

The effect of surface functional groups of nanosilica on the properties of polyamide 6/SiO₂ nanocomposite

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The present study investigated the effect of the surface functional groups of nanosilica on the interfacial, crystallization, and thermal stability of polyamide 6/SiO₂ (PA6/SiO₂) nanocomposite, in which nanosilica was modified *in situ* with both 3-triethoxysilylpropylamine and 3-methacryloxypropyltrimethoxy silane- γ (KH-550 and KH-570). The FTIR analysis results showed the chemical bonding action between the reacting amino groups of nanosilica and end carboxyl groups of polyamide 6 enhanced with increasing the ratio of KH-550 and KH-570. The XRD spectrum indicated that the crystal structure of PA6/SiO₂ nanocomposites tended to form α crystal type that was beneficial to an improvement of mechanical properties, and which was in agreement with the results of mechanical strength measurements. It was also found that crystallization temperature and crystallization rate of PA6/SiO₂ nanocomposites were lower than that of neat polyamide 6.

Keywords: nanosilica; polyamide 6, nanocomposite, *in situ* polymerization.

INTRODUCTION

Nanosilica used as a filler has been applied in rubber, polyamide, polyolefin, and unsaturated polyester resin, etc. Unfortunately, because of hydroxy groups on silica surfaces, the probability of nanosilica aggregation would increase with decreasing the size. As a consequence of aggregation of silica in polymer matrix, the tensile and impact strength, thermal stability, and process ability of nanocomposite were seriously affected. Surface-modified nanosilica becomes an interesting research topic that is beneficial to improve the dispersion of nanosilica inside polymer matrix, the compatibility and interfacial strength between polymer and nanosilica. The incorporation of surface-modified nanosilica inside polyamide 6 has proved to be an effective way of improving the mechanical properties and the dispersion of nanosilica.

Hasan¹, Mahfuz², Tung³ all have studied the synthesis of SiO₂/polyamide 6 (PA6/SiO₂) nanocomposite by melt blending method and found that the mechanical properties, modulus, and thermal stability of nylon 6 can be improved. Li⁴, Zhao⁵, and Fang⁶ all have prepared PA6/SiO₂ nanocomposite via *in situ* polymerization method by addition of functionalized nanosilica, which has been confirmed as a more excellent method compared with a melt blending method for an improvement of the properties of polyamide 6. In addition, masterbatch method is also a conducive method to disperse nanosilica and improve the properties of polyamide matrix. Tang^{7, 8} have synthesized PA6/SiO₂ masterbatch, and then PA6/SiO₂ nanocomposite was fabricated in the polymerization process of masterbatch and ϵ -caprolactam monomer, the results showed both the dispersion inside polyamide and the compatibility of polyamide and SiO₂ were both improved. The reported results indicated that the surface functional groups of nanosilica greatly affected the properties of nanocomposite.

Surface modified *in situ* nanosilica with two or more functional groups as the filler is seldom to apply in the polymer matrix. In the present study, we synthesize PA6/SiO₂ nanocomposites via *in situ* polymerization method

by using functional nanosilica modified *in situ* with two kinds of silane coupling agents (KH-550 and KH-570) and ϵ -caprolactam monomer. And then, the effect of the different ratio of KH-550 and KH-570 on the properties of PA6/SiO₂ nanocomposites, which conclude the mechanical strength, the interfacial properties, thermal stability, and crystallization properties, will be studied by FTIR, TG, DSC, and XRD.

EXPERIMENTAL

Materials

RA0, RA1, RA2, RA3, RA4, and RA5 represent surface-modified *in situ* nanosilicas by the different ratios of two silane coupling agents (KH-550 and KH-570), in which the total amount of silane coupling agent is 10% (m/m), and the amount of KH-570 is 10%, 6.7%, 3.3%, 0.83%, 0.42%, and 0 respectively, at the same, the amount of KH-550 is 0, 3.3%, 6.7%, 9.17%, 9.58%, and 10%. They are obtained from Henan Province Nano-Materials Engineering Technology Center. The ϵ -caprolactam was supplied from Yelang Chemical Co. Ltd of Wuhan. Adipic acid was supplied by Paini Chemical Reagent Factory of Zhengzhou. Formic acid was purchased from Kemel Chemical Reagent Co. Ltd of Tianjin.

Sample preparation

Adipic acid, ϵ -caprolactam, RA0, and distilled water were added to a 250 mL three necks flask. The temperature was then elevated from room temperature to 190°C over a period of about 3 h with stirring. At the following step, the reaction was allowed to proceed at 230°C, in which the temperature was gradually elevated to 260°C within 1.5–2 h. Then, the pressure of the system was gradually pumped to -0.08 MPa within about 1.5 h. Thereafter, the dumbbell type samples followed by a casting model and noted as PRA0 (here and later in the text). And then, the extracted nanosilica sample by dissolving in formic acid was denoted by ERA0, in which PRA0 was dissolved in formic acid, and extracted

for 6 times until polyamide 6 could not be detected by infrared spectroscopy in suspension⁴. Among other nanosilica including RA1, RA2, RA3, RA4, and RA5, the same process procedures were used for preparing polyamide 6 and PA6/SiO₂ nanocomposites, the samples were noted as PA6, PRA1, PRA2, PRA3, PRA4, and PRA5, respectively, and the extracted nanosilica were denoted as ERA1, ERA2, ERA3, ERA4, and ERA5.

Characterization

The infrared spectrum of the samples of polyamide 6 and the extracted silica were recorded inside KBr pellets on Fourier Transform Infrared Spectrometer (FTIR/Avatar360, Nicolet, American). Thermogravimetry Analysis (TG/SDTA851^e, Mettler Toledo, Sweden) was carried out for the purpose of detecting the thermal stabilities of the samples, and heated to 1000°C from room temperature at a heating rate of 10°C/min. The crystallization and melting behaviors of polyamide 6 and PA6/SiO₂ nanocomposites were investigated by differential scanning calorimetry (DSC/851^e, Mettler Toledo, Sweden), and the samples about 5 mg were heated from 25°C to 300°C at a rate of 10°C/min, and then, the samples were cooled back to room temperature. X-ray diffraction patterns (X-pertpro, Philips, Holland) patterns was recorded for studying crystal forms of PA6/SiO₂ nanocomposites on a D/max 2550 V X-ray diffractometer with Cu K α radiation ($\lambda=1.54178$ Å) and a graphite monochromator, operating at 40 kV and 200 mA. The tensile strength of polyamide 6 and PA6/SiO₂ nanocomposites were measured on a WDW-10D testing machine according to GB/T 1040-1992, and the impact strength were evaluated on a ZBC-1400-2 testing machine according to GB/T 1040-1993.

RESULTS AND DISCUSSION

Grafted reaction on the surface of nanosilica

The interfacial interaction is an important factor to know whether and to what extent the reaction between surface functional groups of nano-inorganic particles and the molecular chains of polymer occurred. Generally, the chemical grafting of polymer chains which are compatible to the polymer matrix on the inorganic particles improve the interfacial strength, and that leads to strong mechanical properties.

Figure 1 showed the FTIR spectrum of PA6 and extracted silica. Compared with the absorption of PA6, those in the spectrum of extracted silica ERA1, ERA2, ERA3, ERA4, and ERA5 at 1647 cm⁻¹ and 1551 cm⁻¹ are of polyamides, while the peaks at 3431 cm⁻¹ corresponds to N-H bond, and that at 2944 cm⁻¹, 2875 cm⁻¹ represent the oscillation of C-H bond; but the similar absorption peaks in ERA0 is not found. These observations reveal that ERA1, ERA2, ERA3, ERA4, and ERA5 were coated with the molecular chain of PA6, but ERA0 was not coated. As the samples were separated with formic acid from the nanocomposites via repeated dispersion/centrifugation, any homopolymer should not remain on the surface of nanosilica. Therefore, we can conclude that the molecular chain of PA6 had been chemically grafted onto the silica surface including ERA1, ERA2,

ERA3, ERA4, and ERA5 through chemical bonding rather than physical absorption, but ERA0 was excluded.

For the nanosilica modified *in situ* with the different ratio of KH570 and KH550, the introduced KH570 is beneficial to the dispersion of nanosilica inside PA6 matrix and to reduce the aggregation of nanosilica, and the amino groups of the KH550 can be capable of reacting with carboxyl groups of PA6 that can improve the interfacial strength between nanosilica and PA6 matrix.

Thermogravimetry analysis

TGA spectrum of PA6 and extracted nanosilica from nanocomposites were shown in Fig. 2. It can be seen that the weight loss content of ERA1, ERA2, ERA3, ERA4, and ERA5 were 37%, 42%, 48%, 51%, 52%, respectively, that of RA5 was 20%, and that of RA0 and ERA0 were both only 7%. Additionally, the weight loss at the initial stage ($\leq 100^\circ\text{C}$) corresponds to the surface adsorption of water. The results of the nanosilica weight loss of the following stages were concluded that (1) RA0 and ERA0 without reacting groups had the same weight loss content due to lack of molecular chain of PA6 on the surfaces of two nanosilica; (2) the TG curve of RA5 modified only with KH550 with reacting amino groups was

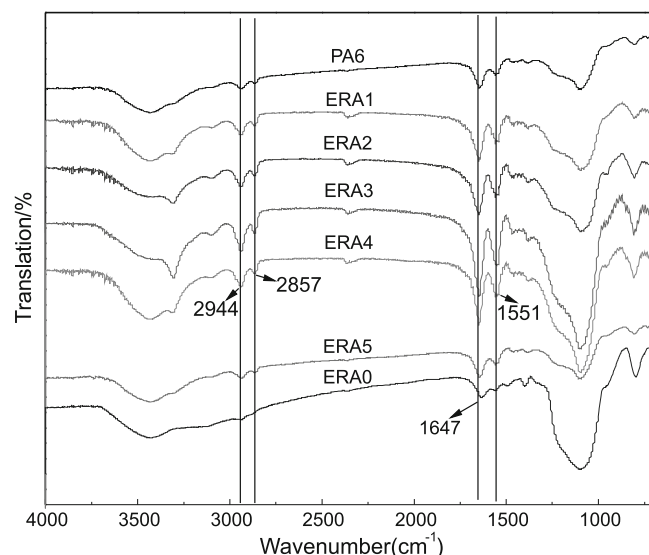


Figure 1. FTIR spectrum of PA6 and extracted silica

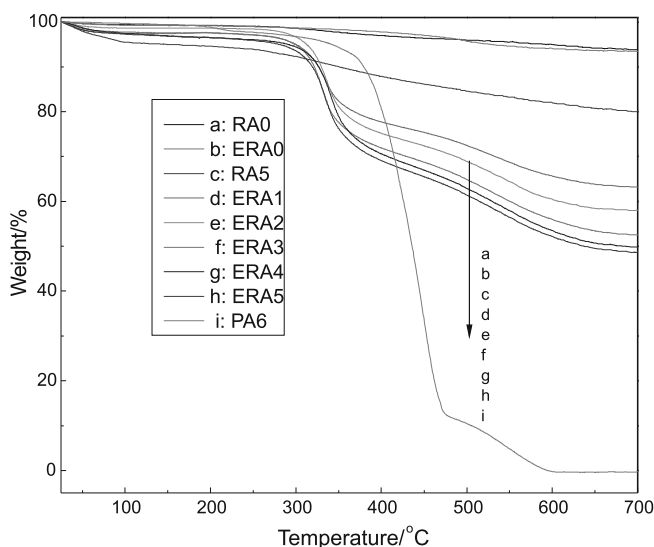


Figure 2. TGA curves of extracted silica and polyamide 6

different from that of RA0 due to aminolysis of surface amino groups of nanosilica, while the previous report had a similar conclusion⁴; (3) the weight loss contents of the extracted nanosilica were gradually increased with increasing the ratio of KH550 and KH570 due to the amino groups reacted with carboxyl groups increased the content of molecular chain of PA6 onto the surface of nanosilica, which led to the increasing weight loss content, the result was in agreement with that of FTIR spectrum and indicated the molecular chains of PA6 onto nanosilica surface were chemically grafted via chemical bonding rather than physical absorption; (4) in addition, the temperature of weight loss of extracted nanosilica (320°C) was lower than that of PA6 (400°C), the possible reason included that the molecular chain of PA6 broke in the process of dissolving nanocomposites with formic acid, and the hydrogen bonds between PA6 molecular chains were also destructed. These phenomena may also affect the crystallization properties of nanocomposites, the following context will be introduced. However, the thermal decomposition temperature of nanocomposites had no influence on different nanosilica as the filler.

The crystallization and melting behaviors

In order to understand the effect of nanosilica on the crystalline and melting properties of PA6/SiO₂ nanocomposites, thermal characterization of PA6 and PA6/SiO₂ nanocomposites evaluated by using DSC were shown in Fig. 3 and Table 1.

Figure 3(a) showed that the melting temperature of PA6 was almost the same as that of PA6/SiO₂ nanocomposites and the ratio of two silane coupling agent had no effect on the melting temperature of PA6 matrix.

However, compared with the crystalline temperature of PA6, that of PA6/SiO₂ nanocomposites gradually decreased with decreasing the ratio of KH-550 and KH-570 in Fig. 3(b) (from RA5 to RA0). The two possible reasons were responsible for the effect of nanosilica modified *in situ* with different the ratio of KH-550 and KH-570 on thermal properties of PA6 and its nanocomposites. Firstly, the nanosilica usually hindered the movement of PA6 molecular chains, particularly, while the amine of the surface of nanosilica reacted with the molecular chains of PA6 was reduced; secondly, the crystallization behavior of PA6 in size would be smaller and more imperfect due to the heterogeneous nucleation of nanosilica^{10, 11}. The above results were also beneficial to the improvement of mechanical properties and crystallization rate of PA6/SiO₂ nanocomposites.

The DSC crystal characteristic parameters in Table 1 showed that the crystallinity (χ_c) of PA6 was almost the same as that of PA6/SiO₂ nanocomposites. However, the crystallization rate ($\Delta T_{c1/2}$) increased with decreasing the ratio of KH-550 and KH-570, the chemical bonding action of the amino group on the surface of nanosilica and the molecular chains of PA6 might weaken the heterogeneous nucleation action of nanosilica, in addition, the nanosilica without reacting amino could hinder the movement of the molecular chains of PA6¹¹.

Crystal structures analysis

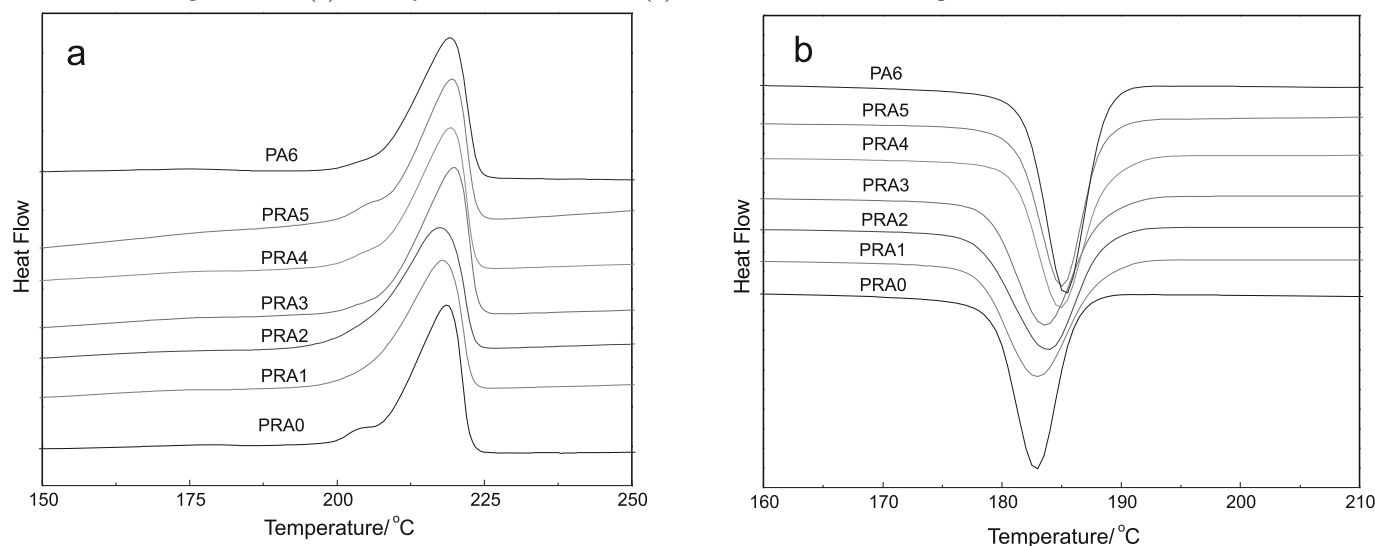
Usually, two crystal forms, α and β type, exist inside the PA6 structure, and α type is advantageous in raising the strength of nylon 6 whereas the β type for the improvement of the toughness of nylon 6. Figure 4 showed the XRD patterns of PA6 and PA6/SiO₂ nanocomposites.

Table 1. DSC crystal characteristic parameters of PA6 and nano-SiO₂/PA6 hybrid materials

	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	χ_c (%)	$\Delta T_{c1/2}$ (min)
PA6	219.52	54.02	183.38	60.68	26.37	0.58
PRA0	218.46	58.90	184.54	61.62	26.78	0.42
PRA1	218.02	56.93	184.17	60.84	26.44	0.45
PRA2	217.58	57.72	182.92	61.85	26.88	0.56
PRA3	217.27	59.73	183.18	62.79	27.29	0.51
PRA4	219.52	56.43	182.23	60.31	26.21	0.59
PRA5	219.01	55.23	184.17	63.14	27.44	0.53

T_m , melting temperature; T_c , crystallization temperature; ΔH_m , the heat of fusion; ΔH_c , the heat of crystallization; χ_c , crystallinity; and $\Delta T_{c1/2}$, full width at half maximum of crystallization peak

Figure 3. Melting behavior (a) and crystallization behavior (b) of PA6 and its nanocomposites



The diffraction peaks at 19.84° and 23.47° corresponded to α crystal form of PA6, and at position of 21.00° corresponded to the γ crystal form. The crystalline form of PA6/SiO₂ nanocomposite was obviously different from that of PA6. The γ crystal form of 23.47° gradually became strong with increasing the ratio of KH570 and KH550. The two possible reasons were indicated: (1) the heterogeneous nucleation effect of SiO₂ inside PA6 increased the nucleation density and the degree of crystallinity; (2) with the reducing the reacting amino groups, SiO₂ hindered the continue growth of crystalline nearby that tended to generate imperfect crystal form. The functional nanoparticles could increase the force point for dispersing the stress and avoiding the stress concentration when the nanocomposite was under the external force, and the impact strength of nanocomposite was improved greatly¹⁰⁻¹².

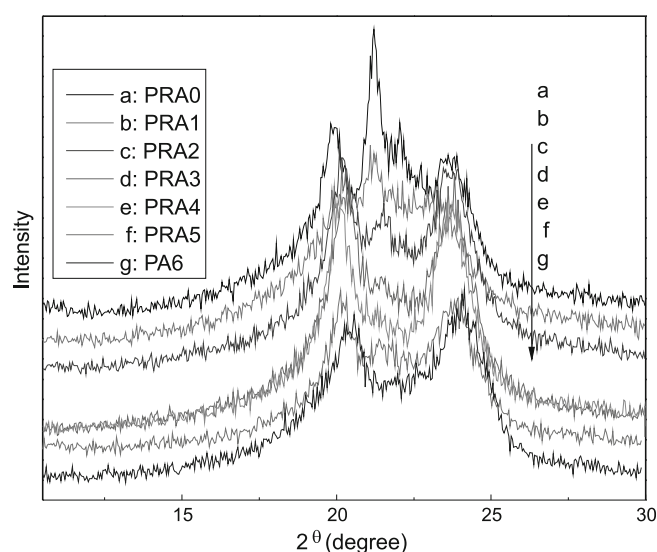


Figure 4. XRD spectrum of PA6 and nanocomposites

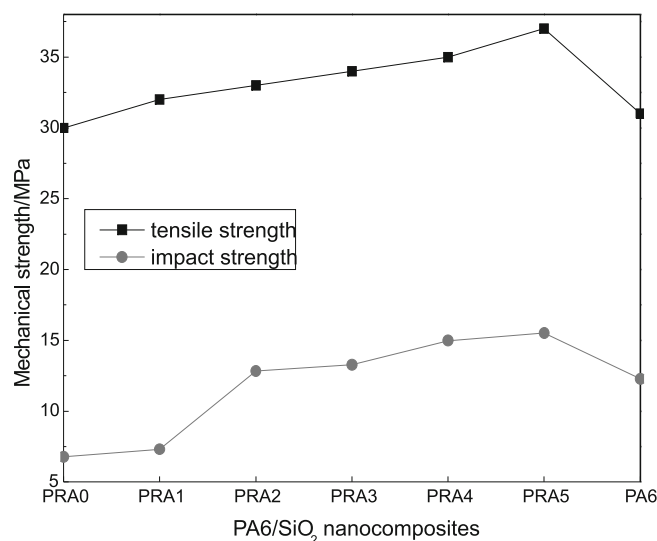


Figure 5. Mechanical strength of PA6 and nanocomposites

The mechanical strength

Figure 5 showed the effect of nanosilica on the tensile and impact strength of PA6/SiO₂ nanocomposites, while the amount of nanosilica was 0.4% (m/m), in which tensile and impact strength gradually increased with increasing the ratio of KH-550 and KH-570. The phenomenon is understood by analyzing the interfacial

strength and the crystal structure of PA6/SiO₂ nanocomposites. The interfacial strength between nanosilica and PA6 is a key factor where the surface amino groups of nanosilica can form the chemically bonding action with the end carboxyl groups of PA6, and whether and to what extent the reaction between the surface amino groups of nanosilica and the end carboxyl groups of PA6 occurred usually affect the mechanical strength. The results also indicated that the reacting amino groups was beneficial to improve the mechanical properties due to the tiny lattice structure via the reaction between surface amino groups and molecular chains of PA6^{9, 13}. In addition, the crystal structure inside PA6 is also an important factor for understanding the mechanical properties of PA6/SiO₂ nanocomposites where the α crystal type is beneficial to the improvement of mechanical strength of nanocomposites^{14, 15}, while the diffraction peaks of α crystal gradually increased from PRA0 to PRA5.

CONCLUSIONS

PA6/SiO₂ nanocomposites were prepared by in situ polymerization by using nanosilica modified *in situ* as the filler. The interfacial strength between nanosilica and PA6 increased with increasing the ratio of KH550 and KH570 due to the reacting amino groups of KH550 can form the chemically bonding action with the terminal carboxyl groups of PA6; and the diffraction peaks of α crystal form also enhanced with increasing the ratio of KH550 and KH570. These results led to the improvement of mechanical strength. Additionally, the decomposition temperature and crystallization temperature were also affected due to heterogeneous nucleation action of nanosilica and hindering action to the movement of the molecular chains of PA6.

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