Preparation and Characterization of Functionalized SiO₂ Nanoparticles with Crosslinking Structure†

MINGHUA LI^{1,2,*}, ZIQIANG ZOU^{1,2}, MING DING¹, CHANGAN TIAN¹, YUNRAN ZHANG¹ and XIN WANG¹

¹Department of Chemistry and Materials Engineering, Hefei University, Hefei 230601, P.R. China

²Department of Mechanical and Electrical Engineering, Beijing University of Chemical Technology, Beijing 100029, P.R. China

*Corresponding author: Tel: +86 551 62158393; E-mail: minghualiahu@hfu.edu.cn

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In this study, we have grafted polyurethane onto the surface of silica (SiO₂) nanoparticles dispersed in the organic solvent *via* crosslinking reaction, synthesizing a new functionalized SiO₂ nanoparticles successfully. The resultant SiO₂ nanoparticles sample was characterized by FT-IR, TG and SEM, demonstrating that the polyurethane chains has grafted onto the surface of SiO₂ nanoparticles and have given rise to a crosslinking structure between SiO₂ nanoparticles and polyurethane. After surface modification, SiO₂ 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 compounds³.

In this study, we have investigated chemical modification of SiO₂ 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 m²/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 SiO₂ nanoparticles

Preparation of polyurethane chains functionalized SiO₂ nanoparticles suspending liquid: The preparation of polyurethane chains functionalized SiO₂ nanoparticles suspending liquid is shown in the **Scheme-I**. First the measured proportion of raw materials isocyanate, SiO₂ 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 °C 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 SiO₂ 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 SiO₂ 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 SiO₂ nanoparticles (a)⁴. The polyurethane chains functionalized nano-SiO₂ of the FTIR spectrum of functionalized SiO₂ nanoparticles (b) can observe the typical polyurethane structure characteristic of infrared absorption peaks. The stretching vibration peak of the methyl and methylene (ν_{CH₂} and ν_{CH₃}) can be seen in 2955-2855 cm⁻¹, while stretching vibration for C=O bond (ν_{C=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 SiO₂ 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 SiO₂ nanoparticles was grafted polyurethane chains.

Fig. 1. FT-IR spectra of original SiO₂ (a) and functionalized SiO₂ (b) nanoparticles

Thermogravimetric analysis: In Fig. 2(1), the thermal decomposition temperature range of original SiO₂ nanoparticles is 60-450 °C. The loss of quality may resulting from the surface decomposition of polyurethane when functional group react and form functionalized SiO₂ nanoparticles. From the DTG differential curve, we can determine the temperature range of 50-400 °C as the main decomposition and weight loss at 5.8 %.

Surface functionalized SiO₂ nanoparticles was washed by butyl acetate and dried. Its thermal decomposition curves are shown in Fig. 2(2). When compared decomposition curves of functionalized SiO₂ 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 °C due to small molecule. From 300 to 600 °C, SiO₂ nanoparticles decompose quickly, mainly because of the decomposition of grafted polymer. From its DTG differential curve we can deter-

Fig. 2. (1) the original SiO₂ nanoparticles (a. TGA curves, b. DTG differential curve); (2) functionalized SiO₂ nanoparticles (a. TGA curves, b. DTG differential curves)

mine the 220-450 °C as the main decomposition temperature range and weight loss was 10.5 %.

Scanning electron microscopic analysis: In Fig. 3(a,b), after comprehensive comparison between original SiO₂ nanoparticles and functionalized SiO₂ nanoparticles there are some differences between them. Original SiO₂ nanoparticles size ranges 10-50 nm while functionalized SiO₂ nanoparticles size range 20-100 nm. The increase of nanoparticles size indicated that SiO₂ nanoparticles had grafted polymer chains. Light gray area is SiO₂ nanoparticles surface which was coated with the polyurethane chains and reduced the reunion. That means functionalized SiO₂ nanoparticles have formed a chemical bonding, indicating that organic chains connected to the SiO₂ 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 SiO₂ nanoparticles suspending liquid. By FTIR, TG and SEM, show that the SiO₂ nanoparticles and polyurethane chains react and form a chemical bond and the surface of SiO₂ nanoparticles was grafted polymer materials.

Fig. 3. SEM of original SiO₂ nanoparticles (a₁, 20,000 times, a₂, 40,000 times) and functionalized SiO₂ nanoparticles (b₁, 20,000 times, b₂, 40,000)

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