Surface Grafting Modification of Fibrous Silicates with Polyvinylpyrrolidone and Its Application in Nanocomposites

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ABSTRACT: Chemical surface modification of fibrous silicate with polyvinylpyrrolidone (PVP) or its derivates via grafting-from and grafting-to methods was investigated. The grafting-from method was based on the immobilization of reactive end functional groups of silane coupling agents on silicate surface, followed by chain growth via radical polymerization of N-vinylpyrrolidone (NVP) to form grafted polymers with different molecular weight. In the grafting-to method, a novel copolymer PVP-171 with side functionalized groups and designed molecular weight was synthesized by radical polymerization of NVP and vinyltrimethoxysilane (DB171) and then bonded to the surface of fibrous silicates. Evidences from FTIR, XPS, TGA, and BET test indicate that there are ∼ 68,000 reactive sites per square meters on the surface with the grafted vinyl concentration of 59 mequiv per 100 g of clay. XRD patterns and SEM images demonstrate that grafting modification was bound on the silicate surface and make the surface rough with the increase of graft-loading quantity. In contrast with grafting-to approach, grafting-from approach facilitates the dispersion of silicates in PET composites. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 566–575, 2009

Key words: surface grafting; palygorskite; polyvinylpyrrolidone (PVP); clay; nanocomposites

INTRODUCTION

Over the past several decades, the plentiful and low-cost clay minerals, such as montmorillonites and palygorskites (PTs), have received widespread attention and numerous applications because they own the native layered or fibrous structure in nanometer scales, ion-exchange properties, swelling capacity, and high surface areas.[1–4] For example, the dispersion of nanometer-size silicate particles in a polymer matrix leads to nanocomposites exhibiting excellent mechanical properties,[5] thermal stability and flame retardancy,[6,7] and gas permeability.[8] Nevertheless, the problems of dispersion of silicate particles in polymer and insolubility of silicates in most common solvents limit the extensive use of them, which make the steadily increasing interest in silicate surface modification. According to the recently reported strategies, there are three different types for surfactants in organoclay, (1) surfactant molecules physically adsorbed on the external surface of clay,[9] (2) surfactant cations exchanged into clay galleries via cation-exchanged reaction,[10,11] (3) surfactant molecules located on the clay surface through reaction with the edged SiOH groups.[12,13] Although physical adsorption and cation-exchanged reaction can improve the solubility and dispersion of silicate particles, the surfactants in these two methods were not located on the clay surface through covalent bonds, and can be fallen off easily in certain cases. Covalent modification of silicates is always by means of condensation reactions taken place between the alkoxy- or chloro- silane end groups and the surface hydroxyl function groups. These organosilanes bonded onto the surface can shift characteristics of objects dramatically and weaken the interaction between clay and polymer matrix. However, the coatings at silicate surface are mostly small molecules, such as alkoxy chain, and the organic loading quantity is limited in number compared with that of polymer grafting.[14–16]

Polymer grafting is a widely used method for modification of solid surfaces because of their novel structures and properties.[17–19] Other than small molecules, polymer chains have been chemically attached to the surface of silicates, with the purpose of making silicates dispersible in organic solvents and within host polymer matrices. In this respect, "grafting-from" and "grafting-to" approaches have

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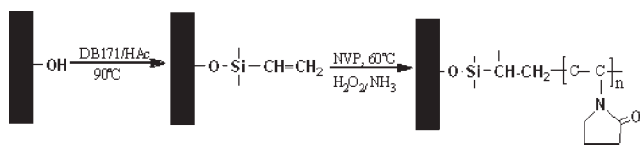
Scheme 1 Grafting-from approach.

been proposed.[20] Usually, the "grafting-from" method firstly immobilized the initiators for polymerization on the surface of silicates, followed by chain growth from the surface initiators and formation of the so-called polymer brushes. As the sample of free-radical surface-initiated polymerization of styrene, the initiators can electrostatically adsorb onto the clay layer for their cationic end groups.[21] The "grafting-to" method aims at attaching polymers to a surface used a system where the polymer carries an "anchor" group either as an end group or in a side chain. This anchor group can be reacted with appropriate sites at the substrate surface, thus yielding surface-attached monolayers of polymer molecules.[22–25]

Although most grafting studies have been performed on planar surfaces, there is also significant interest in grafting of polymer on nanoparticle substrates. Qin et al. investigated functionalization of single-walled carbon nanotubes (SWNT) with polystyrene by both grafting methods, and the final functionalized SWNT dissolved and dispersed well in organic solvents.[26,27] Viville et al. prepared well-dispersed nanocomposites via ring-opening polymerization of ε-caprolactone directly from the montmorillonites surface.[28] Gunaranjan et al. applied grafting polystyrene chains to SWNTs to prepare exfoliated nanocomposites.[29] However, up to now, chain growth of most polymers grafting is always from the immobile initiators or exchanged cations at surface, and the functionalized groups at surface with covalent bond reaction or grafting polymerization have little been utilized.

In this article, polyvinylpyrrolidone (PVP) was selected for grafting modification at the surface of silicates because of its water-soluble properties and high thermal stability.[30] PT, also called attapulgite usually, is clay mineral with wide variety of industrial application based on its physicochemical properties, principally on composition, surface area, porosity, and especially its fibrous structure.[31–33] We report here the details of surface modification of PT with PVP by two approaches shown in Schemes 1 and 2. The morphology and microstructure of the synthesized organoclays and grafting clays were studied by scanning electron microscopy (SEM), FTIR spectroscopy, thermogravimetric analysis, and X-ray photoelectron spectroscopy (XPS). Compared with the physical adsorption of PVP at surface of

PT, grafting modification of PVP may aid in exfoliation of clay in polymer systems. Such grafting modifications are of high importance for understanding the structure, properties, and potential applications of clays.

## EXPERIMENTAL

Materials

PT clay (CEC = 25–50 mequiv/100 g) was obtained from Jiangsu Autobang International Co. Ltd. (Xuyi County, Jiangsu Province, PRC). Vinyltrimethoxysilane (DB171) and N-vinylpyrrolidone (NVP) were supplied from Diamond New Material of Chemical Inc. and Boai Mkypharmaceuticals Ltd., respectively. Dimethy terephthalate (DMT) was a commercial product from Mitsubishi Chemical Corp. (Japan). Azodiisobutyronitrile (AIBN), ethanol glycol (EG) and other agents were purchased from Beijing Chemical Reagents Company (China). AIBN was recrystallized from ethanol, and toluene was dried with molecular sieves.

Preparation

"Grafting-from" approach

Procedure 1: Modification of PT with coupling-agent DB171. PT (10 g) was dispersed into 500 mL deionized water with a magnetic stirrer about 24 h at room temperature. Then, the mixture was dispersed by the ultrasonic wave with an output of 200 W for 0.5 h. A predissolved DB171 solution (50 g H_2O, 50 g ethanol, 60 g acetic acid, and 5 g DB171) was slowly added to the clay suspension and stirred vigorously for 4 h at 90°C. The resultant mixture was filtered and washed with distilled water for six times to remove the residual acid and free coupling agents, as shown by universal indicator articles. The acquired clay was dried at 100°C and then ground into powders. This sample was labeled as PT-DB.

Procedure 2: PVP grafted from PT-DB. A 250 mL round-bottomed flask was charged with PT-DB (1.00 g), NVP (50.0 g), and H_2O (116 g). After stirring for 10 h at room temperature, the desired quantity of initiator (H_2O_2, $NH_3 \cdot H_2O = 1$, 1, wt %) was introduced. The system was purified for 0.5 h under nitrogen flow and then immersed in silicon oil bath with the temperature at 60°C. The reaction was maintained under nitrogen atmosphere for 4 h to obtain a gray suspension with some viscosity. After
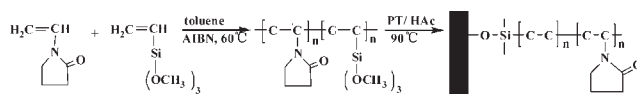
Scheme 2 Grafting-to approach.

polymerization, the product was diluted into 1000 mL ethanol. Afterward, the mixture was centrifuged with a speed of 4800 r/min for 0.5 h. The upper clear solution, which contained free polymer, was decanted, and the polymer was isolated for molecular weight analysis. The underlaying deposits were washed by ethanol for five times. Finally, the glycol ethanol was used to remove the free polymers from the clay surface at 190–200°C with vigorous stir for 3 h. The product was dried and ground into powders. The samples were labeled as PTf-0.5, PTf-1.0, and PTf-3.0, corresponding to the quantity of initiator of 0.5%, 1.0%, and 3.0% of NVP in weight, respectively.

"Grafting-to" approach

Procedure 1: Synthesis of copolymer of PVP and DB171 (PVP-DB171). In a 250 mL round-bottomed flask, NVP (20 g), DB171 (1.00 g), dried toluene (48 g), AIBN (0.2 g) was stirring at room temperature under nitrogen for 0.5 h. Then, the reaction system was heat to 60°C and kept stirring for 3 h. After the toluene was distilled out, the white solid powder was gained, which was named PVP-DB171.

Procedure 2: PVP-DB171 grafted to PT. Just like Procedure 1, in grafting-from approach, the suspension (10 g PT and 500 g H_2O) was treated through stirring, ultrasonic, a predissolved solution with PVP-DB171 (10 g), H_2O (50 g), ethanol (50 g), and acetic acid (60 g) was slowly introduced into the clay suspension at 90°C, and vigorously stirred for 4 h. The clay was washed for five times with ethanol carefully. Finally, the slurry was stirred vigorously in glycol ethanol (180 g) at 190–200°C for 3 h, then centrifuged, dried, ground to powders. The afore-mentioned product was named as PTt.

Physical adsorption of PVP at PT surface

Just as the procedures of "grafting-to" approach with the absence of DB171, pure PVP was synthesized. The pure PVP was used to modify the PT through physical adherence at the surface of PT. After washing with ethanol and glycol ethanol, respectively, the desired samples were tested with TGA.

In situ polymerization of PET/PT nanocomposites

Hundred parts of DMT by weight, 72 parts of EG by weight, a zinc acetate catalyst, and 3 parts of the given PT by weight were introduced in a homemade 500 mL four-necked flask with a nitrogen inlet and a mechanical stirrer. The reactor was heated to 180°C in nitrogen atmosphere, whereupon methanol was generated. After a theoretical amount of methanol was removed, an antimony trioxide catalyst was added to the reaction system, and the temperature was raised to 260–280°C under a pressure of less than 30 Pa for 3 h. Then the polymerization was completed, and PET/PT nanocomposites were produced.

Characterization

FTIR spectra were taken with a Perkin–Elmer FTIR system 2000 spectrometer for the grafted PT powders and PVP-DB171. TGA measurements were performed under nitrogen gas (20 cm^3/min) at a heat rate of 20°C/min from 50 to 750°C with a Perkin-Elmer 7 Series thermogravimetric analyzer. The morphological images of clays were inspected in SEM named HITACHI *S*-530. The fibrous silicates were coated with gold and observed under 10 KV accelerating voltage. Wide angle XRD was performed on powders of samples at room temperature by a Ragaku Model D/max-2B diffractometer at a generator voltage of 40 kV and a generator current of 100 mA. Testing data were collected from 3° to 40° at a scanning rate of 2°/min.

To determine the exact amount of coupling agent grafting to the PT-DB surfaces, XPS experiments were performed with ESCALab220I-XL Spectrometer equipped with a monochromized Al Ka X-ray source of 300 W at 20 mA. Spectra were recorded for the two samples, PT and PT-DB. To determine elemental ratios, normalized peak areas were calculated from peak areas of survey spectra. Specific surface areas of clay samples were determined by a Micromeritics gas adsorption analyzer (OMNISORP 100CX) in liquid nitrogen by means of the BET equation. Prior to these earlier measurements, the samples were pretreated in a vacuum at 120°C for 4 h.

In grafting-from polymerization, the intrinsic viscosity (η) of free polymers in upper solution was measured at 20°C in a Ubbelohde viscometer with deionized water as solvent. The viscosity molecular weight (M_v) can be determined from the Mark-Houwink equation

$$M_v = (\eta/a)^{1/b}$$

where a and b both are content number (1.4×10^4 and 0.7, respectively).[30]

In grafting-to polymerization, the structure of copolymer PVP-DB was proved by the ^{1}H NMR spectrum. A new peak appeared at 3.3 ppm was assigned to the ─OCH_3. The chain structure of PVP-DB was also measured by FTIR spectrum.

Transmission electron microscopy (TEM) images of the PET/PT nanocomposites were obtained by means of a JEOL 100CX electron microscope with an acceleration voltage of 200 kV. The ultrathin slices
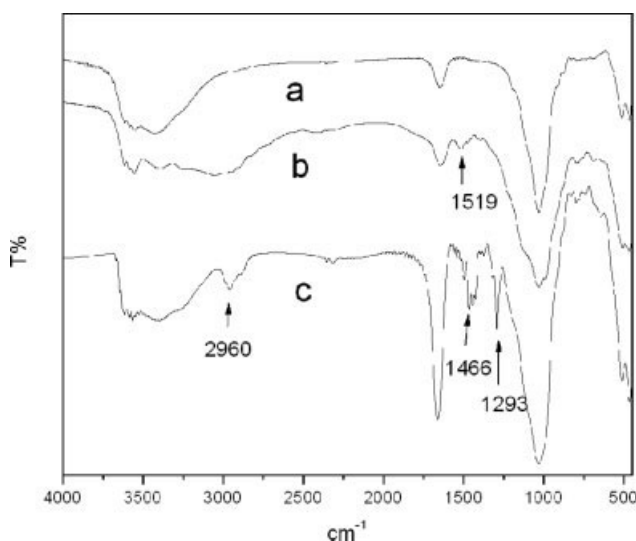
Figure 1 FTIR spectra of pure PT (a), PT-DB (b), and PTf-0.5 (c).

($\sim$ 70 nm) were prepared by a microtome equipped with a diamond knife.

RESULTS AND DISCUSSION

"Grafting-from" approach

The "grafting-from" approach is illustrated in the Schematic 1. First, the PT was modified by the coupling agent (vinyltrimethoxysilane, DB171), which can react with the hydroxyl functional groups at the PT surface through condensation reaction. After the step of coupling reaction, vinyl functional groups can be grafted at the PT surface with covalent bond, which is crucial for next process of radical polymerization of NVP. Therefore, it is important to verify DB171 coupled at PT surface. IR spectroscopy gives direct evidence for covalent surface modification as shown in Figure 1. Compared with the spectrum of pure PT, the new absorbing peaks at 1519 cm^{-1} are

observed in the spectrum of PT-DB samples, which is due to the stretching vibration of C=CSi bond. After radical polymerization, the new absorption peaks at 2960 cm^{-1}, 1466 cm^{-1}, and 1293 cm^{-1} are assigned to the characteristic peak of PVP chains, which indicates the existence of PVP grafted at PT surface.

In addition, XPS measurements were used to qualitatively verify the presence of DB171 and to quantify the number of coupling agent with covalent bond onto the modified clay surface. It should be pointed out that every sample was thoroughly washed for several times to remove the physically absorbed coupling agent before surface analysis. Figure 2 shows C (1s) and Si (2p) XPS spectra of pure PT and PT-DB. After coupling modification, the carbon content of clay surface as determine by XPS increased from 10.6% to 19.0%, and the silicon content increased from 22.2% to 23.1%. XPS atomic composition analysis demonstrated that DB171 is in existence at PT surface. Through the condensation reaction between methoxylsilane of D171 and the HO—Si groups of PT, vinyl function groups were located onto the PT surface by means of C=C—Si—O—Si. As a result, the C and Si elements should be increased, and oxygen should be constant. According to the earlier reaction, the graft-loading quantity ($x\%$, $w\%$) of DB171 to PT-DB was calculated by the following equation,

$$(1 + x\%) \times \text{Si}\%_{\text{PT-DB}} - x\% \times (W_{\text{Si}}/W_{\text{CH2=CH—Si}})$$
$$= \text{Si}\%_{\text{PT}}$$

where Si$\%_{\text{PT-DB}}$ and Si$\%_{\text{PT}}$ were the Si atomic concentrations of PT-DB, and PT (23.1% and 22.0%, respectively), and ($W_{\text{Si}}/W_{\text{CH2=CH—Si}}$) was the Si content of the added surface graft-loading segment of DB171 (CH$_2$ =CH—Si—). The value of $x\%$ can be calculated out to be 3.2%, which means that there
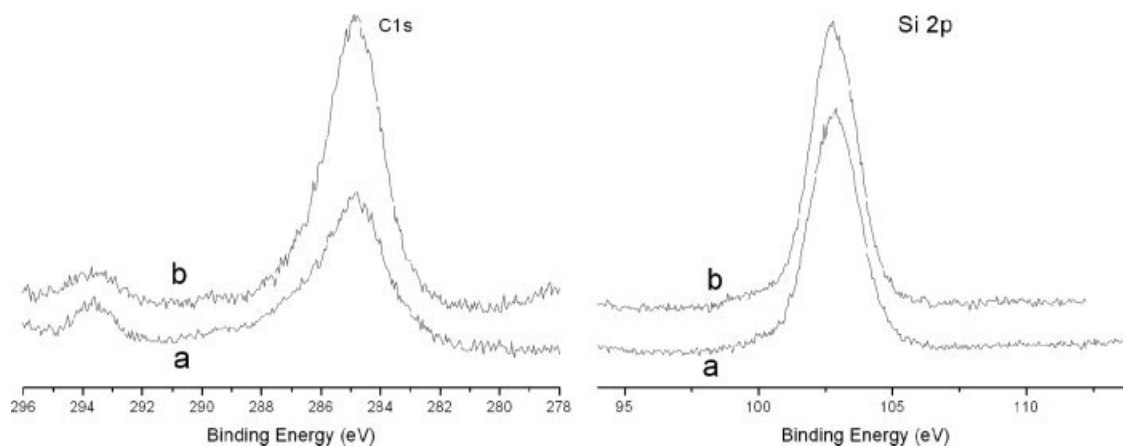

Figure 2 C (1s) and Si (2p) XPS spectra of pure PT (a) and PT-DB (b).
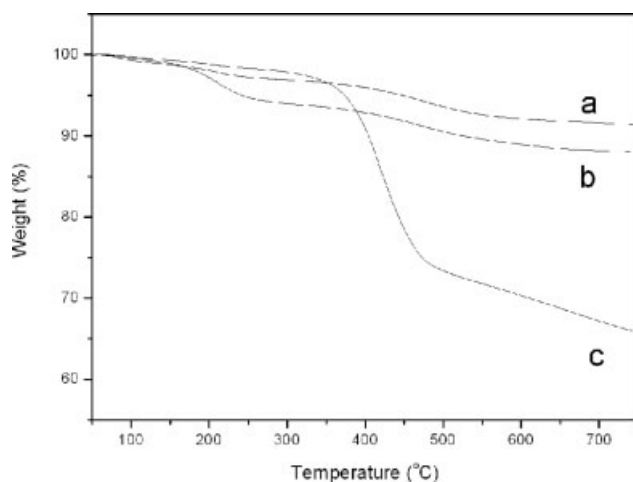
Figure 3 TGA thermograms of pure PT (a), PT-DB (b), and PTf-0.5 (c).

are 3.2 g of coupling agents grafted on the surface of PT sample (100 g).

TGA analysis demonstrated the graft-loading quantity at PT surface, also. In Figure 3, at the temperature of 750°C, the residual weight of pure PT is 91.4%, but the residual weight of PT-DB reaches 88.0%. Thus, we can calculate the graft-loading quantity from these two data for the lost weight of coupling agents, and the value of $x\%$ is 3.4%. This result is in good agreement with that of XPS measurement. According to the graft-loading quantity of PT-DB (the average data of TGA and XPS, 3.3%), there are ~ 3.3 g $\times N_A/$ (56 g/mol) $= 3.548 \times 10^{22}$ vinyl groups per 100 g of clay, where N_A is Avogadro's number (6.02×10^{23} mol^{-1}), and 56 g/mol is the mole mass of grafted function groups of CH_2=CH—Si—. With the nitrogen adsorption–desorption (BET) measurements, the specific area of pure PT is 163.1 m^2/g. On the basis of data of specific surface area and graft-loading quantity, there are ~ 2.175 reactive grafted sites per square nanometer. This means that each reactive site occupies an equivalent square of about 6.8 Å $\times$ 6.8 Å, which is responding to the bond distance of silicon atoms in clay. From the previous literature, each rod-like crystal of PT has an average diameter of 20 nm and length of 500 nm.[31–34] Hence, we can calculate that each rod-like crystal of PT has about 68,000 reactive grafted sites, and the grafted vinyl density is 59 mequiv per 100 g of clay.

Otherwise, the thermal stability of modified PT can be measured by TGA too. As shown in Figure 3(b), the onset decomposition temperature of PT-DB is around 215°C, and there is a step of weight loss between 150°C and 250°C. Normally, the pure PT does not undergo thermally induced change in the temperature range of 150–250°C, hence, the mass lost (3.4%) should be attributed to decomposition of

the vinyl groups grafted at PT-DB surface. Subsequently, after radical polymerization of NVP, the PVP macromolecule chains grow from the vinyl groups at PT-DB surface. The onset decomposition temperature of PTf-0.5 increased to about 370°C, which is consistent with that of pure PVP in other literatures.[9,30,34] Compared with PT-DB, PTf has very high thermal stability that can resist the high temperature during polymerization and processing of most polymer composites. Similar to PT-DB, the graft-loading quantity of PTf-0.5 can be calculated out as 26.1%.

Figure 4 shows XRD patterns of PT, PT-DB, and PTf-0.5. The location of the characteristic diffraction peaks (110, $2\theta = 8.32°$) of PT derivatives did not shift compared with that of PT. The result indicates that all the organic modifications were processed on the surface of rod-like crystals, and the crystal structure of PT was unaltered. This is different from layered clays, and the cause has been presented in our previous article.[34]

SEM is used to observe the surface morphology of clays directly. As shown in Figure 5(a), pure PT agglomerated massively in bundles together, and it is difficult to find the single fibrous crystal. After coupling modification, the interaction between the PT single crystal rods was weakened. Consequently, in Figure 5(b), the good dispersion of rod-like crystals was observed, and there were numerous single crystal rods. Because of the low quantity of grafted coupling agents, the morphology of the surface is smooth. Nevertheless, after graft-from polymerization, the graft-loading quantity became up to quarter of the total weight of PTf-0.5, and these PVP chains deposited at clay surface as "random clew" form. Therefore, the surface of PTf-0.5 becomes rough, and
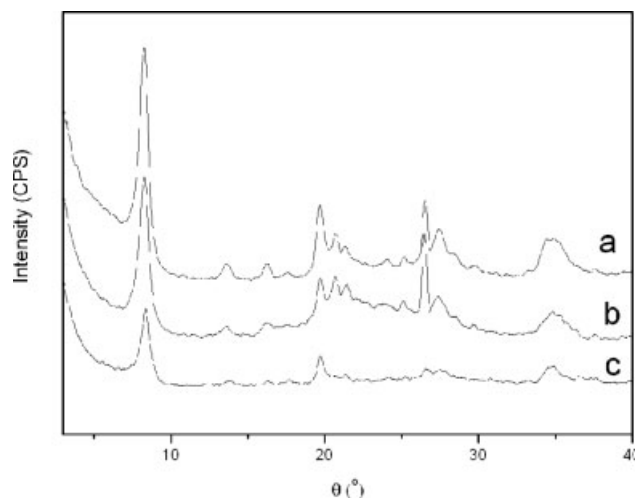

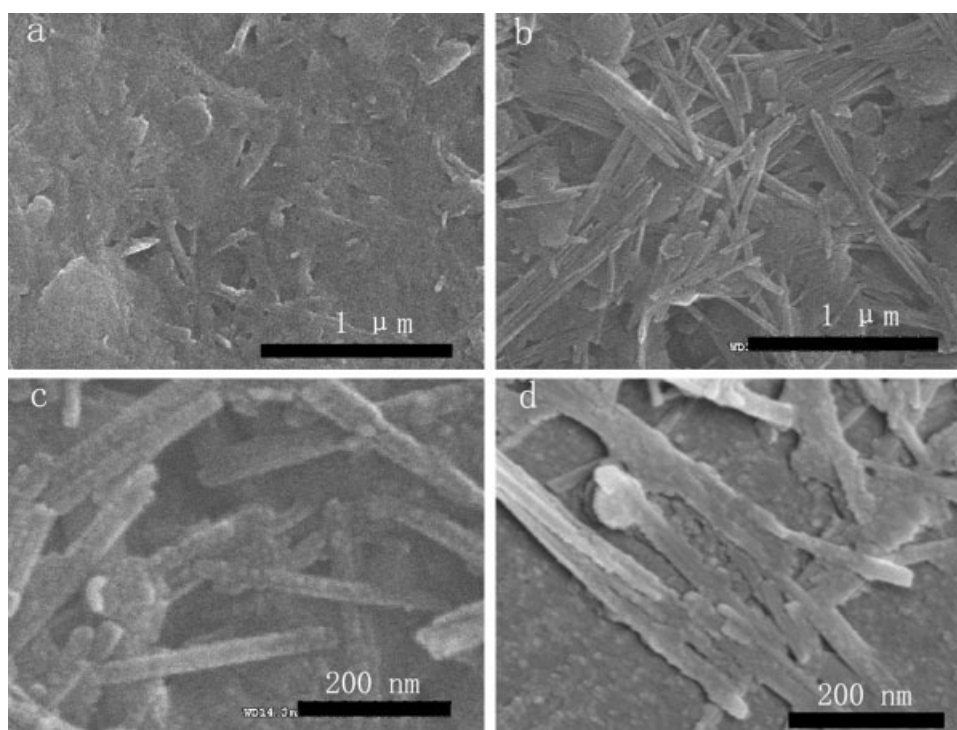**Figure 4** XRD patterns of pure PT (a), PT-DB (b), and PTf-0.5 (c).

Figure 5   SEM images of pure PT (a), PT-DB (b), PTf-0.5 (c), and PTt (d).

lots of small raised spots appear at rod-like crystal surface obviously in Figure 5(c).

The radical polymerization of NVP grafting from PT-DB was carried out with mixed solution of H_2O_2 and $NH_3 \cdot H_2O$ as initiators. The chain length of PVP can be controlled well by the amount of initiators. The more the initiators, the shorter the chain length of PVP is. The molecular weights (M_v) can be measured by means of intrinsic viscosity. The relative graft-loading quantity of polymer at PT surface, compared with that of pure PT, can be determined by TGA. Figure 6 shows the thermograms of PT,
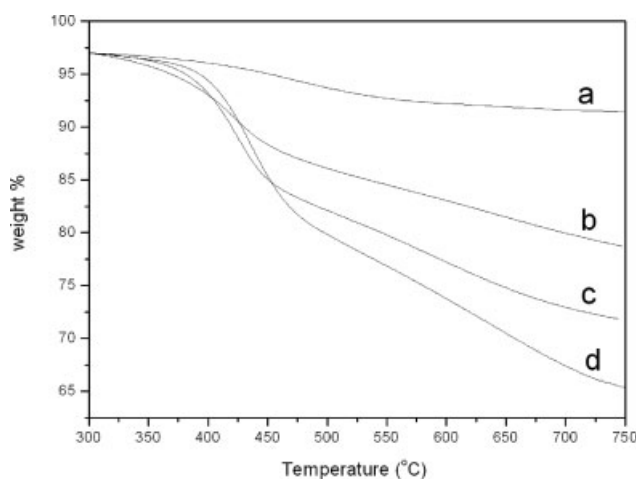
PTf-0.5, PTf-1.0, and PTf-3 under nitrogen. All of coupling agents and grafted polymers are assumed to be lost completely at 750°C, leaving residual PT. With the decrease of amount of initiators, molecular weight of PVP increased, and the graft-loading quantity of modified PT increased too. It is reasonable that PVP with high molecular weight occupies good thermal stability. Figure 7 shows that the loading quantity of grafted polymer increases linearly with M_v of the free polymer. Therefore, the number
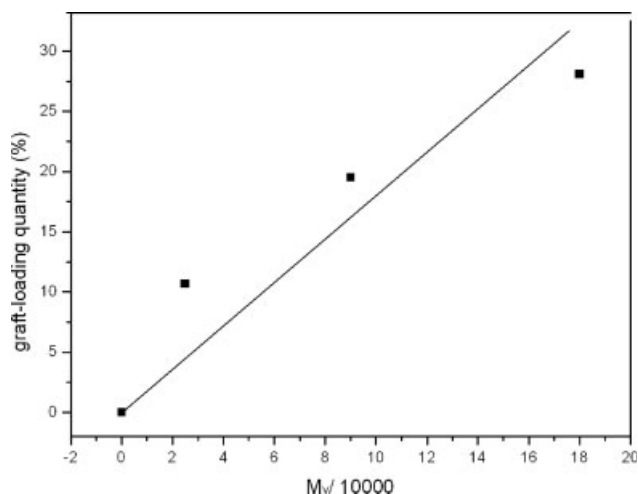

Figure 6   TGA thermograms of pure PT (a), PTf-3.0 (b), PTf-1.0 (c), and PTf-0.5 (d).

Figure 7   Relationship of amount of polymer grafted onto PT and M_v of the three polymers produced with 0.5%, 1.0%, and 3.0% initiator.
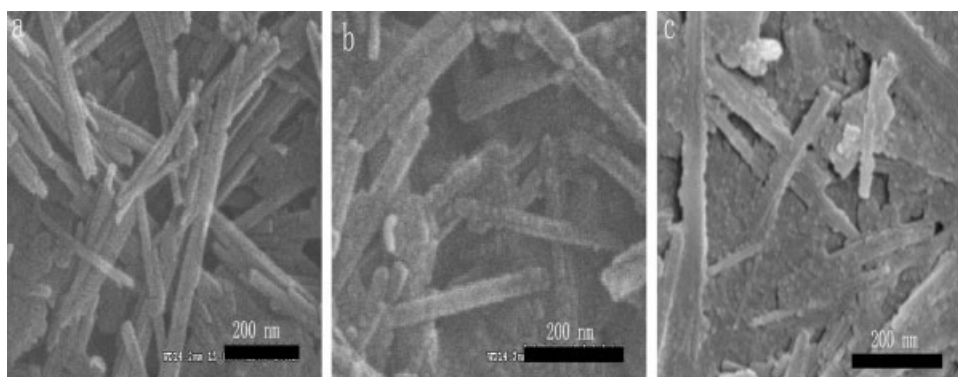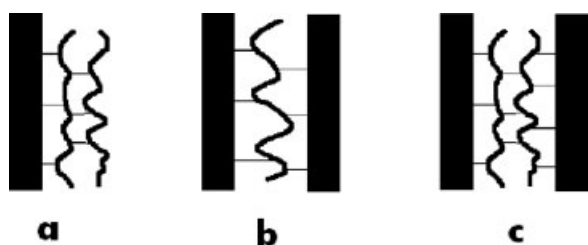
Figure 8 SEM images of PTf-3.0 (a), PTf-1.0 (b), and PTf-0.5 (d).

of graft sites on PT is almost constant during the course of polymerization.

The surface morphology of PTf-0.5, PTf-1.0, and PTf-3.0 was indicated by SEM images (Fig. 8). With the increase of graft-loading quantity or M_v, the surface becomes rough and scraggy. This phenomenon is in agreement with that of images in Figure 5.

"Grafting-to" approach

"Grafting-to" technique involves the bonding of pre-formed functionalized polymer to reactive surface groups on the substrate as shown in Scheme 2. Usually, the polymer is functionalized at end groups, and the so-called polymer brush can be synthesized through the end groups located onto the substrate surface. The limitation of the end group is that attachment of a small number of the chains hinders diffusion of additional macromolecules to the surface, thereby leading to low-grafting density. In this article, the preformed polymer is the copolymer of NVP and DB-171 with the functionalized groups (CH₃O—Si— of DB171) located at the side of chains. After the inner copolymer grafted to the surface hydroxyl groups of PT, the outside copolymer can be attached at surface through condensation reaction between the residual CH₃O—Si— of inner copolymer and the CH₃O—Si— of outside PVP-DB as shown in Scheme 3(a). The advantage of this technique is that

the coating polymer with high loading density is easily synthesized.

The copolymer (PVP-DB) was prepared by radical polymerization of NVP and DB171 in dried toluene at 60°C for 4 h, using purified AIBN as initiator. The number of side functionalized groups and molecular weight can be controlled by the ratio of DB171 to NVP and the amount of initiator, respectively. In polymerization of PVP-DB, It is crucial that the side functionalized groups exist by means of SiOCH₃ because the existence of SiOCH₃ is the premises of grafting reaction with surface hydroxyl groups. The chain structure of copolymer (PVP-DB) was proved by the ¹H NMR spectrum. A new peak appeared at 3.3 ppm, which was assigned to the CH₃OSi— side groups. FTIR spectroscopy of PVP-DB gives direct evidence for side functionalized groups as shown in Figure 9. Generally, a strong and sharp peak at 1668–1682 cm⁻¹ was assigned to the stretching vibration of —C=O, and the peak at 1287–1289 cm⁻¹ was attributed to —C—N. The two peaks confirmed the existence of PVP chain sections in the copolymer PVP-DB. Moreover, in contrast to pure PVP, the new absorption at 1084, 1192, and 2843 cm⁻¹ appeared
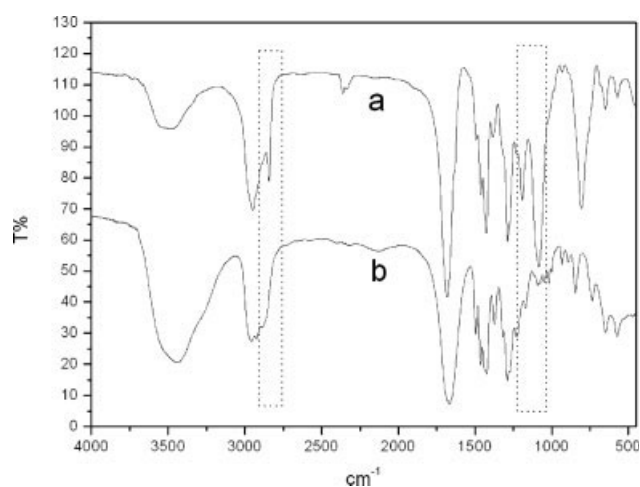

Scheme 3 Copolymer grating to the surface of rod-liked clays.

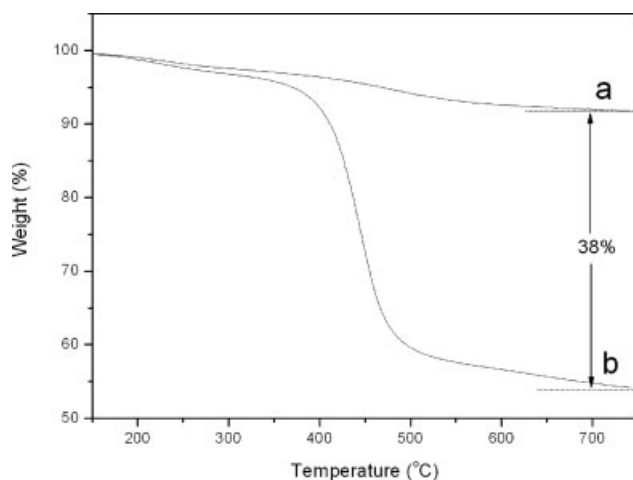**Figure 9** FTIR spectra of PVP-DB (a) and PVP (b).

Figure 10 TGA thermograms of pure PT (a) and PTt (b).

due to the stretching vibration of Si—OCH$_3$, SiO—CH$_3$, and SiOC—H$_3$, respectively. This also proved that the self-condensation reaction of SiOCH$_3$ did not occur in the process of PVP-DB synthesis.

After grafting PVP-DB to Pt, free PVP-DB was removed from the PTt by extensive washing with ethanol and glycol ethanol. As shown in Figure 10 of TGA thermograms, although the molecular weight of PTt ($M_v = 5300$) is lower than that of PTf-3.0 ($M_v = 1.8 \times 10^5$), the graft-loading quantity is up to 38%, which is higher than that of PTf-3.0 via graft-from approach. The SEM image of PTt powders is shown in Figure 5(d). It is similar to PTf-0.5 in Figure 5(c) via grafting-from approach that the surface of PTt became rough after grafting modification. With increasing the grafting-loading quantity, the density and size of small raised spots at PTt rod-like crystal surface increased. This indicates that both approaches of grafting-from and grafting-to are effective to chemically bonded PVP chains on clay surface.

Physical adsorption of PVP at PT surface

To determine that the PVP chains are covalently bound to the surface of PT, not just adsorbed, pure PVP was used to physically adsorb on PT just as the procedures of grafting-to approach without the coupling agents. After sufficient washes with ethanol, the sample was added to the boiling glycol ethanol and stirred for several hours. Then, the product was collected via centrifugation, redispersed in distilled water, and collected again via centrifugation. All the afore-mentioned grafted clays were treated with this process also. As a result, the ethanol wash was inadequate at removing the adsorbed PVP chains, as polymer presence was seen by TGA in Figure 11(c). However, after washing the boiling glycol ethanol,

the TGA thermogram curve in Figure 11(b) is very close to that of pure PT [Fig. 11(a)]. This indicates that the washing with boiling glycol ethanol can remove all physically absorbed PVP chains. In contrast, PVP chains grafted at the clays surface cannot be removed by boiling glycol ethanol washing. It is powerful evidence that polymer chains were grafted onto PT surface with chemical covalent bonds via both grafting approaches. This test was performed to develop an effective procedure for washing organoclays.

In situ polymerization of PET/PT composites

One of the most applications of surface grafting modification of PT is just as fillers to synthesize polymer/clay composites. For example, surface grafting modification with PVP can weaken the interaction between the PT single crystal rods dramatically, which is helpful to clay dispersion in polyester matrix. Generally, TEM can provide the most powerful direct evidence to describe polymer/clay nanocomposites that are exfoliated or intercalated. The TEM images of PET composites with pure PT, PT-DB, PTf-0.5, and PTt were shown in Figure 12. Because of the strong adherence between the rod-like crystals of pure PT, the significant agglomerations were seen above the size of micron obviously in Figure 12(a). After coupling modification of PT, the size of agglomerations in Figure 12(b) decreased compared with that of pure PT, which indicated that coupling modification was benefited to the dispersion of silicate in polymer matrix. Moreover, after grafting-from approach, PVP chains grafted at PT surface effectively prevent composites
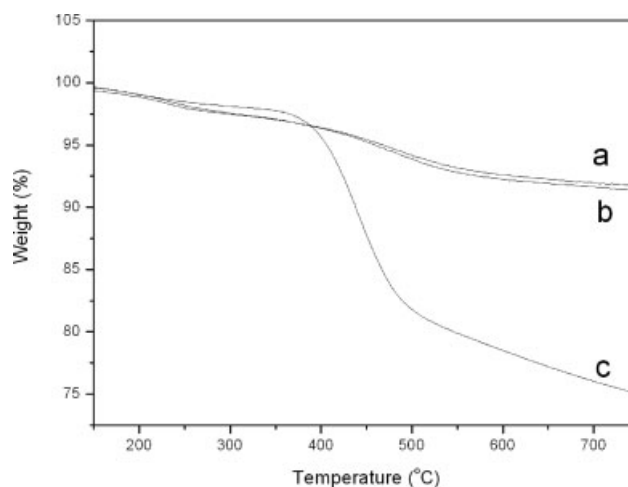

Figure 11 TGA thermograms of pure PT (a), physical adsorbed PT after boiling glycol ethanol washing (b), and physical adsorbed PT before boiling glycol ethanol washing (c).
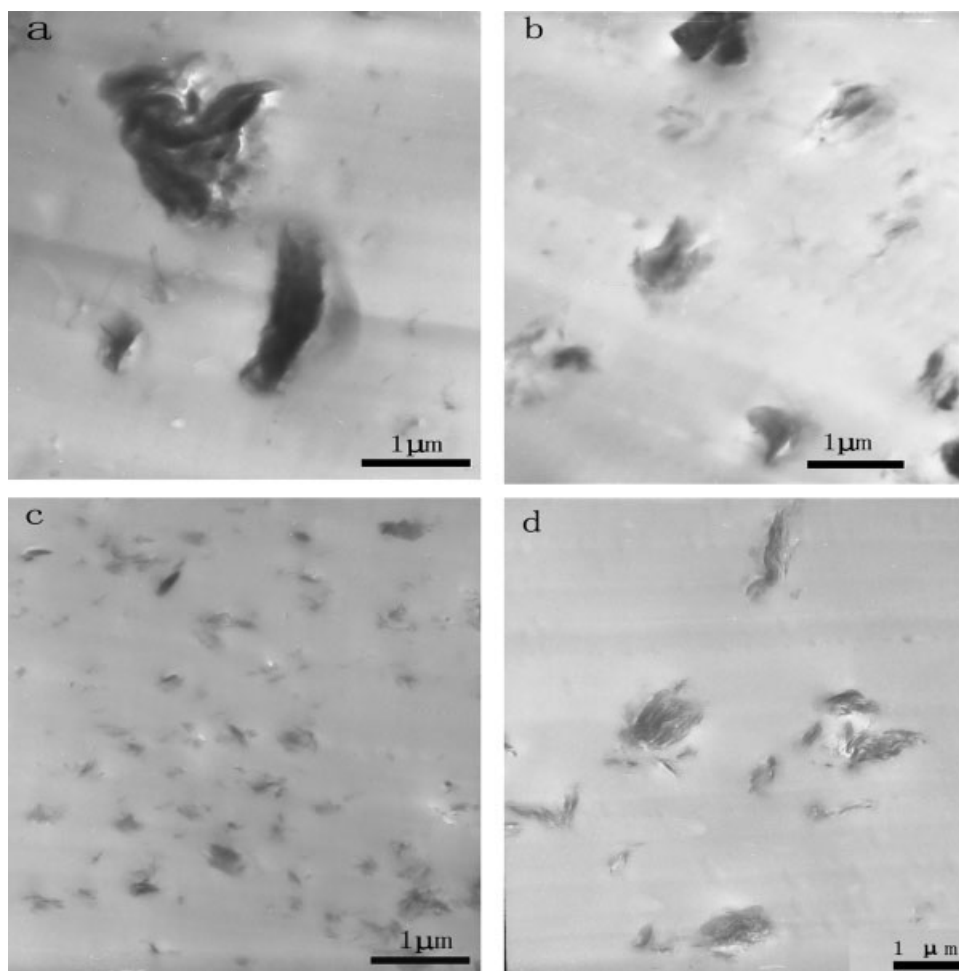
Figure 12 TEM images of pure PT (a), PT-DB (b), PTf-0.5 (c), and PTt (d).

particles from agglomeration, and the silicate particles dispersed disorderly throughout PET matrix. The size of PTf-0.5 particles is almost an order of magnitude smaller than that of pure PT or PT-DB, and the fibrous structure of the particles is discernible in Figure 12(c). It indicates that PET chains can effectively intercalate into the galleries of PT rod-like crystals. In sharp contrast, there are many obvious agglomerates of PTt particles in Figure 12(d). Compared with the grafting-from approach, grafting-to approach was failed to exfoliate silicate. The reason may be that the condensation reaction of PVP-DB chain took place between different rod-like crystals of PT as shown in Scheme 3(b,c). According to the multifunctions of PVP-DB, the same chain can graft at the different rod-like crystals surfaces. As a result, the dispersion of fibrous crystal rod was limited. Because the structure of PT mineral results in zeolite-like channels, which are $\sim 3.7 \times 6.4$ Å wide,[35] it is reasonable and justifiable that one or two PVP-DB chains occur in the earlier reaction in the gallery between two crystal rods.

CONCLUSIONS

The chemical grafting of polymer chains onto fibrous clay nanoparticles is obtained by radical polymerization of PVP. This work demonstrated two generic routes to covalently modify PT clay via grafting-to and grafting-from methods. FTIR, XPS, TGA, and BET test show that there are $\sim 68,000$ reactive grafted sites per square meters on surface with the grafted vinyl concentration of 59 mequiv per 100 g of clay. TGA showed that the amount of polymer grafted on PT surface increased with the increase of initiators quantity, and the number of graft sites on PT surface is almost constant. Simultaneously, the thermal stability enhanced with the increasing molecular weight of polymer grafted at PT surface. XRD patterns and SEM images demonstrate that grafting modification was bound onto the silicate surface and make the surface rough with the increase of graft-loading quantity. In contrast with physical absorption polymer at clay surface, both grafting approach were determined effectively to

graft polymer onto clay surface with covalent bond. Compared with grafting-to approach, grafting-from approach facilitates the dispersion of silicates in PET matrix.

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