Preparation and Characterizations of Poly(amic acid) Grafted Silica Nanoparticles

Peng Liu*

Institute of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, P.R. China

A B S T R A C T

Poly(amic acid) grafted silica nanoparticles (PAA-SNs) were successfully prepared by the grafting polymerization of poly(amic acid)s based from the in-situ condensation polymerization of pyromellitic dianhydride (PMDA) and three diamines (4,4í-diaminodiphenyl ether (DDE), 4,4í-diaminodiphenyl methane (DDM) and 4,4í-diaminodiphenyl sulphone (DDS)) from the surfaces of the γ-aminopropyl silica nanoparticles (APSNs) with *N,N*-dimethyl acetamide (DMAc) as solvent. The products were characterized by elemental analyses (EA), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectrometry (XPS), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). The percentage of grafting (PGs) (the weight ratios of the PAA grafted and the charged silica nanoparticles) of PAADDE-SNs, PAADDM-SNs, PAADDS-SNs, calculated from the results of C elemental analyses (EA), were 56.77%, 38.97% and 46.05%, respectively. The TEM analysis showed that they could be dispersed in organic solvents. Therefore, the systems could be used as reactive nanofillers or nano-cross-linkers for polymer nanocomposites because of their better organic solubilities and the large numbers of carboxyl acid groups on their surfaces.

INTRODUCTION

Silica nanoparticles (SNs) have been widely used as fillers in the manufacture of coatings [1], rubber [2], plastics [3], binders [4], functional fibres [5] and so on. In order to improve the dispersibility and compatibility of nanoparticles in organic matrices or solvents, the surface modifications of nanoparticles have been studied widely.

The modifications with small molecules such as butyl alcohol [6] and organofunctional silanes [7] or polymers [8,9] could decrease the

(∗) To whom correspondence should be addressed.
E-mail: pliu@lzu.edu.cn

surface energy of inorganic nanoparticles efficiently. The modified inorganic nanoparticles could be dispersed in carbon-chain polymer materials and could be used as nanofillers for nanocomposites. The hyperbranched polymers, polyamidoamine (PAMAM) [10,11] and poly(amine ester) [12] (PAE), had been also self-assembled from SNs. They could be applied not only as nanofillers for polyesters and polyamides but also as solidification agents for epoxy resin because of the large numbers of surface amino or hydroxyl groups.

The poly(amic acid), the main precursor for polyimide (PI), had also been used for the functional materials [13-15] or cross-linker for epoxy resin [16,17] because of its particular structure.

Here, we report the preparation and characterization of the poly(amic acid) grafted silica nanoparticles (PAA-SNs), prepared by in-situ condensation polymerization of pyromellitic dianhydride (PMDA) and three diamines (4,4í-diaminodiphenyl ether (DDE), 4,4í-diaminodiphenyl methane (DDM) and 4,4í-diaminodiphenyl sulphone (DDS)) in presence of γ-aminopropyl silica nanoparticles (APSNs). They were expected to be used as reactive nanofillers for other resins.

EXPERIMENTAL

Raw Materials
Silica nanoparticles used was MN1P obtained from Zhoushan Mingri Nano-materials Co. Ltd., Zhejiang, China. The surface area and particle size were 640 m^2 g^{-1} and 10 nm, respectively. It was dried in vacuum at 110ºC for 48 h before use. γ-Aminopropyltriethoxysilane (APTES) (Gaizhou Chemical Industrial Co. Ltd., Liaoning, China) were used as received. 4,4í-Diaminodiphenyl ether (DDE), 4,4í-diaminodiphenyl methane (DDM) and 4,4í-diaminodiphenyl sulphone (DDS)) are analytical reagent grades from Shanghai Chemical Co. of China Medicine Group and re-crystallized in acetonitrile, benzene and methanol, respectively. Pyromellitic dianhydride (PMDA) is analytical reagent grade from Beijing Jinlong Chemical Reagents Ltd. *N,N*-dimethyl acetamide (DMAc) and other solvents used are all analytical reagent grade.

Preparation of PAA-SNs
γ-Aminopropyl silica nanoparticles (APSNs), with an amino content of 3.34 mmol/g, were prepared by the self-assembly of APTES onto the surfaces of silica nanoparticles as reported previously[18]: 5.0 g of silica nanoparticles, 300 mL toluene and 50 mL APTES were added into a 500 mL flask and the mixture was dispersed with ultrasonic vibrations for 30 min. Then the mixture was refluxed for 8 h under stirring with a magnetic stirrer. After the reaction, the mixture was centrifuged (4×10^3 rpm for 1 h) and the precipitate was dispersed into 300 mL ethanol with ultrasonic vibrations for 30 min and centrifuged again. The washing operation was repeated for three times.

3.0 g APSNs and 0.20 mol PMDA were mixed in 250 mL DMAc with ultrasonic vibrations for 30 min, bubbling with Helium. Then, 0.20 mol diamines were added and stirred with a magnetic stirrer for 12 h at room temperature. After the condensation polymerizations, the reaction mixtures were poured into 500 mL warm water, respectively and the precipitates were dried in vacuo at 40ºC. The resulting products were the mixtures of the free poly(amic acid)s and poly(amic acid) grafted silica nanoparticles (PAA-SNs).

PAA-SNs were separated from the free poly(amic acid)s by cycles of dispersion in DMAc and centrifugation at 1.0×10^4 rpm for 1 h, the similar method as for APSNs.

Characterizations
Elemental analysis (EA) of C, N and H was performed on Elementar vario EL instrument. Bruker IFS 66 v/s infrared spectrometer was used for the Fourier transform infrared (FTIR) spectroscopy analysis. Thermogravimetric analysis (TGA) was used for the thermal stability of the PAA-SNs performed with a Perkin-Elmer TGA-7 system by a scan rate of 10ºC min^{-1} at 700ºC in N$_2$. The morphologies of silica nanoparticles (SNs) and the PAA-SNs were characterized with a JEM-1200 EX/S transmission electron microscope (TEM). The powers were dispersed in DMAc in an ultrasonic bath for 5 min, and then deposited on a copper grid covered with a perforated carbon film. The surface characterization of the PAA-SNs was accomplished using a PHI-5702 multi-functional X-ray photoelectron spectrometer (XPS) with pass energy of 29.35 eV and an Mg K$_\alpha$ line excitation source. The binding energy of C 1s (284.6 eV) was used as a reference.
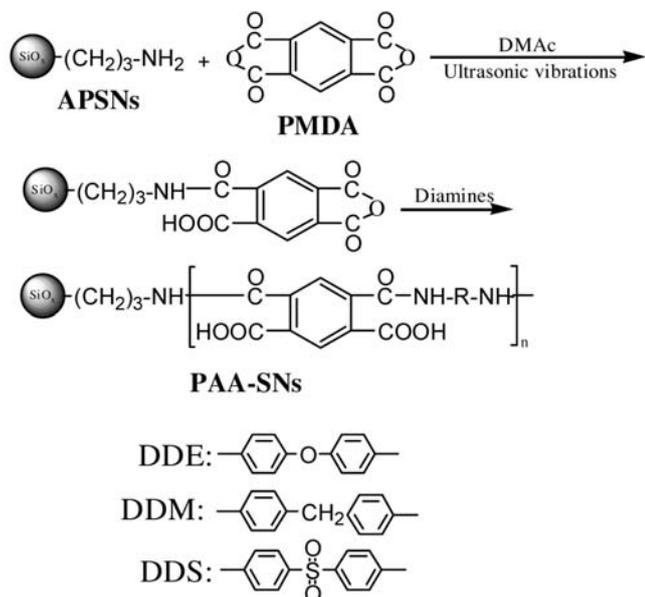
The percentage of grafting (PG) was calculated

Figure 1. Preparation procedure of PAA-SNs.

according to the following relationships from the results of C elemental analyses:

PG (%) = Grafted PAA (g)/Charged silica nanoparticles (g) × 100%

RESULTS AND DISCUSSION

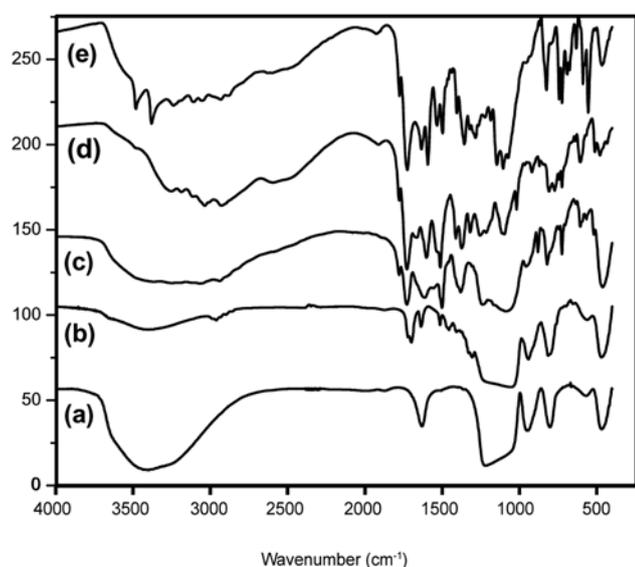The preparation procedures of PAA grafted silica

Figure 2. FTIR Spectra of: (a) SNs, (b) APSNs, (c) PAADDE-SNs, (d) PAADDM-SNs, and (e) PAADDS-SNs.

Table 1. The surface compositional data from XPS.

Samples	XPS analysis (at.%)				
	Si	O	C	N	S
SNs	19.94	51.09	28.69	-	-
APSNs	7.01	19.52	69.35	4.13	-
PAA$_{DDE}$-SNs	3.53	20.74	72.50	3.23	-
PAA$_{DDM}$-SNs	3.21	21.21	72.44	3.14	-
PAA$_{DDS}$-SNs	3.28	20.50	71.90	3.11	1.21

nanoparticles could be shown schematically as Figure 1: one of the anhydride group of some PMDA could be reacted with the amine groups on the surfaces of the APSNs and the other react with the diamines to form poly(amic acid) chains. The percentage grafting (PGs) of PAA$_{DDE}$-SNs, PAA$_{DDM}$-SNs, PAA$_{DDS}$-SNs, calculated from the results of C elemental analyses (EA), were 56.77%, 38.97% and 46.05%, respectively. And they were all lower than those calculated from the N elemental analyses. It was investigated that only a part of the amino groups bonded onto the surfaces of APSNs had been reacted with pyromellitic dianhydride (PMDA) to form the grafted poly(amic acid)s. This was caused by the greater space-hindrance of the monomers. And the different PGs from the same polymerizing condition maybe due to the different reactivities of the diamines used.

The surface elemental contents from the XPS analyses are shown in Table 1. The surface C content increased and the surface Si content decreased after the
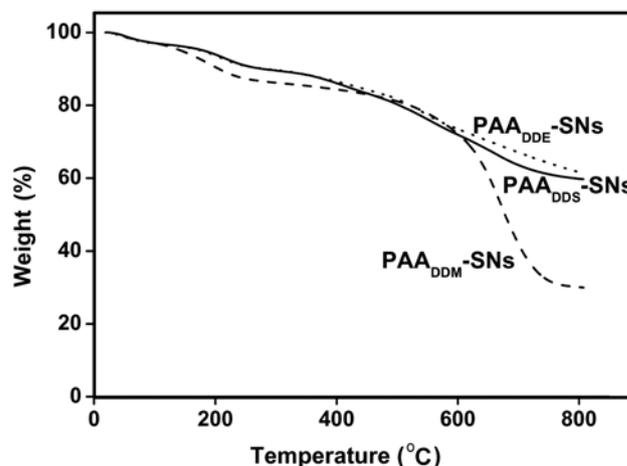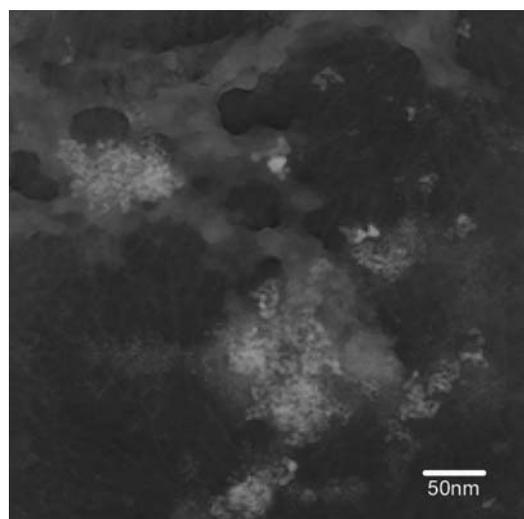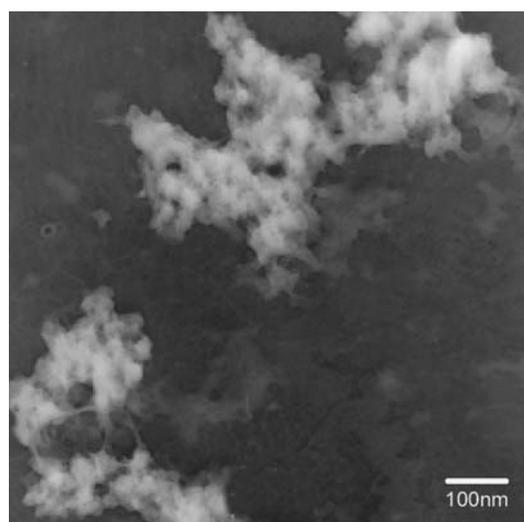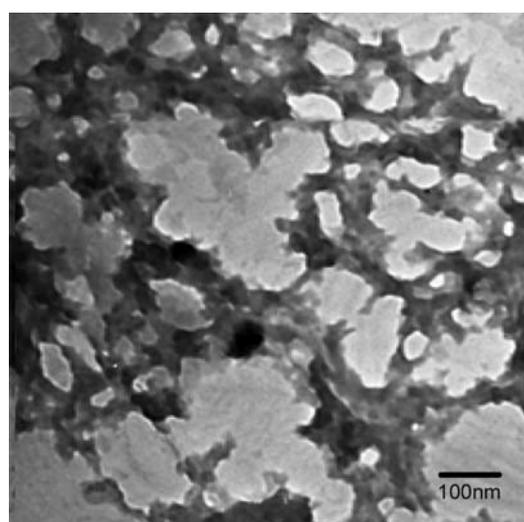

Figure 3. TGA Curves of the PAA-SNs.

(a)

(b)

(c)

Figure 4. TEM images of: (a) PAADDE-SNs, (b) PAADDM-SNs, and (c) PAADDS-SNs.

self-assembly of APTES and grafting of poly(amic acid)s. The surface O content decreased from 51.09% of SNs to 19.52% of APSNs because the γ-aminopropyl groups do not contain any O element. However, it increased after the surface condensation polymerization because the grafted poly(amic acid)s contained O element. The surface N contents decreased after the grafting of poly(amic acid)s. The results showed that the poly(amic acid)s had been grafted onto the surfaces of SNs successfully.

In the FTIR spectra (Figure 2), the appearances of the bands at 1775 cm^{-1} and 1725 cm^{-1} of asymmetric and symmetric stretching of carboxyl groups, the bands at 1654 cm^{-1} and 1550 cm^{-1} of characteristics of amic acid groups, the bands at 1092 cm^{-1} and 830 cm^{-1} of Si-O groups also showed that the poly(amic acid)s had been grafted onto the surfaces of SNs. The three characteristic bands: 1237 cm^{-1} of asymmetry stretch of aromatic ether groups, the band 2927 cm^{-1} of methylene groups and the band 1150 cm^{-1} of sulphone groups, of the DDE, DDM and DDS were also found in their FTIR spectra, respectively.

The TGA curves are shown in Figure 3. The weight losses of the products at about 200ºC were resulted from the volatilization of the solvent, DMAc, which was used in the separation procedure. It was found that the thermal decomposition temperatures of the products are all higher than 400ºC.

The TEM images (Figure 4) showed that the poly(amic acid)s grafted silica nanoparticles could be dispersed in organic solvent. So it could be used as nanofillers or nano-crosslinkers for polymer nanocomposites.

CONCLUSION

Three kinds of poly(amic acid) grafted silica nanoparticles (PAA-SNs) were successfully prepared by in-situ condensation polymerization of pyromellitic dianhydride (PMDA) and different diamines from the surfaces of the γ-aminopropyl silica nanoparticles (APSNs) with *N,N*-dimethyl acetamide (DMAc) as solvent. The PAA-SNs could be better dispersed in organic solvents and had numbers of carboxyl acid groups on their surfaces, so it is expected to be used as reactive nanofillers or nano-crosslinkers for polymer nanocomposites.

ACKNOWLEDGEMENTS

REFERENCES

1. Zhou S.X., Wu L.M., Sun J., Shen W.D., The change of the properties of acrylic-based polyurethane via addition of nano-silica, *Prog. Org. Coat.,* **45**, 33-42 (2000).

2. Arrighi V., McEwen I.J., Qian H., Serrano P.M.B., The glass transition and interfacial layer in styrene-butadiene rubber containing silica nanofillers, *Polymer,* **44**, 6259-6266 (2003).

3. Arkhireeva A., Hay J.N., Synthesis of organically-modified silica particles for use as nanofillers in polymer systems, *Polym. Polym. Compos.,* **12**, 101-110 (2004).

4. von Hohenesche C.F., Unger K.K., Eberle T., Agglomerated non-porous silica nanoparticles as model carriers in polyethylene synthesis, *J. Mol. Cat. A Chem.,* **221**, 185-199 (2004).

5. Kim Y.K., Lewis A.F., Patra P.K., Warner S.B., Mhetre S.K., Shah M.A., Nam D., Nanocomposite fibres, *Mater. Res. Soc. Symp.-Proc.,* **740**, 441-446 (2002).

6. Fuji M., Ueno S., Takei T., Watanabe T., Chikazawa M., Surface structural analysis of fine silica powder modified with butyl alcohol, *Colloid Polym. Sci.,* **278**, 30-36 (2000).

7. Guillet A., Treatment of fillers with organofunctional silanes, technology and applications, *Macromol. Symp.,* **194**, 63-74 (2003).

8. Yoshinaga K., Functionalization of inorganic colloidal particles by polymer modification, *Bull. Chem. Soc. Jpn.,* **75**, 2349-2358 (2002).

9. Liu P., Tian J., Liu W., Xue Q., Surface initiated graft polymerization from inorganic nano-sized particles, *Chem. Bull. (in Chin.),* **66**, 73-77 (2003).

10. Tsubokawa N., Ichioka H., Satoh T., Hayashi S., Fujiki K., Grafting of 'dendrimer-like' highly branched polymer onto ultrafine silica surface, *React. Funct. Polym.,* **37**, 75-82 (1998).

11. Liu P., Tian J., Liu W., Xue Q., Fabrication dendrimer-like PAMAM based on silica nanoparticles, *Chin. J. Chem.,* **21**, 960-963 (2003).

12. Liu P., Liu W., Xue Q., Facile preparation and characterization of hyperbranched poly(amine ester) grafted silica nanoparticles, *J. Mater. Sci.,* **39**, 3825-3827 (2004).

13. Levine K.L., Iroh J.O., Kosel P.B., Synthesis and properties of the nanocomposite of zink oxide and poly(amic acid), *Appl. Surf. Sci.,* **230**, 24-33 (2004).

14. Hsu S.L.C., Wang U., King J.S., Jeng J.L., Photosensitive poly(amic acid)/organoclay nanocomposites, *Polymer,* **44**, 5533-5540 (2003).

15. Li N.J., Lu J.M., Yao S.C., Xia X.W., Zhu X.L., Synthesis and fluorescent properties of PAA-based new side chain polymers, *Mater. Lett.,* **58**, 3115-3118 (2004).

16. Zhao S.L., Qin C.X. Zhang H.B., Study on polyamic acid cured epoxy adhesive, *Chin. Adh.,* **9**, 1-4 (2000).

17. Kevin G., Mitsutoshi J., Masa-aki K., Yoshio I., Amane M., Adhesion behaviour of polyamic acid cured epoxy, *Polymer,* **38**, 4413-4415 (1997).

18. Liu P., Xue Q., Tian J., Liu W., Self-assembly of functional silanes onto nano-sized silica, C*hin. J. Chem. Phys.,* **16**, 481-486 (2003).