The Influence of Silane Treatment on Nylon 6/nano-SiO$_2$ *In Situ* Polymerization

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ABSTRACT: Silane treatment has been applied to the preparation of nylon 6/nano-SiO$_2$ composites through *in situ* polymerization. The influence of such treatment on the reactivity of silica, polymerization of nylon 6, and the mechanical properties of the achieved composites has been studied. Fourier transform infrared (FTIR) spectroscopy and thermal gravimetric analysis (TGA) of silicas isolated from the composites have shown that the conversion of surface silanol groups to amino and epoxy groups did not cause a significant change in the reactivity of silica and that the percentage of silica surface grafting was around 15% for all treated and untreated silicas. End group analysis has shown that the presence of silica (pretreated or not) in the composite system resulted in the decrease of the average molecular weight of the polymer matrix. However, dynamic mechanical analysis and mechanical tests revealed that treating silica with silane improved the strength and toughness of the composite materials, while untreated silica improved their strength at the expense of toughness. This can be attributed to the existence of the flexible interlayer introduced by silane treatment. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 827–834, 2002; DOI 10.1002/app.10349

Key words: silane treatment; nylon 6; nano-silica; *in situ* polymerization; composite

INTRODUCTION

In recent years, polymer-based organic/inorganic nanocomposites have gained increasing attention in the field of material science. By changing the materials and conditions of synthesis, various organic/inorganic nanocomposites can be prepared that possess physical and mechanical properties that are superior to conventional microcomposite counterparts because of the nanometer dimension effect, large specific surface area of the inorganic fillers, and strong interaction between the dispersed phase and the matrix.

To obtain dispersed phases on a nanometer scale, preparation methods include sol–gel process, intercalation, blending, and *in situ* polymerization. There have been numerous reports describing the preparation and characterization of polymer/silica nanocomposites, mostly synthesized via the polymerization of silicon alkoxide in a polymer matrix through the well-known sol–gel process.[1–8] This method can be carried out under mild conditions and can achieve a good degree of dispersion. However, formation of a crosslinked network of organic metal oxides makes the sol–gel process difficult to carry out uniformly. Also, owing to the volatilization of solvents, water, and other small molecules, shrinkage and rupture may occur during the desiccation of the gel, which greatly reduces the utility of this method.

With regard to nanocomposites of nylons, a large number of reports[9–14] have focused on the intercalation method used to prepare nylon/clay

nanocomposites. Using the inherent characteristics of the alumino-silicate layer (e.g., swelling behavior and cation exchange), the inorganic phase could be evenly dispersed on a nanometer scale, generating strong interaction between the inorganic and organic phases. This method, however, is only suitable for clay minerals.

In situ polymerization is a method in which fillers or reinforcements are dispersed in monomer first and then the mixture is polymerized using a technique similar to bulk polymerization. Using this method, inorganic particles may be evenly dispersed in the polymer matrix, creating composites with good processability as a result of their flow properties. Ou et al.[15,16] reported on the preparation of nylon 6/silica nanocomposites by using *in situ* polymerization, in which silica was pretreated with aminobutyric acid. The effects of the unmodified and modified silica on the dispersion, interfacial adhesion, isothermal crystallization, and mechanical properties of nylon 6/silica nanocomposites were investigated. The results showed that silica was dispersed homogeneously in the polymer matrix and that the addition of silica increased the glass transition temperature and crystallization rate of the nylon 6 matrix. The mechanical properties of nylon 6/unmodified silica nanocomposites decreased gradually with the increase of silica content, whereas those of the nylon 6/modified silica system had maximum values at 5% silica content. On the basis of the relationship between the impact strength of the nanocomposites and the matrix ligament thickness τ, a new criterion was proposed to explain the unique mechanical properties of the nylon 6/silica nanocomposites.[16]

It is well-known that silanes have an important role in the fast-growing field of organic/inorganic composites, acting as adhesion promoters, coupling agents, and surface primers. Organofunctional silanes have been widely used to modify the surface properties of fillers, especially those having surface hydroxyl functional groups. It has been demonstrated that the nature of the interlayer between the filler and the polymer matrix, introduced by silane treatment, plays a significant part in the effectiveness of improving the mechanical properties of composites.[17] As for nylon 6/SiO$_2$ *in situ* polymerization, the previous study[15,16] only confirmed its feasibility for preparing organic/inorganic nanocomposites, while the surface treatment of SiO$_2$ by silane-coupling agents and the possible reactions between SiO$_2$ and nylon have not yet been investigated.

In this work, we applied silane treatment to nylon 6/nano-SiO$_2$ *in situ* polymerization. The possible reactions between silica surface functional groups and the nylon matrix were studied by isolating silicas from the final composites and characterizing them by infrared spectroscopy and thermogravimetric analysis. The effect of such reactions on the molecular weight of the polymer matrix was studied by end group analysis. The characteristics of the achieved composites were evaluated by means of dynamic mechanical analysis and mechanical tests.

EXPERIMENTAL

Materials

ϵ-Caprolactam and ϵ-aminocaproic acid were used to prepare nylon 6. Silica used is from Zhoushan Mingri nanomaterial company (China; type MN1P, mean size 10 nm, specific surface area 640 m^2/g). Two commercially available silane compounds, γ-aminopropyl-triethoxysilane (APS) and γ-glycidoxypropyltrimethoxysilane (GPS) from Shuguang Chemical General Company (Nanjing, China) were used as surface modifiers.

Preparation of Nylon 6/ SiO$_2$ Composites

Silica was pretreated with the silane-coupling agents by a dry-blending method, and the silane used was 3 wt% of the silica. In the treatment, APS or GPS in a small amount of toluene was added dropwise to silica under rapid stirring and stirred for 30 min at room temperature. The treated silica was kept in a desiccator before the preparation of nylon 6/silica nanocomposites. A typical procedure is as follows. Into a 500-mL four-necked flask equipped with a mechanical stirrer were placed 200 g of ϵ-caprolactam, 22 g of ϵ-aminocaproic acid, 0.6 g of antioxidant, and 10 g of the modified silica. The mixture was heated to and held at 220°C for 1 h and then heated at 260°C for 5 h in a N$_2$ atmosphere. The products were mechanically crushed and washed with water at 85°C for 1 h. Nylon 6/unmodified silica composites were also prepared by this procedure.

Isolation of Silicas from Nylon 6/SiO$_2$ Composites

To isolate silica from the composite system, the product was extracted with formic acid as follows: 0.1 g of pellets were dissolved in 10 mL formic acid, assisted by ultrasonic irradiation, and then

the suspension was centrifuged until the silica was completely precipitated. The supernatant solution was removed and the procedure was repeated until no more polymer could be detected in the supernatant. The residue was washed with methanol and dried. The percentage of grafting was calculated by the following equation:

$$\text{Grafting } (\%) = \frac{\text{polymer grafted (g)}}{\text{silica used (g)}} \times 100$$

Characterization

The infrared (IR) spectra of the isolated silica from nylon 6/silica composites and the original silica were recorded in KBr pellets on a Nicolet 560 FTIR spectrometer. TGAs of the silicas isolated from nylon 6/silica composites were carried out on a TA 2050 instrument with a heating rate of 10°C/min in N_2 atmosphere. The content of amino end groups (mol/10^6g polymer) in pure nylon 6 and the composites were measured as follows: Polymer chips (0.3 g) were dissolved in 25 mL of 50/50 (v/v) phenol-methanol under stirring; then this solution was titrated with 0.01M hydrochloric acid using phenol blue as an indicator; and finally the amino content was calculated according to the following formula:

$$X = \frac{(A - B)n}{W} \times 10^{-3}$$

where X is the amino content in mol/10^6g; A is the volume of hydrochloric acid consumed by the samples in mL; B is the blank value of the solvents in mL; n is the concentration of hydrochloric acid in mol/L; and W is the weight of the samples in g.

Dynamic mechanical properties of nylon 6/silica nanocomposites were measured with a DMA 2980 from TA instruments. The storage modulus E′ and the loss modulus E′′ were determined at 1 Hz in the temperature range between −50 and +200°C.The specimens were heated at a rate of 5°/min. Specimens were prepared for mechanical tests by injection molding. Charpy impact tests were carried out with an impact test machine (HB-5) on specimens preconditioned to 50% relative humidity (RH) for 24 h. Tensile properties were measured on a LJ-1000 testing machine, also using preconditioned specimens.
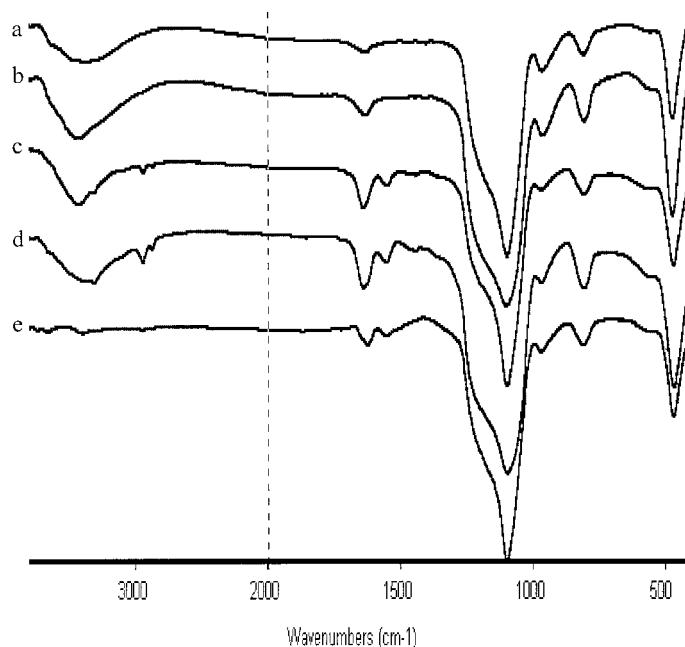
RESULTS AND DISCUSSION

Treatment of Silica with Silane Coupling Agents

Two silane-coupling agents, γ-aminopropyltriethoxysilane (APS) and γ-glycidoxypropyltrime-
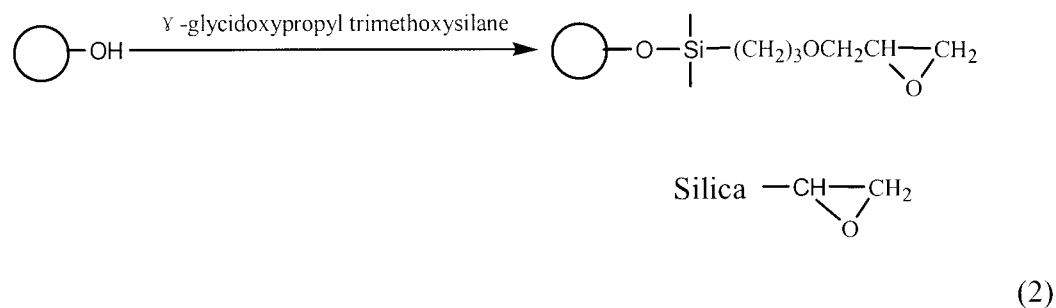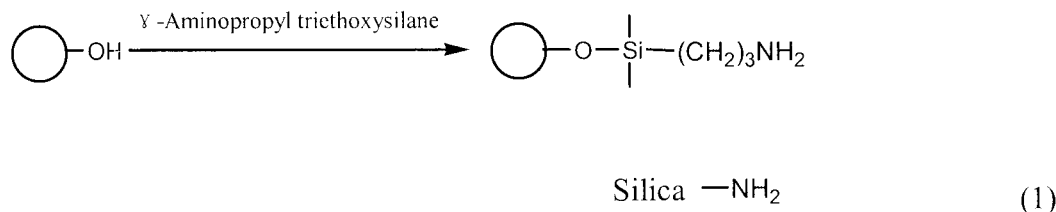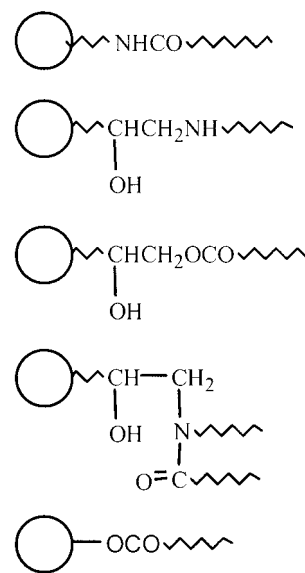

Scheme 1

Figure 1   Fourier transform infrared spectroscopy spectra of silicas: (a) raw material (as received); (b) modified with APS; (c) isolated from nylon 6/SiO_2 composite (SiO_2 was premodified with APS); (d) isolated from nylon 6/SiO_2 composite (SiO_2 was premodified with GPS); (e) isolated from nylon 6/SiO_2 composite (SiO_2 was unmodified).

thoxysilane (GPS), were used to pretreat silica. It is well known that silanol groups of such coupling agents generated by hydrolysis of alkoxy groups react with silanol groups on the silica particle surface via dehydration and condensation to form siloxane bonds,[18,19] as seen in Scheme 1. By such treatment, the functional groups of silica ($-OH$) are partly converted into amino and epoxy terminal groups with extended organic chains from the silica surface.

Characterization of Silicas Isolated from Nylon 6/ SiO_2 Composites

It is important to know whether and to what extent the reaction between silica surface functional groups and the polymer matrix occurred. Therefore, silica samples were isolated from the composites by thorough washing with formic acid and then characterized by IR and TGA. Figure 1 shows IR spectra of the isolated silicas. Compared with the original silica, there are several new peaks appearing in the spectra of silicas isolated from the composites (Fig. 1[c–e]): those at 1640 cm^{-1} and 1550 cm^{-1} are of polyamides, while the peaks at 2950 cm^{-1} and 2875 cm^{-1} represent the oscillation of C–H bond, and that at 3300 cm^{-1}

corresponds to N–H bonds. These observations suggest that whether the silica surface was pretreated or not, it was covered with nylon 6 molecules. As the samples were well washed with formic acid, any homopolymer should have been

Scheme 2
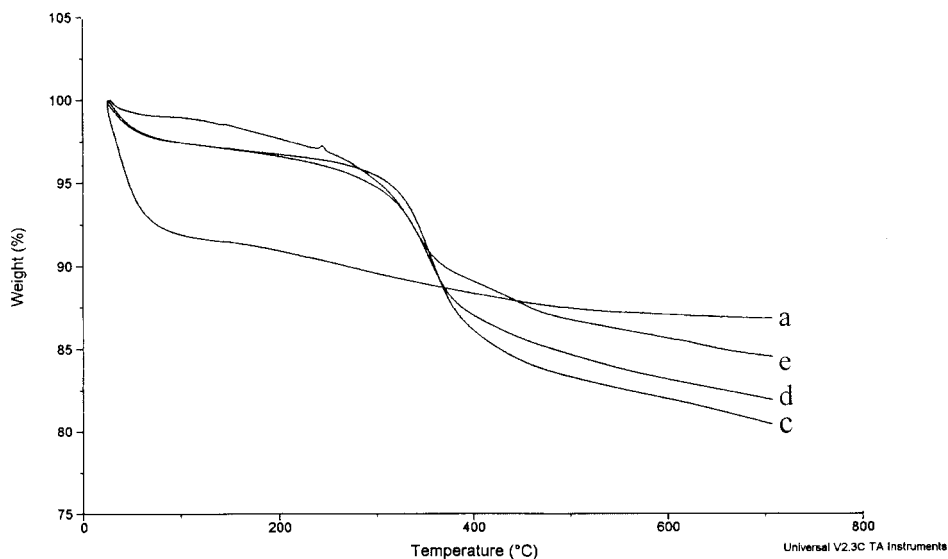
Figure 2 TGA curves of isolated silicas, where a, c, d, and e are in accordance with the Figure 1 caption.

washed off. We can conclude that nylon 6 macromolecules had been chemically grafted onto the silica surface through chemical bonding rather than physical absorption.

For the silica pretreated with APS, the introduced amino groups are capable not only of reacting with terminal carboxyl groups of nylon 6 but also of causing aminolysis of polymer amide groups. As to epoxy-functional silica, the epoxy groups on the silica surface can react with both NH_2 and COOH groups, while previous reports[20,21] showed that the reactivity of epoxide with amines was substantially greater than with carboxyls. In addition, there is the possibility of reaction between epoxy groups and the secondary amide groups of nylon 6 to produce graft polymers. According to one report,[20] these reactions typically occur in the temperature range of 190°–230°C, and it can be safely assumed that they are quite likely to take place at the polymerization temperature (i.e., 220°–260°C). With regard to unmodified silica, the hydroxyl groups on the surface may react with terminal carboxyl groups of nylon 6 as well as through alcoholysis of amide groups. Therefore, the possible bonding modes of the surface grafting are shown in Scheme 2.

Figure 2 shows the results of thermogravimetric analysis of the silicas isolated from nylon 6/silica composites. The weight loss at the initial stage ($\leq 100°C$) results from surface adsorption of water. For the particles isolated from *in situ* polymerization systems, the weight loss increases up to 300°C,which could be concluded to correspond with the initial decomposition temperature of the polymer grafted onto silica surface.

As can be seen from Table I, the percentages of grafting for samples c, d and e were all around 15%, indicating no striking difference among the activity of different functional groups. It is note-

Table I The Grafting (%) of Silicas Isolated from Nylon 6/SiO$_2$ Composites

Serial Number	Grafting (%)
C	16.13
D	14.54
E	13.06

C isolated from nylon 6/SiO$_2$ composite (SiO$_2$ was premodified with APS); D isolated from nylon 6/SiO$_2$ composite (SiO$_2$ was premodified with GPS); E isolated from nylon 6/SiO$_2$ composite (SiO$_2$ was unmodified)

Table II Amino Content of Nylon 6 and Nylon 6/SiO$_2$ Composites

Sample	Silica Content (%)	[NH$_2$] (mol/10^{6}g)
Nylon 6	0	22.68
Nylon 6 + (silica-NH$_2$)	4.3	34.90
Nylon 6 + (silica-epoxy)	4.3	26.64
Nylon 6 + (silica-OH)	4.3	26.85
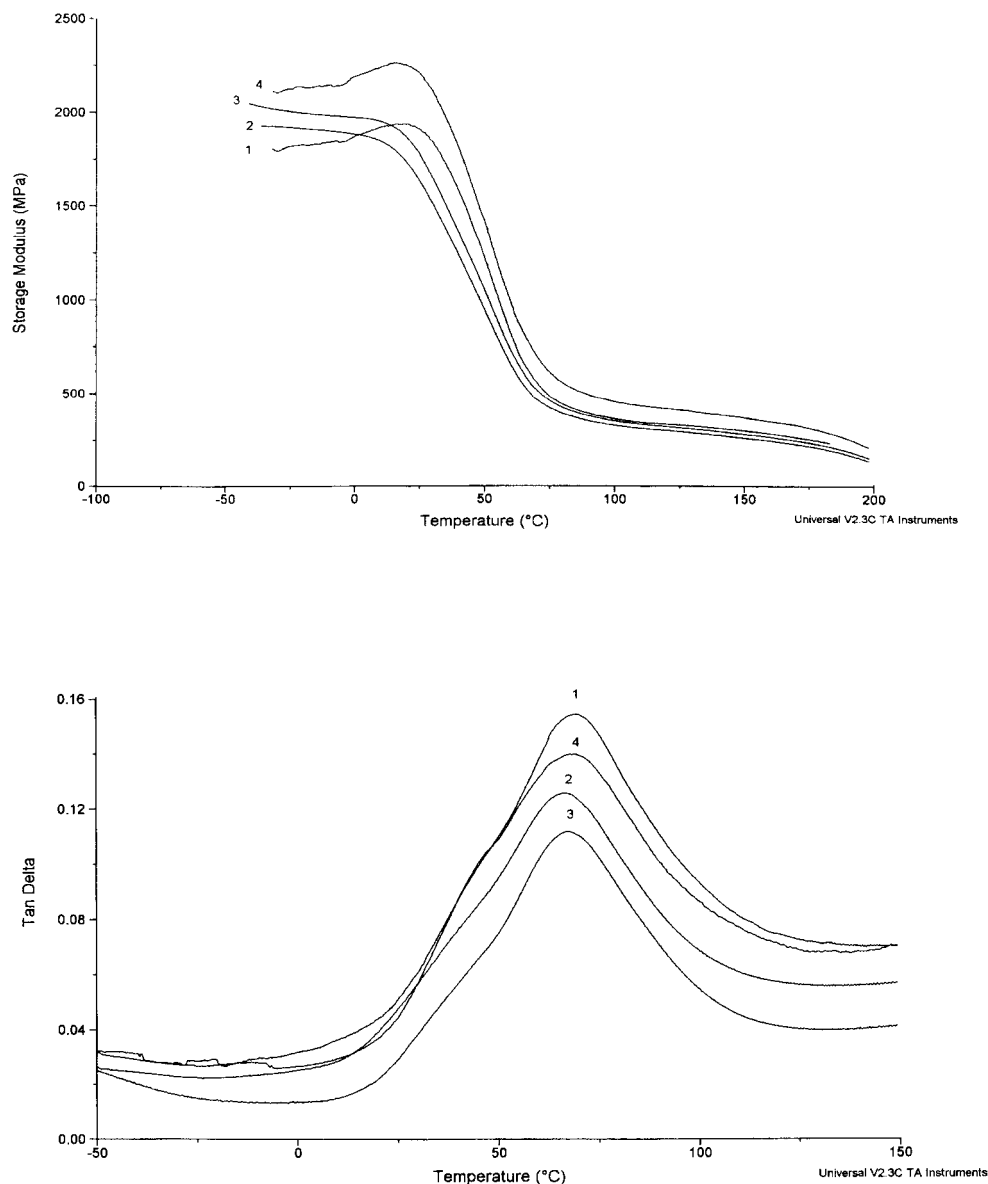
Figure 3   Dynamic mechanical spectra of nylon 6 and nylon 6/SiO$_2$ composites, where (1) pure nylon 6; (2) nylon 6 + (silica-NH$_2$); (3) nylon 6 + (silica-epoxy); and (4) nylon 6 + unmodified silica.

worthy, however, that whether silica was pretreated or not, the amount of grafting was low in relation to the large number of functional groups that exist on the silica surface. In fact, only approximately 0.3% of the surface functional groups reacted, as estimated by the amount of grafting and the amino content shown in Table II. These results confirmed that nanometer silica participated in the polymerization process. In addition, our further study showed that the addition of more coupling agent in the pretreatment process

resulted in an increase of grafting, up to 28% when the APS used was 15 wt% to silica.

Amino Group Content of Nylon 6/SiO$_2$ Composites

Control and determination of molecular weight are common problems in polymer science and are important for processing behavior and toughness. For linear nylons, the average molecular weight can be determined by end-group analysis. In the polymerization of ϵ-caprolactam, the reactive groups should correspond to a 1 : 1 mole ratio; any

Table III   Mechanical Properties of Nylon 6/SiO$_2$ Composites

Serial Number*	Tensile Strength (MPa)	Tensile Elongation (%)	Impact Energy (kJ/m^2)**
1	66.7	277.5	131.6
2	71.9	307.2	154.3
3	71.0	303.6	165.5
4	74.5	57.4	66.2

*Numbers 1, 2, 3, and 4 are absolutely in accordance with Figure 3.
**The impact energy was measured according to a nonstandard method and with only comparative meaning.

increase in NH$_2$ can be related to a decrease in polymer molecular weight. As seen from Table II, the addition of nanometer silicas (pretreated or not) resulted in an increase in amino content, indicating a decrease in the molecular weight of nylon 6 formed. It is reasonable that the reaction between silica and nylon 6 would alter the proportion of the two end groups (COOH and NH$_2$). In case of silica–NH$_2$, amino content of the composite derived from both silane treatment and nylon 6; after subtracting the silane contribution, the NH$_2$ content from the nylon was similar in value to those for silica–epoxy and unmodified silica. We conclude that pretreated silicas had similar effects to unmodified silica on nylon 6 polymerization.

Dynamic Mechanical Behavior of Nylon 6/SiO$_2$ Composites

In general, the dynamic mechanical analysis of nylon 6 shows an α peak in the tanδ curve that originates from the movement of the longer molecular chains in the amorphous region, corresponding to the glass transition temperature.[22] As can be seen from Figure 3, the T_g of the composite containing unmodified silica was almost the same as that of nylon 6, while the addition of silane-treated silica resulted in a shift of T_g to a lower temperature.

For the pretreated silica, owing to the existence of flexible segments derived from silane-coupling agent on the particle surface, a flexible interface layer is formed with decreased hindrance of the main chain motion of nylon near the interface layer, resulting in decreased T_g of the composites, as well as a lower value of tanδ compared with the composite containing unmodified silica and pure nylon 6.

Mechanical Properties of Nylon 6/SiO$_2$ Composites

In general, the addition of rigid particles to a thermoplastic matrix results in an increase in strength, modulus, and dimensional stability at the sacrifice of toughness. This was the case when unmodified silica was used. As can be seen from Table III, the tensile strength of the composite (sample 4) was higher than pure nylon 6 (sample 1), whereas the tensile elongation and impact energy decreased dramatically, meaning that the material toughness deteriorated.

When silane-treated silicas were used, namely samples 2 and 3, the tensile strength of the composites got a slight decrease compared with untreated silica but was still higher than pure nylon; the tensile elongation and impact energy increased significantly compared with untreated silica—even better than pure nylon. This means that there was an increase in both strength and toughness when compared with the single polymer. It is interesting to note that there was no obvious difference in mechanical properties between silica–amino and silica–epoxy compounds. As mentioned above, for the premodified silicas, there were flexible interface layers in the composites owing to their having been treated with silane. The existence of flexible layers could expedite the yielding and plastic deformation of the matrix near silica surface, resulting in a decreasing tendency in tensile strength and an increase in impact strength. As the silane-coupling agents used in this study had a relatively small amount of carbon atoms (three or four), the thickness of the formed interlayer was thin; thus, the influence on tensile strength might not be prominent. As seen from samples 2 and 3, only a slight decrease in tensile strength was observed compared with unmodified silica (sample 4). Another reason for this is the existence of certain degree of adhesion between silica and the polymer matrix because of surface grafting. Consequently, the strength and toughness could be improved simultaneously for silane-treated silica composite systems.

CONCLUSION

Functional silane treatment of nano-SiO$_2$ before *in situ* polymerization of nylon 6 did not bring about a significant difference in the reactivity of surface groups of silicas, as shown by TGA of silicas isolated from the composites and an end-group analysis of the composites. However, it can simultaneously improve the strength and toughness of the composites, as indicated by mechanical tests, mainly as a result of the introduction of a flexible layer in the interface.

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