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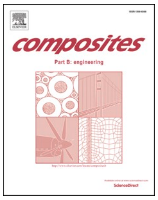

The versatility of hyperbranched epoxy resins containing hexahydro-s-triazine on diglycidyl ether of bisphenol-A composites

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ABSTRACT

Owing to the outstanding mechanical performance, diglycidyl ether of bisphenol A (DGEBA) becomes an important thermoset resin, but its brittleness and difficulties in degradation and recycling retard sustainable development. Herein, we have prepared several hyperbranched epoxy resins containing 1,3,5-hexahydro-s-triazine (HER-HT_n, n = 3, 6, 12, 24) which showed versatility on modifying DGEBA, including simultaneous reinforcing and toughening function, rapid degradation and recycling, and good compatibility. The detailed results showed that the HER-HT_{12} could increase the flexural, impact and tensile strengths of cured DGEBA by 132.7%, 190.4%, and 57.7%, respectively, and also increase degradation degree from 37.2 wt% to 99.9 wt%. The mechanical performance of the cured HER-HT_n/DGEBA reinforced in the beginning and then decreased with an increase in the content and the molecular weight of HER-HT_n, however, their degradation degrees increased distinctly. The reinforcing and toughening mechanism and degradation mechanism of the composites were investigated by SEM micrographs and GC-MS spectra.

1. Introduction

Hyperbranched epoxy resins (HERs) [1,2] as a novel thermoset resin have attracted increasing interests due to their simultaneous reinforcing and toughening effect [3,4] on diglycidyl ether of bisphenol A (DGEBA) [5], and they have been extensively used [6] in adhesives, coatings, and composites, taking advantages of their high reactivity and high solubility [7–10]. Like DGEBA, after curing, the strong chemically cross-linked [11] HERs are insoluble and infusible, resulting in their inability for reprocessing and reshaping by heat or solvent [12], causing extreme difficulties in degradation and recycling [13]. A large amount of cured epoxy resin wastes has become a heavy burden to the environment [14,15]. Landfill and incineration [16] of the wastes create critical pollution to the environment. To solve this problem, both designs of epoxy resins containing reversible dynamic covalent groups and recycling methods of cured epoxy resin wastes should be explored. Recycling and degradation methods *via* chemical bonds cleavage include pyrolysis [17], supercritical fluid process [18], and biodegradation [19], which degrade cured DGEBA into small molecule [20]. In mechanical recycling, cured DGEBA is ground to powders that can be served as fillers of new composite materials. However, the resulting powders exhibited not well compatibility with DGEBA because of their absence of functional groups, resulting in poor mechanical performance [21]. Cured DGEBA printed circuit board and carbon fiber (CF)/DGEBA [22] composites could be degraded at 245 °C and 90 °C, respectively. Cured DGEBA glass fiber composites could also be degraded in nitric acid solution [23,24] in about 19 h. These thermolysis processes could availably degrade cured DGEBA although require long degradation time. The supercritical fluid process could be used to decompose anhydride-cured DGEBA [25] and 4,4′-diamino-diphenyl- sulfone-cured DGEBA [26] in near-critical water and in supercritical 1-propanol, respectively, but the degradation solution is difficult to separate and the trainer is difficult to recover from the

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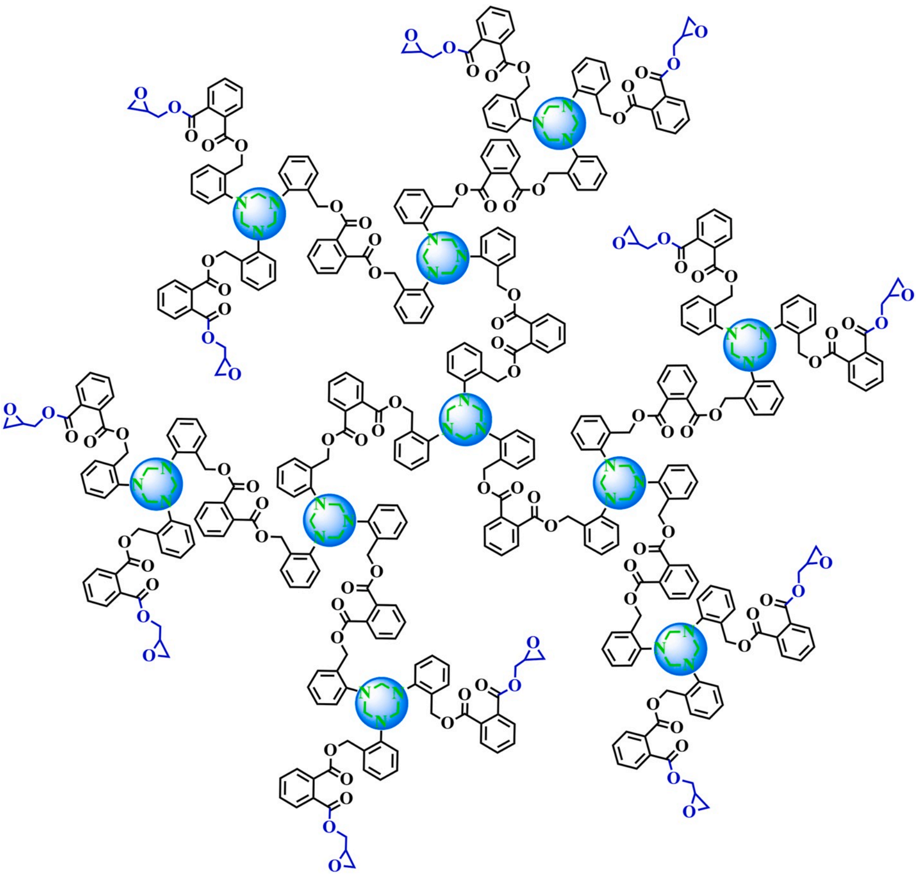


Scheme 1. Chemical structure of HER-HT$_{12}$.

extract [27]. In addition, the design, development, and operation of an industrial supercritical fluid process are difficult. Biodegradation of cured DGEBA takes a long time [28] and it is difficult to separate and recycle the degradation products due to the numerous mineral salts involved [29].

Designing reworkable resins is another method to recycle the cured epoxy resin wastes. Thermally cleavable bonds include mainly sulfonate ester, ester, acetal, disulfide, imine, and hexahydro-s-triazine (HT) structures. Some crosslinked cross-linkable epoxies [30–32] which have thermally cleavable groups could be degraded in water or organic solvents at 120-200 °C. The degradation degree of cycloaliphatic epoxy resin [33] carrying the acetal group increased along with the increase of acidity. The cured epoxy resins containing dynamic acetal [34] or disulfide [35] bonds could also decompose at lower temperatures. Thermoset polyimide resins with imine bonds [36] could degrade at mild conditions to recover CFs. The ratio of imine can control the degradation degree of hyperbranched polymer which has imine bond [37]. Degradable HERs [38,39] containing esters bonds increased the strength and degradability of the DGEBA, although the degradation substances could not be recycled. The epoxy resins without HT bonds and their composites showed poor mechanical performance because of instabilities of the thermally cleavable bonds [40], but have good degradation [41]. Then, trifunctional amine with HT bonds (HT-A) [42] as a curing agent was prepared as a degradable epoxy network, and the CF composites could be degraded to recover the CFs in a dilute acid solution.

The previous studies demonstrate that epoxy resins with HT bonds have excellent properties, including high mechanical performance, high degradability, and recyclability in relatively mild conditions, especially epoxy resins with hyperbranched structure, which increases the degradation degree of cured DGEBA in addition to simultaneously toughening and reinforcing the DGEBA. If HERs containing HT bonds can be used to degrade industrial DGEBA, it would provide an available solution to the challenge of producing high performance and rapidly recyclable epoxy resins. In this study, we prepared hyperbranched epoxy resins containing rapid degradation 1,3,5-hexahydrotriazine (HER-HT$_n$) and investigated the degradation process and mechanism of the resulting HER-HT$_n$/DGEBA composites. HER-HT$_n$ showed multifunctionality in modifying DGEBA, including toughening, reinforcing and improving degradability.

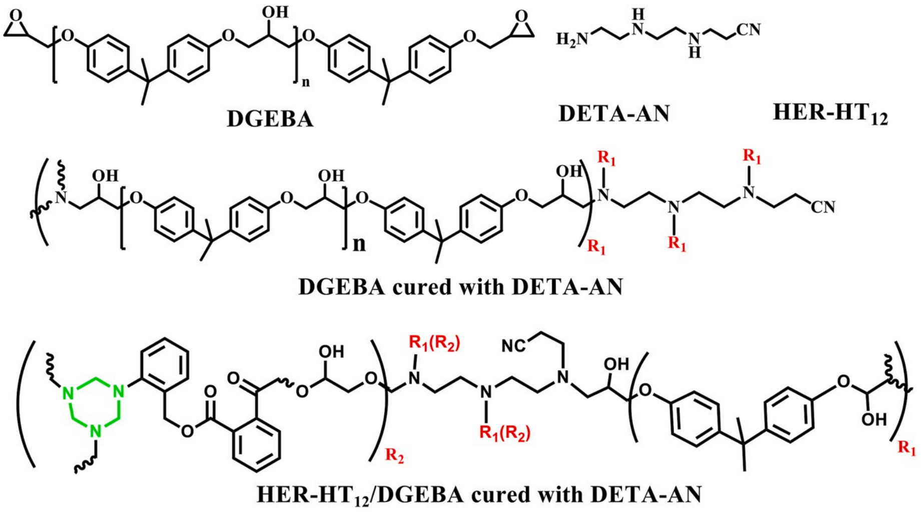
2. Experimental

2.1. Preparation of degradable hyperbranched epoxy resins (HER-HT$_n$)

The 2, 2′, 2''- (1,3,5-hexahydro-s-triazine-1,3,5-triyl) benzyl alcohol and degradable hyperbranched epoxy resins containing hexahydro-s-triazine (HER-HT$_n$) were synthesized according to our group literature (Scheme S1 and Scheme 1) [14]. ^{1}H NMR (400 MHz, $CDCl_3$) of HTA: δ (ppm) 7.24 (H, m, CH; HO-CH_2-Ph), 7.18 (H, m, CH; -N-Ph), 7.00 (2H, s, 2 × C*H*;-Ph-), 4.95 (2H, s, -N-CH2-N-), 4.85 (2H, s, HO-CH2-Ph-), 4.69 (H, s, **H**O-CH2-Ph-). ^{1}H NMR (400 MHz, $CDCl_3$) of HER-HT$_6$: δ (ppm) 7.72 (H, -CO-***Ph***-CO), 7.49 (H, -***Ph***-), 7.12 (H, -CO-CH_2-***Ph***), 6.96 (H, ***Ph***-), 6.88 (H, N-***Ph***), 4.91 (H, -N-C***H***$_2$-N-), 4.82 (H, -C***H***$_2$-Ph), 4.65 (H, -CO-C***H***$_2$-CH-), 4.37 (H, -CH-C***H***$_2$-O), 3.71 (H, -CH_2-C***H***-O). The ^{1}H NMR of HER-HT$_3$, HER-HT$_{12}$, and HER-HT$_{24}$ are similar to those of HER-HT$_6$.

2.2. Preparation of HER-HT$_n$/DGEBA composites

The curing agent of 3-((2-((2-aminoethyl)amino)ethyl)amino)propanenitrile (DETA-AN) was synthesized according to literature [43]. The chemical structure of DGEBA, HER-HT$_n$, DETA-AN, and cured resins are



Scheme 2. Chemical structures of DGEBA, HER-HT$_n$, DETA-AN, and cured composites.

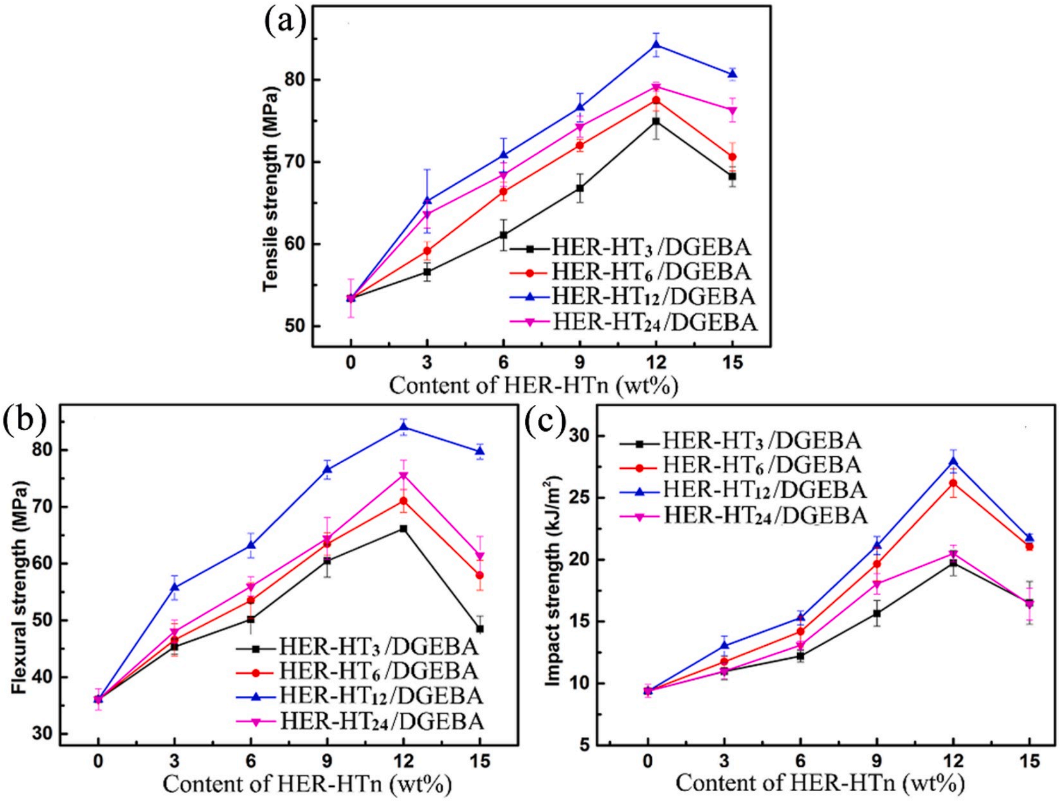


Fig. 1. Mechanical behavior of the cured HER-HT$_n$/DGEBA composites (a. tensile, b. flexural, and c. impact).

shown in Scheme 2. The HER-HT$_n$/DGEBA composites containing 0-15 wt% HER-HT$_n$ (Table S1) were prepared by blending HER-HT$_n$ and DGEBA at 25-30 °C. The curing agent (DETA-AN) with a stoichiometric quantity was appended into the composites. The mixed samples were cured 12 h at room temperature and post-cured 6 h at 80 °C.

3. Results and discussion

3.1. *Mechanical performance of HER-HT$_n$/DGEBA composites*

Fig. 1 shows the mechanical performance of HER-HT$_n$/DGEBA composites with various molecular weight and content of HER-HT$_n$. With the addition of HER-HT$_n$ into DGEBA, the mechanical performance of the cured composites was improved. Accompanied by increasing the content of HER-HT$_n$, their mechanical performance increased first and then decreased, and their maximum values reached 12 wt% HER-HT$_n$ content. The tensile strength of HER-HT$_n$/DGEBA composites after cured ($n = 3$, 6, 12 and 24) with 12 wt% HER-HT$_n$ respectively increased by 40.3%, 45.1%, 57.7%, and 48.3% higher than the pure DGEBA (53.4 MPa) in Fig. 1a. The crosslinking density [44], intramolecular defects, and cavity [9] played key roles in the tensile property of the cured HER-HT$_n$/DGEBA composites. Increasing HER-HT$_n$ content, the crosslinking density of the composites after curing increases and improves the tensile strength. However, the non-crosslinked segments of HER-HT$_n$

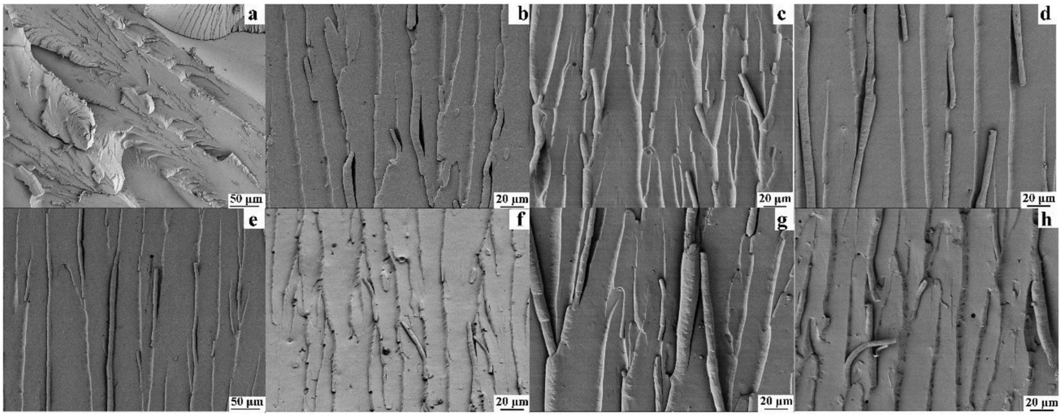


Fig. 2. SEM micrographs of the fracture surfaces of composites (a. DGEBA, b. 3 wt% HER-HT$_{12}$/DGEBA, c. 9 wt% HER-HT$_{12}$/DGEBA, d. 12 wt% HER-HT$_{12}$/DGEBA, e. 15 wt% HER-HT$_{12}$/DGEBA, f. 12 wt% HER-HT$_{3}$/DGEBA, g. 12 wt% HER-HT$_{6}$/DGEBA, h. 12 wt% HER-HT$_{24}$/DGEBA).

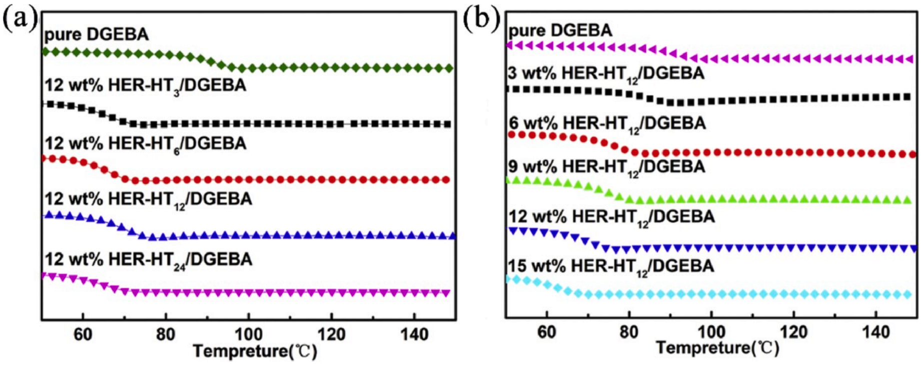


Fig. 3. DSC curves of HER-HT$_n$/DGEBA composites after curing.

caused intramolecular defects and cavity, which adverse impacts on the tensile property of the HER-HT$_n$/DGEBA composites after cured.

In contrast to the DGEBA (36.1 MPa), the flexural strength of the HER-HT$_n$/DGEBA composites with 12 wt% HER-HTn improved by 83.1%, 96.7%, 132.7% and 109.4% in Fig. 1b, respectively. The combination of crosslinking density [44] and intramolecular cavity [7] results in this phenomenon. From Fig. 1c, the maximum impact strength which of 12 wt% HER-HT$_n$/DGEBA was nearly 3 times that of the pure cured DGEBA, caused by the aforementioned intramolecular cavity. With an increase in HER-HT$_n$ content, the crosslinking density of the composites increases, which brittles the composites, whilst the increase of non-crosslinked segments of HER-HT$_n$ cause intramolecular defects and cavity, which increases the impact strength of composites. The comprehensive influences of these factors result in a maximum impact strength at the cured 12 wt% HER-HT$_n$/DGEBA.

SEM of the fracture surfaces of DGEBA and HER-HT$_n$/DGEBA composites after curing in Fig. 2. Fig. 2a shows that there is not any filament and smooth surface of cured DGEBA, indicating a brittle property [45]. Many obvious filaments appear on the fractured surfaces in Fig. 2b–h, as an indicator of ductile fractures. Both HER-HT$_n$ and DGEBA are miscible and can form a homogeneous blend, resulting in no microphase separation after curing. HER-HT$_n$ with the hyperbranched structure and intracavity can disperse into the DGEBA matrix, so a large number of cavities exist inside the composites. The cavities absorb a large amount of energy while impacting and distort, resulting in a filament microtopography. With the increase of HER-HT$_{12}$ content in the composites, the regularity and length of the filament of the impact section continuously increase from Fig. 2b to e, indicating an increase in cavities concentration. This result is consistent with that the cured 12 wt% HER-HT$_{12}$/DGEBA composites show high mechanical performance [46], combining the effect of crosslinked density. The filament concentration of the cured composites containing HER-HT$_n$ (Fig. 2d and 2g) with moderate molecular weights are higher than others (Fig. 2f and 2h), being attributable to the fact that the topological structure of both HER-HT$_6$ and HER-HT$_{12}$ is close to the globular shape and easy to distort [47].

Table 1
The thermal degration data of cured HER-HT$_n$/DGEBA composites.

Typical data	T_g (°C)	T_5 (°C)	T_{10} (°C)	T_{max} (°C)	Residual carbon yields (wt%)
DGEBA	101.2	317.3	337.9	370.4	12.1
12% HER-HT$_3$/DGEBA	66.4	256.5	321.5	358.0	8.1
12% HER-HT$_6$/DGEBA	69.3	256.9	322.9	359.0	8.3
12% HER-HT$_{12}$/DGEBA	71.8	257.1	324.4	359.3	9.9
12% HER-HT$_{24}$/DGEBA	68.1	258.0	326.1	359.8	9.9
3% HER-HT$_{12}$/DGEBA	88.6	300.9	335.4	364.7	8.9
6% HER-HT$_{12}$/DGEBA	80.3	281.3	332.3	363.4	9.5
9% HER-HT$_{12}$/DGEBA	75.9	263.7	328.3	360.1	9.6
15% HER-HT$_{12}$/DGEBA	65.2	241.9	312.5	353.0	9.9

3.2. *Thermal properties of cured HER-HT$_n$/DGEBA composites*

T_g of the cured HER-HT$_n$/DGEBA composites is shown in Fig. 3 and

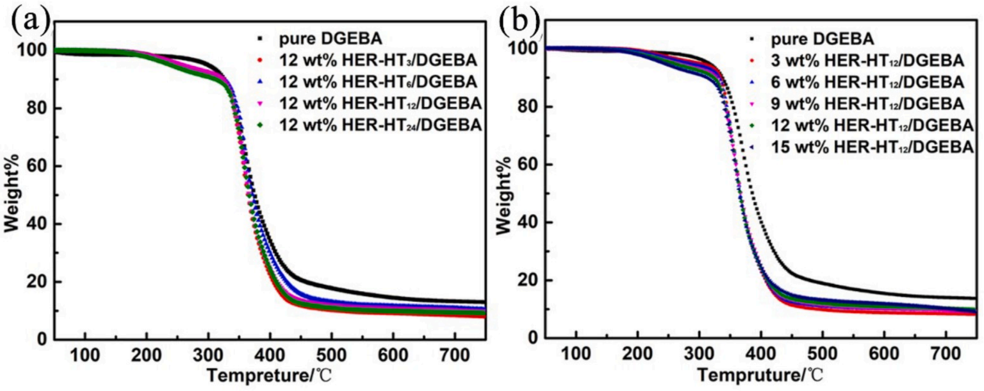


Fig. 4. The thermogravimetric analysis of HER-HT_n/DGEBA composites after curing (a. molecular weight, b. HER-HT_{12} content).

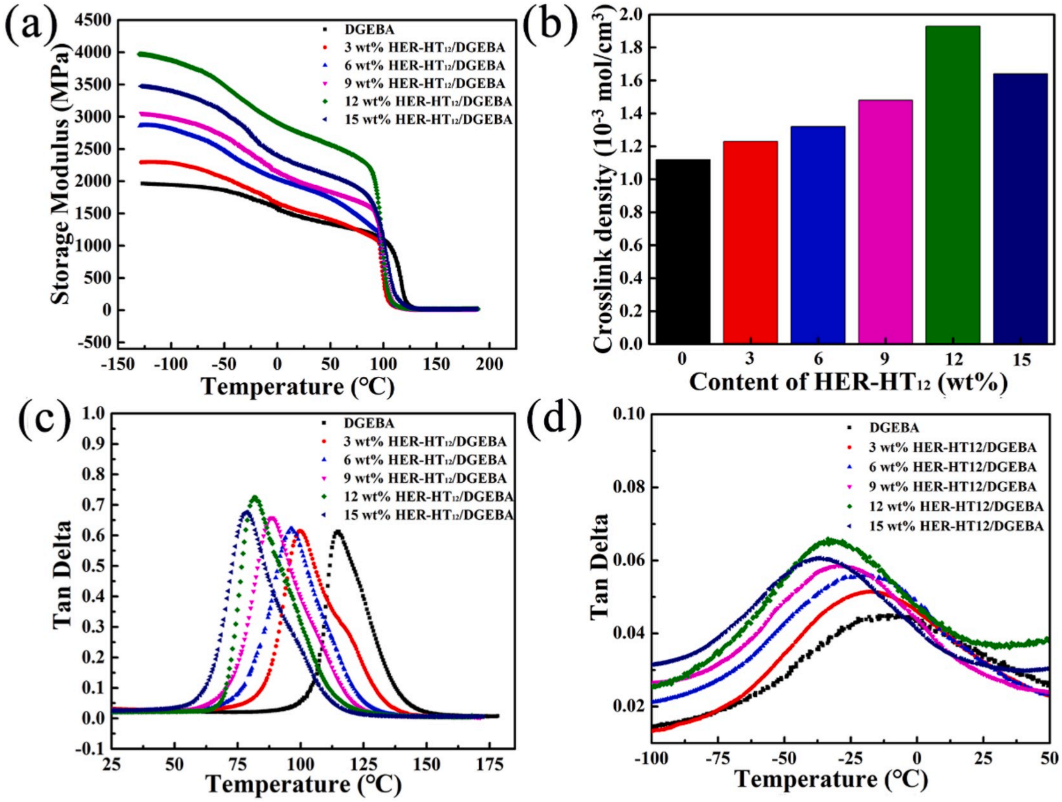


Fig. 5. DMA curves of cured DGEBA and HER-HT_{12}/DGEBA composites (a. storage modulus, b. crosslink density, c and d. tanδ).

Table 1, which is influenced by the molecular weight and content of HER-HT_n. It is found that $T_{5\%}$ and $T_{10\%}$ of HER-HT_n/DGEBA composites were lower than that of neat DGEBA [48]. The T_g of the composites changes a little with a difference in the molecular weight of HER-HT_n in Fig. 3a, and the T_g of the composites decreases slightly as the HER-HT_n content increases, being attributable to the fact that the intramolecular cavities density increases [49] due to the addition of HER-HT_n.

Fig. 4 and Table 1 show the thermogravimetric analysis (TGA) curves of the HER-HT_n/DGEBA composites after curing. The thermal stability changes gently along with the increase of HER-HT_n molecular weight, which are lower significantly than that of the DGEBA after curing. The thermal stability of the composites decreases significantly with increasing HER-HT_{12} content. This is can be explained that the unstable hexahydro-s-triazine structure in composites starts to decompose at 200 °C to produce small molecules.

Fig. 5 shows the dynamic mechanical properties of cured HER-HT_{12}/DGEBA with different HER-HT_{12} contents. The storage modulus of the composites increased significantly after adding HER-HT_{12} in Fig. 5a. Along with the increase of HER-HT_{12} content, the storage modulus of composite increased firstly and then reduced, being attributed to the fact that both rigidity of the HER-HT_{12} chain and the strong interaction between chains increase the storage modulus of the composite [50]. However, a lot of intramolecular cavities or hyperbranched topological structure in HER-HT_{12} reduces the strength of the composites. Therefore, the storage modulus of the composites appears a maximum value when the addition amount is 12 wt%. The crosslink density of composites increases firstly and then reduces with the addition of the HER-HT_{12} in Fig. 5b, and the crosslink density of the composites with 12 wt% HER-HT_n/DGEBA appears the maximum value. With the addition of HER-HT_{12}, the number of crosslinkable epoxy groups of the composites increases and improves high crosslink density, but excess HER-HT_{12} may result in an incomplete crosslinking reaction and low

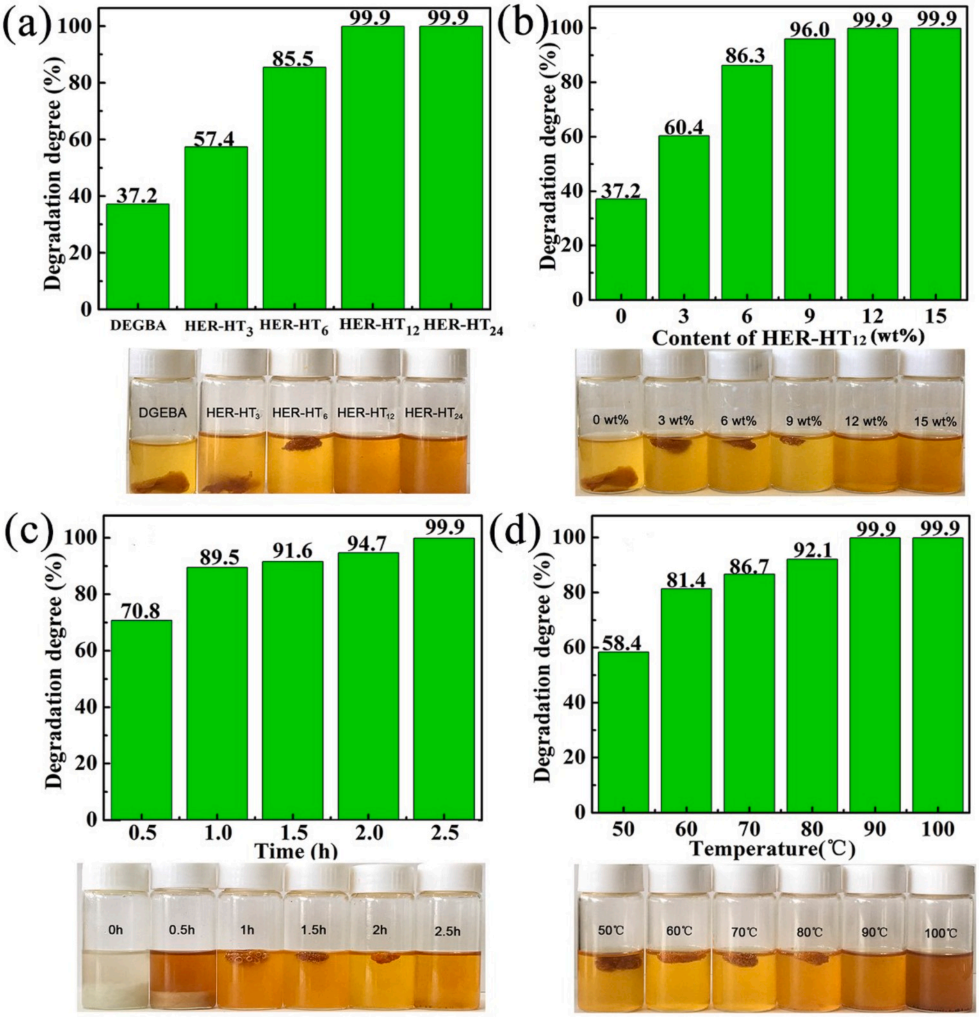


Fig. 6. The degradation behavior of cured HER-HT$_n$/DGEBA composites with various conditions (a. molecular weight, b. HER-HT$_{12}$ content, c. time, and d. temperature).

crosslink density. Fig. 5c shows that there is only one glass transition temperature in the range of 50-200 °C, indicating no micromorphological separation and good compatibility in the composites. After adding HER-HT$_{12}$, the T_{gs} of 3 wt% HER-HT$_{12}$/DGEBA, 6 wt% HER-HT$_{12}$/DGEBA, 9 wt% HER-HT$_{12}$/DGEBA, 12 wt% HER-HT$_{12}$/DGEBA, 15 wt% HER-HT$_{12}$/DGEBA were 100.1 °C, 96.1 °C, 89.4 °C, 81.9 °C, and 78.4 °C, respectively. The molecular cavity or hyperbranched topological structure density in the composites increases due to the addition of HER-HT$_{12}$, leading to a slight decrease in T_g. The peak height and area of β relaxation in the DMA curve (Fig. 5d) can reflect the toughness of the cured resins [9], being agreement with the result in Fig. 1c. The temperatures at β-relaxation peak of pure DGEBA, 3 wt% HER-HT$_{12}$/DGEBA, 6 wt% HER-HT$_{12}$/DGEBA, 9 wt% HER-HT$_{12}$/DGEBA, 12 wt% HER-HT$_{12}$/DGEBA and 15 wt% HER-HT$_{12}$/DGEBA are -9.4 °C, -16.7 °C, -21.8 °C, -27.6 °C, -33.4 °C, and -36.1 °C respectively, suggesting good low-temperature resistance of the composites with high content of HER-HT$_{12}$.

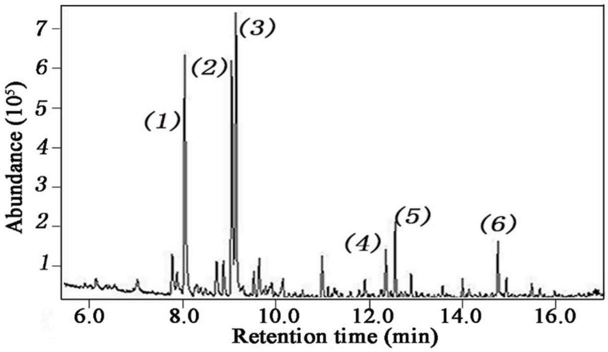


Fig. 7. GC-MS spectrum of the degradation solution of cured 12 wt% HER-HT$_{12}$/DGEBA.

3.3. Degradation of HER-HT$_n$/DGEBA composites

The degradation behavior of the cured HER-HT$_n$/DGEBA composites is shown in Fig. 6. Firstly, the 0.25 g cured 12 wt% HER-HT$_n$/DGEBA powder was put into a solution with 4.41 g phosphoric acid, 3.75 g DMF and 3.75 g of H_2O_2 to degrade 2.5 h at 90 °C, and the effect of HER-HT$_n$ molecular weight and content on degradation degree of the composites is shown in Fig. 6a and b. With an increase in molecular weight and content of HER-HT$_n$, the degradation degree increases gradually. It can be regarded as complete degradation (as shown in Fig. 6a and b) when the content of HER-HT$_{12}$ is 12 wt% [45]. And then, we used 12 wt% HER-HT$_{12}$ as the research object. Fig. 6c and d shows the best degradation time and temperature are 2.5 h and 90 °C, respectively. Because the HER-HT$_n$ contains an easily hydrolyzable ester group structure and an easily digested triazine structure [51], which are more easily degraded than ether bonds in DGEBA [41]. With the increase of

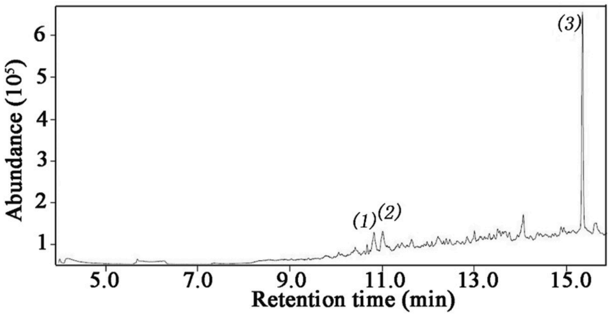
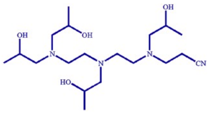
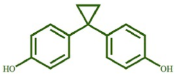
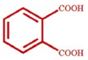
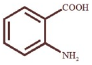
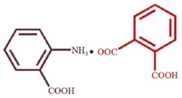


Fig. 8. The GC-MS spectrogram of the degradation solution of DGEBA after curing.

Table 2

Degradation products of cured 12 wt% HER-HT$_{12}$/DGEBA composites.

Main degradation products	RT (min)	*m/z*	Molecular formula
(1)	8.05	388	
(2)	9.06	226	
(3)	9.15	136	
(4)	12.35	168	
(5)	12.56	137	
(6)	14.75	305	

molecular weight and content of HER-HT$_n$, the number of both triazine and ester groups increased and the degradation degree of the composites increased [45]. Prolonging the degradation reaction time and increasing temperature can improve the degradation of composites.

The degradation mechanism of the cured HER-HT$_n$/DGEBA composites was then investigated. From their GC-MS spectra (Figs. 7-8), the degradation products of the HER-HT$_{12}$/DGEBA composite after curing and the DGEBA after curing were displayed in Tables 2-3 According to Fig. 7 and Table 2, there are six degradation products *(1), (2), (3), (4), (5)* and *(6)*. The product *(1)* is degradation products from the curing agent chains. The products *(2), (3), (4), (5)* and *(6)* contain benzene ring structure. The products *(2)* and *(3)* are from the DGEBA chains. The degradation product *(4)* may be inferred to be phthalic acid due to the same molecular weight. However, the molecular weights of products *(5)* and *(6)* cannot be directly obtained through the breakdown of the segment. The presence of product *(4)* proves that the ester group was broken. At the same time, the product *(5)* is obtained by oxidization of 2-aminobenzyl alcohol. The sum of the molecular weight of the product *(4)* and *(5)* is that of the product *(6)*, indicating that the product *(6)* is a salt formed by complexation of anthranilic acid and phthalic acid. Therefore, the degradation mechanism of the composite can be supposed from Table 2 and Fig. 7, as shown in Scheme 3. The formation of small molecules is mainly attributed to the fracture of the C-N bond in the triazine ring, the ester group in HER-HT$_{12}$, and the ether bond in DGEBA.

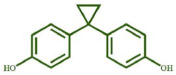
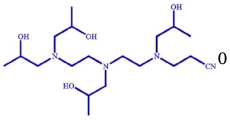
Compared with HER-HT$_{12}$/DGEBA composite, the degradation of cured DGEBA can be obtained (Fig. 8 and Table 3) by the following analysis. The products *(1)* and *(2)* are degradation products from cured DGEBA chains. The product *(3)* is obtained by the fracture of the C-N bond. The degradation mechanism of DGEBA after curing is similar to the cured HER-HT$_{12}$/DGEBA composite in Scheme 3. Compared with degradation products of cured DGEBA, the degradation of HER-HT$_{12}$/DGEBA composites can be completely degraded to smaller molecules, suggesting that the degradation degree of composites is higher than DGEBA. And the above analysis substantiates that the HER-HT$_{12}$ can effectively improve the degradation of cured DGEBA.

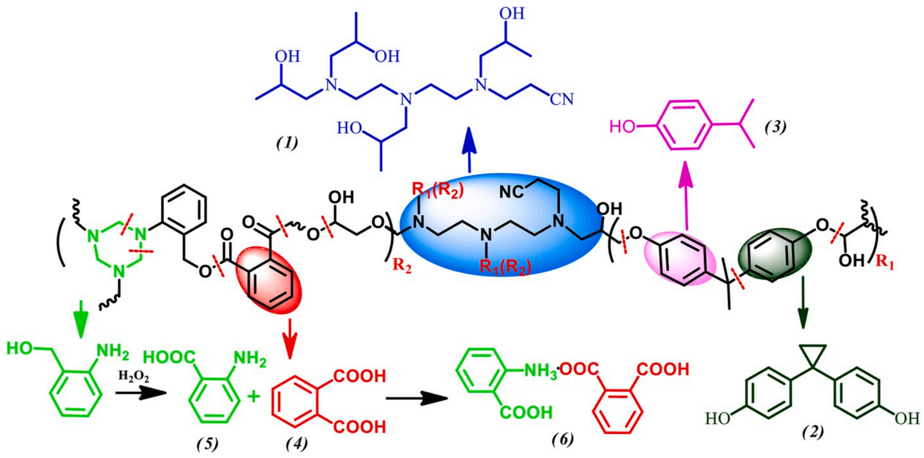
4. Conclusions

The hyperbranched epoxy resins (HER-HT$_n$, n = 3, 6, 12, 24) were synthesized and used to modifying DGEBA. The HER-HT$_n$ could improve

Table 3

Degradation products of DGEBA after curing.

Main degradation products	RT (min)	*m/z*	Molecular structures
(1)	10.67	226	
(2)	10.85	136	
(3)	15.35	388	



Scheme 3. Degradation mechanism of cured 12 wt% HER-HT$_{12}$/DGEBA composites.

distinctly the mechanical performance and degradation degree of the DGEBA. Compared with the tensile strength (53.4 MPa), flexural strength (36.1 MPa) and impact strength (9.4 kJ/m^2) of cured DGEBA, the mechanical performance (tensile, flexural and impact strengths) of 12 wt% HER-HT$_{12}$/DGEBA composites were 84.2 MPa, 84.0 MPa, and 27.3 kJ/m^2, respectively, which increased by about 57.7%, 132.7%, and 190.4%, respectively. The HER-HT$_n$ can improve the degradation property of the composites, and the cured HER-HT$_{12}$/DGEBA with 12 wt % HER-HT$_{12}$ could be completely degraded at 90 °C about 2.5 h, however, the degradation degree of pure DGEBA was only about 37.2 wt% at same degradation condition. This result supports an available approach to recycling and reusing cured DGEBA and its composites, helping the sustainable development of DGEBA.

Declaration of competing interest

The authors declare no competing financial interest.

CRediT authorship contribution statement

Xu Ma: Methodology, Data curation, Writing - original draft. **Yeyun Liang:** Data curation, Writing - original draft. **Zejun Xu:** Writing - original draft. **Sufang Chen:** Data curation. **Juan Cheng:** Writing - review & editing. **Menghe Miao:** Writing - review & editing. **Daohong Zhang:** Supervision, Writing - review & editing.

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Appendix A. Supplementary data

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