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Environment-friendly synthesis and performance of a novel hyperbranched epoxy resin with a silicone skeleton†

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Hyperbranched epoxy resins have attracted increasing attention for their excellent comprehensive performance in toughening and reinforcing the diglycidyl ether of bisphenol-A (DGEBA). However, the tedious synthetic procedure, high cost, and the use of large amounts of organic solvents have hampered their industrial application. This paper presents an environment-friendly method to synthesize a novel hyperbranched epoxy resin with a silicone skeleton (HERSS) through a hydrosilylation reaction catalyzed by a heterogeneous halloysite-supported platinum catalyst. The reaction involves only one solvent and affords a high yield (>90%). The chemical structure, molecular weight, and degree of branching of the HERSS were characterized by FT-IR, GPC and NMR. The resulting HERSS was used to modify a DGEBA based epoxy resin and showed excellent performance. With the incorporation of 9 wt% HERSS, the impact, flexural and tensile strength of DGEBA are increased by about 92.5%, 36.0% and 88.6%, respectively. The toughening and reinforcing mechanism was attributed to the ''sea-island'' structure of the cure composite, as shown by the SEM micrographs of the fractured surfaces. An initial thermal decomposition temperature of about 380.0 °C of the cured HERSS/methyl nadic anhydride resin also indicates promising applications with regard to high-temperature-resistance.

1. Introduction

Hyperbranched polymers (HBPs) are of interest in many applications because they are easier to synthesize than dendrimers and yet possess similar properties.[1] Moreover, HBPs generally have better solubility and lower viscosity than linear polymers with similar molar mass and chemical repeat units. It is interesting to note that HBPs are also important tougheners[2–4] for epoxy resins. Epoxy resins are a vital class of thermosetting polymers and have a broad range of applications,[5] including coatings, paintings, adhesives, laminates, encapsulants, and electrical insulating materials. However, their poor toughness or inherent brittleness, high viscosity and low thermal decomposition temperature have limited their applications.[6]

Toughening modification of epoxy resins has been a subject of intense investigation throughout the world. Compared with rubbers,[7] graphene oxide,[8] epoxidized oleic esters,[9] thermoplastic polyetherimide,[4] and core–shell particles,[4] HBPs[2–4,10–15] demonstrated better overall performance. Hydroxyl-functionalized HBPs,[4,14] epoxy-functionalized HBPs (Boltorn E1, Boltorn E2),[13,15–17] hydroxyl and epoxy-functionalized hyperbranched block copolyethers with core/shell structures,[18] and amine-terminated HBP[19] can increase several fold the fracture toughness of commercial diglycidyl ether of bisphenol-A (DGEBA), with the use of only 5–20 wt% of HBP. However, the tensile strength, flexural strength and glass transition temperature are usually impaired to some extent. These HBPs/epoxy resin composites are also difficult to process since the HBPs are either solid or of high viscosity. In 2006, we synthesized several novel hyperbranched epoxy resins with low viscosities of 350–5000 cp and a low epoxy equivalent weight.[20] An interesting result was that these hyperbranched epoxy resins could toughen and reinforce DGEBA at the same time.[3,21] An *in situ* reinforcing and toughening mechanism was suggested first[3] and further confirmed through research of unsaturated HBP/linear unsaturated polyester resins composites[22] and hyperbranched polyphosphate ester/DGEBA composites.[23] The toughening effect was attributed to the intramolecular cavity from the non-crosslinking structure of HBPs which may absorb a significant amount of energy upon impact. The reinforcing function was regarded as a result of the rigid phenyl structure of

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hyperbranched epoxy resin.[3] The toughening effect was further substantiated by a novel low-viscosity hyperbranched epoxy resin[2] containing similar chemical structures as Boltorn E1. Other functional HBPs, including hyperbranched polyglycerol containing carbonate groups,[24] hydroxyl-functionalized HBPs,[25] and hyperbranched poly(ester-amide)[26] could also increase the strength of DGEBA by about 5–20% as a results of the toughening effect.

Different approaches to synthesize hyperbranched epoxy resins have been researched for their production and application on an industrial scale. Aliphatic and aromatic hyperbranched epoxy resins were prepared by proton transfer polymerization[27–29] and ATRP.[30] Polyester hyperbranched epoxy resins could be obtained by grafting epoxy groups to HBPs[2,6,20,31–38] with epichlorohydrin. Liquid crystalline hyperbranched epoxy could be synthesized by a reaction between benzylidene cyclopentanone biepoxy monomers and trimesic acid.[39] Hydrosilylation has also been adopted to prepare organic silicone hyperbranched epoxy resin[40] and epoxy-terminated carbosiloxane.[41]

Although these techniques were successful in preparing hyperbranched epoxy resins, many of them were obtained only in labs, with the exceptions of Boltorn E1 and E2 (Perstorp Corp., Sweden) and our HyperT E1, E2, E3 and E4 series (HyperT Resins, China). A great deal of organic solvents, such as DMF,[39] and tedious processes involving synthetic epoxy monomers[27–29] are involved in some methods. In other methods, a large amount of water is wasted in the washing and removal of the byproduct NaCl.[2,6,20,31–38] Another disadvantage of these hyperbranched epoxy resins is their low glass transition and thermal decomposition temperature. Hyperbranched silicone resins[42,43] have good heat-resistance, whereas the synthetic processes are not only expensive, based on organic silane coupling agents[42] and unrecyclable homogeneous platinum catalysts, but also harmful to the environment due to the release of a great deal of HCl during the hydrolysis of chlorosilanes.[43] Many of the other hyperbranched epoxy resins reported need to be diluted with a thinner or solvent during application since they are either a solid[41] or a high viscosity liquid,[27–29] and can not be applied in solvent-free conditions.

In this paper, we present an environment-friendly method for preparing a novel hyperbranched epoxy resin with a silicone skeleton (Fig. 1). Firstly, phenyltriallylsilane (PTAS) was prepared by a reaction between allylmagnesium chloride (AMC) and phenyltrichlorosilane (PTCS). Secondly, an allyl-ended hyperbranched resin with a silicone skeleton (AHRSS) was obtained by a hydrosilylation between the PTAS and 1,1,3,3-tetramethyl-disiloxane (TMDS) using halloysite-supported platinum as a catalyst. Then, the hyperbranched epoxy resin with a silicone skeleton (HERSS) was synthesized by a similar hydrosilylation between AHRSS and 1,1,3,3-tetramethyl-disiloxane-propylglycidyl ether (TDPGE) that resulted from an addition of equal molar TMDS and allylglycidyl ether (AGE). In all the synthetic processes, the catalyst, excess materials and THF can be recycled, and the yield of every

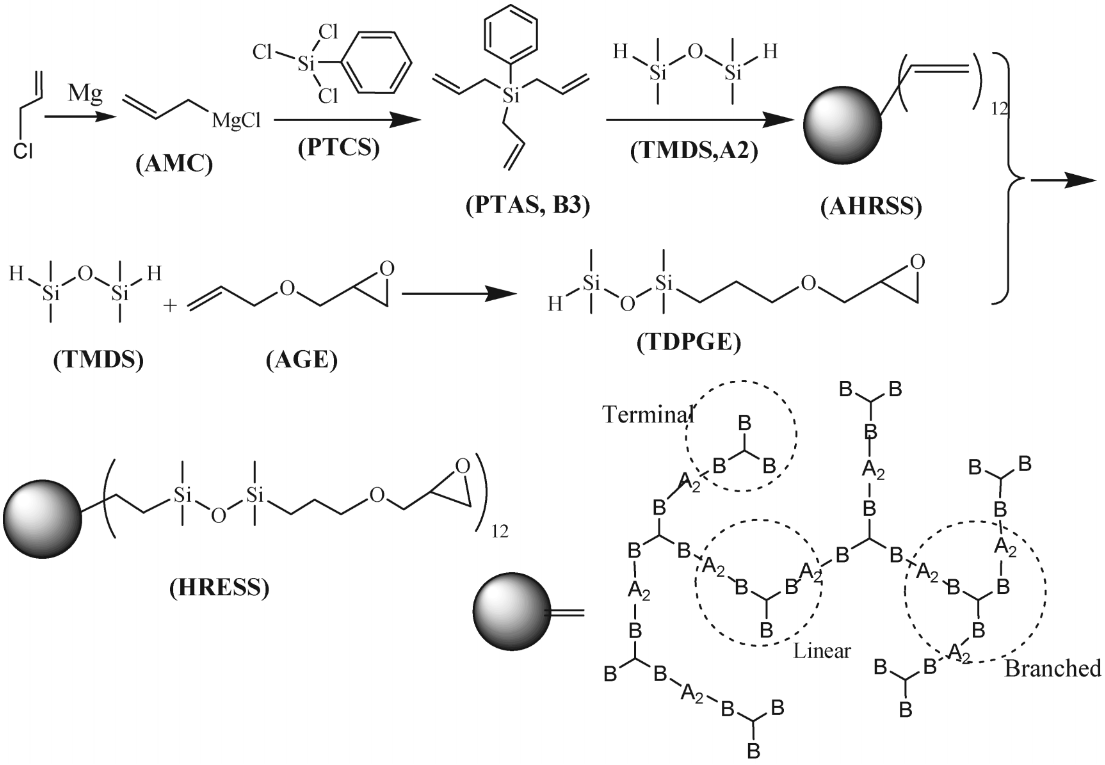

Fig. 1 Synthetic schemes of AHRSS and HERSS.

reaction involved was more than 90%. This method is not only suitable for large-scale production but also for solvent-free applications. The resulting HERSS was used to modify DGEBA and showed an excellent toughening and reinforcing ability. HERSS also showed good heat-resistance and may be used as a vacuum pressure impregnation insulation resin in high-power (over 2.5 MW) wind driven generators.

2. Experimental

2.1 Materials and measurements

Allylglycidyl ether (AGE), styrene (St), methyl nadic anhydride (MNA) and other materials were purchased from commercial sources and used without further purification unless noted otherwise. Tetrahydrofuran (THF), 1,1,3,3-tetramethyl-disiloxane (TMDS), allyl chloride (AC) and phenyltrichlorosilane (PTCS) were purified by distillation. AC, TMDS, AGE and PTCS were dried over 24 h with 4 Å molecular sieves before using. A heterogeneous halloysite supported platinum catalyst (Pt-Halloysite) with 0.4 wt% of platinum was prepared as described in our previous paper.[44] DETA-AN as curing agent, was prepared by an addition reaction between acrylonitrile (AN) and diethylene triamine (DETA)[3] at equal molar ratio.

Infrared spectra were taken using a NEXUS 470 Fourier transform infrared spectrometer. ^{1}H and ^{13}C NMR measurements were conducted using an AVANCE III-400 (Bruker) nuclear magnetic resonance spectrometer. The molecular weights and distributions (PDI) were determined with a gel permeation chromatograph (PL GPC-50) using a PL-RTLS 15/90 dual-angle LSD as a detector and THF as the eluent. The viscosity of AHRSS and HERSS was measured using a Brookfield DV-III+ viscometer with an RV-S06 spindle at 25 °C and 20 rpm. A transmission/reflection polarizing optical microscope (TRPOM, XPV-203E, China) equipped with a thermal platform was used to study micro-phase separation of the sample during curing.

The no-notch impact strength of the cured samples (80 mm × 10 mm × 4 mm) was determined using a XJJ-5 simple-supported-beam impact testing machine (ChengDe Precision Testing Machine Co., Ltd, China) at room temperature (25 °C) according to ASTM D256-81. The tensile strength of the dumbbell samples (75 mm × 5 mm × 5 mm) was measured by a WSM-20KN computer-controlled universal testing machine (ChengDe Precision Testing Machine Co., Ltd, China) according to ASTM D368-91a with a loading rate of 10 mm min^{-1}. The flexural strength of the samples (80 mm × 10 mm × 4 mm) was determined according to ASTM D790M-92 by a WSM-20KN testing machine using a three-point bending mode.

A scanning electron microscope (SEM) (XL-30FEG, Philip) was used to examine the morphology of the fractured surface. A thin section of the fractured surface was cut and mounted on an aluminum stub using conductive (silver) paint and was sputter-coated with gold prior to fractographic examination. SEM micrographs were obtained under conventional secondary electron imaging conditions, with an accelerating voltage of 20 kV.

Differential scanning calorimetry (DSC) measurements were performed with a differential scanning calorimeter (NETZSCH DSC204 F1) using a 1.8–3.0 mg sample in standard aluminum pans at a heating rate of 10 K min^{-1}. Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (NETZSCH TG209) at a heating rate of 20 K min^{-1} and a nitrogen flow of 20 mL min^{-1}.

2.2 Synthesis of silicone skeleton hyperbranched epoxy (HERSS) resin

Preparation of TDPGE. A mixture of AGE (5.71 g, 0.05 mol) and TMDS (6.70 g, 0.05 mol) was added dropwise to a three-necked flask containing TMDS (13.43 g, 0.10 mol) and Pt-Halloysite (6.0 g). The flask was equipped with a stirrer, cooler and thermometer, and the reaction was allowed to proceed for 10 h at about 60 °C. Then the catalyst was filtered and the excess TMDS was removed under a pressure of 5 mmHg at 60 °C to yield 12.30 g (98.95%) of a yellowish transparent liquid 1,1,3,3-tetramethyl-disiloxane-propylglycidyl ether (TDPGE).

Preparation of AHRSS. A mixture of PTAS (11.42 g, 0.05 mol) and THF (20 mL) was added dropwise to a three-necked flask containing TMDS (6.04 g, 0.045 mol), THF (15 mL) and Pt-Halloysite (10.0 g) as a catalyst. The flask was equipped with a stirrer, cooler and thermometer, and the reaction continued for 12 h at about 65–70 °C. Then the catalyst was filtered and the solvent was removed under a pressure of 5 mmHg at 65–70 °C to yield 17.06 g (97.7%) of a yellowish transparent liquid (AHRSS, M_n = 1637 Da, M_w = 3315 Da, M_z = 6795 Da, PDI = M_w/M_n = 2.03) with a viscosity of 252.5 mPa s (25 °C).

Preparation of HERSS. AHRSS (5.24 g), THF (15 mL), TDPGE (8.05 g) and Pt-Halloysite (5.0 g) was added to a three-necked flask, and the reaction continued for 10 h at temperature between 65 °C and 70 °C. A yellowish transparent liquid (HERSS, M_n = 2163 Da, M_w = 4525 Da, M_z = 10 464 Da, PDI = M_w/M_n = 2.09) of 9.70 g (99.5%) was afforded after the catalyst was filtered and the solvent THF was removed. The viscosity of the product is 1102 mPa s (25 °C) and the epoxy equivalent weight is 550 g mol^{-1}.

2.3 Preparation of HERSS/DGEBA composites

The HERSS/DGEBA blends containing 0–15 wt% of HERSS were prepared by mixing HERSS with DGEBA in a glass cup which was stirred with a glass stick at about 25 °C. A stoichiometric amount of DETA-AN was added with continuous stirring for 5 min. After the bubbles in the HERSS/DGEBA blend was removed under vacuum for 10 min, the blend was put into a silicone rubber mold and cured at 25 °C for 12 h, at 80 °C for 3 h and then post-cured at 180 °C for 6 h. After that, the samples were cooled gradually to room temperature and stored for about 12 h. The mechanical performances were then measured by corresponding standard methods.

3. Results and discussion

3.1 Recycle times of the halloysite-supported platinum catalyst

The halloysite-supported platinum catalyst (0.7 g) was used to catalyze the hydrosilylation between St (0.06 mol, 6.24 g) and

TMDS (0.025 mol, 3.36 g) at 323–328 K for 2 h with mechanical stirring. Then the catalyst was recycled by filtration and reused. The conversion of the Si–H bond of TMDS was measured by FT-IR after the reaction. The effect of the number of times the halloysite-supported platinum catalyst has been recycled on the FT-IR spectra of the product is shown in Fig. S1, ESI.† According to a relative ratio of peak area at 2123 cm^{-1} (Si–H) to that at 1494 cm^{-1}, a relationship between the conversion of the Si–H bond of TMDS and number of times the halloysite-supported platinum catalyst is recycled can be obtained and is shown in Fig. S2, ESI.† When using the same sample of catalyst for the seventh time the conversion of the Si–H bond of TMDS remains 98.4%, demonstrating the excellent recyclability of the halloysite-supported platinum catalyst.

3.2 Characterization of TDPGE, AHRSS and HERSS

FT-IR spectra of AGE, TMDS, TDPGE, PTAS, AHRSS and HERSS are shown in Fig. 2. Characteristic bonds of TMDS in FT-IR (KCl, cm^{-1}) are supplied in ESI† (S1).

The disappearance of the absorption peak of the =C–H group at 3059 cm^{-1} and 1646 cm^{-1} in Fig. 2c indicates that there is a complete reaction between AGE and TMDS, and the diminishment of the peak at 3060 cm^{-1} and the disappearance of the peak at 1629 cm^{-1} (Fig. 2f) also suggests complete conversion of the double bonds of AHRSS.

The ^{1}H NMR spectra and ^{13}C NMR spectra of the resulting compounds are shown in Fig. 3 and 4, respectively. The chemical shift data are summarized in ESI† S2 and S3, respectively.

NMR spectroscopy is a common tool[45,46] for measuring the degree of branching (DB) of hyperbranched polymers according to eqn (1). The DB refers to the ratio of branched and terminal units to total units, *i.e.*

$$DB = (N_b + N_t)/(N_b + N_t + N_l) \quad (1)$$

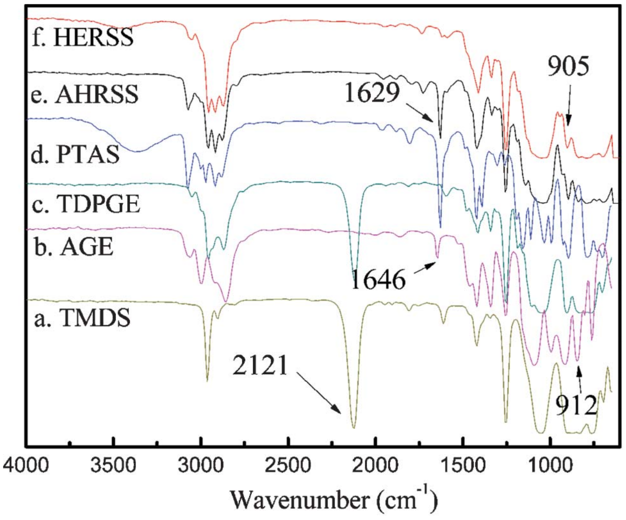

Fig. 2 FT-IR spectra of TMDS, AGE, TDPGE, PTAS, AHRSS and HERSS.

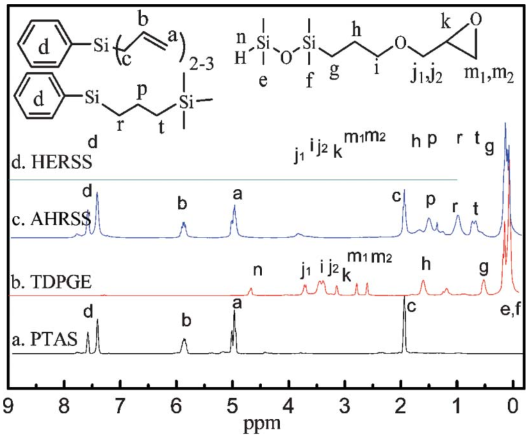

Fig. 3 ^{1}H NMR spectra of TDPGE, PTAS, AHRSS and HERSS.

According to the chemical structure of the AHRSS and its reaction mechanism, the chemical chains of AHRSS should be composed of three different structure units, including (1) branched units (N_b), (2) linear units (N_l) and (3) terminal units (N_t) (Fig. 5).

Since the difference in structural variation among the three units is very small, it is very difficult to designate directly the attributions of these hydrogen atoms in the range of 0.5–1.8 ppm (Fig. 6). The ^{1}H NMR-minus spectrum of model compound with a similar chemical structure is a convenient strategy used to analyze effectively these attributions for simplifying the calculation process and obtaining the DB.[32] Herein, we designed and synthesized a model compound tri-(1,1,3,3-tetramethyl-disiloxane)-phenylpropylsilane (**A$_3$**) by a reaction between the TMDS and the PTAS through a similar synthetic process as for TDPGE. Chemical shifts at δ 1.37–1.57 (a, 2H), δ 0.91–1.09 (b, 2H) and δ 0.60–0.80 (c, 2H) are observed clearly in the ^{1}H NMR (Fig. 6) of **A$_3$**. Comparing the corresponding chemical shifts of **A$_3$** to the chemical shifts of the hydrogen atoms in AHRSS, the three kinds of units (Fig. 5) can be assigned as following: δ 1.37–1.57 (T_2–H, 2H and B_2–H,

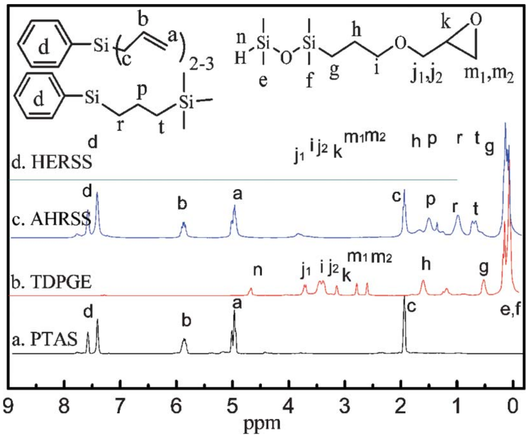

Fig. 4 ^{13}C NMR spectra of TDPGE, PTAS, AHRSS and HERSS.

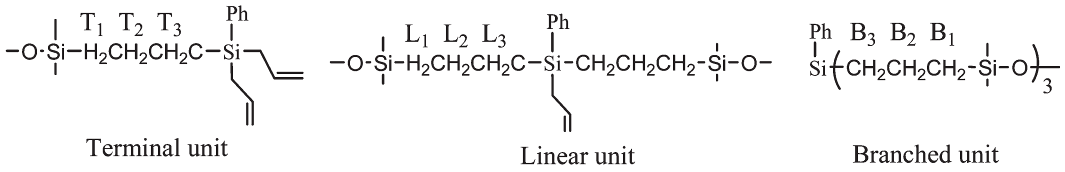

Fig. 5 Chemical structures of terminal, linear and branched units.

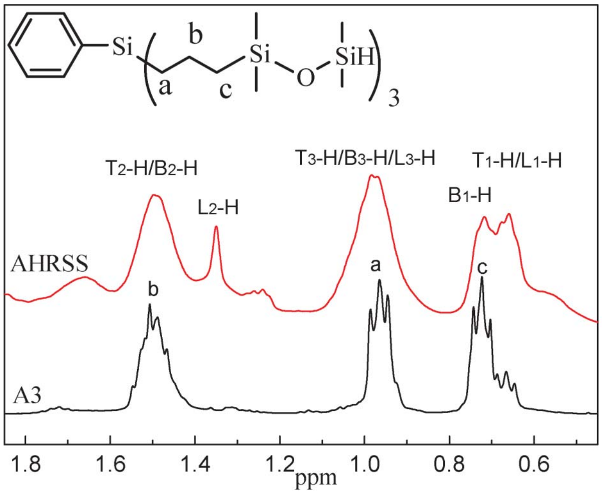

Fig. 6 ^{1}H NMR spectra of $\mathbf{A_3}$ and AHRSS between δ 0.5–1.8 ppm.

6H), δ 1.34 (L_2–H, 4H), δ 0.81–1.09 (T_3–H, 2H, B_3–H, 6H and L_3–H, 4H), δ 0.67–0.78 (B_1–H, 6H), and δ 0.54–0.67 (T_1–H, 2H and L_1–H, 4H) (Fig. 6). The relative areas of all these peaks are obtained and summarized in Table 1 according to their relationships among chemical structures. The precise DB (0.72) of the AHRSS can be calculated by eqn (2). The DB of HERSS is also 0.72 because it has same silicone skeleton as AHRSS.

$$\mathrm{DB}=\frac{\dfrac{(T_1+T_2+T_3)}{2}+\dfrac{(B_1+B_2+B_3)}{6}}{\dfrac{(T_1+T_2+T_3)}{2}+\dfrac{(B_1+B_2+B_3)}{6}+\dfrac{(L_1+L_2+L_3)}{4}} \tag{2}$$

3.3 Application and performance of HERSS

One of the major applications of hyperbranched epoxy resins is to toughen and reinforce the commercial DGEBA,[3,4,15,36,47] however, their glass temperature usually decreases by over 20%. The novel hyperbranched epoxy resin with a silicone skeleton structure (HERSS) was applied to modify DGEBA using DETA-AN as a curing agent. The mechanical performance of HERSS/DGEBA composites first increases and then decreases with an increase of the HERSS content (Table 2), and when the modified DGBEA contains 9 wt% HERSS, the HERSS can increase the impact, flexural and tensile strength by about 92.5%, 36.0% and 88.6%, respectively.

However, compared with the homogeneous microstructure of HTDE/DGEBA composites,[3] it is interesting to note that a micro-phase separation ''sea–island'' structure appears clearly in the morphology of the fractured surface (Fig. 7). An increase in HERSS content results in an increase in the number and volume content of ''islands'' on the surface (Fig. 7). The volume contents of the islands observed in SEM micrographs are close to the theoretical values (Table 3) calculated from their formula, indicating that the composition of the islands should be cured HERSS. The difference in solubility parameters of DGEBA (δ 17.91 (J cm^{-3})$^{0.5}$) and HERSS (δ 15.19 (J cm^{-3})$^{0.5}$) changes their compatibility during curing and inducts micro-phase separation. A real-time transmission/reflection polarizing optical microscope (TRPOM) equipped with a thermal platform was used to study the micro-phase separation (Fig. S3, ESI†) of 9 wt% HERSS/91 wt% DGEBA blend during curing on the surface of a glass slide at 80 °C, and the result indicates that the micro-phase separation size of ''sea–island'' structure increases with the curing time.

The clear smooth morphology in Fig. 7a is substantial evidence of the brittle nature of DGEBA. The appearance of many ''islands'' (Fig. 7b–f) in the matrix indicates excellent toughness of the HERSS/DGEBA composites because the non-crosslinkable hyperbranched structure in the islands may absorb energy upon impacting.[3] At the same time, improvement in tensile strength and flexural strength is attributable to the increase in crosslinking density of the composites due to a large number of epoxy groups in HERSS and strong surface interactions between ''islands'' and ''sea'' (Fig. 7g–h). However, the crosslinking density and non-crosslinkable hyperbranched structure have opposite effects on the strength and toughness of the composites. A balance was found with the incorporation of 9 wt% HERSS, which demonstrated not only increased toughness but also excellent tensile and flexural strength.

Table 1 Peak areas and DB calculations of the AHRSS

δ/ppm	0.54–0.67		0.67–0.78	0.81–1.09			1.34	1.37–1.57		DB
Hydrogen atoms	T_1	L_1	B_1	T_3	L_3	B_3	L_2	T_2	B_2	
Areas	0.81	1.11	1.89	0.81	1.11	1.89	1.11	0.81	1.89	0.72

Table 2 Effects of the HERSS content on the mechanical performances of HERSS/DGEBA composites

Performance	Tensile strength/MPa	Flexural strength/MPa	Impact strength/kJ m^{-2}	Glass temperature/°C
DGEBA	31.98	31.14	1.99	126.0
3 wt% HERSS	41.79	35.35	2.99	118.0
6 wt% HERSS	57.16	37.38	3.50	112.3
9 wt% HERSS	60.31	42.34	3.83	108.3
12 wt% HERSS	56.18	41.64	3.60	107.5
15 wt% HERSS	53.38	39.54	3.51	105.5

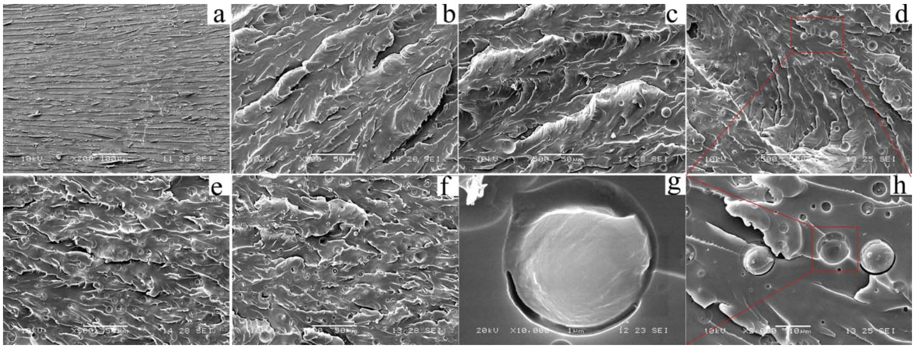

Fig. 7 SEM micrographs of the fractured surface of HERSS/DGEBA composites and DGEBA: (a) DGEBA, (b) 3 wt% HERSS, (c) 6 wt% HERSS, (d) 9 wt% HERSS, (e) 12 wt% HERSS, (f) 15 wt% HERSS, (g–h) local magnified images.

Table 3 Volume contents of the islands in all composites

HERSS content	Volume content calculated from SEM micrographs/%	Volume content calculated from theoretical formula/%
3 wt% HERSS	2.86	2.82
6 wt% HERSS	5.67	5.64
9 wt% HERSS	8.52	8.45
12 wt% HERSS	10.28	11.27
15 wt% HERSS	14.00	13.06

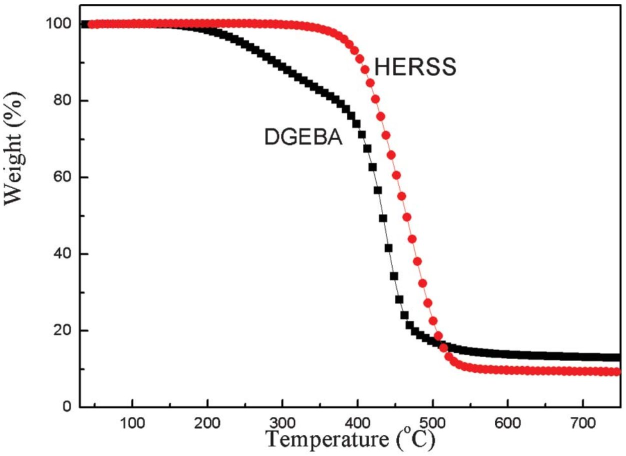

Fig. 8 TGA curves of cured HERSS and DGEBA with MNA.

The glass transition temperature (T_g) of the HERSS/DGEBA composites decreases slowly with an increase in HERSS content as shown in Fig. S4, ESI† and Table 2. The T_g (108.3 °C) of 9 wt% HERSS/DGEBA composites only decreases by about 14.0% compared with that of DGEBA (126.0 °C), suggesting a better heat-resistance than other hyperbranched epoxy resins reported.[3,36] For example, the T_g of 9 wt% HTDE-2/DGEBA composites decreased by about 30.3%.[3] Thermal decomposition temperature, T_I (initial thermal decomposition temperature or temperature at 5% weight loss), of the HERSS/DGEBA composites increases slightly (Fig. S5 and Table S1, ESI†) with increase in HERSS content. All the composites have higher thermal decomposition temperatures of about 340 °C than previous results.[3,36] Methyl nadic anhydride (MNA) is the primary curing agent in preparing solvent-free insulation materials with high-temperature resistance. The T_I of about 380.0 °C (Fig. 8 and Table S1, ESI†) of the cured HERSS-MNA materials is not only much higher than that of DGEBA-MNA (99.1 °C), but also approaches that of cured pure silicone,[42] indicating the excellent high-temperature-resistance of HERSS.

4. Conclusions

An allyl-ended hyperbranched resin with a silicone skeleton (AHRSS) was synthesized by a hydrosilylation between phenyltriallylsilane (PTAS) and 1,1,3,3-tetramethyl-disiloxane (TMDS), and a novel hyperbranched epoxy resin with a silicone skeleton (HERSS) was then prepared from 1,1,3,3-tetramethyl-disiloxane-propylglycidyl ether (TDPGE) and AHRSS using a recyclable heterogeneous halloysite supported platinum catalyst. The chemical structure, molecular weight and distribution and degree of branching of the HERSS were characterized by FT-IR, GPC and NMR. The impact, flexural and tensile strength of DGEBA can be increased by about 92.5%, 36.0% and 88.6% respectively with the incorporation of 9 wt% HERSS. A micro-phase separated ''sea–island'' structure was observed and attributed to the weak compatibility between HERSS and DGEBA. Moreover, the high initial thermal decomposition temperature of about 380.0 °C of cured HERSS/methyl nadic anhydride (MNA) resin indicates a promising application in high-temperature-resistant solvent-free resins. The use of less solvent, the recyclability of the catalyst and excess materials, and the high yields (>90%) of the corresponding compounds all suggest that this product should be produced economically on a large scale.

Acknowledgements

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Notes and References

1 B. I. Voit and A. Lederer, *Chem. Rev.*, 2009, **109**, 5924.
2 S. Chen, D. Zhang, S. Jiang and D. Jia, *J. Appl. Polym. Sci.*, 2012, **123**, 3261.
3 D. Zhang and D. Jia, *J. Appl. Polym. Sci.*, 2006, **101**, 2504.
4 L. Boogh, B. Pettersson and J. A. E. Månson, *Polymer*, 1999, **40**, 2249.
5 B. Ellis, *Chemistry and technology of epoxy resins*, Blackie Academic & Professional, 1993.
6 B. De and N. Karak, *J. Mater. Chem. A*, 2013, **1**, 348.
7 G. Qi, X. Zhang, B. Li, Z. Song and J. Qiao, *Polym. Chem.*, 2011, **2**, 1271.
8 D. R. Bortz, E. G. Heras and I. Martin-Gullon, *Macromolecules*, 2011, **45**, 238.
9 X. Cheng, Y.-X. Chen, Z.-L. Du, P.-X. Zhu and D.-C. Wu, *J. Appl. Polym. Sci.*, 2011, **119**, 3504.
10 G. Cicala, A. Recca and C. Restuccia, *Polym. Eng. Sci.*, 2005, **45**, 225.
11 X. Fernández-Francos, J. M. Salla, A. Cadenato, J. M. Morancho, A. Serra, A. Mantecón and X. Ramis, *J. Appl. Polym. Sci.*, 2009, **111**, 2822.
12 A. Gopala, H. Wu, J. Xu and P. Heiden, *J. Appl. Polym. Sci.*, 1999, **71**, 1809.
13 R. Mezzenga, L. Boogh and J.-A. E. Månson, *Compos. Sci. Technol.*, 2001, **61**, 787.
14 D. Ratna and G. P. Simon, *Polym. Eng. Sci.*, 2001, **41**, 1815.
15 R. J. Varley and W. Tian, *Polym. Int.*, 2004, **53**, 69.
16 D. Ratna, R. Varley, R. K. S. Raman and G. Simon, *J. Mater. Sci.*, 2003, **38**, 147.
17 J. Verrey, Y. Winkler, V. Michaud and J. A. E. Manson, *Compos. Sci. Technol.*, 2005, **65**, 1527.
18 J. Fröhlich, H. Kautz, R. Thomann, H. Frey and R. Mülhaupt, *Polymer*, 2004, **45**, 2155.
19 S. Lu, C. Wei and X. Yang, *Trans. Nonferrous Met. Soc. China*, 2006, **16**(Supplement 2), 665.
20 D. Zhang and D. Jia, *Eur. Polym. J.*, 2006, **42**, 711.
21 Y. Zhang, D. Zhang, C. Qin and J. Xu, *Polym. Compos.*, 2009, **30**, 176.
22 D. Zhang, X. Cheng, A. Zhang and D. Jia, *Funct. Mater. Lett.*, 2011, **4**, 351.
23 D. Zhang, H. Wu, T. Li, A. Zhang, Y. Peng and F. Jing, *Polym. Compos.*, 2011, **32**, 36.
24 P. G. Parzuchowski, M. Kiźlińska and G. Rokicki, *Polymer*, 2007, **48**, 1857.
25 J.-P. Yang, Z.-K. Chen, G. Yang, S.-Y. Fu and L. Ye, *Polymer*, 2008, **49**, 3168.
26 M. Morell, M. Erber, X. Ramis, F. Ferrando, B. Voit and A. Serra, *Eur. Polym. J.*, 2010, **46**, 1498.
27 T. Emrick, H. T. Chang and J. M. J. Fréchet, *Macromolecules*, 1999, **32**, 6380.
28 T. Emrick, H. T. Chang and J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 4850.
29 L. Ma, H. Wang, L. He and X. Li, *Chin. J. Polym. Sci.*, 2011, **29**, 300.
30 V. Coessens, J. Pyun, P. J. Miller, S. G. Gaynor and K. Matyjaszewski, *Macromol. Rapid Commun.*, 2000, **21**, 103.
31 X. Wang and W. Feast, *Chin. J. Polym. Sci.*, 2002, **20**, 585.
32 D. Zhang, D. Jia and S. Chen, *Macromol. Chem. Phys.*, 2009, **210**, 1159.
33 D. Zhang, D. Jia and Z. Zhou, *Macromol. Res.*, 2009, **17**, 289.
34 X. Fernández-Francos, D. Foix, À. Serra, J. M. Salla and X. Ramis, *React. Funct. Polym.*, 2010, **70**, 798.
35 D. Zhang, D. Jia and Y. Chen, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 2010, **47**, 957.
36 J. Fu, L. Shi, S. Yuan, Q. Zhong, D. Zhang, Y. Chen and J. Wu, *Polym. Adv. Technol.*, 2008, **19**, 1597.
37 A. Vora, M. J. Nasrullah and D. C. Webster, *Macromolecules*, 2007, **40**, 8586.
38 J. Lv, Y. Meng, L. He, T. Qiu, X. Li and H. Wang, *J. Appl. Polym. Sci.*, 2013, **128**, 907.
39 M. Murali, V. Srinivasa Rao and A. B. Samui, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 3116.
40 C. Gong and J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 2970.
41 N. Kang, Z. Du, H. Li and C. Zhang, *Polym. Eng. Sci.*, 2012, **52**, 868.
42 B. Zhang, A. Gu, G. Liang, J. Hu, D. Zhuo and L. Yuan, *Polym. Adv. Technol.*, 2011, **22**, 2415.

43 Q. Li, J. Zhong, Y. Li, K. Wang, Q. Jiang and H. Chen, *IEEE Trans. Dielectr. Electr. Insul.*, 2010, **17**, 785.

44 D. Zhang, W. Huo, J. Wang, T. Li, X. Cheng, J. Li and A. Zhang, *J. Appl. Polym. Sci.*, 2012, **126**, 1580.

45 C. J. Hawker and J. M. J. Frechet, *J. Am. Chem. Soc.*, 1990, **112**, 7638.

46 D. Yan, A. H. E. Müller and K. Matyjaszewski, *Macromolecules*, 1997, **30**, 7024.

47 M. DeCarli, K. Kozielski, W. Tian and R. Varley, *Compos. Sci. Technol.*, 2005, **65**, 2156.