



Surface Modification of Nano-Silicon Nitride with Silane Coupling Agent†

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In this work, a silane coupling agent was used for surface modification of native nano-sized silicon nitride (Si_3N_4) powder. According to the spectra of FT-IR and TGA, it can be inferred that this coupling agent covalently bonds on the surface of nano- Si_3N_4 particles and an organic coating layer was formed. The surface free energy experiments showed that the hydrophobic property of nano- Si_3N_4 modified with coupling agent was improved obviously. Analysis of nanoparticle size and TEM revealed that the modified nano- Si_3N_4 possessed good dispersibility and the average diameter was less than 100 nm.

Key Words: Silicon nitride, Surface modification, Nanocomposite, Dispersibility.

INTRODUCTION

Composite materials are composed of metallic, inorganic non-metallic or polymer material and they are a kind of multi-phase materials, which possess a superior cooperative performance. Composite materials based on polymer with nano-size is a kind of inorganic-organic composite materials and the inorganic fillers are dispersed in the polymer with nano-size.

Silicon nitride (Si_3N_4) is an important inorganic ceramic material used various applications due to its high strength, high fracture toughness, high thermal-shock resistance, low coefficient of thermal expansion and good wear resistance¹⁻⁵. It may be an effective filler of polymeric materials for the properties improvement. Our research group is preparing nano- Si_3N_4 /PPS composites that may exhibit unique hybrid properties including good heat-resistance and good dynamic mechanical properties. However, it is difficult to prepare polymer-based nanocomposites from a conventional polymer because of the strong tendency of nanoparticles to agglomerate. To break down the nanoparticle agglomerates and for improving the dispersivity of nanosized particles in polymer matrix, the technology of surface-modification is used for producing nanostructural composites.

In this study, a surface modification strategy with a silane coupling agent for Si_3N_4 was developed so that the modified nano- Si_3N_4 can be added to the PPS matrix for improving their compatibility and nanoparticles' dispersibility.

EXPERIMENTAL

The silicon nitride powder used in this study was a commercial product from Kaier Nano-materials Co. Ltd., Hefei, P.R. China with following characteristics: average particle size 20-40 nm, specific surface area $> 115 \text{ m}^2\text{g}^{-1}$, total oxygen $< 0.62 \%$ (wt).

Modification agent was purchased from Nanjing Shuguang Chemicals Co., Nanjing, P.R. China. Commercial name: KH-845-4; chemical name: *bis*-(γ -triethoxysilylpropyl)-tetrasulfide. Acetone (A.R) and ethanol (A.R) was purchased from Shanghai reagent company of China national pharmaceutical group Co., Shanghai, P.R. China and petroleum ether (A.R) was purchased from Hangzhou refinery of China petrochemical Co., Hangzhou, P.R. China.

Surface modification: Nano- Si_3N_4 powders were dispersed in petroleum ether and a certain amount (8-18 % of total mass) of coupling agent was added into the flask, mixing round with high speed at 40 °C for 4 h, then vacuum drying for 24 h.

Characterization and measurement: Native nano- Si_3N_4 powders and modified nano- Si_3N_4 powders were investigated by FT-IR (NeuXs-870, Nicole-t); TGA (Pyris-I, Perkin Elmer); Size distributions analyzer (Zetasizer 3000 HS, Malvern), TEM (JEM-100SX, JE-OL). Contact angle and surface free energy were investigated by contact angle measuring instrument (DSA 10-MK2, KRüss Gmb H).

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RESULTS AND DISCUSSION

FT-IR analysis of powder: The surface region of nano-Si₃N₄ powder has a significant amount of Si₂-NH, Si-NH₂ and Si-OH groups³. In Fig. 1, $\nu(\text{OH})$ (hydrogen bonded) + $\nu(\text{NH})$ combination band observed at 3422 cm⁻¹. The detection of absorption at 1064 cm⁻¹ as well as of a broad band at 487 cm⁻¹ in our sample, is probably indicative of the presence of SiO₂.⁷ The band at 1633 cm⁻¹ is assigned to the N-H shear vibration, 974 cm⁻¹ is assigned to the back bone vibrations of Si-N-Si and 1385 cm⁻¹ is attributed to the bending mode of hydroxyl groups.

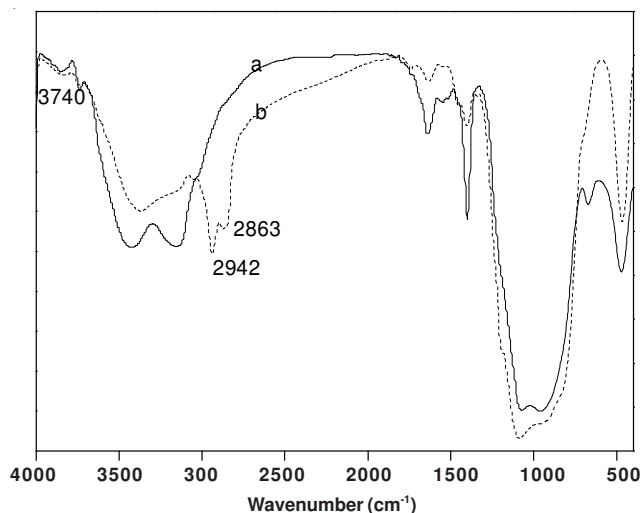


Fig. 1. FT-IR spectra of nano-Si₃N₄ (a) and modified nano-Si₃N₄ (b)

For the modified nano-Si₃N₄ (Fig. 1), the peaks at 2942 and 2863 cm⁻¹ are related to -CH₂, -CH₃ asymmetric stretching mode. This proved that the coupling agent had been tightly adsorbed at the surface of nano-Si₃N₄ by chemisorption and it is still exist in the modified powders even after being extracted by Soxhlets extractor in acetone.

TGA of nano-Si₃N₄: Thermal stability of nano-Si₃N₄, modified nano-Si₃N₄ were measured by dynamic thermogravimetric analysis. The surface modified nano-Si₃N₄ sample was analyzed after being washed with acetone in Soxhlet extractor for 72 h.

Fig. 2 is TG curve of nano-Si₃N₄ and modified nano-Si₃N₄ (the heating rate was monitored at 20 °C/min). As shown in the TG curve, the thermal decomposition of native nano-Si₃N₄ begins at about 40 °C and the continuous mass loss can be seen from 40 to 200 °C. This is likely due to a series of reactions happening on the surface of nano-Si₃N₄ between surface groups or some physical and chemical adsorption substances, then the desorption of H₂O, NH₃ and *etc.* from the surface of nano-Si₃N₄ with increasing temperature results in the continuous mass loss. In contrast with native nano-Si₃N₄, the thermal decomposition process of modified nano-Si₃N₄ can be divided into several stages. The first stage started from 40 to 160 °C, the mass loss is only about 1 %. The second stage is in the range of 160-340 °C. This stage is identical with the main thermal decomposition stage. Thus, we consider that most of the coupling agent coats on the surface of nano-Si₃N₄ particles and strong chemical bonding establishes between the coupling

agent and nano-Si₃N₄. The third stages of decomposition is above 340 °C and powder quality changed little. Compared with native nano-Si₃N₄ and modified nano-Si₃N₄, the result indicates that owing to the strong chemical bonding, the decreasing number of -NH₂ and -OH group on the surface of modified nano-Si₃N₄ results in the reduction of gas desorption quantity on the surface of modified nano-Si₃N₄ below 210 °C. The thermal stability of modified nano-Si₃N₄ has been proved.

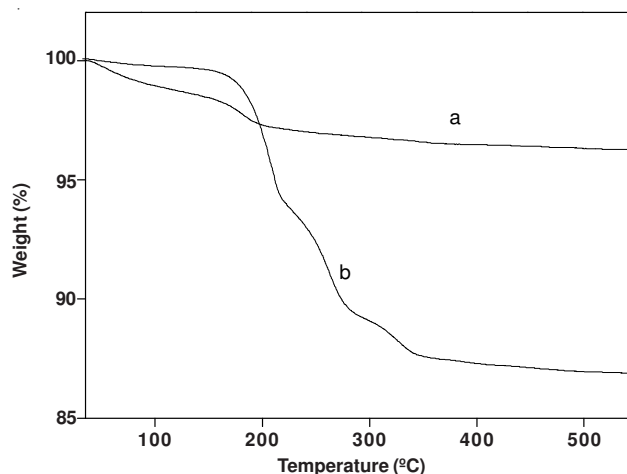
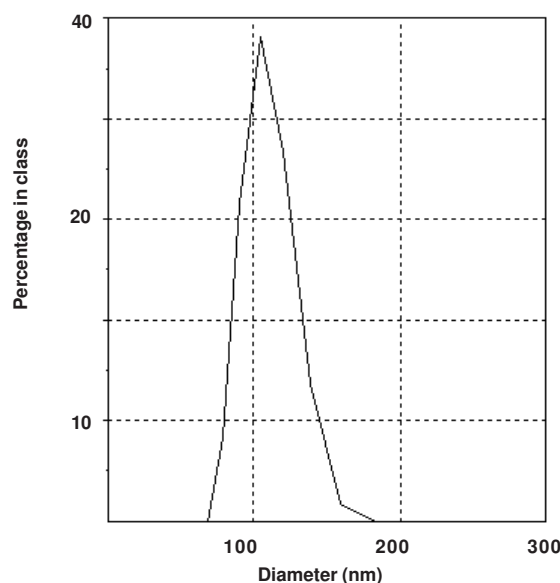
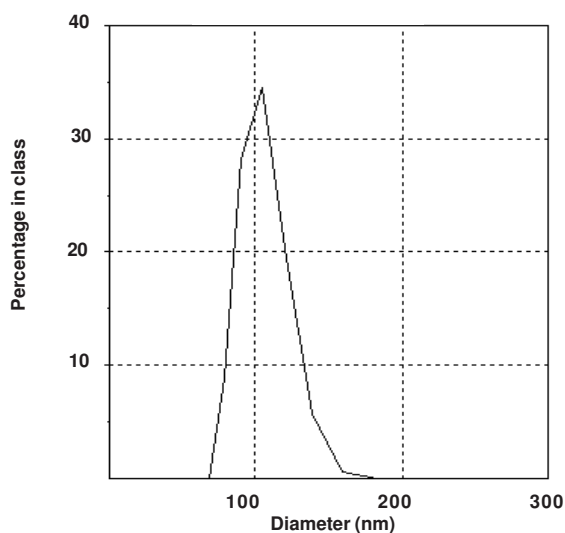
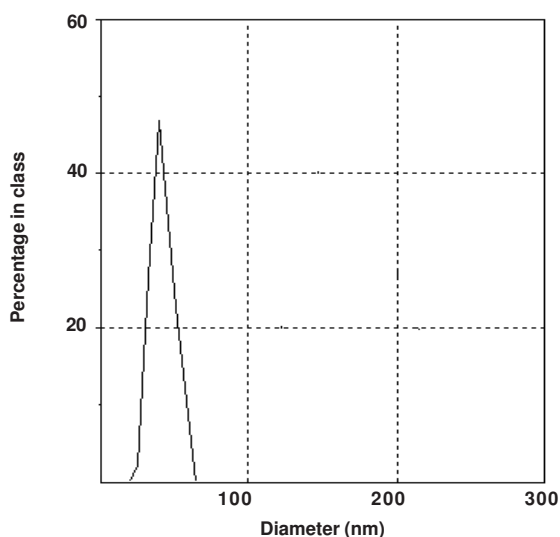
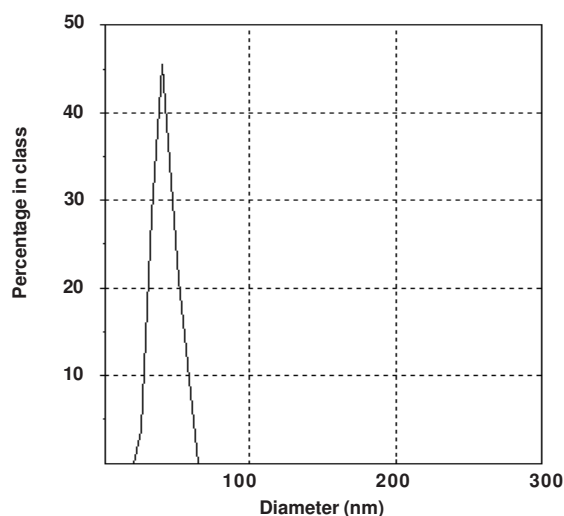


Fig. 2. TG curves of nano-Si₃N₄ (a) and modified nano-Si₃N₄ (b)

Analysis of nanoparticle size and distribution: The number average diameter and size distribution of nano-Si₃N₄ suspension were analyzed using size distributions analyzer (3000 HS, Malvern) (Fig. 3). The nano-Si₃N₄ suspension in alcohol was prepared through ultrasonic dispersion for 0.5 h. According to the result, the average diameter of native nano-Si₃N₄ is about 110 nm while that of modified nano-Si₃N₄ decreased obviously. It was suggested that the dispersing effect of nano-Si₃N₄ in alcohol be improved obviously after modified.



a1. Volume distribution of nano-Si₃N₄

a2. Number distribution of nano-Si₃N₄b1. Volume distribution of modified nano-Si₃N₄b2. Number distribution of modified nano-Si₃N₄Fig. 3. Size distribution of nano-Si₃N₄ (a1, a2) and modified nano-Si₃N₄ (b1, b2)

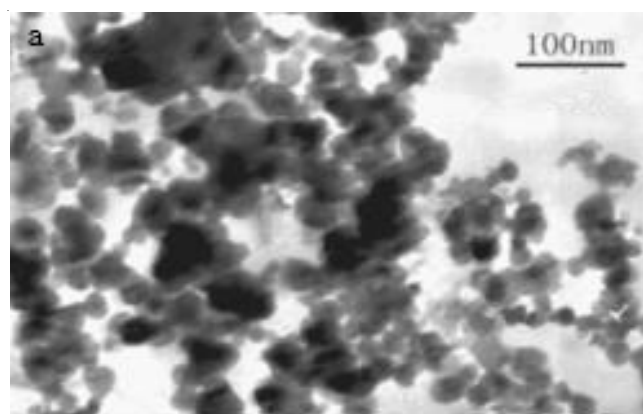
The native nano-Si₃N₄ particles were dispersed poorly in alcohol and the serious agglomerations were formed due to the existence of Si-OH group on the surface of the native nano-Si₃N₄ powders. Compared with the native powders, the nano-Si₃N₄ modified with KH-845-4 showed good dispersibility in alcohol. Because of the new chemical bond's forming between the coupling agent and nano-particles, the interaction among nano-particles was broken down and the agglomeration was controlled effectively.

Analysis of surface free energy: The change of surface hydrophilicity was investigated by contact angle measurements. Surface free energy was calculated by corresponding contact angle. Table-1 shows an obvious change of surface free energy after modifying nano-Si₃N₄ surfaces. After the surface modification, the surface free energy decreased from 108.12 to 25.36 J/m², suggesting increased surface hydrophobicity. These changes are likely due to the carbon backbone of the silane coupling agent, which is hydrophobic. Thus, it is concluded that the nano-Si₃N₄ modified with coupling agent can be dispersed in polymer more easily than native nano-Si₃N₄ powder.

TABLE-1
SURFACE FREE ENERGY OF NANO-Si₃N₄ at 20 °C

Sample	Different percentage of coupling agent			
	0 %	9 %	10 %	12 %
Surface energy (J.m ⁻²)	108.12	77.60	42.30	25.36

Comparison of nano-Si₃N₄ and modified nano-Si₃N₄'s dispersion by TEM: TEM photographs of native nano-Si₃N₄ and modified nano-Si₃N₄ suspensions in alcohol, prepared with ultrasonic vibrating method, are shown in Fig. 4. The obvious agglomeration can be seen in the photograph of native nano-Si₃N₄ [Fig. 4(a)] while a better dispersion can be seen in the photograph of modified nano-Si₃N₄ [Fig. 4(b)]. Based on Fig. 4, the conclusion can be drawn that the surface modification effectively improved the dispersability of nano-Si₃N₄ in acetone, the size of particles is less than that of the unmodified nano-Si₃N₄. And, Fig. 4(b) shows that the coating layers are clearly seen as the gray area, which coated on the surface of nano-Si₃N₄ particles and reduced the agglomerations. This suggests that condensation reaction should take place on the surface of nano-Si₃N₄ particles, then the organic chain of the agent is grafted onto the nano-particles surface, thus the surface free energy reduced and the agglomeration was controlled.



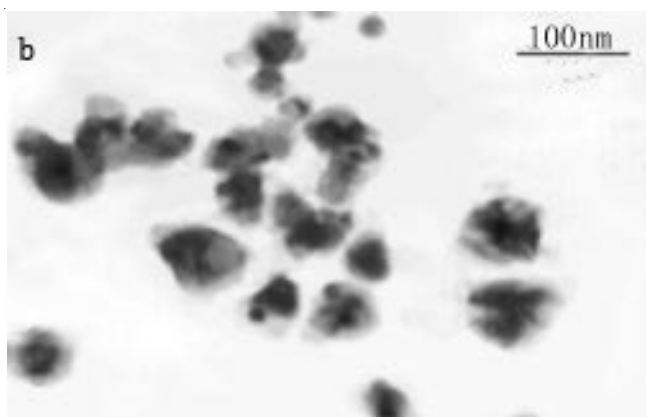


Fig. 4. TEM micrographs of nano-Si₃N₄ (a) modified nano-Si₃N₄ (b)

Conclusion

Nano-Si₃N₄ powder can be modified with silane coupling agent, which may be applied to prepare polymer composites. An organic coating layer formed on the surface of nano-Si₃N₄ powders and chemical bond combination happened between the coupling agent and nano-Si₃N₄ powders surface. The

hydrophobic property of nano-Si₃N₄ modified with coupling agent was improved obviously. Modified nano-Si₃N₄ possessed good dispersibility and the average diameter was less than 100 nm.

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