J Mater Sci (2007) 42:4967–4975
DOI 10.1007/s10853-006-0537-2

Surface structure, grafted chain length, and dispersion analysis of PBT prepolymer grafted nano-silica

Jianfei Che · Yinghong Xiao · Baoyong Luan · Xiaoming Dong · Xin Wang

Received: 2 December 2005 / Accepted: 6 June 2006 / Published online: 6 March 2007

Abstract Dispersion of nano-particles plays a key role in preparing high-performance nano-composites. Steric hindrance stability mechanisms can be applied to improve the dispersibility and stability of nano-particles. The steric hindrance layer can be established when graft polymerization of PBT prepolymer is performed onto the surface of nano-particles. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) characterization revealed the chemical linkage between nano-silica and the grafted prepolymer. Based on XPS and thermal gravimetric analysis (TGA), it is conjectured that the grafted PBT prepolymer was mainly distributed on the surfaces of nano-silica. From transmission electron microscopy (TEM) images the polymer coverage can be observed. System vacuum played an important role in determining the graft amount and the length of the grafted chains. The relationship between vacuum and chain length was investigated by calculating $\overline{M}_v$ and TGA. The lower the vacuum, the more the weight loss, and thus the longer the grafted chains. Sedimentation experiments and atomic force microscope (AFM) characterization showed that the grafted nano-silica prepared under the vacuum of 3.9 kPa had the best dispersibility and could disperse homogeneously in tetrachloroethane. Under these conditions, the length of the grafted molecule chains was approximately, 16 units.

J. Che (✉) · Y. Xiao · B. Luan · X. Dong ·
X. Wang
School of Chemical Engineering, Nanjing University
of Science and Technology, Nanjing 210014, P.R. China
e-mail: xiaoche@mail.njust.edu.cn

Introduction

The dispersion of nano-particles and the interface between the nano-particles and polymer matrix play key roles in the preparation of nano-composites with excellent properties. Nano-particles have high surface activity and a great inclination to agglomerate due to the lack of coordinate atoms on the surfaces. Moreover, the poor interfacial compatibility between the nano-particles and the polymer matrix prevents the formed nano-composite from obtaining the expected excellent properties. Therefore, it is necessary to modify the surface of nano-particles when nano-composites are prepared. The modification is expected to improve the wettability, compatibility, and the dispersibility and increase the interfacial adhesion [1–5].

A lot of work has been done to modify the surface of nano-particles. Conventional methods include surfactant modification [6–8], organic acid modification [9, 10], and coupling agent modification [11–13]. The surface of nano-particles can be changed to hydrophobic one by these methods and the modified nano-particles can be used to modify PP [14], PE [15], and PS [16]. However, in order to modify some engineering plastics, such as polybutylene terephthalate (PBT), polyethylene terephthalate (PET), polycarbonate (PC), and polyamide (PA), etc., nano-particles must have amphoteric property to obtain good compatibility with engineering plastics. In our study, surface grafting with PBT prepolymer (pre-PBT) was performed to modify the surface of nano-particles.

Stable dispersion of nano-particles refers to the phenomenon that the particles can shield off the London-Van de waals bonds with the help of static electricity repellence and steric hindrance repulsion

[17]. It is known that most organic solvents and polymer melts have low ability for disassociation. Hence, for nano-particle filled polymers, steric hindrance stability mechanisms and steric stabilizers can be applied to improve the dispersibility and stability. Effective molecules used as steric hindrance stabilizers have two characteristic parts. One is the anchored group that has strong adsorption and high reactivity with nano-particles. The other part is easily solvated and can stretch sufficiently in the surrounding media [18–20]. Grafted pre-PBT has similar polarity and solubility parameters to most of the engineering plastics. As a result, grafted pre-PBT and engineering plastics have mutual solubility. Grafted pre-PBT can stretch sufficiently and form a steric hindrance layer in the above engineering plastics melts. The layer exhibits a stabilizing effect and can keep nano-particles from aggregating. The above effect helps the particles disperse uniformly and remain stable in the polymer matrices. The advantages are the following:

(1) Chemical bonds are formed in between the nano-particles and grafting prepolymer. This chemical force (anchored mediate) is obviously stronger than the physical adsorption that usually occurs between the nano-particles and the surfactants or ultra-dispersants.
(2) Structure design of the solvated molecule chains is important since steric hindrance is derived from solvation. It is required that the grafted chains have good compatibility with the dispersing medium. The pre-PBT chains can stretch sufficiently in engineering plastics melt and thus dispersion stability increases [21–23].
(3) The length of the solvated molecule chains plays an important role in the dispersion process. The hindrance layer must have a certain thickness in order to make the nano-particles disperse uniformly. Effective layers should be approximately 5–10 nm thick for nano-particles. The grafting molecule chains have sufficient length compared to the conventional dispersing reagents thus can form effective steric hindrance layers [24].

In our study, the grafted nano-particles were dispersed homogeneously in tetrachloroethane and no agglomeration or adhesion was observed from AFM images. By terminating the graft reaction at various steps, we studied the relationship between the dispersibility of nano-particles and molecule chain length of the grafted prepolymer, and determined optimal molecule chain length. Furthermore, the chemical structure and compatibility of the nano-particles were investigated. The method may be applied to other surface grafting polycondensation and thus provide a novel way to improve the dispersibility of nano-particles in engineering plastics.

Experimental

Materials

The nano-silica, provided by Hai-Tai Co. Ltd, Nanjing, China, had a specific area of 380 m^2/g (N_2, BET), an average diameter of 22 nm, and 4.12 surface hydroxyl groups per square nanometer. Dimethyl-p-phthalate, 1,4-butanediol, butyl titanate, phenol, tetrachloroethane, dimethylformamide, and acetone were purchased from Shanghai Lingfeng Chemical Reagents Co. Ltd, China. All reagents were identified as being of analytical grade and were used without further purification.

Preparation

Preparation of grafted prepolymer on the surfaces of nano-silica

Nano-sized SiO_2 was pretreated at 200 °C for 4 h under vacuum to eliminate the possiblity water existing on the surface. 5 g of pretreated SiO_2 and 27×10^{-6} m^3 (0.3 mol) 1,4-butanediol were added to a flask and mixed using ultrasonic oscillation for 10 min. Then 38.8 g (0.2 mol) dimethyl-p-phthalate were added. After the mixture was heated to melting temperature, three drops of butyl titanate (0.1 mmol) as the catalyst were added. The reaction system was heated slowly with stirring and outgassing methanol until the temperature reached 200 °C. After 20 min, the temperature was raised to 220 °C. The pre-condensation was performed under appointed vacuums for 1 h.

The above reaction products were placed into a 250×10^{-6} m^3 beaker. A solvent mixture of phenol and tetrachloroethane (3:2 in volume)was added. Ultrasonic oscillation was used to help eliminate the residual polymer. The grafted nano-silica was separated by centrifugation, and further, twice washed with the solvent mixture of phenol and tetrachloroethane, dimethyl formamide, and acetone, respectively. The washed, grafted nano-silica was extracted for 8 h with acetone in a Soxhlet extractor to ensure that all the substances adsorbed on the surfaces of the particles were washed away. The grafted nano-silica was dried at 80 °C for 4 h under vacuum. Finally the grafted nano-particles were obtained.

Characterization of the modified nano-silica

Fourier transform infrared spectroscopy (FTIR, Bruker Vector-22) was used to analyze the chemical structure of the nano-particles. Samples were prepared in KBr pasties. The weight of the samples was 5×10^{-3} g and the weight of KBr was 0.5 g. The pasties were made under the press of 5×10^{8} Pa. The measurement range was from 400 to 4000 cm^{-1}.

Thermal gravimetric analysis (TGA, Shimadzu DTA –50) was used to determine the amount of the grafted polymer on the surfaces of the nano-particles. N_2 was applied at a flow rate of 20×10^{-6} m^3/min. The heating rate was 20 °C /min and the temperature range covered was from 25 to 600 °C.

X-ray photoelectron spectroscopy (XPS) was used to analyze the linkage between the nano-particles and the grafted prepolymer. XPS analyses were performed using a VG ESCALAB MK II spectrometer equipped with a monochromatic Mg Ka ($h\upsilon$ = 1253.6 eV) source at a power of 240 W(12 kV × 20 mA).The total pressure in the main vacuum chamber during analyses was typically 5×10^{-8} Pa. The analyzer's pass energy was set at 160 eV and the step was set at 0.5 eV to record survey spectra, 20 eV and 0.05 eV respectively, to take high-resolution spectra. The carbon peak at 285.0 eV was used as a reference to correct for charging effects.

Viscometry was applied to test the molecular weight of PBT prepolymer. The procedure was as follows. After centrifugal separation of the reaction system, two parts were obtained. The prepolymer was obtained from the upper clear liquid using rotation evaporation. A solution of prepolymer at a concentration of 1×10^3–10×10^3 $\mathrm{g/m}^3$ was made with a mixture of phenol- tetrachloroethane (volume ration of 3:2)as the solvent. The molecular weight of the prepolymer was tested with a capillary viscometer at 30 °C after the solution was filtered.

Transmission electron microscopy (TEM, Philips 450) was used to study the size and morphology of the grafted nano-silica. 0.2 g nano-particles were dispersed in 15×10^{-6} m^3 water with ultrasonic wave before characterization.

Sedimentation was performed as follows: 0.2 g nano-particles and 15×10^{-6} m^3 tetrachloroethane were placed into the test tubes. Ultrasonic oscillations were applied for 10 min to help the particles disperse in the solvent. Following this, the test tubes were kept stationary and sedimentation could be observed. The time when the interface of the SiO_2 colloid reached the half-height was recorded.

Atomic force microscope (AFM, Dimension 3100) was used to study the dispersion of the grafted nano-silica in tetrachloroethane. 0.2 g nano-particles were dispersed in 15×10^{-6} m^3 tetrachloroethane with ultrasonic wave before characterization.

Results and discussion

FTIR spectroscopy

The introduction of organic groups onto the surfaces of the nano-particles was confirmed by FTIR spectrum, as shown in Fig. 1. Compared with the original version, the modified nano-silica exhibits new absorptions at 2960–2865, 1720, 1600–1500, 1270, and 730 cm^{-1}, which are characteristic of PBT [25]. In detail, the band at 2960–2865 cm^{-1} is attributed to the stretching modes of C–H in the saturated hydrocarbyls. The absorption at 1720 cm^{-1} refers to the stretching vibration of the ester carbonyl. The band at 1600–1500 cm^{-1} represents the stretching vibration of the backbone of benzene. The peak at 1270 cm^{-1} is attributed to the stretching mode of C–O in the ester. The peak at 730 cm^{-1} corresponds to the bending mode of C–H in the benzene ring. Another significant phenomenon is the absorption at 3450 cm^{-1}, which suggests that the stretching mode of –OH becomes weak in the modified version. It indicates that part of the hydroxyl groups reacted with other substances and consequently caused the number of the hydroxyls on the surfaces to be reduced. As for the more commonly observed peak located at about 1100 cm^{-1} related to Si–O–C linkages, it is mixed with Si–O–Si absorption in SiO_2 and it is very difficult to find the change of the intensity. The evidence of Si–O–

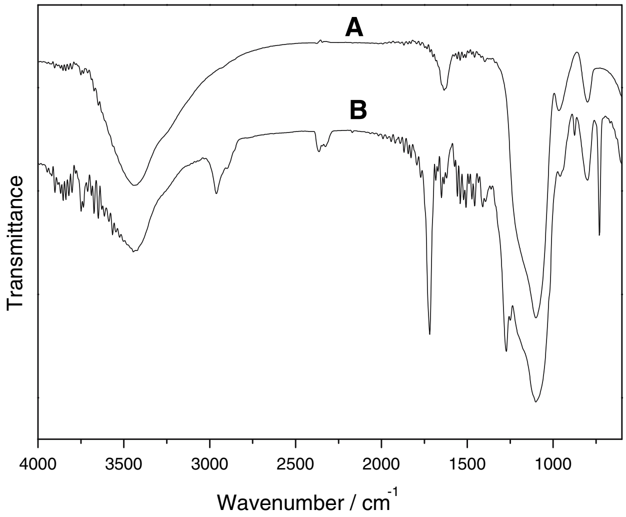

Fig. 1 FTIR spectra of (**a**) the as-received nano-SiO_2 and (**b**) the grafted SiO_2

C linkages can be found in XPS analysis. As mentioned in the experimental session, the samples were washed thoroughly with different solvents. Thus, physical adsorption did not exist. From the analysis we conclude that the surfaces of nano-silica were grafted with the prepolymer of PBT.

TG analysis

The polymerization of PBT is a polycondensation reaction, which is reversible. The molecular weight and thus the viscosity of the reaction system increase during polymerization. With high viscosity, small molecule by-products are difficult to outgas from the reaction system, which inhibits further polymerization. Therefore, vacuum is needed to eliminate the by-products in order to obtain a high molecular weight prepolymer. Vacuum plays an important role in determining the degree of grafting and the length of the grafted chains.

From Fig. 2 we see that the weight loss is being increased by using vacuum for the system. Regardless of the weight loss percentage, the shape of all the curves is similar, being in two steps, at 280–310 °C and 360–440 °C, respectively. The first step corresponds to the decomposition of the butanediol end-group, while the second one is caused by the thermal cracking of the whole molecules. It can be seen that the weight loss of all the samples in the first stage is the same. The difference caused by the vacuum is exhibited only at the second stage. It shows that the vacuum has an effect on the length but not on the number of the grafted chains on the surfaces of the nano-particles. This can be explained by the fact that new grafted chains could not be formed due to the steric hindrance of the prepolymer. The change of the vacuum gave rise to the propagation of the grafted chains. The stronger the vacuum, the longer the grafted chains, and thus the greater the weight loss.

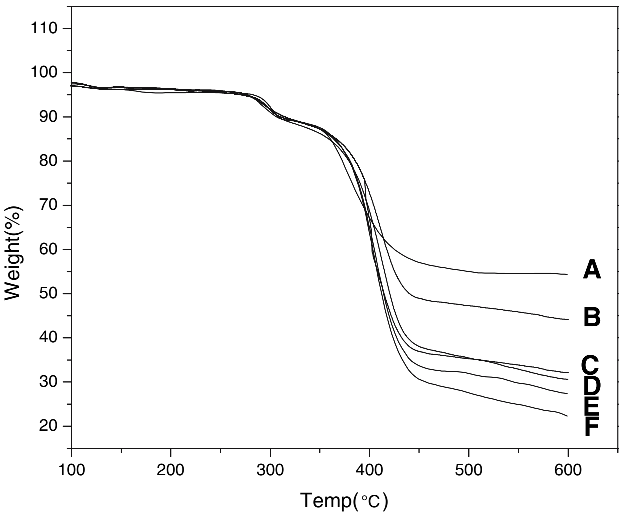

Fig. 2 **TGA** of the grafted SiO_2 prepared under different vacuums (**a**) 101 kPa; (**b**) 20 kPa; (**c**) 3.90 kPa; (**d**) 2.66 kPa; (**e**) 1.33 kPa; (**f**) 0.266 kPa

XPS characterization

XPS is used for the surface analysis of materials. It can analyze over a surface thickness from 3 to 5 nm beneath the surface. The Si2p peak of the grafted SiO_2 almost disappeared due to the coverage of the grafted PBT prepolymer. As a result, the peak of C1s increased. The ratio of elements can be obtained from the peak area and sensitivity factor. The sensitivity factors of C1s, O1s and Si2p are 0.25, 0.66 and 0.27, respectively. The results are shown in Table 1.

Data from Thomason's XPS study [26] of 'epoxy compatible' glass fiber indicate that below 10–20 of C/Si the XPS data are dominated by the glass-fiber surface while above this value the data are dominated by the organic sizing. With the increasing organic sizing, only photoelectrons in the sizing can be detected and presented in XPS. Hence, C/Si ratio will tend toward infinity, and C/O ratio will be determined by stoichiometry of the sizing mixture. From Table 1 it is seen that the as-received SiO2 has very low C/Si ratio (0.4) and C/O ratio (0.15), since only carbon atoms from surface contamination are detected. After nano SiO2 particles are grafted with pre-PBT, the C/Si ratio increases to 11.6. The C/O value is 1.9, approaching to the value of 3.0 calculated from the pre-PBT. Since all the samples have been purified by acetone extraction, this may be the evidence for chemically bound layer of the grafted pre-PBT, which is difficult to remove by extraction.

From TGA curve (Fig. 2), it is seen that the weight loss of the grafted version is 67.3%. The C/Si atom ratio of 6.8 is obtained via Eq. (1).

$$\text{C/Si ratio} = \frac{\frac{W_1}{M_1} \times n_C}{W_2/M_2} \tag{1}$$

Table 1 Concentrations of various elements on nano- SiO_2 surfaces

Sample	Content (%)			C/Si	C/O
	C1s	O1s	Si2p		
As-received SiO_2	9.7	63.2	27.1	0.4	0.15
Grafted SiO_2*	61.5	33.2	5.3	11.6	1.9

*The grafted SiO_2 was prepared under 3.90 kPa where W_1, the weight of organic substance in the grafted version; M_1, molecular weight of PBT constitutional unit; W_2, the weight of SiO_2 in the grafted version; M_2, molecular weight of SiO_2; n_C, number of carbon atoms in PBT constitutional unit

From XPS analysis, the C/Si atom ratio on the surfaces is greater than 6.8. It indicates that the grafted prepolymer is mainly distributed on the surfaces of nano-silica.

The Si2p XPS high-resolution spectrum of the modified SiO_2 was obtained by fine scan, with the as-received version as control. From the XPS spectrum (Fig. 3) it is seen that the binding energy of Si2p in the modified version is 103.2 eV, while it is 103.7 eV in the original version. There is a 0.5 eV shift to lower binding energy after the nano-particles are grafted. This shift was caused by the variation of the chemical environment of the atoms [27]. The shift of Si2p to lower binding energy indicated that the surfaces of nano-silica were grafted with PBT prepolymer, and Si–O–C bond thus is being formed. Since the C–O groups bound with Si are strong electron-repellent aromatic ester groups the density of the electron cloud around Si becomes higher. The shielding effect was increased, this causing the binding energy to decrease.

Study on the length of the grafted prepolymer molecule chains on the surfaces of nano-silica

The length of the grafted chains has a crucial role on the dispersion stability of the nano-particles as well as on the interfacial adhesion of the nano-composites. With the same graft density, longer grafted chains can provide stronger repellence due to steric hindrance.

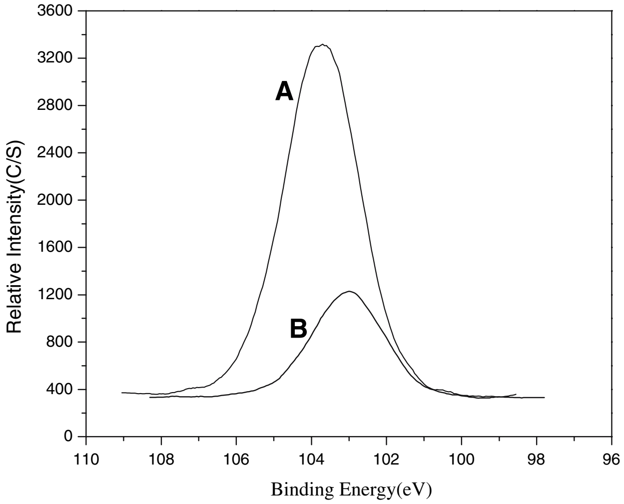

Fig. 3 Si2p XPS high-resolution spectra of (**a**) the as-received nano-SiO_2 and (**b**) the grafted nano-SiO_2

Graft polymerization can be terminated at any step if the ratios of the starting materials, the temperature and time, or the vacuum of the reaction system are changed. Thus a grafted prepolymer with different degrees of polymerization can be obtained. The length of the grafted chains can be controlled by using the aforementioned methods. However, the chain length is difficult to determine directly. Polymer structure on nano-silica surfaces is normally characterized by using the base solution method [1]. Nano-silica particles are dissolved in a strong base solution, and as a result the grafted polymer is separated. However, degradation of PBT prepolymer will occur when pH > 7. The generally used base solution method can't be applied to our study. In this case, we applied TGA and $\overline{M}_v$ calculation in order to investigate the relationship between the vacuum and chain length.

Degrees of PBT prepolymer separated from the reaction system under different vacuums were studied. Furthermore the length of the grafted polymer chains on SiO_2 surfaces was estimated by using an approach, which is elaborated below.

Molecular weight of PBT prepolymer was measured by using a capillary viscometer. The relationship between $\overline{M}_v$ and the intrinsic viscosity is shown by Mark-Houwink empirical equation as follows:

$$[\eta] = K\,\overline{M}_v^{\alpha} \tag{2}$$

where $K = 1.166 \times 10^{-8}$ m^3/g, and $\alpha = 0.871$.

Hence,

$$\overline{X}_n = \overline{M}_v/\mathrm{M}_1 \tag{3}$$

where M_1, molecular weight of PBT constitutional unit; $\overline{X}_n$, degree of polymerization.

It is well known that both end groups react when condensation polymerization is being performed. However, in the grafted chains one end group of the PBT prepolymer was anchored onto SiO_2 surfaces, thus losing its reactivity. Only the other end group can perform a chain propagation reaction, and as a result, the degree is half that of the normally synthesized polymer. Thus the length of the grafted chains (γ_2) on nano-silica surfaces should be revised to Eq. (4).

$$\gamma_2 = \overline{X}_n/2 \tag{4}$$

The experiment data are shown in Table 2.

The weight loss from the TG experiments was caused by the chemically combined prepolymer on the nano-silica surfaces, since the samples were thoroughly washed as described in the preparation section. The

Table 2 The analyses of the grafted chain length by Mv

Vacuum (kPa)	101	20	3.90	2.66	1.33	0.266
γ_2	7.48	12.08	16.05	18.35	20.30	23.36
σ	0.47	0.57	0.82	0.78	1.11	0.94

σ, standard deviations

density of the hydroxyls on the surfaces of the nanoparticles was 4.12 per square nanometer. Of these hydroxyl groups, some have high chemical stability and therefore do not participate in the graft polymerization due to hydrogen bond association. Only single hydroxyls have high chemical activity and can react with the PBT prepolymer. On the other hand, the molecule chains of the prepolymer are relatively long, and thus the steric hindrance has a shielding effect on the hydroxyls of nano-silica surfaces. The number of the grafted chains on the surfaces is less than that of the actual hydroxyls. Maitra [28] reported that the number of grafted Poly(ethylene oxide) chains on the surface of fumed silica can change with the grafted polymer molecular weight and the empirical value is approximately 0.2–1.4 molecules/nm^2 with the grafted polymer molecular weight 520–5000. The steric hindrance should be weaker because the in-situ modification was performed in our study. Considering that the grafted polymer molecular weight of all the samples estimated by intrinsic viscosity approach was 1645($M_1 \times 7.48$)–5139($M_1 \times 23.36$) in Table 2, we revised the number of the grafted chains on the surfaces to approximately 0.8–1.2 molecules/nm^2 based on Maitra's report. On the other hand, the kinetics of the reaction is enhanced at higher vacuum, which would lead to an increase in the molecular weight of the chain along with a large number of chains grafted onto the surface. It is very difficult to differentiate between these two effects. From TGA analysis (Fig. 2), it is shown that the weight loss of butanediol end-groups did not change much with the reaction vacuums. The vacuum had an effect on the length but not on the number of the grafted chains on the surfaces of nano-silica. Thus the hypothesis was proposed that the number of grafted polymer chains in this study did not change much with vacuums and can be neglected.

The number of PBT prepolymer units chemically bound on nano-SiO$_2$ surfaces per square nanometer can be calculated from the following equation:

$$\delta = (\text{g PBT/molar PBT units})\,N_A \,/[\,(\text{g silica})(380\ \text{m}^2/\text{g})(10^{18}\ \text{nm}^2/\text{m}^2)] \tag{5}$$

where N_A is Avogadro's number (6.02×10^{23})

Hence, the length of the grafted chains is

$$\gamma_1 = [\delta\ \text{units/nm}^2]/[(0.8 - 1.2)\ \text{molecules/nm}^2] \tag{6}$$

Influence of the vacuum on the grafted chain length was studied and the results are shown in Table 3.

It is concluded that the grafted molecule chains are longer, thus the molecular weight of the grafted PBT prepolymer is higher when vacuum is applied. Although the above TG and $\overline{M}_v$ were indirect characterization procedures, the same conclusions were obtained.

The morphologies of the nanoparticles

Figure 4 shows the TEM image of the grafted nano-silica with the as received material. In this study, the diameter of the single original particle was 20 nm. However, the size can reach microns or sub-microns after agglomeration (Fig. 4a). After modification the particles present linear arrays instead of agglomerations (Fig. 4b, c). The adhesion phenomena happened only at the edges and the adhesion was weaker than that in the agglomerates. In image C, the irregular edge of nano-particles became spherical. For a single particle, the colour in the centre is dark whereas it is light around the particle. This shows that the surface of the nano-particles was covered with PBT prepolymer. However, the grafted layers became thicker when stronger vacuum was applied. In this case, the grafted chains became longer. The chemical linkage would occur between the grafted chains on different particle surface. These would cause adhesion and agglomeration between the particles (Fig. 4d).

Table 3 The analyses of the grafted chain length by TG

Vacuum(kPa)	101	20	3.90	2.66	1.33	0.266
Weight loss[a](%)	45.29	54.17	67.79	69.23	71.52	76.55
δ[b](units/nm^2)	5.96	8.51	15.15	16.20	18.08	23.51
γ_1[c]	7.45–4.97	10.64–7.09	18.94–12.63	20.25–13.05	22.60–15.07	29.39–19.59
σ[d]	0.89	1.38	1.24	0.95	0.78	1.09

[a] TGA weight loss from 100 to 600 °C; [b]number of BT units/nm^2 SiO$_2$; [c]The higher number was calculated assuming that the number of molecules/nm^2 SiO$_2$ is 0.8 molecules/nm^2, The lower number was calculated assuming that the number of molecules/nm^2 SiO$_2$ is 1.2 molecules/nm^2; [d]Standard deviations.

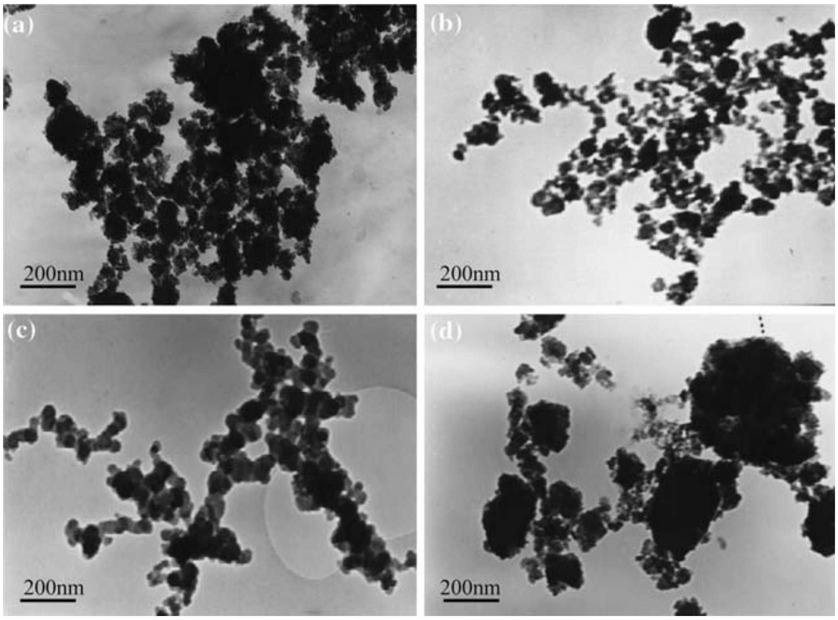

Fig. 4 TEM image of nano-SiO_2 (**a**) as-received; (**b**, **c**, **d**) grafted under the vacuums of 101, 3.9, and 0.266 kPa

The dispersion of the nanoparticles

When nano-silica is dispersed in a medium, a colloid is usually formed. However, when the dispersibility is poor, the nano-sized particles easily agglomerate, leading to sedimentation. This will lead to separation of the particles from the colloid and form a clear interface between the phases. The bigger the agglomerate is, the faster the interface declines. The dispersion stability can be evaluated on the basis of the half-height sedimentation time.

The sedimentation experiments were performed using tetrachloroethane as the solvent. The strategy is based on the fact that the solubility parameter of tetrachloroethane is similar to that of PBT resin. Similar dispersion of the particles can be observed in tetrachloroethane and in the PBT melt resin. Results are shown in Fig. 5.

It is seen from Fig. 5 that the suspension stability increased initially with vacuum, followed by a decrease. It is indicated that the steric hindrance layer on the surfaces of nano-particles became thicker and the stability of the particles increased. The optimum vacuum was 3.9 kPa. Under these conditions, the length of the grafted molecule chains was approximately 16 units. The number of carbon atoms was 180, corresponding to a layer thickness of approximately 10 nm. With the pressure further decreasing, the grafted chains became benting on the nano-silica surfaces. The steric hindrance layer was compressed and twists between the chains occurred, causing the nano-particles to re-agglomerate. As a result, the stability decreased.

Microscopic characterization of the dispersion of the grafted nano-particles can not be performed by TEM. The reason is that the dispersion medium for TEM characterization was water, which has poor compatibility with the grafted organic polymer. Therefore, dispersion of PBT prepolymer grafted nano-silica in tetrachloroethane was studied by AFM.

AFM images (Fig. 6) demonstrated the ideal dispersion state of the grafted nano-silica in the dispersing medium of tetrachloroethane. The as-received nano-silica agglomerated in tetrachloroethane (Fig. 6a). On the contrary, the grafted nano-particles were dispersed homogeneously and no agglomeration or adhesion was

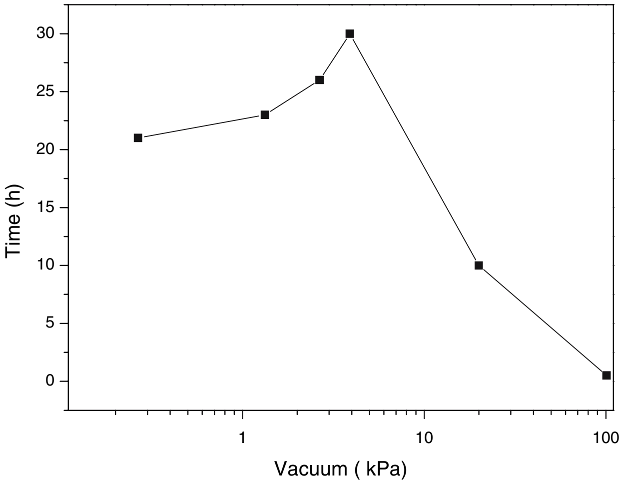

Fig. 5 The half-height sedimentation time of the grafted SiO_2 prepared under different vacuums (in tetrachloroethane)

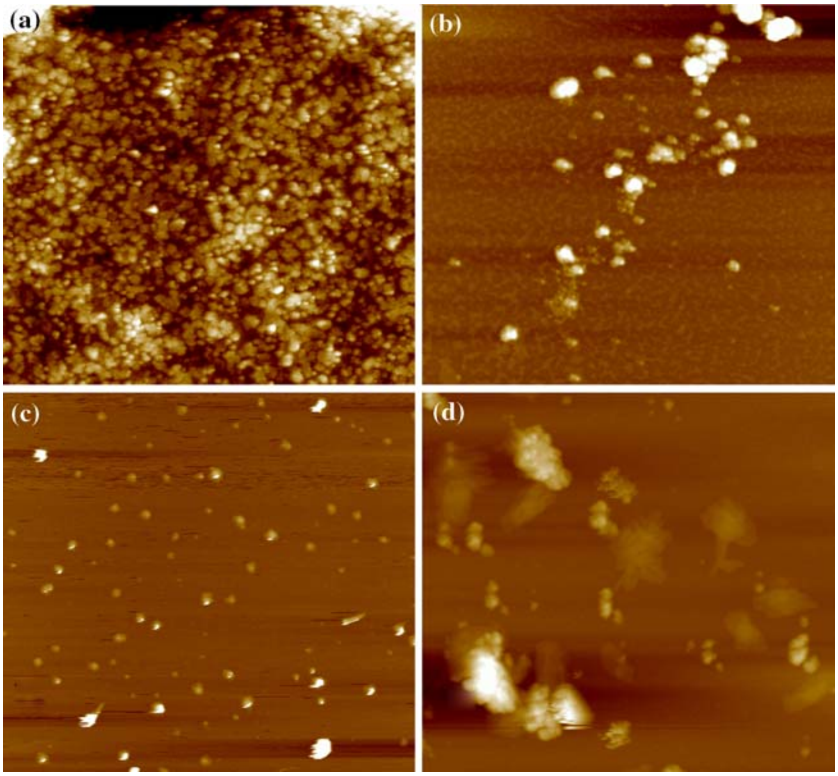

Fig. 6 AFM topographical image of nano SiO_2 in tetrachloroethane (**a**) as-received; (**b**, **c**, **d**) grafted under the vacuums of 101, 3.9, and 0.266 kPa (Scan size, 5.00 µm; Data scale, 20.00 nm)

observed (Fig. 6b, c). This can be explained by the similarity of the solubility parameters of the grafted prepolymer and tetrachloroethane. It is predicted that when filled in PBT, the grafted prepolymer would form a stable hindrance layer between the particles. The layer effectively inhibits the agglomeration and thus improves greatly the dispersing stability of the nanoparticles.

When stronger vacuum was applied, the chemical linkage would occur between the grafted chains on different particle surface. It would result in insolubility of pre-PBT on the particle surface and cause the adhesion and agglomeration between the particles (Fig. 6d).

Conclusion

Graft polymerization with PBT prepolymer has been performed on the surfaces of nano-silica. A steric hindrance layer was established on the surfaces improving the dispersion stability of the particles as well as the compatibility with the polymer matrix.

(1) FTIR and XPS analyses of grafted nano-silica indicated that a PBT prepolymer layer formed on SiO_2 surfaces. The grafted layer was chemically bound with nano-SiO_2, and Si–O–C bonds were formed. Based on XPS and TG analysis, it is exhibited that the grafted PBT prepolymer mainly distributed on nano-SiO_2 surfaces.

(2) The length of the molecule chains can be controlled via the in situ vacuum during polymerization. The relationship between the vacuum and chain length was investigated by TG and $\overline{M}_v$ calculation. The optimum vacuum was found to be 3.9 kPa. Under these conditions, the length of the grafted chains was about 16 units. The number of carbon atoms was 180, corresponding to a layer thickness of approximately 10 nm.

(3) TEM images show that PBT prepolymer was grafted onto the surface of nano-silica, and the polymer cover can be observed. After modification the particles present linear arrays instead of agglomerates.

(4) The sedimentation experiments demonstrated that the grafted nano-silica has good suspension stability. The suspension stability increased initially with vacuum, followed by a decrease. The grafted nano-silica polymerized under a vacuum of 3.9 kPa has the best dispersibility. From AFM images the ideal dispersion state of the grafted nano-silica in the dispersion medium of tetrachloroethane was found.

Acknowledgement This work was supported by NJUST Funding, XKF05010.

References

1. Wu CL, Zhang MQ, Rong MZ, Friedrich K (2002) Compos Sci Technol 62:1327
2. Jana SC, Jain S (2001) Polymer 42:6897
3. Li JX, Silverstein M, Hiltner A, Baer E (1994) J App Polym Sci 52:255
4. Wang YJ, Huang S (1996) J App Polym Sci 60:1779
5. Jongsomjit B, Chaichana E, Praserthdam P (2005) J Mater Sci 40:2043
6. Oda M, Abe T, Suzuki T, Iwashige H, Kutluk G (2002) Mater Res Soc Symp Proc 704:3
7. Huang CC, Hwu JR, Su WC, Shieh DB, Tzeng Y, Yeh C-S (2006) Chem Eur J 14:3805
8. Xu G, Zhang X, He W, Liu H, Li H (2006) Powder Technol 3:202
9. Kuwabata S, Sato K, Tachibana Y, Torimoto T (2005) 207th Meeting of the Electrochemical Society, p 987
10. Taira S, Yokoyama K (2005) Biotechnol Bioeng 89:835
11. Sun Y, Zhang Z, Wong CP (2005) J Colloid Interface Sci 292:436
12. Wang J, White WB, Adair JH (2006) J Phys Chem B 110:4679
13. Cezar N, Xiao H (2005) Ind Eng Chem Res 44:539
14. Garcia M, van Zyl WE, ten Cate MGJ, Stouwdam JW, Verweij H, Pimplapure MS, Weickert G (2003) Ind Eng Chem Res 42:3750
15. Jeong SH, Hwang YH, Yi SC (2005) J Mater Sci 40:5413
16. Zhang J, Wang X, Lu L, Li D, Yang X (2003) J Appl Polym Sci 87:381
17. Mackor EL, Van der Waals JH (1952) J Colloid Interface Sci 7:535
18. Wang LW, Sigmund W, Aldinger F (2000) J Am Ceram Soc 83:691
19. Wang LW, Sigmund W, Aldinger F (2000) J Am Ceram Soc 83:697
20. Nishizawa N, Nishimura J, Saitoh H, Fujiki K, Tsubokawa N (2005) Prog Org Coatings 5:306
21. Ottewill RH, Rennie AA, Schofield A (1990) Colloid Polym Sci 81:1
22. Bergstrom L, Shinozaki K, Tomiyama H (1997) J Am Ceram Soc 80:291
23. Bauer F, Freyer A, Ernst H, Gläsel HJ, Mehnert R (2001) Appl Surf Sci 179:119
24. Bergstrom L (1996) J Am Ceram Soc 79:3033
25. Silverstein RM, Webster FX (1998) Spectrometric Identification of Organic Compounds. John Wiley & Sons, New York
26. Thomason JL, Dwight DW (1999) Composites: Part A 30:1401
27. Briggs D (1998) Surface analysis of polymer by XPS and static SIMS. Cambridge University Press, Oxford
28. Maitra P, Ding J, Huang HS, Wunder L (2003) Langmuir 19:8994