

Preparation of PA6/Nano Titanium Dioxide (TiO₂)

Composites and Their Spinnability

Meifang Zhu,*¹ Qiang Xing,¹ Houkang He,¹ Yu Zhang,¹ Yanmo Chen,¹
Petra Pötschke,² Hans-Jürgen Adler³

¹ College of Material Science & Engineering, State Key Laboratory for Modification of Chemical Fiber & Polymeric Materials, Dong Hua University, 200051 Shanghai, China

² Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany

³ Institute of Macromolecular Chemistry & Textile Chemistry, Dresden University of Technology, Mommsenstr. 13, D-01069 Dresden, Germany
E-mail: zmf@dhu.edu.cn

Summary: In this work, surface modification technique with coupling agents and anchoring polymerization was adopted to tailor the surface properties of nanoscaled titanium dioxide (TiO₂). Ethyl glycol sols with TiO₂ were prepared in order to simulate the dispersibility of differently modified TiO₂ in a molten polyamide 6 (PA6) matrix. The modified TiO₂ were melt compounded with PA6 and composites and fibers were prepared. The average filler diameter of 47 nm (in composites) and 44 nm (in fibers) indicated homogeneous dispersion of TiO₂ in the matrix, whereas unmodified TiO₂ showed agglomerated structures in the PA6 matrix. The mechanical properties of the composite fibers were improved as compared to pure PA6 fibers and composite fibers with unmodified TiO₂.

Keywords: composites; mechanical properties; nano-TiO₂; PA6; surface modification; spinnability

Introduction

As one of novel high-tech materials, composite materials and functional fibers of polymer/inorganic nanosized particles are attracting more and more attention and interest these years^[1,2]. In these kinds of materials, the inorganic phase is dispersed at a nanoscale level in the polymer matrix phase. Due to the special structural characteristics of polymer/inorganic nanocomposites, they can exhibit high-order characteristics such as optical transparency, special dielectric properties, electrical conductivity (in case of conductive fillers), nonlinear optical effects, quantum confinement effects, biological compatibility, and biological

activity^[3]. The properties of such nanocomposites can be widely controlled by the state of nanofiller dispersion. In this context, the dispersibility of nanofillers in organic solvents or polymeric matrices is one of the hotspot and puzzle of research and application^[4, 5].

Among inorganic nanoparticles, nanosized titanium dioxide (TiO₂) is one of the most promising materials in research and application fields because of its versatile functions such as photocatalytic activity, far-infrared radiation, anti-bacterium properties, UV-resistance, antistatic behaviour et al.^[6]. A lot of novel composites and fibers with good functions were prepared based on its special properties^[7-8].

Many reports were published about polyolefin or polyester based nano-TiO₂ composites, but the work is rare on polyamide based composites. This work concerns to improve the dispersibility of modified nano-TiO₂ in polyamide 6 (PA6) matrix. Silane coupling agents and anchoring polymerization were used to modify the surface properties of TiO₂. An ethyl glycol sol with nanoparticles was prepared in order to simulate the dispersibility of modified TiO₂ in a molten PA6 matrix. The structure and properties, such as dispersion of the nanofillers, spinnability, and mechanical properties of the obtained polyamide/TiO₂ nanocomposite and fibers prepared theirfrom were characterized.

Experimental Section

Materials

The PA6 ($T_m=226^{\circ}\text{C}$) was supplied by Shanghai Yu Hang Special Chemical Fiber Factory, China and nanoscale TiO₂ (NT) particles were commercially produced by Jiangsu Hehai Nano Science & Technology Ltd., China. A silane coupling agent (CA) was used to modify the surface properties of TiO₂ with structures as RO-Si-R'-C=C. The solvents ethanol, acetone, and glycol and monomers such as vinyl dianhydride (VDA) as well as initiator benzoyl peroxide (BPO) were analytical class.

Surface modification of TiO₂

Coupling agent modification

The dried TiO₂, silane coupling agent, and ethanol as solvent were premixed and added into

the flask. Stirred for 5 min and dispersed for 30 min with an ultrasonic disintegrator (Model CQX 25-06) the mixture completed reaction after 5 hr at 80°C in circumfluence condition. The dosages of coupling agents are given in Table 1.

Table 1. Dosages of coupling agents

Samples No.	Coupling agent (g /10g TiO ₂)
NT0	0
NT3	0.3
NT5	0.5
NT8	0.8
NT10	1.0

Anchoring polymerization modification

The anchoring polymerization modification is based on the modified TiO₂- NT10. The dried NT10, monomer VDA, and initiator BPO were mixed and added into the acetone and dispersed for 30 min with an ultrasonic disintegrator. The reaction took place at 60°C for 5 hr in order to prepare the anchoring polymerization modified TiO₂ (APNT10).

Characterization

Preparation of ethyl glycol/ TiO₂ sol and sedimentation properties test

The ethyl glycol (EG) sol with TiO₂ was prepared with 0.005g modified TiO₂ added in 50 ml EG dispersing for 30min with an ultrasonic disintegrator. The sedimentation of TiO₂-EG sol was proceeded by a Centrifuger (Model 800, Shanghai Ultrasonic Instrument Factory, China), using a centrifugation speed of 3250 rpm at 0, 0.5, 1, 2, 4, 8, 15, 30 min. The absorbance of the sol was detected by an UV-Vis spectrometer (Model 7520, Shanghai Analyse Instrument Factory, China, wavelength= 536 nm). The sedimentation characteristics of nano-TiO₂ in EG as measured by the absorbance of the sol at different centrifugation times, was used to estimate the dispersibility of TiO₂ in molten PA6.

Chemical surface analysis of TiO₂

The surface of the modified TiO₂ was analysed using FTIR spectroscopy. A FTS-185 (Bio-Rad, USA) was used. The dried TiO₂ and KBr were mixed and pressed into flakes.

Preparation of the nanocomposites and fibers

The mixing of the composites (PA6/TiO₂: 97/3 wt%) was proceeded in a DACA Micro Compounder (DACA Instruments, USA) with 4.5 ccm volume applying a rotation speed of 100 rpm at 250°C for 8 min.

As-spun PA6 and PA6/ TiO₂ composites fibers were prepared on an ABE Spinner Instrument (ABE Corp., Japan) at 270°C and a take-up velocity of 800 m/min was used. The as-spun fibers were drawn using a Barmag 3010 Drawer (BARMAG, Germany) set to 70°C for the heat roller and to 120°C for the winding roller.

Morphology observation

The morphology of nano-TiO₂ particles was investigated using TEM (Model: JEM-100CX II, JEOL, Japan). Samples for scanning electron microscopy (SEM) of composites and fiber were prepared by cryo-fracturing in liquid nitrogen. The fractured sections were sputtered with gold and observed at 10 kV acceleration voltage on a JSM-5600LV (JEOL, Japan).

Results and Discussion

TiO₂ surface modification

Coupling agent modification

Most nano inorganic dioxides contain abundant hydroxyl groups^[9]. As shown in Figure 1, the methoxy- or ethoxygroups of the coupling agent can react with the hydroxyl groups on the inorganic particles surface. The created long alkyl tails have a good compatibility with the polymer matrix^[10]. Figure 2 and 3 show the Ti-O-Si transmittance peak at 1042 cm⁻¹ evidently, implying that the coupling agent was grafted onto the surface by chemical bonds.^[10] The peaks at 1378cm⁻¹ and 1639 cm⁻¹ predicated the C=C bond which is suitable for the compatibility with the polymer matrix since it can act as the active point for the further surface modification^[11]. The grafted coupling agents formed an organic layer on the inorganic TiO₂ particle surface which can serve as the compatibilizer for an organic medium, solvent, or polymer matrix.

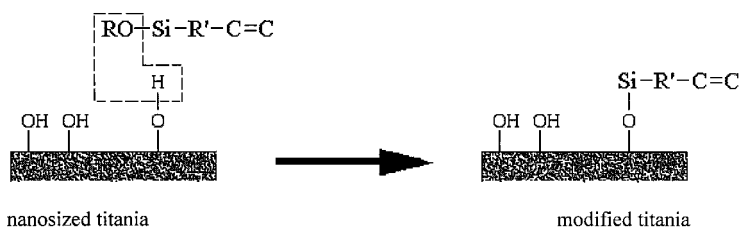


Figure 1. Reaction scheme for modification of nanosized titania with coupling agent

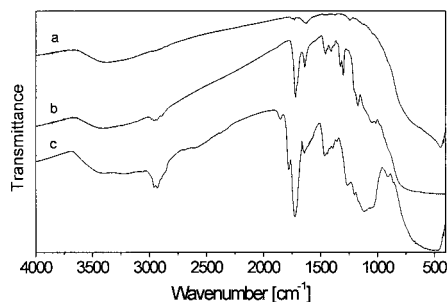


Figure 2. FTIR spectra of NT0 (a), NT10 (b), and APNT10 (c), curves horizontally shifted

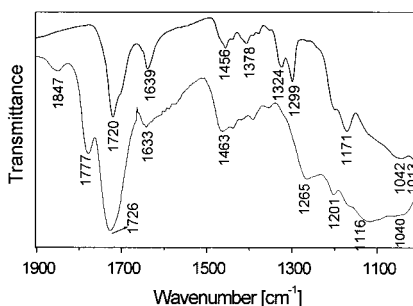


Figure 3. FTIR finger mark spectra of NT10 (upper curve) and APNT10 (lower curve)

Anchoring polymerization modification

The surface graft polymerization is imported to improve the coverage ratio and to obtain long organic tails onto a substrate in order to get better compatibility and dispersibility in a medium. The anchoring polymerization surface modification is one of the free-radical surface graft polymerizations emerged as a simple method for obtaining a high surface chain coverage^[12-13]. In this case, the active sites, vinyl groups on surface graft polymerization of vinyl monomers, were introduced by the formerly coupling agent modification as shown in Figure 4. The FTIR spectrum (Figure 2,3) of the PVDA-grafted TiO_2 (APNT10) particles displays a series of new peaks as compared to the NT10. The spectrum reveals two peaks at 1777 cm^{-1} and 1847 cm^{-1} which are characteristics of the C=O bond stretching introduced by the VDA, and a group of partially overlapped peaks between 1116 cm^{-1} and 1265 cm^{-1} , owing to the O-C bond stretching^[12].

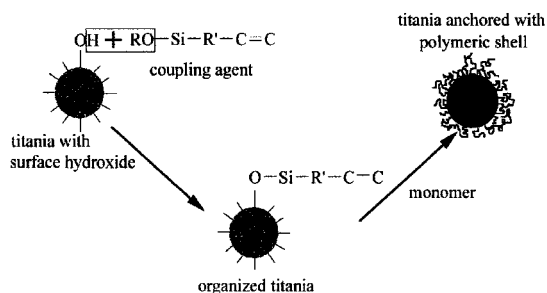


Figure 4. Schematic representation of the modification of TiO_2 through anchoring polymerization

In addition, there is a broad peak around 2930 cm^{-1} corresponding to the H-C bond stretching of the hydrocarbon backbone of the grafted polymer chains^[14]. The Ti-O-Si peak (1042 cm^{-1}) was remained in FTIR spectrum of APNT10 implying the silane coupling agents were not removed during the polymerization. However, the peak at 1633 cm^{-1} becomes weaker than in the NT10. This peak corresponds to the C=C bonds on the TiO_2 surface which are reacting as the active sites with the VDA monomer, thus, reducing their content. From the FTIR results we can conclude that the VDA was polymerized from the silane-coupling agents to get a thick polymer shell around the TiO_2 surface as indicated in Figure 4. This modification should be favourable for the TiO_2 dispersibility.

Morphology of modified TiO_2

Figure 5 shows the morphology as obtained by TEM of differently modified TiO_2 . The unmodified TiO_2 particles agglomerated as shown in Figure 5(a) and separate particles can not be distinguished. It is difficult to break these agglomerates under common process condition, which is also named 'hard agglomeration'. On the contrary, the modified TiO_2 particles, shown in Figure 5(b,c), can be observed as divided particles. Within the agglomerated areas, clear contours are visible between the TiO_2 particles. This indicates that the modified TiO_2 particles are easier to disperse during the composite processing^[15], named 'soft agglomeration'. The APNT10 particles have a looser agglomeration structure as compared to NT10 which is indicative for their thick and complete organic coverage.

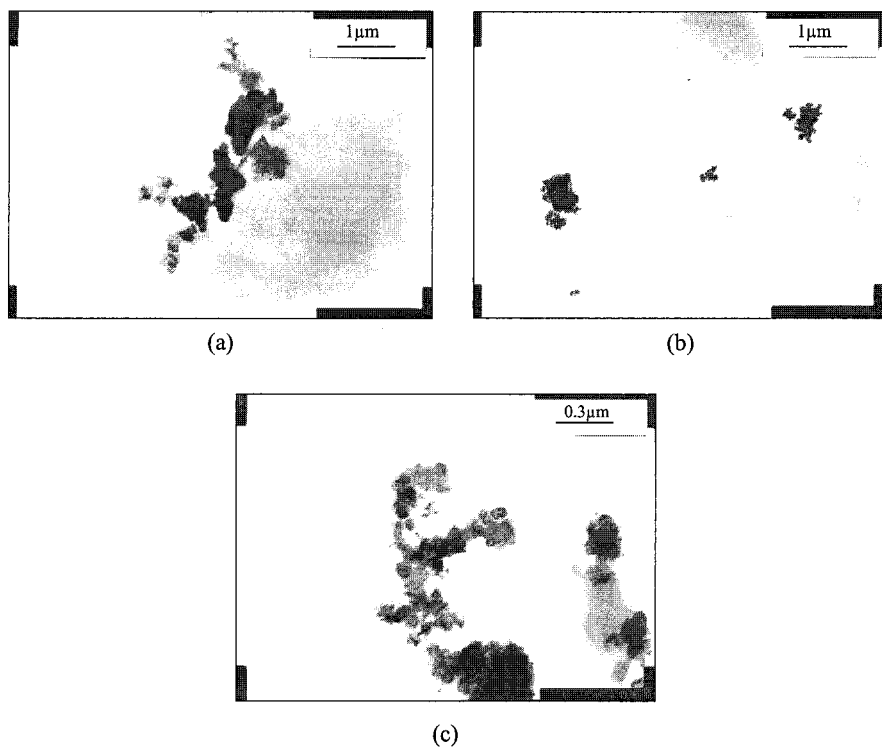


Figure 5. TEM micrographs of NT0 (a), NT10 (b) and APNT10 (c)

Sedimentation properties of modified TiO_2

The dispersion process of nanoparticles in a polymer matrix is difficult to observe and appraise, especially when forming the composites by melt mixing. In order to simulate the dispersibility of TiO_2 in a matrix, the sedimentation of TiO_2 in EG was introduced by using the EG as the substitute of molten PA6. Properties of EG and PA6 are shown in Table 2.

Table 2. The basic properties of ethylene glycol (EG) and PA6

Property	Ethylene glycol	PA6
Polarity $/[\text{cal} \cdot \text{cm}^{-3}]^{1/2}$	15.7	13.6
Density $/\text{g} \cdot \text{cm}^{-3}$	1.1135	1.23/1.08 (ρ_c/ρ_a)
Rheological behavior	Mucous (liquid)	Viscous (melt)

Figure 6 shows the absorbance of EG/ TiO_2 sol with centrifugation time. As lower the sedimentation speed (as slower the absorbance reduction), the better the TiO_2 particles are

dispersed in the EG. With increasing dosages of coupling agent the sedimentation speed is decreasing and the balance adsorbance is increasing. NT10 has the highest balance absorbance implying the best dispersibility and processability in the PA6 matrix.

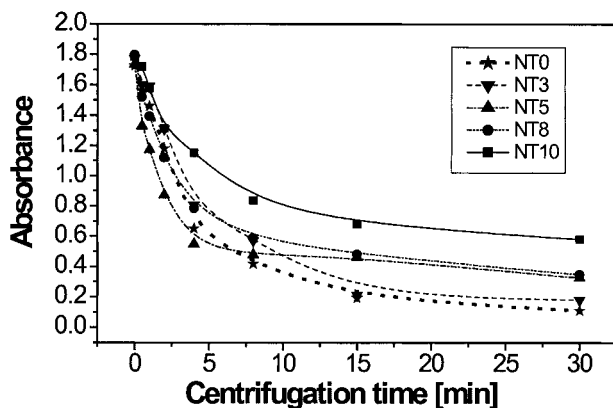


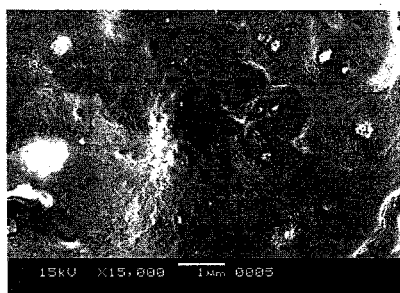
Figure 6. Sedimentation curves of TiO_2 modified with 0, 3, 5, 8, 10 wt% silane coupling agent (relative to the mass of titania)

Morphology of TiO_2 in PA6 composites and fibers

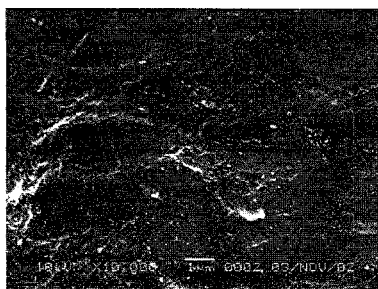
The properties of nanocomposites can be normally controlled by the dispersion of the nanoparticles in the polymer matrix. The dispersibility of the filler becomes the bottleneck problem for the performance of nanocomposites. Therefore, a lot of research is focused on this field. In this study, the grafted polymer layer consisting of the coupling agent and PVDA on the TiO_2 surface can be completely miscible with the surrounding PA6 medium. By this way, polymer detachment is prevented due to the covalent attachment of polymer chains to the substrate which also leads to a better stability of the dispersion.

Figure 7 shows the morphology of differently modified TiO_2 in PA6 composites. Some big agglomerates and black holes are visible in the PA6 matrix in Figure 7(a) where 3 wt% unmodified TiO_2 were added. These agglomerates are caused by the already introduced 'hard agglomeration' of unmodified TiO_2 which could not be broken during the blending process. The holes were produced by TiO_2 breaking off from the PA6 fractured section during the SEM sample preparation because of the poor binding with the PA6 matrix. The average

diameter of the TiO_2 agglomerates is about 100 nm. The TiO_2 particles after surface modifications were dispersed in the matrix homogeneously and their average sizes are less than 50 nm. No holes could be detected on the sections surface. Therefore, the surface modification is effective to improve the dispersibility and the interface adhesion of TiO_2 to the PA6 matrix. This result is in accordance with the sedimentation result of TiO_2 -EG sol. Comparing Fig. 7(b) to 7(c), the anchoring polymerization modification showed an further increase in adhesion.



(a) PA6/NT0
Agglomerate size ~ 100 nm



(b) PA6/NT10
Particle size ~ 47 nm

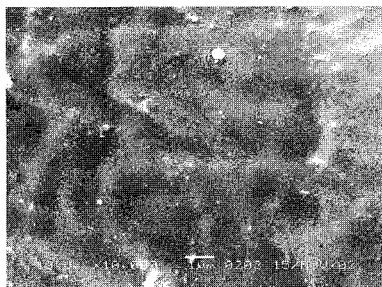


(c) PA6/APNT10
Particle size ~ 40 nm

Figure 7. SEM micrographs of fractured sections of PA6/ TiO_2 = 97/3 wt% composites

The good dispersibility of the modified TiO_2 in composites supplied the precondition for the fiber formation of these composites. The dispersion morphology and statistics of particles size of NT10 in PA6 composite fiber is shown in Figure 8 and 9. The homogeneous dispersion of the modified TiO_2 particles already discussed in the composite is maintained after the spinning procedure. The amount of particles with sizes below 70 nm reached 95%, while the

amount of agglomerates with sizes larger than 100 nm is less than 2%, as shown in Figure 9. During the fiber formation, the shear stress and strain tend to break the agglomerates of TiO_2 and, on the other hand, the high process temperature can destroy the organic layer on TiO_2 surface and can induce agglomeration. These two factors affect the final dispersion of TiO_2 in the PA6 fiber simultaneously. As the results show the particle size in the fibers is comparable to that of the composite indicating no agglomeration of TiO_2 during spinning.



Particle size ~ 44 nm

Figure 8. SEM micrograph of fractured section of PA6/NT10 composite fiber

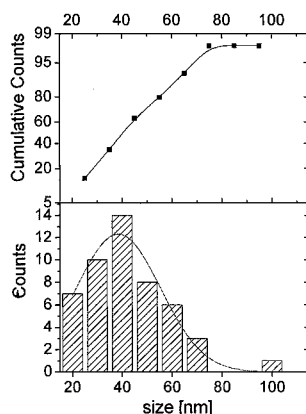


Figure 9. Statistics of TiO_2 particles size distribution in PA6/NT10 composite fiber

Spinnability of nanocomposites and properties of drawn fibers

It is known that lower particles size and more homogeneous dispersion lead to improved composite spinnability and result in better mechanical and functional properties of the fibers. This is the reason that the tenacity at break and the initial modulus of PA6/NT10 composites fiber were improved by about 10% and 20%, respectively, as compared to pure PA6 (Table 3). This indicates that TiO_2 acts as a reinforcing phase in the PA6 matrix^[9]. The modification reagent on the TiO_2 surface also strengthens the interface adhesion to the polymer matrix.

Table 3. Fineness and mechanical properties of drawn fibers

Sample	Fineness /dtex $\cdot\text{f}^{-1}$	Tenacity at break /cN $\cdot\text{dtex}^{-1}$	Initial modulus /cN $\cdot\text{dtex}^{-1}$	Elongation at break /%
100 PA6	143.2/60	3.47	45.3	18.4
97/3 PA6/NT0	135.5/60	3.47	40.8	10.2
97/3 PA6/NT10	135.6/60	3.80	59.9	16.0

Conclusions

The silane coupling agent and anchoring polymerization methods are effective to modify the surface properties of nano TiO₂ with improved dispersibility and interface adhesion in a PA6 matrix. The 'hard agglomeration' state of compactly assembled unmodified TiO₂ particles was replaced by a 'soft agglomeration' of modified TiO₂ particles. The composite with modified TiO₂ showed better spinnability than the composites with unmodified TiO₂ filler as well as improved mechanical properties.

Acknowledgement

The authors thank the National 863 Project (No.2002AA302616), the Shanghai Nano Special Project (No.0219nm039), and the Shanghai Nanotechnology Application Platform (No.0359nm008) for the financial support within the program "211 Engineering" of the "Tenth Five Plan".

- [1] Maiti S N, Ghosh K. *J. Appl. Polym. Sci.* **1994**, 52(8), 1091-103.
- [2] Zhang M, Gao Y-F, Fu W, Jiang Y, Zhou Q-X, Liu D-S, *Acta Materiae Compositae Sinica* **1998**, 15(3), 71-4.
- [3] Novak, B.M. *Adv. Mater.* **1993**, 5, 422-33.
- [4] Nakamura Y, Okabe S, Yoshimoto N, Iida T, *Polymer Composite.* **1998**, 6, 407-14.
- [5] Bories M, Huneault MA, Lafleur PG, *Int. Polym. Process* **1999**, 14(3):34-42
- [6] Hagfeldt A, Gratzel M., *Chem. Rev.* **1995**, 95(1), 49-56.
- [7] Takeda Chemical Inc Ltd. *Medical Textiles* **1998**, 10, 2.
- [8] Japan Patent: 10-259521, 1998.
- [9] Norio T, Akira K, Kazue M, Keiko T, *Polymer Journal* **1990**, 22(9), 827-33.
- [10] Yu S Lipatov. *Polym. Sci. Technol.; Part B: Adhes. Adsorp. Polym.* **1980**, 12, 601-7.
- [11] Tripp C P, Hair M L. *Langmuir* **1992**, 8, 1120-8.
- [12] Brown T, Chaimberg M, Cohen, Y. *J. Appl. Polym. Sci.* **1992**, 44, 671-7.
- [13] Nguyen V, Yoshida W, Jou J. D, Cohen Y. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, 40(1), 26-31.
- [14] Siberzan P, Leger L, Ausserre, D, Benatta J J. *Langmuir* **1991**, 7, 1647-53.
- [15] Pampach R, Haberk K. *Ceramic Powders*. Amsterdam: Elsevier Scientific Pub. Company, 1983, 623.

