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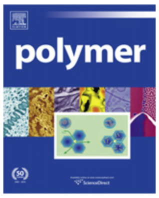

Grafting of hyperbranched aromatic polyamide onto silica nanoparticles

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ABSTRACT

Hyperbranched aromatic polyamide grafted nano-silica particles were successfully prepared via "one-pot" melt polycondensation. The particles were firstly treated with a silane coupling agent to introduce amine groups as the growth points, and then grafting of the hyperbranched polymers started from the modified surface. The percentage grafting can be as high as 32.8%. The key reaction conditions, including feeding ratio, reaction temperature and time, were carefully investigated to determine a set of optimal grafting parameters. It was found that the significant steric hindrance between the hyperbranched polymers during graft polymerization played a key role in controlling molecular structure of the grafted polymers, while adsorption of grafting monomer onto SiO_2 particles prior to the reaction facilitated higher degree of branching and apparent molecular weight of ungrafted polymers.

1. Introduction

Hyperbranched polymers (HBPs) are highly branched macromolecules with three-dimensional spherical architecture [1]. Their properties depend on not only structural characteristics of the branches in their interior, but also the large number of surface end groups that are susceptible to functionalization. As a result, diversified and tailor-made performance (e.g. compatibility and reactivity) can be imparted to the polymers.

Due to the unique structure and properties, HBPs have been used as additives in epoxy resins, where they brought in enhanced flexibility and/or toughness due to phase separation without affecting other properties, including hardness and tensile modulus [2]. They also served as compatibilizer in polypropylene/polyamide 6 blends [3].

In recent years, preparation and application of hyperbranched polymers grafted nano-surfaces have become an attractive field [4–6]. Organic–inorganic conjugates, in which HBPs are chemically grafted onto inorganic particles, nano-tubes or ceramic membranes, are potentially interesting because they combine the properties of multifunctional polymers with the superior mechanical stability and morphology control of inorganic substrates [7]. Grafting of hyperbranched polymers onto nanoparticles surface can interfere with agglomeration of the nanomaterials and increase their surface affinities for organic solvent and polymer matrixes. However, most previous studies dealt with grafting of aliphatic HBPs, and the grafting of aromatic HBPs is yet to be explored. It is anticipated that the grafted aromatic HBPs might find wide applications, such as reinforcing agent for reducing wear rate of thermosets due to their higher thermal stability.

Our previous works demonstrated that incorporation of inorganic nanoparticles pre-treated by graft polymerization is capable of toughening thermoplastics [8] and reducing wear rate of thermosets [9]. In comparison with low molecular surfactants or coupling agents, grafting macromolecules onto inorganic nanoparticles has the following advantages. (i) Interfacial characteristics between the treated nanoparticles and the matrix polymer can be purposely adjusted through a proper selection of species of graft monomers and conditions of graft reaction [10,11]. When reactive groups (i.e. epoxide or amine groups) are introduced onto nano-SiO_2 by graft polymerization, for instance, chemical bonding between the fillers and epoxy matrix is established by the reaction between epoxide groups and curing agent [12]. (ii) After graft modification, fragile agglomerates of nanoparticles become much stronger as they turn into a nanocomposite microstructure consisting of the nanoparticles, the grafted and the ungrafted polymer.

Nevertheless, the aforesaid studies in our lab only consider grafting of linear polymeric chains. As a part of our serial researches dealing with epoxy nanocomposites that are supposed to have excellent tribological properties, the present paper investigates hyperbranched grafting of aromatic polyamide on the surface of nano-sized silica using melt polycondensation method. It is hoped that the specific hyperbranched architecture, excellent thermal resistance and abundant terminal amino groups of aromatic

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polyamide will generate synergistic effect together with nano-SiO_2 in the composites. Aiming at this ultimate target, this report is focused on details of in-situ surface graft polymerization with 3,5-diaminobenzoic acid as the monomer. The two-step reaction route is showed in Scheme 1. Nano-silica is treated with a silane coupling agent to introduce amine groups as the growth points on the surface, and then grafting of hyperbranched aromatic polyamide starts from the modified particles' surface.

In comparison with step-wise propagation, one-pot method is reported to be simpler and more convenient [13–15], when synthesis of hyperbranched polymers grafted nano-surfaces is concerned. Grafting of hyperbranched aliphatic polyester and poly(amidoamine) in solution or solvent-free dry system was carried out in this way, whereas grafting of hyperbranched aromatic polyamide onto silica has not yet been documented.

In general, hyperbranched polymers possess highly, but not perfectly, branched structures. Degree of branching, DB, is a characteristic parameter to describe their architecture [16]. Control of DB value, molecular weight and its distribution is one of the most interesting and important aspects of synthesis of hyperbranched polymers. Especially in the case of graft polymerization, these factors are influenced by the existence of silica. Considering that self-polycondensation of 3,5-diaminobenzoic acid is a complicated procedure that may form dendritic, linear and terminal units [17], effects of polymerization conditions and nano-SiO_2 on percentage grafting, DB value, molecule weight and its distribution, and content of amine end groups are carefully studied hereinafter.

2. Experimental

2.1. Materials

The nano-sized silica (Aerosil) supplied by Degussa Co., Germany has a specific surface area of 380 m^2/g and an averaged diameter of 7 nm, respectively. Prior to usage, the particles were dried in an oven at 120 °C under vacuum for 24 h in order to get rid of the physically adsorbed water. A silane coupling agent, γ-aminopropyl triethoxysilane (γ-APS, provided by Nanjing Shuguang Chemical Industry Co. Ltd., China), was employed to introduce the active amine groups on the surface of nano-SiO_2. The grafting monomer, 3,5-diaminobenzoic acid (DABA, Alfa Aesar Co. Ltd.), was refined by recrystallization in water in advance. Other solvents, like N,N-dimethylacetamide (DMAc), N,N-dimethylform amide (DMF), toluene, ethanol, methanol and HF solution (40 wt.% in water) were analytical grade provided by Guangzhou Chemical Reagent Factory, China, and were used as received without further purification.

2.2. Introduction of amino groups onto nano-silica surface

5.0 g nano-silica and 150 mL toluene were charged into a 250 mL flask, which was then treated with ultrasonic for 30 min. Subsequently, 5 g γ-APS was added, and the reaction proceeded for 8 h under refluxing temperature with the protection of nitrogen. After filtration and extraction with ethanol for 24 h to remove the excess silane adsorbed on the nanoparticles, the γ-APS treated nano-silica (called SiO_2–APS) was dried in vacuum at 50 °C for 24 h. Thermal gravimetric analysis gave a percentage grafting of 12% (meaning 12 g APS has been grafted onto 100 g silica). The content of amino group ($-NH_2$) on the surface of SiO_2–APS was determined by titration with HCl aqueous solution [18], which provided a result of 1.65 mmol/g.

2.3. Melt grafting of hyperbranched aromatic polyamide from silica surface

The AB_2 monomer, DABA, was melt grafted from the surface active amino groups of SiO_2–APS. A typical procedure is as follow. 1.0 g SiO_2–APS and a certain amount of DABA were charged into a 100 mL flask. The self-polycondensation was performed at 240 °C with agitation under argon gas stream for 30 min. Having been cooled down to room temperature, the product was extracted by DMAc in a Soxhlet apparatus for 72 h to completely remove the ungrafted hyperbranched polyamide, as convinced by the inspection of the HBP concentration in the extraction solvent by UV spectroscopy. At last, the grafted product (i.e. the extracted SiO_2-g-HBP) was washed with methanol and dried in vacuum at 50 °C for 24 h. Some of them were transferred to a Netzsch TG-209 thermogravimeter to determine the percentage grafting, γ_g (meaning the weight of HBP has been grafted onto 100 g silica).

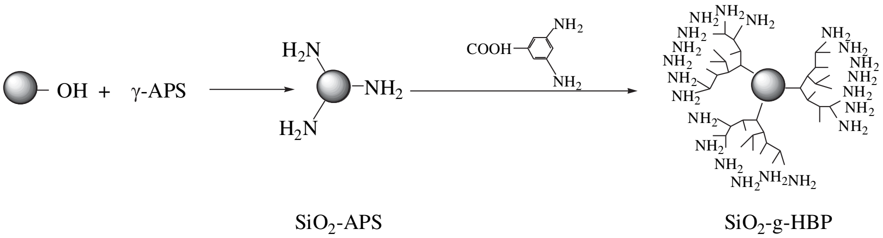
To collect the ungrafted hyperbranched polyamide, the aforesaid DMAc solution was poured into methanol containing 0.1% LiCl. The precipitated ungrafted product was filtered and dried in vacuum at 50 °C. The density of hyperbranched polyamide was determined to be 1.35 g/cm^3 by density bottle method.

To highlight the effect of silica on the architectures of grafted hyperbranched aromatic polyamide, a comparative experiment was conducted in terms of a direct polycondensation of DABA in the absence of silica (named as homopolymerization) [17]. The reaction conditions and procedure are similar to those applied for preparing SiO_2-g-HBP except that no agitation was used.

2.4. Isolation of grafted hyperbranched polyamide from nano-silica

A typical procedure is described as follows. Extracted SiO_2-g-HBP and 20 wt.% HF solution (SiO_2/HF = 1/1.1 by equivalent ratio) were charged into a 50 mL plastic beaker, and stirred under room temperature for 2 h until the silica particles were completely dissolved. The residual HBPs were collected by filtering, and washing with H_2O and methanol for several times. Then, the isolated hyperbranched polyamide (dissoluble in DMAc) was obtained after drying in vacuum at 50 °C for 12 h.

It is worth noting that the percentage grafting estimated from weight of the isolated grafted HBP is always lower than that obtained by thermogravimetric analysis of extracted grafted nano-SiO_2 (refer to sub-section 2.3), because certain amount of the isolated grafted HBP might be lost during repeated filtering and washing. It proved the correctness of the percentage grafting



Scheme 1. Two-step route for grafting hyperbranched aromatic polyamide from nano-silica.

offered by the extraction method from another angle. Accordingly, the values of percentage grafting used hereinafter were determined by thermal decomposition of solvent extracted grafted nano-SiO_2 as described in sub-section 2.3.

2.5. Characterization

Fourier transform infrared (FTIR) spectra were recorded using a Nicolet/Nexus 670 spectrometer (Thermo Fisher Scientific Inc., KBr disk method). Nuclear magnetic resonance (^1H NMR) measurements were conducted on a Varian Mercury-Plus 300 spectrometer (Varian, Inc.) with DMSO-d_6 as the solvent. Thermal gravimetric analyses (TGA) were performed with a Netzsch TG-209 instrument (NETZSCH-Gerätebau GmbH) at a heating rate of 20 °C/min in N_2 or air flow (20 mL/min). The apparent molecular weights of grafted, ungrafted and homopolymerized polymers were measured by using a Walter 208LC gel permeation chromatograph (GPC, Waters Corp.) at room temperature with DMF containing 0.05 mol/L LiBr as the solvent. It is worth noting that the apparent molar masses determined with GPC should be smaller than the absolute values due to the smaller hydrodynamic radius than that of linear polystyrene standard [19]. Herein, the apparent molar masses are used for interpreting the influence of reaction conditions, which can be further compared with other references using GPC molecular weights. Differential scanning calorimetry (DSC) measurements were carried out using a TA Instruments DSC Q10 (TA Instruments-Waters LLC) at 10 °C/min under nitrogen. Morphologies of SiO_2 and SiO_2-*g*-HBP were observed with a JEM-2010HR transmission electron microscope (TEM, JEOL Ltd.). The samples were prepared by dispersing SiO_2 or SiO_2-*g*-HBP in ethanol at a concentration of 0.001 g/mL under ultrasonic agitation for 15 min, and then depositing the particles on a copper grid covered with a carbon film. The average size and size distribution of the nanoparticles were determined by dynamic/static light scattering method using a Brooken Haven BI-200SM instrument (Brookhaven Instruments Co., USA; solid-state laser, wavelength: 532 nm, power: 100 mW, cell type: circular quartz sample cell (ϕ25), detector angle: 90°, temperature: 25 °C, dispersant viscosity: 0.92, dispersant refractive index: 1.44). The samples were dispersed in DMAc under ultrasonic for 15 min in advance.

3. Results and discussion

3.1. Characteristics of the surface modified nano-silica

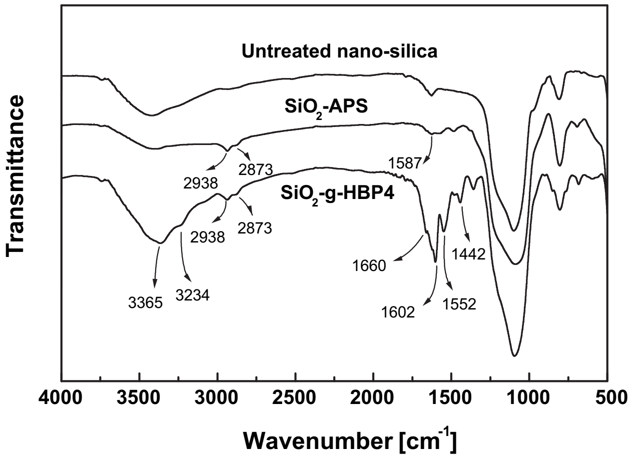


Fig. 1. FTIR spectra of untreated nano-silica, SiO_2–APS and SiO_2-*g*-HBP4.

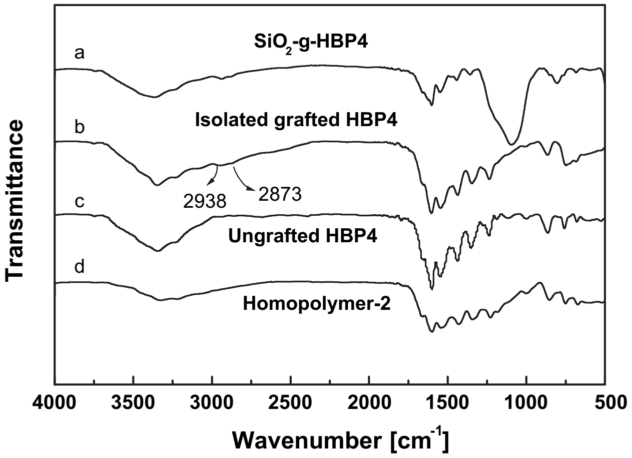


Fig. 2. FTIR spectra of (a) SiO_2-*g*-HBP4, (b) isolated grafted HBP4, (c) ungrafted HBP4 and (d) homopolymer-2.

According to our previous study [12], coupling agent treatment plays an essential role in chemically attaching polymer chains onto nanoparticles. In this work, the amino groups were firstly introduced onto nano-silica surface as an initiator site by the treatment of silica with γ-APS, and then hyperbranched polyamide was grafted from these amino groups. FTIR spectra of the related materials are shown in Fig. 1. The adsorptions of amino group at 3409 and 1587 cm^{-1}, and methylene at 2938 and 2873 cm^{-1} in the spectrum of SiO_2–APS reveal the existence of silane γ-APS on the surface of nano-silica. For the spectrum of SiO_2-*g*-HBP, the peak at 1660 and 1552 cm^{-1} can be assigned to amide besides the peaks of aromatic primary amine at 3365 and 3234 cm^{-1}, and phenyl groups at 1602 and 1442 cm^{-1}. These prove that hyperbranched polyamide chains have been chemically connected to the surface of nano-silica, and the grafted polymer cannot be removed by the extraction procedure.

When the grafted hyperbranched polyamide chains are isolated from the silica, the adsorption of Si–O–Si bonds at 1095 cm^{-1} disappears, while the peaks belonging to methylene of γ-APS are still visible (refer to curve *b* in Fig. 2). It indicates that silica is etched by breaking the Si–O bonds. The FTIR spectrum of ungrafted hyperbranched polyamide is almost the same as that of the homopolymer obtained by thermal polymerization of DABA (cf. curves *c* and *d* in Fig. 2), which implies that no other side reactions occurred during the graft polymerization.

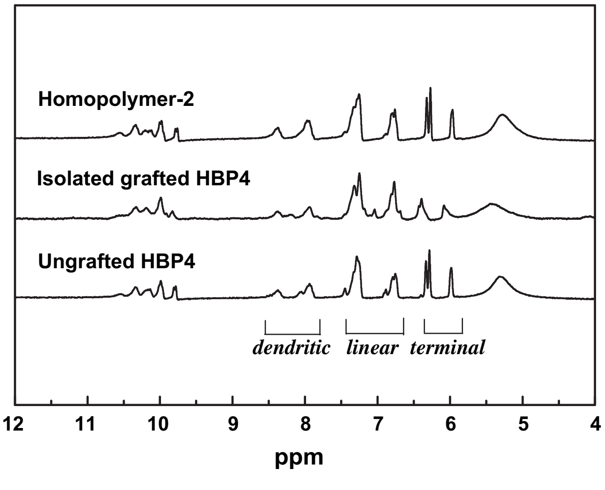
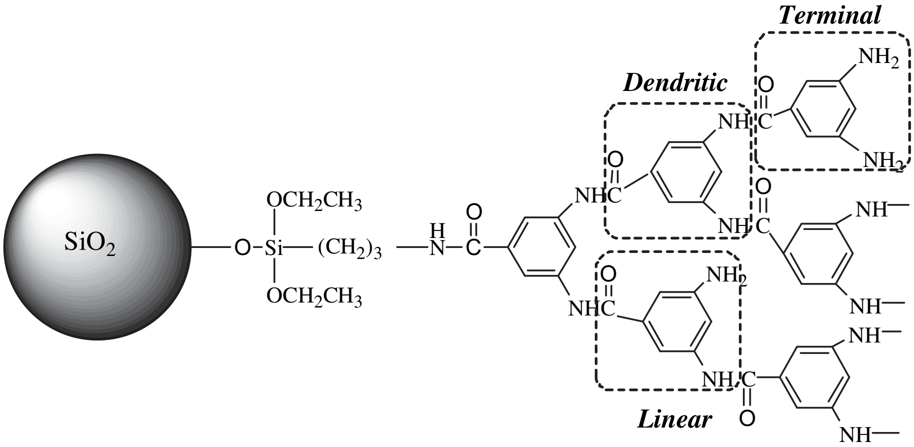


Fig. 3. ^1H NMR spectra of homopolymer-2, isolated grafted HBP4 from SiO_2-*g*-HBP4, and ungrafted HBP4 generated during preparing SiO_2-*g*-HBP4.



Scheme 2. Architecture of hyperbranched polyamide grafted nano-silica.

^{1}H NMR spectra of the resultant polymers are shown in Fig. 3. The characteristic peaks from the aromatic protons are perceived at 8.3, 7.9, 7.3, 6.8, 6.3 and 6.0 ppm for all hyperbranched polyamides. The peaks at 8.3 and 7.9 ppm are attributed to the aromatic protons of the dendritic units (D), while the peaks at 7.3 and 6.8 ppm and those at 6.3 and 6.0 ppm are ascribed to those of the linear (L) and terminal units (T), respectively (Scheme 2). In addition, the signals of terminal amine groups at 5.3 ppm, and the amide groups at 10.6–9.8 ppm are also observed. Evidently, the ^{1}H NMR spectra further demonstrate the hyperbranched architecture of various polyamides. According to Fréchet's equation [16]:

$$\mathrm{DB} = \frac{D+T}{D+T+L}$$

the degree of branching, DB, can be calculated from the integration ratio of the peak areas based on dendritic, linear and terminal units (Tables 1–3). Besides, the number of amino groups per molecule, $N_{\mathrm{NH_2}}$, can also be estimated from:

$$N_{\mathrm{NH_2}} = \frac{M_{\mathrm{n}}}{133a+134b+135c} \times (b+2c)$$

where M_n is the number average molecule weight of the polymer, and the parameters a, b and c represent the contents of dendritic (molar mass: 133 g/mol), linear (containing 1 mol NH_2 group, molar mass: 134 g/mol) and terminal units (containing 2 mol NH_2 group, molar mass: 135 g/mol) determined by ^{1}H NMR, respectively. From Table 1, it is noted that quite a large amount of NH_2 groups are introduced onto nano-SiO_2 particles by the hyperbranched grafting method.

The main chemical shifts in the ^{1}H NMR of the isolated grafted polymer are identical to those of the homopolymer (Fig. 3). It means that both polyamides have the same molecular structure. However, during the separation of grafted hyperbranched polyamide from nano-silica surface, the etching reagent HF may bond with the terminal amino groups to form salts, which induces a mild chemical shift of the aromatic protons peaks connected to terminal amino units from 6.3 to 6.0 to 6.4 and 6.1 ppm. This is because HF attracts electrons, and shifts the adjacent aromatic protons peaks to lower magnetic field. Meanwhile, the resonance of terminal amino groups is also affected by HF, leading to the chemical shift of proton from 5.3 to 5.4 ppm. It should be noted that the interaction between terminal amino groups and HF only shifts the peak position, but does not alter the area of these peaks. Accordingly, the DB values of the grafted polymer determined by ^{1}H NMR are creditable. In comparison with homopolymer, ^{1}H NMR spectrum of the ungrafted polyamide also shows similar characteristic peaks. Again, the two polymers must have the same molecular structure.

Thermal stability of aromatic polyamide homopolymer is shown in Fig. 4, in which the initial decomposition temperatures are estimated to be 430 °C and 325 °C in N_2 and air, respectively. Fig. 5 and Table 4 further compare pyrolytic performance of the homopolymer, SiO_2–APS, SiO_2-*g*-HBP3 and its corresponding ungrafted polymer. The initial thermal decomposition temperature of SiO_2–APS is about 258 °C, while SiO_2-*g*-HBP3 begins the weight loss at about 289 °C. The lower initial decomposition temperatures of SiO_2-*g*-HBP3 and its ungrafted polymer than that of the homopolymer are ascribed to the lower apparent molecular weight of the former (Tables 2 and 3). Nevertheless, the temperatures corresponding to the peak rate of weight loss for SiO_2-*g*-HBP3 and its ungrafted polymer are similar to that of the homopolymer.

T_g of hyperbranched polyamide cannot be directly detected by DSC because of its rigid chains and the strong interaction between

Table 1
Characterization of the resultant HBP homopolymer as a function of reaction conditions of direct polycondensation.

Samples	Temperature (°C)[a]	Time (h)[b]	DB[c]	M_n ($\times10^4$ g/mol)[d]	M_w ($\times10^4$ g/mol)[e]	M_w/M_n[f]	$N_{\mathrm{NH_2}}$[g]
Homopolymer-1	240	1	0.49	2.9	4.5	1.5	213
Homopolymer-2	246	0.5	0.48	3.8	6.5	1.7	273
Homopolymer-3	246	1	0.47	3.6	5.6	1.6	260
Homopolymer-4	246	2	–	–	–	–	–
Homopolymer-5	260	1	–	–	–	–	–

[a] Polycondensation temperature.
[b] Polycondensation time.
[c] Degree of branching.
[d] Number average apparent molecular weight.
[e] Weight average apparent molecular weight.
[f] Apparent molecular weight distribution.
[g] Number of amino groups per molecule calculated based on the number average molecule weight of the polymer.

Table 2
Characterization of grafted HBP isolated from SiO_2-*g*-HBP as a function of reaction conditions of grafting polycondensation.[a]

Samples	Feeding ratio[b]	Time (h)	γ_g (%)	DB	M_n ($\times 10^4$ g/mol)	M_w ($\times 10^4$ g/mol)	M_w/M_n	N_{NH_2}
SiO_2-*g*-HBP1[c]	1:0.25	1	25.8	–	–	–	–	–
SiO_2-*g*-HBP2	1:0.5	1	32.5	0.48	2	2.3	1.1	144
SiO_2-*g*-HBP3	1:1	1	32.8	0.46	2.2	2.5	1.2	164
SiO_2-*g*-HBP4	1:2	1	28.2	0.43	2.3	2.8	1.2	160
SiO_2-*g*-HBP5	1:3	1	31	0.4	2.8	4.4	1.6	195
SiO_2-*g*-HBP6	1:0.5	0.5	31.5	0.4	1.8	2	1.1	119

[a] Reaction temperature is fixed at 246 °C. Other parameters have the same meanings as those in Table 1.
[b] Weight ratio of SiO_2–APS over monomer.
[c] The grafted polymer isolated from SiO_2-*g*-HBP1 cannot be precipitated from DMAc with methanol.

Table 3
Characterization of ungrafted HBP as a function of reaction conditions of grafting polycondensation.[a]

Samples	Feeding ratio	Time (h)	DB	M_n ($\times 10^4$ g/mol)	M_w ($\times 10^4$ g/mol)	M_w/M_n	N_{NH_2}
Ungrafted HBP1	1:0.25	1	–	–	–	–	–
Ungrafted HBP2	1:0.5	1	0.53	2.4	3.2	1.4	190
Ungrafted HBP3	1:1	1	0.51	2.9	4.2	1.5	229
Ungrafted HBP4	1:2	1	0.5	3.4	7.7	2.3	264
Ungrafted HBP5	1:3	1	0.49	3.1	6.6	2.1	235
Ungrafted HBP6	1:0.5	0.5	0.49	2.1	2.9	1.4	163

[a] All the parameters have the same meanings as those in Table 1.

the terminal amino groups. To characterize molecular motion of the polymer, the end groups had been capped by benzoic chloride [17], which was verified by ^{1}H NMR. After the capping modification, the strong hydrogen bond interaction disappears, and then T_g of hyperbranched polyamide homopolymer at around 315 °C was determined by DSC measurement.

On the other hand, all the hyperbranched aromatic polyamides prepared by either grafting or homopolymerization are soluble in DMF, DMAc, NMP and DMSO. Even when the end groups were capped, all the polyamides are still soluble in DMSO, whereas they become partially soluble in DMF and DMAc. It is factually indicative of close relationship between solubility of the hyperbranched polymer and terminal groups.

3.2. *Influence of reaction conditions on graft polymerization*

To understand features of the graft polymerization, effects of direct polycondensation conditions on the architectures of hyperbranched polyamide homopolymers should be known at the beginning.

Since the monomer's melting point is 235 °C, the melt polycondensation temperature should be higher than 240 °C. During polymerization, the system gradually translates from melt to solid with molecular growth. Thus, higher reaction temperature (246 °C) should improve the reaction speed and provide the polymer with higher apparent molecular weight (Table 1). However, the system gelated when the reaction temperature exceeded 260 °C or the reaction time was longer than 2 h due to occurrence of undesired side reactions (such as intermolecular deamination, amide exchange reaction in polyamide, etc). On the other hand, longer reaction time at 246 °C may cause exchange reaction among different polyamide chains, leading to a slight decrease in DB value, apparent average molecular weight and its distribution. Considering that rearrangement of the branching chains is beneficial to the formation of homogeneous architecture of final hyperbranched polyamide, a favorable reaction condition (i.e. 246 °C, 1 h) is chosen for the subsequent chemical graft modification of nano-SiO_2.

Actually, SiO_2–APS particles containing amino groups can act as core monomer with multi-functionalities, and then the grafted polymers grow up from the particles (i.e. in a "grafting from" manner). The grafted polymer can also be built by "grafting onto" approach, during which pre-made hyperbranched polyamide with active end carboxyl groups reacts with the functional amino

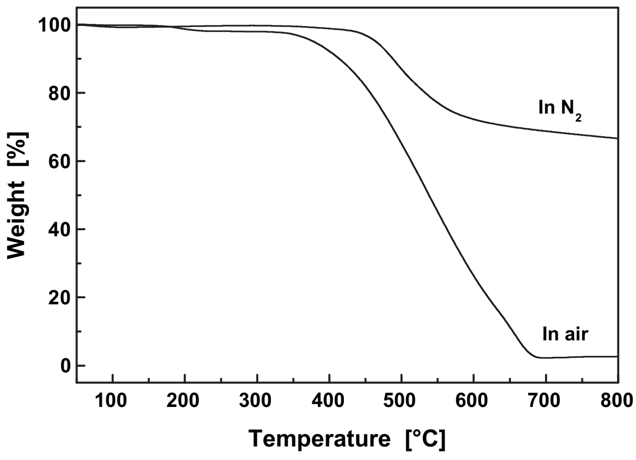


Fig. 4. TGA curves of homopolymer-3 measured in N_2 and air.

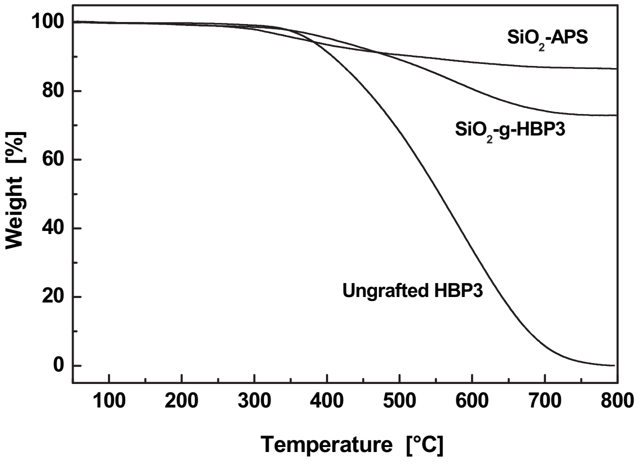


Fig. 5. TGA spectra of SiO_2–APS, SiO_2-*g*-HBP3 and ungrafted HBP3 generated during preparing SiO_2-*g*-HBP3. Testing atmosphere: air.

Table 4
Thermal decomposition temperatures of hyperbranched polyamides estimated from the TGA curves in Figs. 4 and 5.[a]

Samples	Initial decomposition temperature (°C)	Peak decomposition temperature (°C)	Final decomposition temperature (°C)
Homopolymer-3	325	537	725
SiO_2–APS	258	340	490
SiO_2-*g*-HBP3	289	573	694
Ungrafted polymer from SiO_2-*g*-HBP3	322	569	689

[a] Testing atmosphere: air.

groups on the silica surface or numerous functional groups outside the polymer shell. Meanwhile, homopolymers are formed in the system following the general “divergent” or “convergent” mechanisms. It should be pointed out that the grafted polymer shell that covers the particles may hinder contacts between the components. This will be manifested by the following tests. In addition, a strong steric hindrance effect exists between the hyperbranched polymers during the graft polymerization. Another fact that may influence the graft reaction lies in that the monomer melt is completely adsorbed by the silica powder at lower feeding ratio (ratio of monomer/silica $\leq$ 1/3, w/w), implying that there is no state transition from melt to solid, like the case of homopolymerization. In other words, the powder-like system that can be stirred may favor heat exchange, but obstruct diffusion of monomer between particles.

When reaction temperature is fixed at 246 °C, longer reaction time produces grafted hyperbranched polyamide with higher DB value, apparent molecular weight and its distribution (cf. SiO_2-*g*-HBP2 and SiO_2-*g*-HBP6 in Table 2). This phenomenon is quite different from the case of homo-polycomdensation, suggesting that the adsorption of monomers on SiO_2 hinders their diffusion in the system or delays the reaction progress. It is noted that the percentage grafting keeps nearly constant as the reaction time is prolonged from 0.5 to 1 h. Thereby, the longer reaction time (1 h) actually favors the defect diminishing (evident increase in DB value) rather than further growth of the grafted chains (slight increase in M_n).

The dependences of DB value, apparent molecular weight and its distribution on feeding ratio are also exhibited in Table 2. When the feeding ratio is 1:0.25, although the percentage grafting is 25.8%, the isolated product of SiO_2-*g*-HBP1 by HF etching cannot be precipitated from DMAc with methanol, implying that only oligomers or monomers are grafted. No existence of grafted polymer evidences the delay effect of monomers adsorbed onto the particles for polycondensation. If most of monomers are linked with the particles by strong hydroxyl bonds before polycondensation, they tend to directly react with the amido groups on the surface of SiO_2 or give an oligomer as first generation growth. For the cases from SiO_2-*g*-HBP1 to SiO_2-*g*-HBP5, the monomer layers that cover the

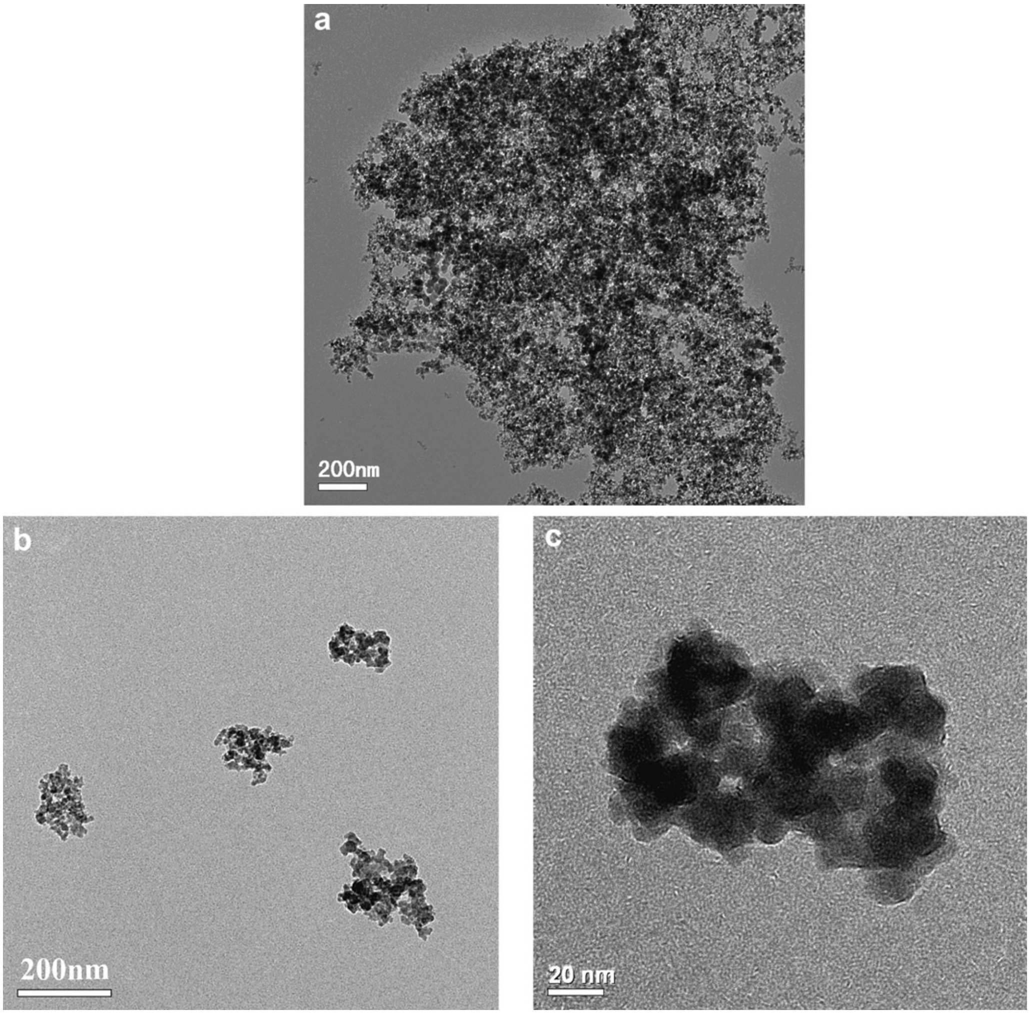


Fig. 6. TEM photos of (a) nano-silica, (b) and (c) SiO_2-*g*-HBP3 dispersed in ethanol.

particles are thick enough to induce grafted polymer. With a rise in feeding ratio of monomer, apparent molecular weight and its distribution of the grafted polymers increase, while the percentage grafting is nearly unchanged. It indicates that the percentage grafting depends on the starting sites formed during the first generation grafting rather than the propagation of grafted polymers. Since there exists strong steric hindrance effect, only a few grafted chains can grow from the particles. A higher monomer concentration (feeding ratio) promotes the polycondensation rate for both grafted and ungrafted polyamide, resulting in the increase in apparent molecular weight and its distribution (see Tables 2 and 3). However, the numbers of grafted polymer may be reduced as a result of the fast growth of hyperbranched chains. On the other hand, the gradual decrease of DB value with feeding ratio for both grafted and ungrafted polyamide means that more defects appear due to higher reaction rate.

It is noted that the ungrafted polymers possess higher DB values, apparent molecular weights and their distributions than those of the corresponding grafted polymers (cf. Tables 2 and 3). This can be explained by different polymerization loci. For the grafting process, the preferential polymerization loci are on the surfaces of the nanoparticles. Owing to strong steric hindrance effect, the grafted chains have to grow up with more defects and low reaction rate. In contrast, the three-dimensional growth of the ungrafted polymer chains present more possibilities for contacts of the components. Accordingly, free and quick propagation of ungrafted polymer chains endows them with higher DB values and apparent molecular weights. In fact, the presence of nano-SiO_2 makes grafted polymer only grow from the particles surface, which certainly limits development of the hyperbranched architecture. In addition, radiation growth of the grafted polyamides starting from the core of SiO_2 should facilitate formation of uniform molecules (narrower apparent molecular weight distribution) as the monomers or oligomers can only approach the propagating ends outside the polymer shell (Note: herein radiation growth means that HBP can only grow from the particles surface rather than the opposite direction).

The influence of SiO_2 on the growth of ungrafted polymers can be perceived by comparing the results of ungrafted HBP4 with those of ungrafted HBP5 in Table 3. Unlike the grafted polymer, further increase of monomer concentration in the system of ungrafted HBP5 decreases apparent molecular weight and its distribution. Here the monomer cannot be completely adsorbed by silica. The extra amount of monomer turns to solid during polycondensation, and combines some particles into an aggregate bulk. This transition should be detrimental to diffusion of monomers and oligomers, leading to incomplete reaction of the ungrafted polymers. Still, the system of ungrafted HBP5 differs from the homopolymerization one because most of monomers are adsorbed by the nanoparticles. On the whole, the homopolymers have higher apparent molecular weights and wider molecular weight distributions, but lower DB values in comparison with the ungrafted polymers. Clearly, adsorption of monomers on SiO_2 delays the growth of ungrafted polymers due to lower monomer concentration, but facilitates development of the hyperbranched architecture. Indeed, for ungrafted HBP2 and ungrafted HBP3 systems, DB $>$ 0.5 is realized, implying that the significant difference in reactivity between linear and terminal units favors linear units [16]. This work demonstrates that the situation can be achieved when the monomers are adsorbed on the surface of SiO_2 before the graft reaction.

3.3. Morphology of the grafted nano-silica

Fig. 6 shows the morphology of nano-SiO_2 before and after the graft treatment. Due to the serious agglomeration resulting from the high specific surface area, the untreated nano-SiO_2 particles get together forming clusters of several microns (Fig. 6(a)). When the nanoparticles are grafted by HBP, their dispersion in ethanol is significantly improved (Fig. 6(b)). It is noted that the grafted HBP is insoluble in ethanol, so that the dispersion status of the grafted nano-SiO_2 shown in Fig. 6(b) is not a result of solvent-HBP interaction but originates from mechanical stirring, reflecting the separation effect of HBP grafted onto the nanoparticles during graft polymerization. That is, the separation of SiO_2 agglomerates should be ascribed to the continuous growth of HBP from the surface of nano-silica that facilitates isolation among the particles. A comparison between Fig. 6(a) and (b) obviously demonstrates that the graft treatment is rather effective in separating the agglomerated nanoparticles, which would benefit the subsequent composites manufacturing. The argument is further supported by the results of dynamic light scattering measurements (Fig. 7). The average diameters of SiO_2 and SiO_2-g-HBP3 are 1567 and 181 nm, respectively, which coincide with the TEM observation.

Fig. 6(c) shows a vague layer around the dark particles, demonstrating the existence of grafted HBP. On the basis of percentage grafting and density of HBP, the average thickness of the HBP attached onto the surface of nano-SiO_2 can be estimated. In the case of SiO_2-g-HBP3, for example, its percentage grafting, density of HBP and specific surface area of nano-SiO_2 are 32.8%, 1.35 g/cm^3 and 380 m^2/g, respectively. Hence the thickness of HBP is calculated to be 0.6 nm (i.e., $(0.328 \times 10^9)/(1.35 \times 10^6 \times 380) = 0.6$ nm).

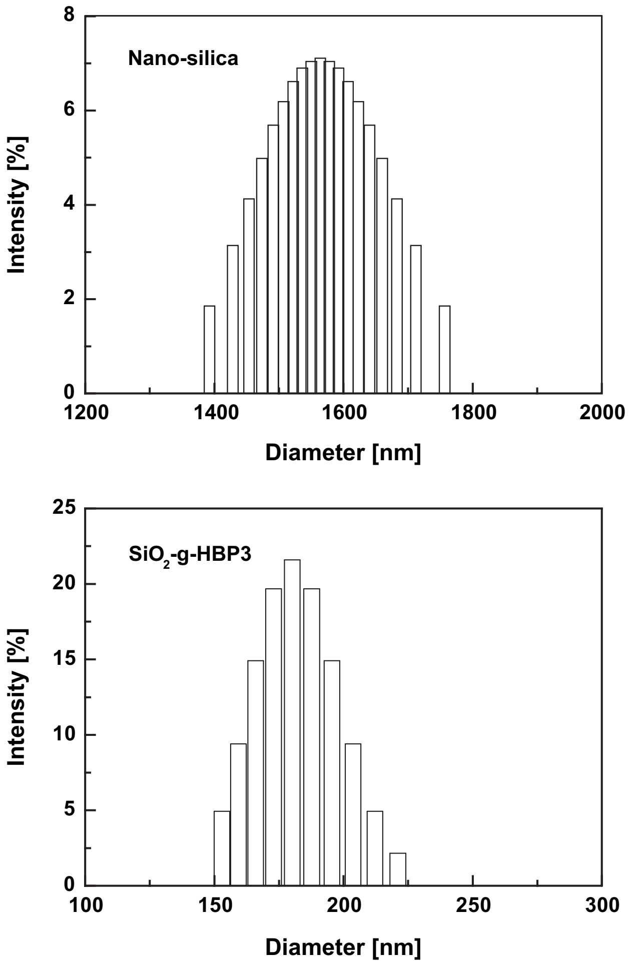


Fig. 7. Distribution histograms of the diameters of nano-silica and SiO_2-g-HBP3 measured by dynamic light scattering tests.

4. Conclusions

To provide nano-silica particles with better dispersion and stronger interfacial interaction while maintaining their higher thermal stability in future epoxy composites, hyperbranched aromatic polyamide was grafted onto silica nanoparticles by a two-step method. The key issue lay in the “one-pot” melt polycondensation of the monomer 3,5-diaminobenzoic acid, which led to radiation growth of the hyperbranched polymers from SiO_2 surface. The results indicated that the proposed technical route proceeded as expected, which proved to be convenient and effective.

Due to the significant steric hindrance between the grafted chains, only a few hyperbranched polymers can grow up from the particles. A higher monomer concentration promoted the rate of grafting, resulting in higher apparent molecular weight and wider molecular weight distribution, but reduced DB value. In addition, adsorption of monomer onto SiO_2 that hindered its diffusion in the system or delayed the reaction progress explained the main difference between ungrafted polymer and homopolymer. The slow growth of ungrafted polymers owing to lower monomer concentration facilitated development of the hyperbranched architecture, but resulted in lower apparent molecular weight accordingly.

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