excessive HPB, leading to the decrease of I_3 . In addition, I_3 is significantly lower at low temperature than at RT, which may be because the sample temperature decrease weakens the cross-linking of the three-dimensional network [48].

The variations of impact, compression, and tensile properties at both RT and 77 K as functions of free volume hole size are shown in Fig. 5, to understand better the relationship between the microstructure and the mechanical properties of HPB/epoxy composites. From Fig. 5a, we can see that there is a negative correlation between the impact strength at RT and the free volume hole size. At 77 K, there is a positive correlation between the impact strength and the free volume hole size. In Fig. 5, we can find a strange point (the black point) that does not correlate with mechanical properties. As shown in Fig. 4c, this point is the

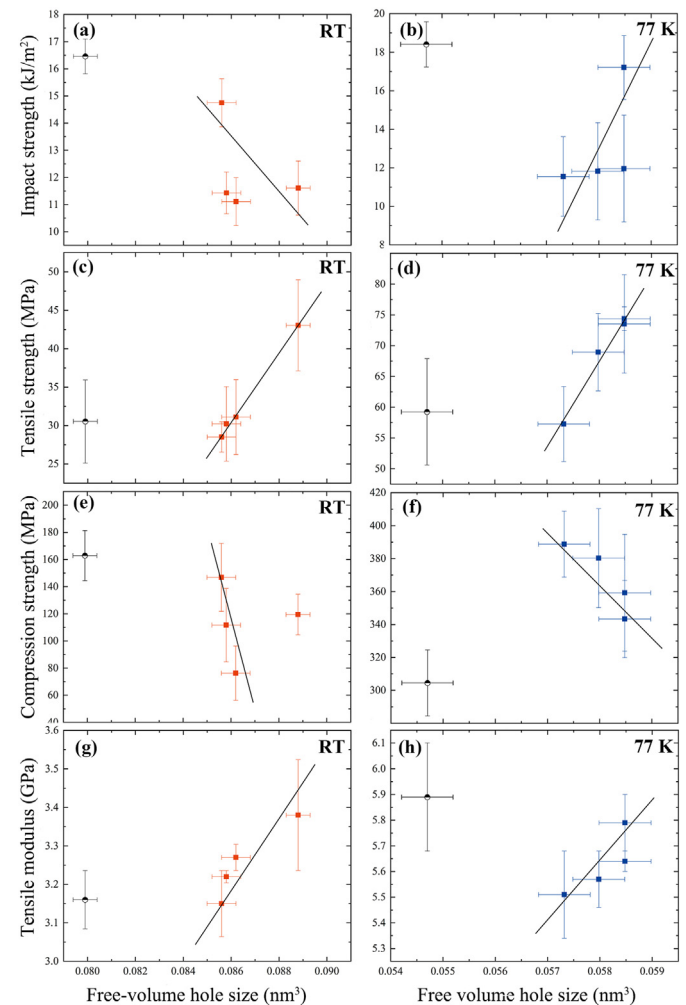


Fig. 5. Effect of free volume hole size (V_f) on impact strength, tensile strength, compression strength, and tensile modulus at both RT and 77 K. The black lines are to guide the eyes.

HPB/epoxy composites with 10 wt% HPB. This may be because with the addition of too much HPB, the molecular chains squeeze each other, making the size of the existing free volume smaller. As a result, the effect of free volume holes on mechanical properties was suddenly changed. In Fig. 5c and d, there is a positive correlation between the tensile strength and the size of the free volume hole at RT and 77 K. Similarly, there is also a positive correlation between the tensile modulus and the size of the free volume hole at RT and 77 K (in Fig. 5g and h). But for the compression strength, whether it is at RT or 77 K, there is a negative correlation between the compression strength and the size of the free volume hole (in Fig. 5e and f). That is because the larger size of the free volume hole, the internal micro-cracks are more likely to occur during compressing.

In addition, Fig. 6 shows the relationship between impact, compression, and tensile properties and the relative fraction of the free volume at RT and 77 K. It is obvious that the relationship between the mechanical properties and the relative fractional free volume is completely different at RT and 77 K. Similarly, it can be found in Fig. 6 that when the addition amount of HPB is 10 wt%, the correlation between free volume distribution and mechanical strength changes. There is no clear correlation between mechanical properties and the relative fractional free volume at RT. At 77 K, the impact strength, tensile strength, and tensile modulus are positively correlated with the relative fraction of free volume, while the compression strength was negatively correlated with

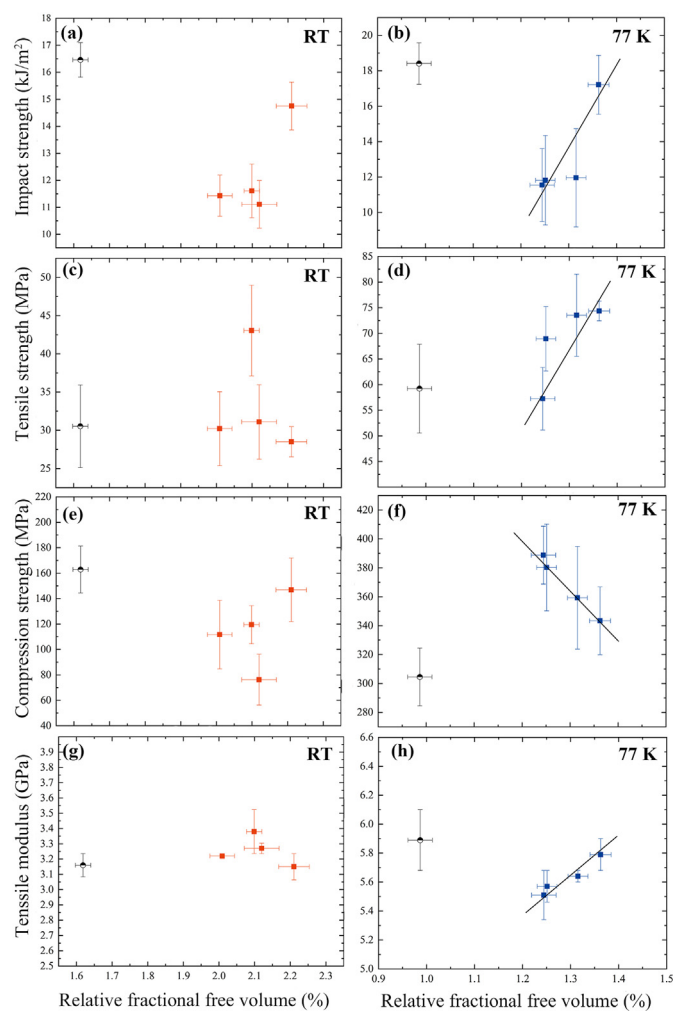


Fig. 6. Effect of relative fractional free volume on impact strength, tensile strength, compression strength, and tensile modulus at both RT and 77 K. The black lines are to guide the eyes.

the relative fractional free volume. Therefore, we can know that increase the relative fraction of the free volume is beneficial to improve the impact and tensile properties of the HPB/epoxy composites. This is also consistent with our assumption of the cryogenic mechanical properties of toughened epoxy resins using hyperbranched polymers.

4. Conclusions

In summary, this study demonstrated an effective approach to enhance the cryogenic mechanical properties of epoxy composites filled with hydroxy-terminated hyperbranched polyester HPB. The mechanical properties of the HPB/epoxy composite were significantly higher at 77 K compared with that at RT. The composites with the addition of 7.5 wt% HPB exhibited enhancements of ultimate tensile strength at 77 K. And the maximum cryogenic impact strength is obtained for the composites with 10 wt% HPB. And the SEM image of the fracture surfaces the HPB/epoxy composites results further demonstrated the effect of HPB on the impact strength of epoxy resin. In addition, the PAL measurements were carried out to explain the free volume size and fraction in composites and their effects on mechanical properties at RT and 77 K. This work reveals the correlation between the mechanical properties of epoxy resin and their microstructure, providing a direction for further improvement of the mechanical properties of epoxy resins. Moreover, the data at 77 K provide valuable information for improving the cryogenic mechanical properties of epoxy resins for cryogenic engineering applications in the future.

Data availability

All data in this study are available upon request by contact with the corresponding author.

Author contribution

Conceptualization: Yalin Zhao, Rongjin Huang, Hongjun Zhang.
Investigation: Yalin Zhao, Zhengrong Zhou.
Formal analysis: Yalin Zhao, Zhixiong Wu, Hua Zhang, Laifeng Li.
Software: Yun Dong, Mi Luo, Bangjiao Ye, Hongjun Zhang.
Writing - original draft: Yalin Zhao, Rongjin Huang, Hongjun Zhang.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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