JOURNAL OF MATERIALS SCIENCE **39** (2004) 3825–3827 LETTERS

Facile preparation and characterization of hyperbranched poly(amine ester) grafted silica nanoparticles

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Silica nanoparticles (SN) have attracted increasing attention because of their superior properties over conventional micrometer particles [1]. They have been widely used as a filler in the manufacture of paints, rubber, plastics, binders, functional fibers, anti-virus materials and so on. However, agglomeration and incompatibility with the organic matrix are impeding problems, which limit their efficient use. It is known that surface modification by grafting of polymers is an effective way to improve dispersibility of the nanoparticles in an organic matrix or solvents and improve their compatibility with the matrix, thus enhancing the properties of the composite materials [2, 3].

Hyperbranched polyamidoamine (PAMAM) dendrimer had been grafted onto silica nanoparticles [4, 5] and the products have been applied for the curing of epoxy resins [6] and complexed to rhodium and palladium, being useful as effective catalysts for hydroformylation and the Heck reaction [7, 8]. It also had been grafted onto bacterial magnetic nanoparticles (AMB-1) for the enhanced extraction of DNA from fluid suspensions [9]. The Frechet-type polyether dendrimers were also grafted onto silica nanoparticles by the convergent approach [10, 11]. The preparation procedures used in the works mentioned above all used dendrimer synthesis methodology. However, their percentages of grafting (PG) were lower and the preparation procedures were time-consuming.

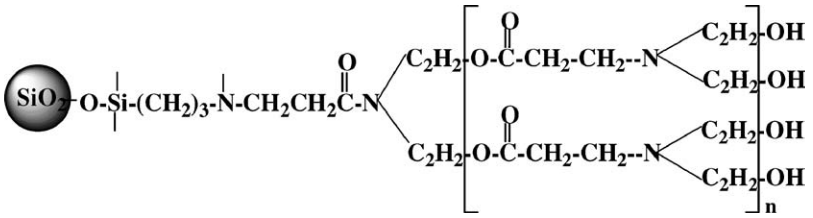
In the current study, we report the preparation of hyperbranched poly(amine ester) (HPAE) grafted silica nanoparticles (HPAE-SN) from methyl acrylate (MA) and diethanol amine (DEA), cored by γ-aminopropyl silica nanoparticles (APSN) [12] with a one-pot method [13]: 1.0 g APSN, 0.10 mol MA, 0.10 mol DEA and 10^{-5} m^3 methanol were mixed ultrasonically and stirred for 30 min at room temperature and heated for 4 h at 35 °C with N_2 bubbling throughout. Then 0.60 g p-methyl benzenesulfonic acid (p-BSA) was added as catalyst into the mixture and methanol was distilled. The residual mixture was heated at 120 °C for 4 h. The product was a mixture of non-grafted HPAE and HPAE-SN.

HPAE-SN was separated from the non-grafted HPAE by several cycles of dispersion in methanol with ultrasonic vibrations for 30 min and precipitated by centrifugation at 10^4 rpm for 30 min. The ideal structure of HPAE-SN is shown in Scheme 1.

The elemental analysis (EA) results (Table I) of HPAE were almost the same as the theoretical values. The element content ratios of C:N of HPAE-SN were much bigger than that of HPAE. It demonstrated that the amino groups content of the APSN used was bigger and the amino groups could not react with the monomers completely because of the space hindrance.The percentage of grafting (PG) was calculated by the following equation from the elemental analysis results:

$$\mathrm{PG}(\%) = (A/B) \times 100\%$$

In which A was the mass of the HPAE grafted (g) and B was that of the silica nanoparticles charged (g). The PG of 83.11% was obtained with the proposed "grafting onto" method. It was near to those of



Scheme 1 Ideal structure of HPAE-SN.

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TABLE I Elemental analysis results

Sample	C%	H%	N%	PG%
APSN	12.69	4.31	4.68	–
HPAE	52.76	7.49	8.92	–
HPAE-SN	33.87	5.33	6.19	83.11

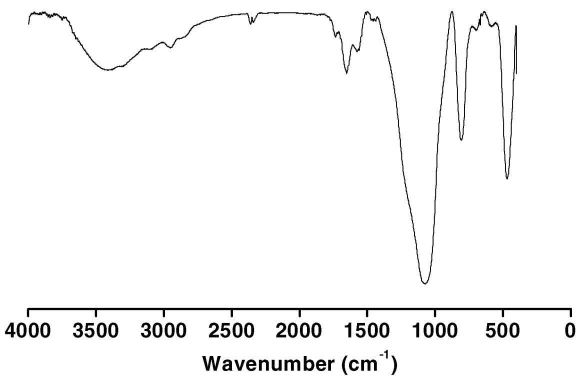


Figure 1 IR of HPAE-SN.

the 10th generation hyperbranched PAMAM grafted inorganic nanoparticles with the dendrimer synthesis methodology.

Fig. 2 shows the Thermogravimetric Analysis (TGA) results of the non-grafted HPAE, and HPAE-SN. The PG value calculated from the TGA results was almost the same as that calculated from the EA results. It was also found that the thermal stability of HPAE could be improved remarkably by being grafted onto silica nanoparticles.

In the FT-IR spectrum of HPAE-SN (Fig. 1), the 1653 and 1566 cm^{-1} bands were characteristic of amide groups, and the 1728 cm^{-1} band was that of ester groups. Furthermore, the 2950 and 3295 cm^{-1} bands were characteristic of –CH_2-groups and the amino groups remained. The FTIR spectrum also confirmed the analysis results of EA and TGA. They all showed that the hyperbranched poly (amine ester) had been grafted onto the surfaces of the silica nanoparticles successfully by the one-pot method. The transmission electron microscopy (TEM) analyses (Fig. 3) showed that the dispersibility in methanol of HPAE-SN was better than that of the bare silica nanoparticle. It indicated that the grafting of the hyperbranched poly (amine ester) could improve the dispersibility of silica nanoparticles in methanol.

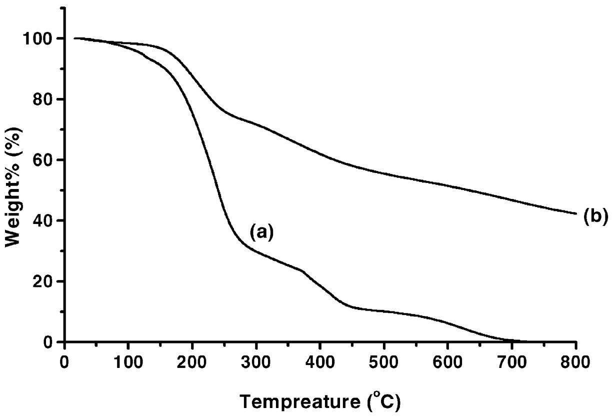
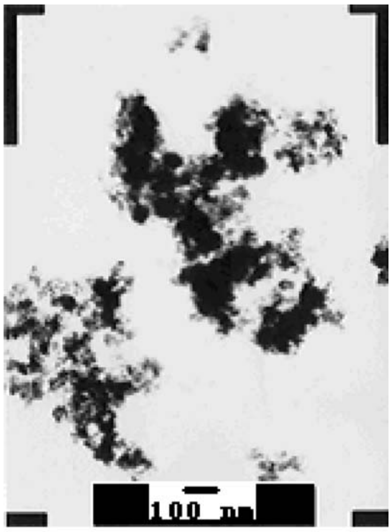
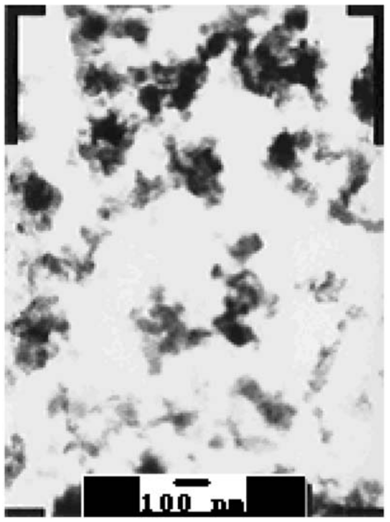


Figure 2 TGA of (a) HPAE and (b) HPAE-SN.



(a) Bare Silica Nanoparticle



(b) HPAE-SN

Figure 3 TEM images of the bare SN and HPAE-SN.

The hyperbranched poly (amine ester) (HPAE) grafted silica nanoparticles (HPAE-SN) were successfully prepared with a one-pot method. The "grafting onto" procedure is simpler and the PG obtained is satisfactory. The modification of silica nanoparticles with HPAE could improve its dispersibility in polar organic solvents. The HPAE-SN is expected to be used as nanofillers for polymers such as polyesters and nylons.

Acknowledgments

This work was supported by the DSFC of Lanzhou University (2001) and the K. C. Wong Education Foundation, Hong Kong (2001).

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Received 30 September 2003
and accepted 12 January 2004