

## Simultaneous improvements in the cryogenic tensile strength, ductility and impact strength of epoxy resins by a hyperbranched polymer

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### ABSTRACT

Improvements in mechanical properties at low temperatures are desirable for epoxy resins such as diglycidyl ether of bisphenol A (DGEBA) that are often used in cryogenic engineering applications. In this study, a hydroxyl functionalized hyperbranched polymer (H30) is employed to improve the mechanical properties of a DGEBA epoxy resin at liquid nitrogen temperature (77 K). The results show that the tensile strength, failure strain (ductility) and impact strength at 77 K are simultaneously improved by adding a proper content of H30. The maximum tensile strength at 77 K is increased by 17.7% from 98.2 MPa of pure epoxy resin to 115.6 MPa of modified epoxy system for the 10 wt% H30 content. The failure strain at 77 K increases consistently with the increase of H30 content. The maximum impact strength at 77 K is attained by introduction of 10 wt% H30 with an improvement of 26.3% over that of pure epoxy resin. For the purpose of comparison, the mechanical properties of modified epoxy resins at room temperature (RT) are also investigated. It is interesting to note that the impact strength is not lower at 77 K than that at RT for the modified systems. Moreover, the glass transition temperature ( $T_g$ ) is not reduced by the addition of H30 in appropriate amounts.

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### 1. Introduction

Thermosetting epoxy resins have wide applications in coatings, adhesives, electrical laminates and structural components [1–4]. With the rapid development of spacecraft and superconductive technologies, epoxy resins and their composites are increasingly applied in the cryogenic engineering fields [5–7]. However, the use of thermosetting epoxy resins is often limited owing to their brittleness (insufficient toughness) problem [8]. This problem becomes more severe when the thermosetting epoxy resins are employed in extremely low temperature environments (e.g. liquid nitrogen medium (77 K), etc.) [6,9,10]. When the temperature is decreased down to cryogenic temperature, micro-cracking of the epoxy matrix in a fiber-reinforced composite would take place since the internal stresses are generated as a result of the unequal coefficients of thermal expansion between the fibers and the matrix [11]. Sometimes even fracture of the epoxy resin can happen if the thermal-stress induced stress intensity factor exceeds the fracture toughness of the epoxy resin [6]. Therefore, improvement of the

mechanical properties including strength, ductility and toughness or impact strength of epoxy resins at low temperatures is desirable in development of high performance thermosetting epoxy resins for cryogenic engineering applications.

In order to develop high performance epoxy resins for cryogenic engineering applications, the cryogenic mechanical properties of epoxy resins have been extensively investigated [6,7,12–16]. Ueki et al. [6] reported that the control of the chemical and network structures is very important to optimize epoxy systems for cryogenic engineering applications and they found that the network structure should be given priority over the chemical structure in improving the fracture toughness at cryogenic temperature. Nishijima et al. [7,17] used free space defined as the unoccupied space within the molecules and free volume defined as the unoccupied space between molecules in three-dimensional epoxy networks to explain the toughening mechanism at cryogenic condition. They proposed that the unoccupied spaces would still be present at cryogenic temperature and thus relax stresses within the epoxy resins, consequently leading to the increase in the fracture toughness of cured epoxy resins. Sawa et al. [16] mixed two types of epoxy resins with different numbers of epoxy groups, namely they used multifunctional epoxy tetraglycidyl-*meta*-xylenediamine (TGMXDA) as a modifier to improve the fracture toughness of diglycidyl ether of bisphenol A (DGEBA) resin system at cryogenic temperature. Their results suggested

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that epoxies with larger molecular weights between cross-linkings relaxed stress at the crack tip at cryogenic temperature; intermolecular forces and stress relaxation at the crack tip were found to be important for high fracture toughness. Moreover, long chain aliphatic resin [12], polyurethane–epoxy [13], flexible diamines (D-230 and D-400) [14] and poly(ethersulfone) [15] were also reported to modify the cryogenic impact behavior of the brittle epoxy resins. Flexible chains or groups were regarded to contribute to the increase in the cryogenic impact strength.

Hyperbranched polymers (H30, see Fig. 1) called dendrimers have been explored as a novel and intriguing new class of modifiers for brittle epoxy resins [18–20]. It has been shown that hyperbranched polymers can effectively improve the mechanical properties (such as tensile strength, flexural and impact strength) of epoxy resins at room temperature (RT) [8,21–23]. In comparison with linear polymers, H30 possesses high density hydroxyls grafted on the shell of its molecules. The hydroxyls can react with the curing agent and hence the network structure of the cured epoxy systems can be tailored [24,25]. It was reported that epoxies of three-dimensional networks contain a plenty of unoccupied spaces in the networks and they would still exist at cryogenic temperature [7,17]. The unoccupied spaces in the cured networks will increase due to the introduction of H30 as shown in Fig. 2. On the other hand, the flexible polymer chains of H30

could contribute to improvement of the toughness or impact strength of cured epoxy resins. Thus, it can be expected that introduction of H30 to epoxy resins can also improve the mechanical properties at low temperatures. Another advantage of H30 is its lower viscosity and hence better processability at a given molecular weight compared to the linear analogue due to its highly branched architecture and spherical nature, namely there is a lack of chain entanglements between molecules [26].

However, to our best knowledge, no work has been reported on the mechanical properties at cryogenic temperatures of epoxy resins modified by hyperbranched polymers. DGEBA has been frequently used in cryogenic engineering applications [6,13,14]. Therefore, in this work, the cryogenic mechanical behaviors at 77 K of methyltetrahydrophthalic anhydride (MeTHPA) cured DGEBA modified by H30 are reported in terms of the tensile and impact properties. The mechanical properties at RT were also investigated for the purpose of comparison. Interestingly, it was observed that the impact strength is not lower at 77 K than that at RT for the modified systems though the cryogenic impact strength is generally lower than that at RT since epoxy resins are normally more brittle at cryogenic temperature than at RT [12–15]. Moreover, the glass transition temperature ( $T_g$ ) as a function of H30 content was examined by DSC analysis.

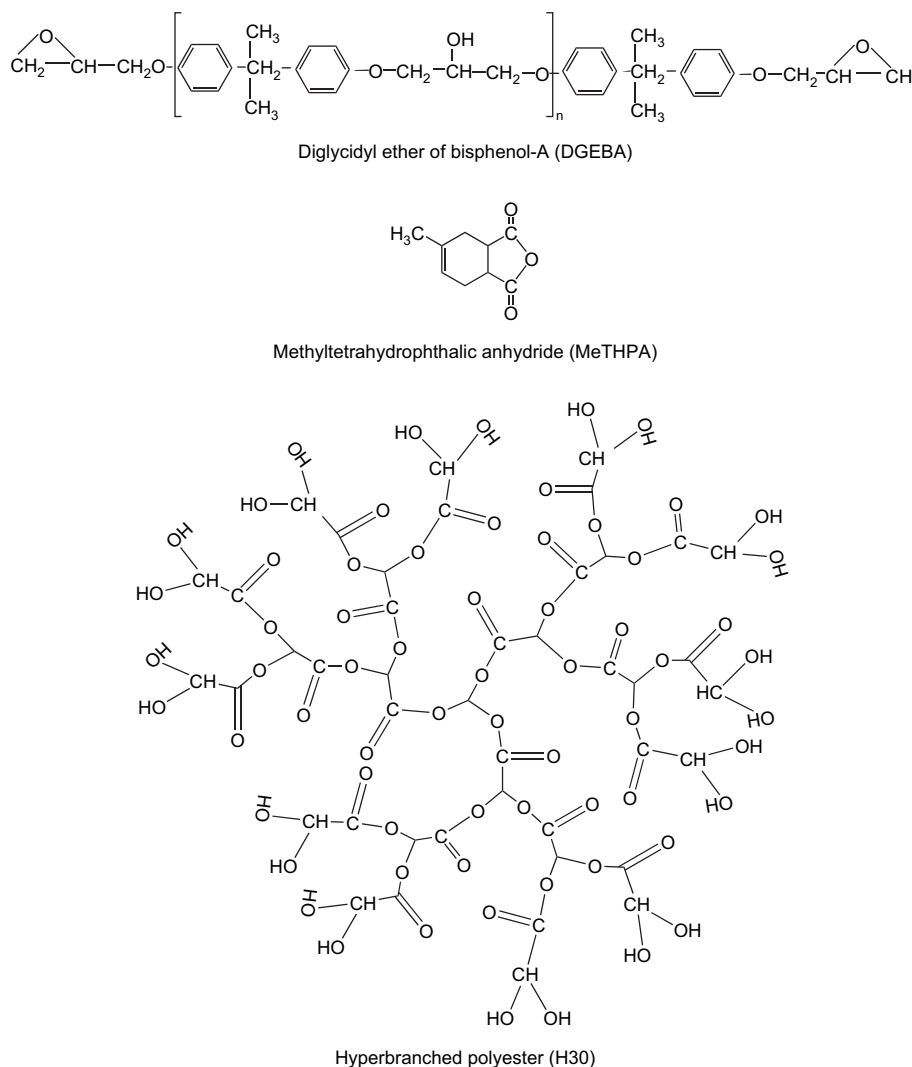


Fig. 1. Chemical structures of epoxy resin (DGEBA), curing agent (MeTHPA) and hyperbranched polyester (H30).

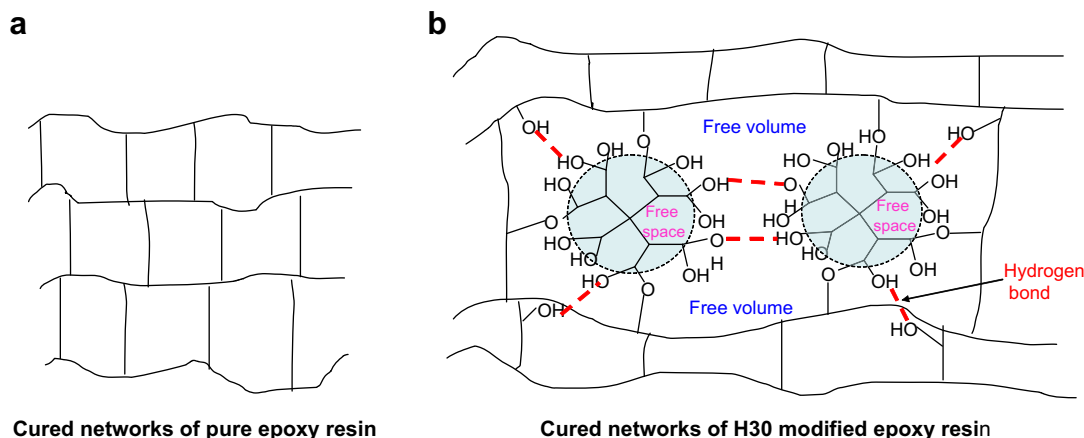


Fig. 2. Schematic illustration of (a) pure epoxy networks and (b) hydrogen bonds, free space and free volume in H30-modified epoxy networks.

## 2. Experimental

### 2.1. Materials

The epoxy resin used was a bisphenol A diglycidyl ether CYD-128 with an epoxy equivalent of 184–194 from Yueyang Refinery Plant, China. The curing agent was methyltetrahydrophthalic anhydride from Shanghai Li Yi Sci. and Technol. Development Co. Ltd, China. The accelerator was benzyl dimethylamine (BDMA) from Shijiazhuang Wells Electronic Material Co. Ltd, China. The hyperbranched polymer (HBP) used in this work was polyester Boltorn H30 kindly donated by Perstorp Speciality Chemicals. Boltorn H30 is a third-generation hyperbranched polyester with 32 primary hydroxyl groups on the shell and it is an amorphous solid at RT. The chemical structures of epoxy resin, curing agent and hyperbranched polyester (H30) are shown in Fig. 1.

### 2.2. Preparation of samples

The solution of H30 in acetone (2 ml/g) was firstly mixed with the epoxy resin and the mixture was stirred and heated at 60 °C for 2 h until a homogenous mixture was observed. Most of the acetone was evaporated when the mixing progresses. The H30 content in the blended mixtures varied from 0 to 15% in weight. A stoichiometric amount of curing agent was added to the H30/epoxy mixtures at 60 °C, which was then degassed under vacuum for 30 min. A homogenous solution was obtained, and cast in a preheated steel mold at 80 °C, then cured at 130 °C for 3 h, 150 °C for 10 h, and post-cured at 170 °C for 5 h.

### 2.3. Characterization

#### 2.3.1. Mechanical testing

The tensile samples were prepared according to the recommendation of ASTM D638-96. The tensile properties of the cured specimens at RT and 77 K were measured by an RGT-20A Reger Mechanical Tester using a 10 kN load cell with a crosshead speed of 2 mm/min. The cryogenic temperature condition was achieved by dipping clamps and samples in a liquid nitrogen filled cryostat designed in our laboratory. The entire test was conducted while the specimen and its loading fixture were submerged in liquid nitrogen. A schematic diagram of the loading fixture is shown in Fig. 3 [27].

The impact strength of the cured specimens was measured with a REGER Impact Tester according to ASTM D-256. The impact specimens were prepared with the size of 4 mm (thickness) × 10 mm (width) × 80 mm (length). Impact testing at 77 K was performed

with the specimens dipped in a liquid nitrogen filled cryostat for over 10 min, and it was quickly completed within a couple of seconds after taking the specimens out from the cryostat. At least five specimens were tested for each composition. The temperature inside the samples was examined, showing no obvious change after the specimens were taken out from the cryostat for a few seconds using cryogenic thermocouples embedded inside the specimens. Therefore, the temperature for the impact testing was approximately considered to be 77 K.

#### 2.3.2. PALS and DSC measurements

The positron annihilation lifetime spectroscopic (PALS) measurements were carried out at RT by an EG&GORTEC fast-slow coincidence system with a resolution of 180 ps. The source of  $^{22}\text{Na}$  ( $5 \times 10^5$  Bq) was sandwiched between two pieces of sample. Three million counts were collected for each spectrum. The positronium lifetime  $\tau_3$  and intensity  $I_3$  of the long-lived components analyzed were studied using the computer program "POSFIT88".

Differential Scanning Calorimetry (DSC) was performed on unmodified and modified epoxy mixtures under nitrogen atmosphere with various heating rates of 5, 10, 15 and 20 °C/min using a NETZSCH STA 409PC.

#### 2.3.3. SEM

The fracture surfaces of the impact specimens were observed by scanning electron microscopy (SEM) using a HITACHI S-4300 microscope (Japan). Prior to examination, the fracture surfaces were

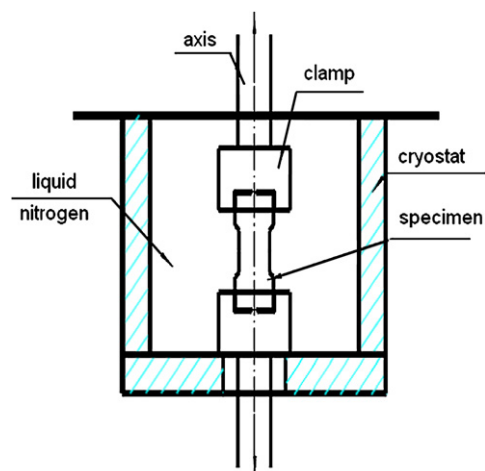


Fig. 3. Schematic diagram of the fixture for cryogenic tensile testing [26].

cleaned with alcohol and spray coated with a thin layer of evaporated gold to improve conductivity.

### 2.3.4. Measurement of glass transition temperature

The glass transition temperature ( $T_g$ ) of the cured specimens was measured in nitrogen gas environment at a heating rate of 10 °C/min using a NETZSCH STA 409PC. The heating temperature ranges from 30 to 200 °C.

## 3. Results and discussions

### 3.1. Tensile properties

The stress–strain curves of the unmodified and H30-modified epoxy resins at both RT and 77 K are shown in Fig. 4. It can be seen that the stress–strain curves shift from the left-hand side to the right-hand side as the H30 content increases. The data for the tensile strength, tensile modulus and the failure strain of the epoxy resins at RT and 77 K were obtained from these stress–strain curves via the REGER Testing Software. The results are shown in Table 1 and will be discussed later.

In order to interpret the dependence of mechanical properties of modified epoxy resins on H30 content, schematic illustration of cured networks in the pure epoxy and hydrogen bonds, free spaces and free volumes of cured networks in the H30-modified epoxy systems is presented in Fig. 2. Two hyperbranched polymer molecules are included in one unit of the epoxy network in order to conveniently display the hydrogen bonds between H30 molecules. Of course, one or three H30 molecules can also be included in one unit of the epoxy network in the schematic illustration of the epoxy networks. There are a large number of hydroxyl groups at the ends of H30 polymer chains as shown in Fig. 1. Since MeTHPA was stoichiometric with epoxy resin, there would be a large number of unreacted hydroxyl groups in H30-modified resins after curing. A large number of hydrogen bonds would form among the unreacted hydroxyl groups (Fig. 2(b)), when compared with the unmodified system (Fig. 2(a)).

By the addition of H30, free spaces defined as the unoccupied spaces within the molecules would exist in the cured systems. The free volumes defined as the unoccupied spaces between molecules in three-dimensional epoxy networks would increase because of the steric effects associated with the large volume of the hyperbranched structure of H30 molecules during the reacting process with MeTHPA. Fig. 5(a) and (b) shows the simulated structures of

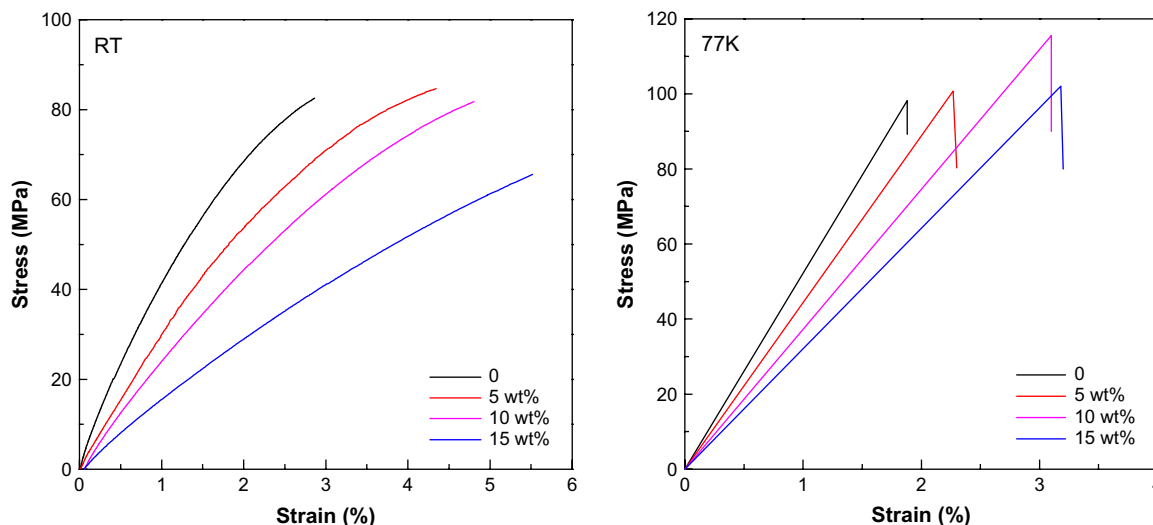
**Table 1**  
Tensile properties at RT and 77 K of unmodified and H30-modified epoxy resins

H30 content (wt%)	Tensile strength (MPa)		Young's modulus (GPa)		Failure strain (%)	
	RT	77 K	RT	77 K	RT	77 K
0	82.6 ± 5.0	98.2 ± 2.8	3.78 ± 0.6	5.2 ± 0.5	2.9 ± 0.2	1.9 ± 0.3
5	84.4 ± 2.3	100.7 ± 6.5	2.6 ± 0.5	4.4 ± 0.2	4.3 ± 0.4	2.3 ± 0.3
10	83.4 ± 2.8	115.6 ± 4.0	2.2 ± 0.6	3.8 ± 0.5	4.8 ± 0.2	3.1 ± 0.3
15	66.8 ± 4.7	102.1 ± 4.8	1.3 ± 0.2	3.2 ± 0.2	5.5 ± 0.2	3.2 ± 0.3

single H30 and two H30 molecules in the cured networks of a modified epoxy resin using the well known Chemoffice3D Ultra 10.0 Software, illustrating free spaces and free volumes in a nanometer scope. The nanometer molecular size of H30 results in excellent miscibility and no phase separation on the fracture surfaces of modified epoxy systems will be observed. The corresponding SEM micrographs will be shown later.

The above supposition about the free volumes was proven by the PALS results. Table 2 exhibits the measured results for the positronium lifetime ( $\tau_3$ ), an indication for the average size of free volumes as a function of H30 content, and the intensity  $I_3$ , a measure of the concentration of free volumes [7,28] within the cured epoxy networks. It can be seen from Table 2 that the  $\tau_3$  values of H30-modified epoxy systems are higher than those of the unmodified epoxy resin system. Moreover, Table 2 shows that  $I_3$  for the modified epoxy systems is obviously larger than that for the unmodified epoxy system, indicating that the mean size of the holes forming the free volumes in the H30-modified cured epoxy systems should be obviously larger than that in the unmodified epoxy system [7,28]. Furthermore, the increase of  $I_3$  with increasing H30 content displays that the concentration of free volumes in the cured epoxy networks increases with increasing H30 content.

Fig. 6 shows the DSC scans of unmodified and H30-modified epoxy systems, illustrating the effect of H30 addition on the epoxy anhydride cure reaction. The modified epoxy system containing 10 wt% H30 displays peak exotherm at the same temperatures (173.7, 188.7, 198.4 and 205.2 °C) as unmodified DGEBA (172.9, 188.8, 198.5 and 204.7 °C), respectively, for the heating rates of 5, 10, 15 and 20 °C/min. At the peak exotherm, there is the greatest amount of heat given off and therefore assumed to be related to the point where the reaction is most rapid. Therefore, the hyperbranched polymer (H30) has little effect on the cure kinetics and this has also been reported in the literature [22,26].



**Fig. 4.** Stress–strain curves at RT and 77 K of H30-toughened epoxy systems with different H30 contents.

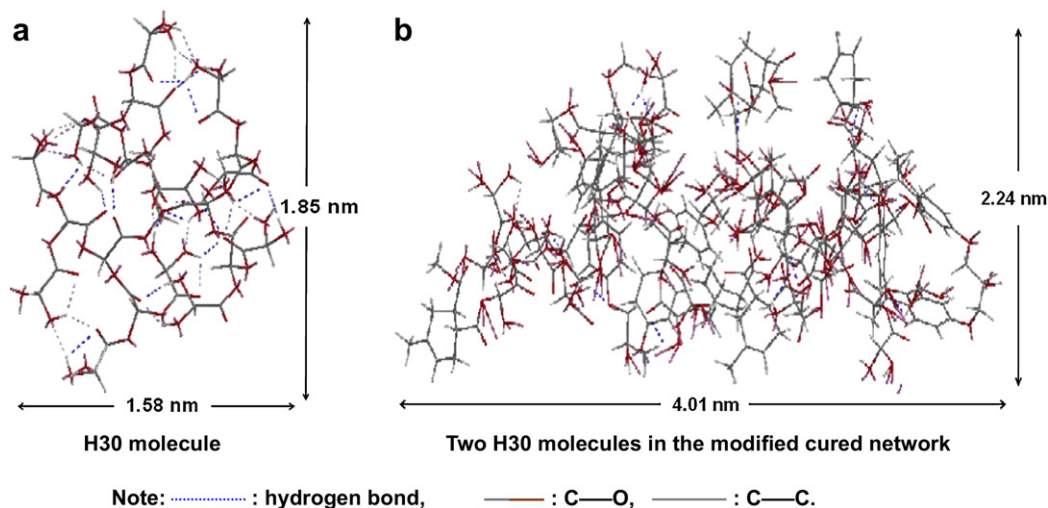


Fig. 5. Simulated structures of (a) single H30 molecule and (b) two H30 molecules in the modified cured network.

Effects of the H30 content on the tensile strength of the cured epoxy at both RT and 77 K are shown in Table 1. It shows that the cryogenic tensile strength is higher than the RT strength. Moreover, the tensile strengths at RT and 77 K show completely different dependencies on H30 content. Tensile strength at RT (RT tensile strength) doesn't change apparently until H30 content is increased to 15 wt% at which the RT tensile strength is decreased from 82.6 MPa for the pure epoxy resin to 66.8 MPa for the modified system. However, the tensile strength at 77 K increases with increasing the H30 content and reaches the maximum value 115.6 MPa for the modified system with 10 wt% H30, showing an improvement of 17.7% over that for the pure epoxy resin. Afterwards, the tensile strength at 77 K decreases when the H30 content is further increased to 15 wt%, but it is still higher than that of the pure epoxy resin. The tensile strengths at RT and 77 K are discussed below.

The RT tensile strength is discussed first. On the one hand, a large number of hydrogen bonds (in Figs. 2(b) and 5(b)) would contribute to enhancement of the RT tensile strength of the cured systems [29]. The introduction of a certain amount of soft matters (here flexible groups of H30) into brittle epoxy resins would reduce residual internal stresses, also leading to enhanced strength [14]. On the other hand, flexible polymer chains in the H30 molecule structure would decrease the rigidity of polymer chain, and hence lead to the reduction of the tensile strength at RT. It is similar to the case that the addition of soft matters like rubber and polyurethane to epoxy resins generally results in reduction of tensile strength at RT [30,31]. Besides, introduction of free spaces within H30 molecules and free volumes between H30 molecules into the cured epoxy networks would lead to a decrease in the cross-linking density of the H30-modified epoxy systems since free spaces and free volumes would take space in the cured epoxy networks, and hence to a decrease in the tensile strength at RT [21,32]. As a result, when the H30 content is relatively low ( $\leq 10$  wt%), the reduction of tensile strength caused by the above negative factors would be offset by the increment due to the above positive factors. However, when the H30 content is further increased to 15 wt%, the amount of

flexible polymer chains of H30 and the free spaces and free volumes introduced into the epoxy resins would be too much, hence the positive contribution by the positive factors to the strength is not enough to offset the negative contribution by the negative factors to the strength. Therefore, the tensile strength at RT is reduced by introduction of 15 wt% H30, which is similar to the previous reports [21,33].

The cryogenic tensile strength is discussed here. The formed hydrogen bonds in the cured epoxy systems become stronger at 77 K due to the shorter chemical-bond length caused by thermal shrinkage compared to the RT case. The free spaces and free volumes in the cured systems due to the introduction of H30 with hyperbranched structure would be smaller at 77 K due to thermal shrinkage [7,17], which contributes to an increased intermolecular force compared to the RT case, also leading to a higher tensile strength at 77 K compared to the RT. Consequently, these would result in a higher tensile strength at 77 K compared to RT. On the other hand, it is well recognized that the internal residual stress in epoxy resins cured at high temperature is produced by bulk shrinkage occurring during the cooling process from the curing temperature to RT [34,35]. At low temperature, the internal stress can become severer due to thermal shrinkage [6,11]. The internal stress within the bulk epoxy material can greatly influence the performance of the finished samples by creating micro-cracks and voids. The incorporation of soft flexible segments into brittle epoxy resins can dramatically reduce the internal stress [14,34–36]. Thus, the increase in the cryogenic tensile strength by introduction of suitable amounts of H30 could be attributed to the reduction of internal stress in the samples by the introduction of soft flexible groups of H30 into the brittle epoxy network. Similar observation was reported in our previous work on flexible diamine modified diglycidyl ether of bisphenol A (DGEBA) epoxy resins [14]. As the content of H30 is further increased, the tensile strength at 77 K decreases, this is similar to the RT case and won't be discussed in detail for simplicity.

Table 1 also shows the tensile modulus of the epoxy resins at both RT and 77 K. The tensile modulus at both RT and 77 K tends to decrease linearly with increasing the H30 content. This can be attributed to the fact that the presence of H30 would decrease the rigidity of polymer chains and the cross-linking density of the cured systems as mentioned above. Moreover, it can be observed that tensile modulus at 77 K is larger than that at RT with the same composition. Similar results were reported in our other works [10,14,15]. This is because the binding force and intermolecular force at 77 K are greater than those at RT due to thermal shrinkage,

**Table 2**  
The positronium lifetime  $\tau_3$  and intensity  $I_3$  of unmodified and modified epoxy resins

H30 content (wt%)	$\tau_3$ (ns)	$I_3$ (%)
0	$1.72 \pm 0.01$	$20.7 \pm 0.2$
5	$1.73 \pm 0.01$	$22.4 \pm 0.2$
10	$1.74 \pm 0.01$	$22.6 \pm 0.2$
15	$1.74 \pm 0.01$	$23.0 \pm 0.2$



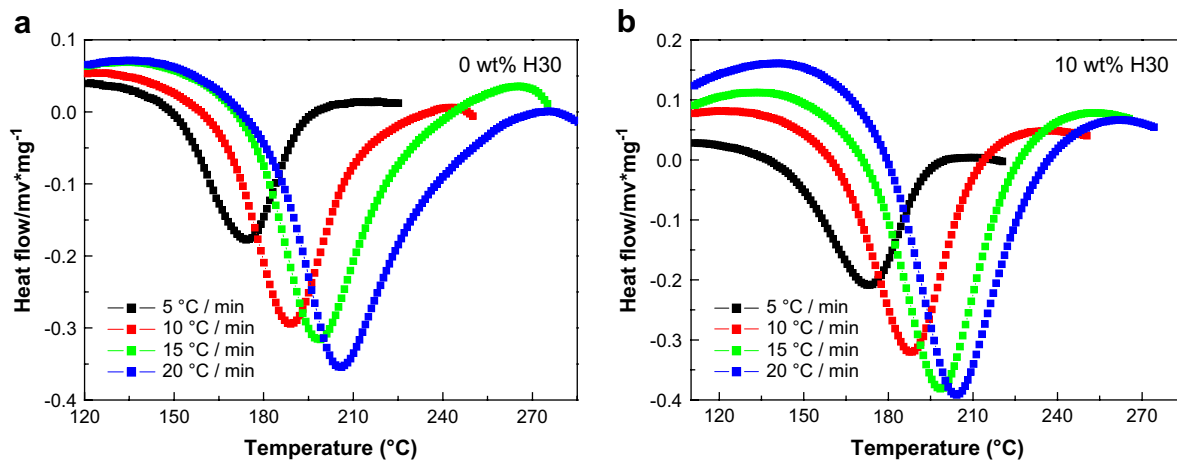


Fig. 6. DSC scans of (a) MeTHPA/DGEBA system and (b) HBP/MeTHPA/DGEBA system containing 10 wt% H3O at different heating rates.

which would make contribution to the increase of the tensile modulus.

The failure strains of the epoxy resins are also shown in Table 1. It shows that the failure strains at 77 K are much lower than those at RT. This is because most of macromolecules are frozen up and the free volumes and free spaces become smaller at 77 K than at RT, resulting in reduction of the ductility. Table 1 also displays that the failure strain at both RT and 77 K increases consistently with the increase of H3O content, showing the enhanced ductility by introduction of H3O. It is attributed to the easier motilities by introduction of flexible structures from H3O in the rigid epoxy network structure. The presence of free volumes and free spaces due to introduction of H3O provides room for facilitating polymer chain mobility when the cured epoxies are subjected to a tensile force, which also contributes to an increase in the failure strain as the H3O content increases.

### 3.2. Impact strength and SEM analysis

Effects of the H3O content on the RT and cryogenic impact strength of the cured epoxies are shown in Table 3. It is clear from Table 3 that the impact strength at both RT and 77 K increases up to the maximum by adding the 10 wt% H3O and decreases afterwards with the increase of H3O content. The maximum impact strength at RT and 77 K of modified epoxy systems is 31.2 and 32.0 kJ/m<sup>2</sup>, respectively. It is generally expected that the impact strength of epoxy resins at 77 K should be lower than that at RT since epoxy resins become normally more brittle at low temperatures [12–15]. However, it is interesting to note that the impact strength at 77 K of the modified epoxy systems is not lower than that at RT for the same H3O content. The maximum improvements in the impact strength at RT and 77 K are, respectively, 20.3 and 26.3% over those of the pure epoxy resin by the introduction of 10 wt% H3O.

The RT impact strength is first discussed. The flexible groups (namely ester segments in H3O) can dissipate the impact energy by their segmental motion in molecular chains, which contributes to

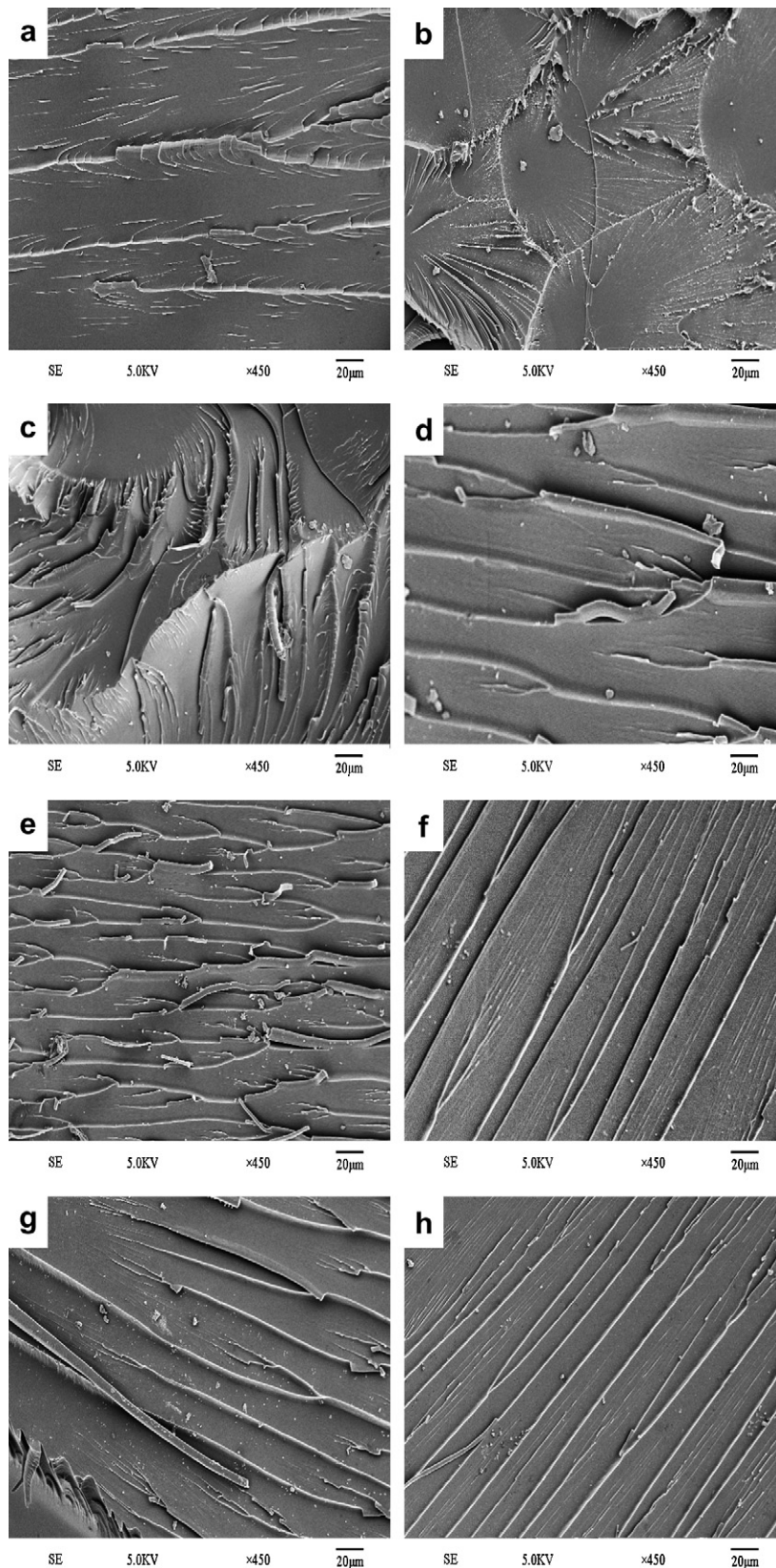
the increase of impact strength at RT [4,14,32]. The nanometer sized free spaces and free volumes as shown in Fig. 6 can also absorb much energy by distorting themselves and providing motion space for the molecules in the network during impacting [7,17]. Thus, the impact strength at RT of the cured epoxy resins increases with increasing the H3O content until 10 wt% H3O, which is similar to the results in the literature [23,38,39]. As the H3O content is increased beyond 10 wt%, the stereo-hindrance effect of the component H3O would become prominent and suppressed hydrogen bonding, and therefore, the impact strength would be deteriorated.

At 77 K, flexible ester segments in H3O are not completely frozen and can dissipate the impact energy by their segmental motion [14,16,37]. The nanometer sized free volumes and free spaces shown in Fig. 6 become smaller but still exist in the cured epoxies when the temperature goes down to 77 K. They can also absorb much energy by distorting themselves and providing motion space for the molecules in the network during impacting at 77 K [7,14,17]. The two factors will attribute to the increase of cryogenic impact strength of the cured systems by introduction of 5–10 wt% H3O. As the H3O content further increases beyond 10 wt%, the impact strength decreases. This is similar to the RT case and will not be discussed for simplicity. Furthermore, it is also observed that the impact strength at 77 K of the cured systems is not lower than that at RT except for the pure epoxy resins. Explanation can be given in terms of the effect of hydrogen bond on the impact strength [33]. The stronger hydrogen bonds because of the presence of large numbers of hydroxyl groups from H3O and hence higher intermolecular forces at 77 K will make a much larger contribution than at RT to the impact strength at 77 K, leading to the higher impact strength at 77 K than at RT.

The impact behavior of the cured epoxies can be examined in terms of the morphology observed by SEM. Scanning electron micrographs of the representative fracture surfaces at RT and 77 K are shown in Fig. 7(a)–(h). The smooth and glassy surfaces as shown in Fig. 7(a) and (b) are substantial evidence of brittle failure of the pure epoxy resin. The fracture surfaces for the H3O-modified epoxies with 5–15 wt% of H3O in Fig. 7(c)–(h) were quite different from those of the pure epoxy. As for the modified systems, the fracture surfaces show relatively rough and irregular appearance. A lot of “protonema” (referring to filar strips) have been observed in SEM micrographs of H3O-modified epoxy resins, and the similar phenomenon was also reported elsewhere [21]. The formation of “protonema” results likely from the distortion of intramolecular cavities (also called free spaces) that would occur when the samples are subjected to impacting [21]. The “protonema” is the indication of the characteristics of toughening fracture. So, an

**Table 3**  
Impact strength at RT and 77 K of unmodified and H3O-modified epoxy resins and glass transition temperature ( $T_g$ ) of the cured epoxy resins

H3O content (wt%)	Impact strength (kJ/m <sup>2</sup> )		Glass transition temperature (°C)
	RT	77 K	
0	25.9 ± 3.2	25.4 ± 2.7	118.5
5	27.1 ± 3.3	29.1 ± 3.3	118.8
10	31.2 ± 2.7	32.0 ± 1.0	118.7
15	24.9 ± 1.6	27.3 ± 1.4	112.2



**Fig. 7.** SEM micrographs of fracture surfaces after impact testing with different H30 contents (a) 0 wt%, RT; (b) 0 wt%, 77 K; (c) 5 wt%, RT; (d) 5 wt%, 77 K; (e) 10 wt%, RT; (f) 10 wt%, 77 K; (g) 15 wt%, RT; (h) 15 wt%, 77 K.

improvement in impact strength has been observed by the addition of 5–10 wt% H30. When the H30 content is beyond 10 wt%, the stereo-hindrance effect would become prominent and therefore,

the impact strength is deteriorated by the addition of 15 wt% H30. In addition, no second phase can be found in the SEM images in Fig. 7(c)–(h), indicating that H30/epoxy systems are homogeneous.

### 3.3. Thermal properties

The glass transition temperature ( $T_g$ ) of the cured epoxies with H30 is also shown in Table 3. It can be observed that  $T_g$  doesn't change much until the H30 content is increased to 15 wt% at which  $T_g$  is decreased from 118.8 °C for the pure epoxy resin to 112.2 °C for the system with 15 wt% of H30. The glass transition temperature depends primarily on the chain flexibility, cross-linking, intermolecular attraction and steric effects, etc. [29,40]. The large number of hydrogen bonds (as shown in Figs. 2(b) and 5(b)) formed in the cured systems leads to the increase of the intermolecular attraction, and hence to restriction of the mobility of the polymer chains, which would enhance  $T_g$  of the cured materials [29]. Steric effects caused by the hyperbranched structure of H30 molecules can also increase  $T_g$  of the cured systems [40]. On the contrary, the introduction of flexible polymer chains, free volumes and free spaces by incorporation of H30 can make the polymer chains to move more easily and hence to decrease  $T_g$  of the cured systems [38]. The decrease of the cross-linking density, which can be proven by the increased size and content of free volumes shown by the PALS results (Table 2), has also a negative effect on  $T_g$  of the cured systems [21,38]. As a result, the variance in  $T_g$  of cured systems as a function of H30 content is determined by both the above competing factors for the cases of low H30 contents up to 10 wt%, leading to the unchanged  $T_g$ . However, when the H30 with an excessive amount is introduced into the pure epoxy resin,  $T_g$  is reduced to some degree since flexible polymer chains, free volumes, free spaces and decreased cross-linking density would dominate in determining the glass transition temperature.

### 4. Conclusions

In this paper, a hydroxyl functionalized hyperbranched polymer (H30) has been successfully used to enhance the cryogenic mechanical properties of DGEBA/MeTHPA system. The results show that addition of H30 of proper amounts can lead to simultaneous improvements in the tensile strength, failure strain and impact strength at 77 K. The maximum tensile strength at 77 K is obtained for the modified system with 10 wt% H30. The elongation at break at 77 K is consistently increased by the addition of H30. The maximum cryogenic impact strength is obtained for the modified epoxy system with 10 wt% H30. The observed "protonema" by SEM on fractured surfaces of modified epoxy resins is used to explain the RT and cryogenic impact strength for the H30-modified epoxy resins. Moreover, it is shown that the addition of appropriate amount of H30 would not reduce  $T_g$ . The data at 77 K provide valuable information for using hyperbranched polymers in modifying epoxy resins for cryogenic engineering applications.

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