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Preparation and Characterization of Functionalized SiO_2 Nanoparticles with Crosslinking Structure†

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In this study, we have grafted polyurethane onto the surface of silica (SiO_2) nanoparticles dispersed in the organic solvent *via* crosslinking reaction, synthesizing a new functionalized SiO_2 nanoparticles successfully. The resultant SiO_2 nanoparticles sample was characterized by FT-IR, TG and SEM, demonstrating that the polyurethane chains has grafted onto the surface of SiO_2 nanoparticles and have given rise to a crosslinking structure between SiO_2 nanoparticles and polyurethane. After surface modification, SiO_2 nanoparticles was dispersed evenly in the organic solvent.

Keywords: Silicon dioxide, Surface modification, Polyurethane, Dispersion.

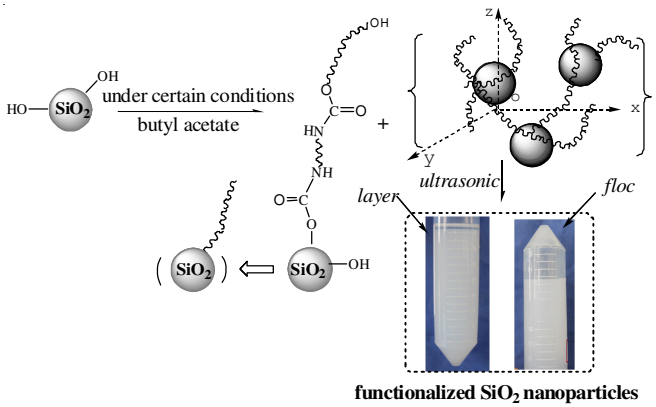
INTRODUCTION

The dispersion of nanoparticles and the interface between the nanoparticles and polymer matrix play key roles in the preparation of nanocomposites with some special properties in mechanical, optical, electric, thermal and magnetic aspects[1,2]. Owing to the lack of coordinate atoms on the surfaces of nanoparticles, they have high surface activity and great inclination to agglomerate. Thus, it is important to modify the surface to nanoparticles for improving the wettability, compatibility, dispersibility and interfacial adhesion. Silicon dioxide nanoparticle are represented as one of the most wide spread nanomaterials in use because it has two features: (i) ease of preparation through hydrolysis condensation reaction, (ii) effective surface modification with various organic compounds[3].

In this study, we have investigated chemical modification of SiO_2 nanoparticles *via* a novel crosslinking reaction (**Scheme-I**) to study its dispersion stability in organic solvent.

EXPERIMENTAL

Silicon dioxide nanoparticles were bought from Guangzhou GBS High-Tech & Industry Co., Ltd. (GBS) (BET:150 m^2/g). All solvents employed and other reagents (isocyanate, polyether diols, catalyst) were commercially available and used without further purification.



Scheme-I: Preparation route of functionalized SiO_2 nanoparticles

Preparation of polyurethane chains functionalized SiO_2 nanoparticles suspending liquid: The preparation of polyurethane chains functionalized SiO_2 nanoparticles suspending liquid is shown in the **Scheme-I**. First the measured proportion of raw materials isocyanate, SiO_2 nanoparticles and butyl acetate was poured into dry 1000 mL three-neck flask fitted with stirrer, thermometer. After ultrasonic machining for 10-25 min, added catalyst and reacted in 70-90 ºC for 2-5 h. A type of polyether diols was then poured into reaction system for another 2 h. The reaction mixture was terminated with

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ethanol. After termination, the functionalized SiO_2 nanoparticles suspending liquid was collected using ultrasounds for 5 min and then placed to observe the layering and sedimentation.

RESULTS AND DISCUSSION

FTIR analysis: FTIR spectra of original and functionalized SiO_2 nanoparticles are shown in Fig. 1. The absorption peaks at 1101, 796 and 470 cm^{-1} in Fig. 1 are the characteristic absorption peaks of original SiO_2 nanoparticles (a)[4]. The polyurethane chains functionalized nano-SiO_2 of the FTIR spectrum of functionalized SiO_2 nanoparticles (b) can observe the typical polyurethane structure characteristic of infrared absorption peaks. The stretching vibration peak of the methyl and methylene (ν_{CH_2} and ν_{CH_3}) can be seen in 2955-2855 cm^{-1}, while stretching vibration for C=O bond (νC=O) is appearing at 1662 cm^{-1}. The new absorption peak of the stretching vibration for the C=O bond and the bending vibration for the N-H bond in the -NH-CO-O- bond are appearing at 1655 and 1590 cm^{-1}, respectively. The peak at 1018 cm^{-1} corresponds to the absorption of Si-O-C bond, shows that SiO_2 nanoparticles and isocyanate had reacted, forming Si-O-C. After the progress of centrifugation, washing, the sample completely exclude the effects of physical adsorption and the surface of SiO_2 nanoparticles was grafted polyurethane chains.

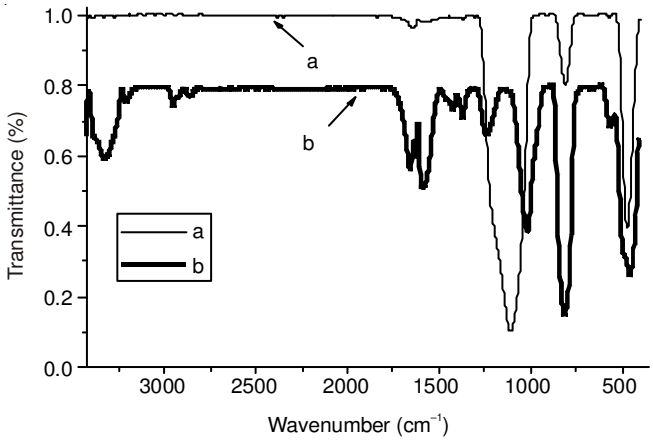

Fig. 1. FT-IR spectra of oiginal SiO_2 (a) and functionalized SiO_2 (b) nanoparticles

Thermogravimetric analysis: In Fig. 2(1), the thermal decomposition temperature range of original SiO_2 nanoparticles is 60-450 ºC. The loss of quality may resulting from the surface decomposition of polyurethane when functional group react and form functionalized SiO_2 nanoparticles. From the DTG differential curve, we can determine the temperature range of 50-400 ºC as the main decomposition and weight loss at 5.8 %.

Surface functionalized SiO_2 nanoparticles was washed by butyl acetate and dried. Its thermal decomposition curves are shown in Fig. 2(2). When compared decomposition curves of functionalized SiO_2 nanoparticles with the curve of decomposition of original nanoparticles it is easy to find that there is a little decomposition when temperature is below 200 ºC due to small molecule. From 300 to 600 ºC, SiO_2 nanoparticles decompose quickly, mainly because of the decomposition of grafted polymer. From its DTG differential curve we can determine the 220-450 ºC as the main decomposition temperature range and weight loss was 10.5 %.

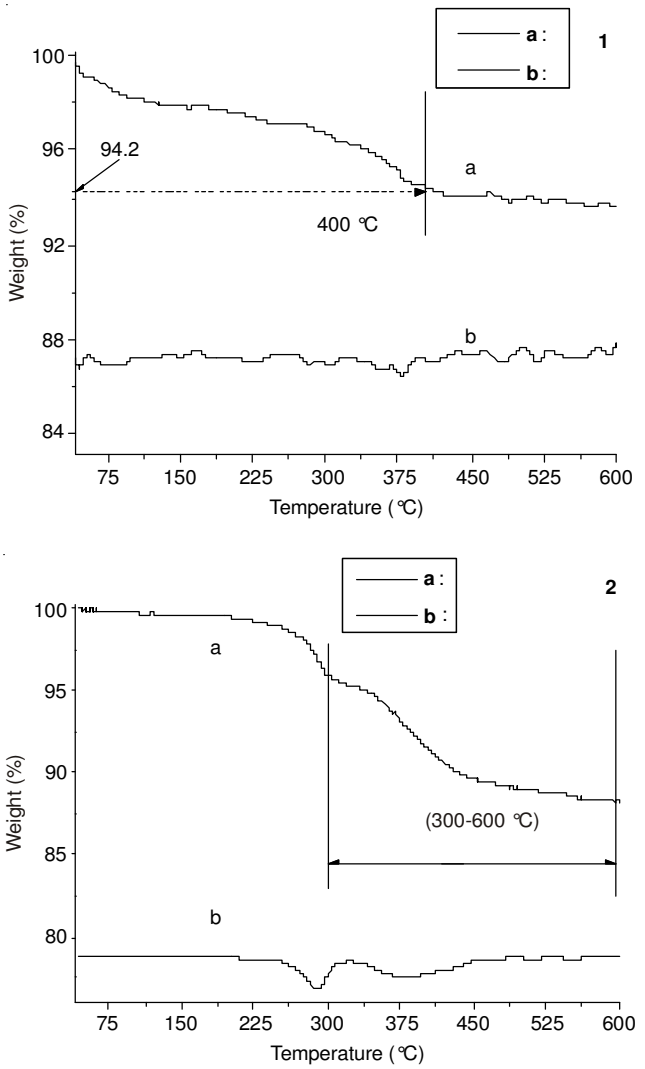

Fig. 2. (1) the original SiO_2 nanoparticles (a. TGA curves, b. DTG differential curve); (2) functionalized SiO_2 nanoparticles (a. TGA curves, b. DTG differential curves)

Scanning electron microscopic analysis: In Fig. 3(a,b), after comprehensive comparison between original SiO_2 nanoparticles and functionalized SiO_2 nanoparticles there are some differences between them. Original SiO_2 nanoparticles size ranges 10-50 nm while functionalized SiO_2 nanoparticles size range 20-100 nm. The increase of nanoparticles size indicated that SiO_2 nanoparticles had grafted polymer chains. Light gray area is SiO_2 nanoparticles surface which was coated with the polyurethane chains and reduced the reunion. That means functionalized SiO_2 nanoparticles have formed a chemical bonding, indicating that organic chains connected to the SiO_2 nanoparticles surface can reduces surface free energy and reunion due to mutual exclusion and steric effects.

Conclusion

In summary, this work studies on synthesis of polyurethane chains functionalized SiO_2 nanoparticles suspending liquid. By FTIR, TG and SEM, show that the SiO_2 nanoparticles and polyurethane chains react and form a chemical bond and the surface of SiO_2 nanoparticles was grafted polymer materials.

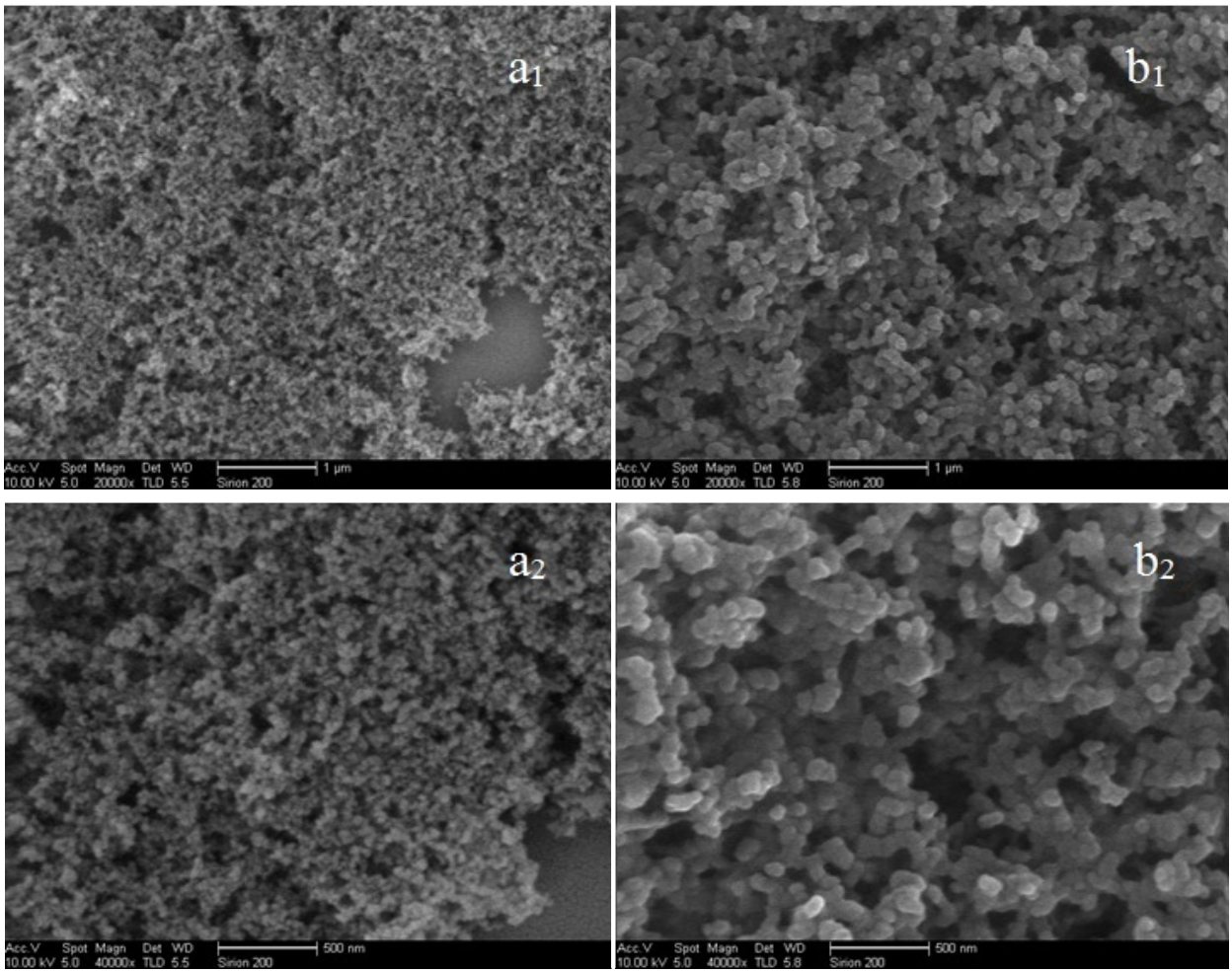

Fig. 3. SEM of oiginal SiO_2 nanoparticles (a_1.20,000 times, a_2. 40,000 times) and functionalized SiO_2 nanoparticles (b_1. 20,000 times, b_2. 40,000)

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REFERENCES

1. 1. Y.N. Pandey, G.J. Papakonstantopoulos and M. Doxastakis, *Macromolecules*, **46**, 5097 (2013).
2. J. Yang, C.R. Han, J.F. Duan, F. Xu and R.C. Sun, *J. Phys. Chem. C*, **117**, 8223 (2013).
3. H. Zou, S.S. Wu and J. Shen, *Chem. Rev.*, **108**, 3893 (2008).
4. E. Moncada, R. Quijada and J. Retuert, *Nanotechnology*, **18**, 335606 (2007).