A Simple Approach to Prepare PMA/TiO$_2$ Composite: The Homogeneous Dispersion of Nano TiO$_2$ in Maleic Anhydride Polymer Matrix

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ABSTRACT: This contribution reports a simple approach for preparing PMA/TiO$_2$ composite. In this method, nano TiO$_2$ powders are previously treated by a combined modification process, namely, the alkali-treatment followed by oleic acid surface-grafting. Before polymerization, the modified TiO$_2$ nanoparticles are dispersed into the maleic anhydride (MA) solution to form stable homogeneous gel. When the reaction temperature is raised to 150°C, the modified nano TiO$_2$ can initiate the *in situ* anionic polymerization of MA. Finally, the PMA/TiO$_2$ composites are obtained, in which all the TiO$_2$ are fully coated by MA polymer (PMA). Therefore, it is not needed to reclaim the nano initiators because they are blended into the prepared polymers as the nano fillers. TEM and SEM experiment results can strongly demonstrate that the TiO$_2$ nanoparticles are homogeneously dispersed in PMA matrix. This approach is easy-to-operate and applicable to the preparation of other nano composites. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3582–3588, 2009

Key words: surface-grafting; TiO$_2$; composite; dispersion; bifunctional material

INTRODUCTION

Modified polymer materials have attracted great concerns for their novel physical or chemical advances.[1–3] One of the most used modification approaches is blending.[4–6] Nano materials, particularly nano metal oxides, are potent fillers improving matrix mechanic or thermo properties.[7,8] However, nanoparticles often form agglomerates because their high surface area to volume ratio provides a tremendous driving force for their bonding. Obviously, this disadvantage can lead to the inhomogeneous dispersion of nanofillers in matrix and further cause the reduced advance. According to some reports, surface-modification to inorganic materials is an effective method to prevent their agglomeration and improve their dispersion status in matrix.[9–11]

In early studies, our group has found that alkali-treated nano TiO$_2$ is an easy-to-operate initiator for the anionic polymerization of maleic anhydride (MA), BMI, and styrene.[12–14] Unfortunately, these nano TiO$_2$ cannot be reclaimed but remains in the polymer products, and usually, they can form big agglomerates in matrix.

To make an improvement to the abovementioned problems, herein we develop a simple approach with advantages that not only avoid reclamation of nanoinitiators, but also effectively improve their dispersion in polymer matrix. In this approach, bare TiO$_2$ nanoparticles undergo a combined modification process: (1) the alkali-treatment, by which TiO$_2$ is enabled to anionic-initiate the MA monomer[9] and (2) the oleic acid surface-grafting, by which the consistency between TiO$_2$ and PMA is improved. Maleic hydride is selected as the matrix monomer because its polymer products are fragile thin pieces, which are convenient for TEM observation on the blended TiO$_2$. The dispersion status of TiO$_2$ in PMA matrix is particularly investigated.

EXPERIMENTAL

Alkali-treatment of nano TiO$_2$ by NaOH (1.0M)

TiO$_2$ (10 g) nanoparticles are added into NaOH solution (1.0M) and stirred for 6 h.[9] Then, centrifugal-separated inorganic materials are rinsed with deionized water until its pH = 7–9. Then, the products are dried in vacuum at 90°C.
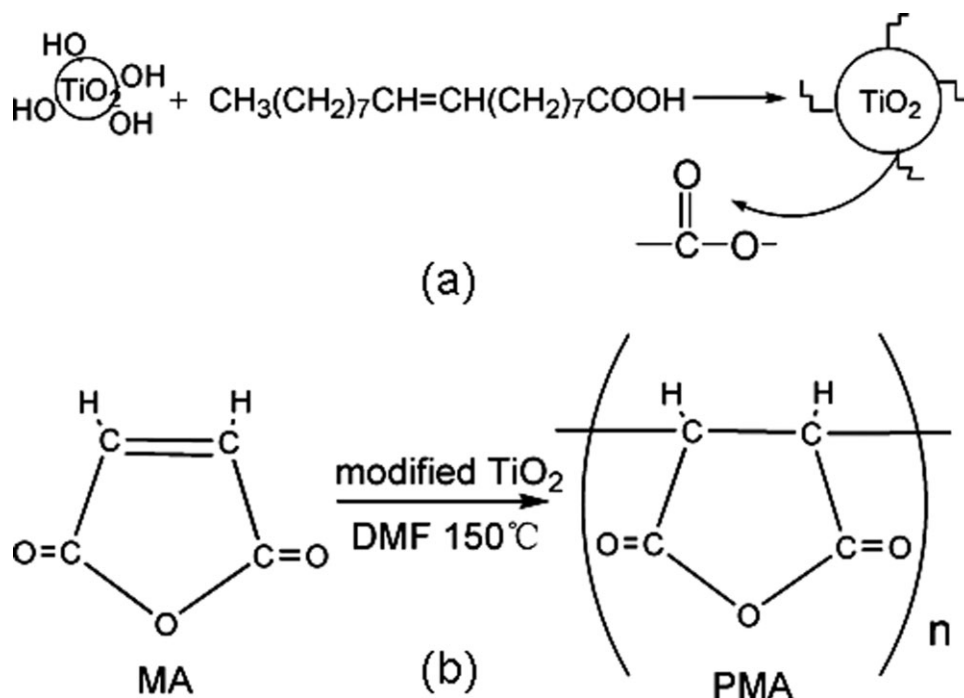
Figure 1 Schematic diagram of: (a) TiO$_2$ surface-grafting by oleic acid via the esterification reaction between the surface hydroxyl and carboxyl; (b) the polymerization equation of MA initiated by modified TiO$_2$.

Oleic acid surface-grafting process of nano TiO$_2$

Figure 1(a) represents the TiO$_2$ surface-grafting process.[10] The alkali-treated TiO$_2$ are added into the hexane (10 mL) solution of oleic acid (20 mL) at 80°C. After refluxed for 8 h, the products that separated are fully washed with hexane and dried in vacuum.

Synthesis of PMA/TiO$_2$ composite

Figure 1(b) presents the polymerization equation of MA initiated by modified TiO$_2$. The previous-modified TiO$_2$ nanoparticles (0.5 g, 10% wt of MA) are added to a DMF solution (10 mL) of MA (4.9 g). A homogeneous gel has been formed after vigorous stirring for 30 min. The reaction system is refluxed for 4 h at 150°C and a color change from white to dark brown can be seen. Afterwards, the reaction temperature is raised to 180°C to evaporate DMF (b.p = 153°C) and the brown solids gradually precipitates. The products after triturating are brown powders and then dried in vacuum under 35°C.

Instrumentation

FTIR spectra are recorded by Bruker Vector 22 Infra Spectrometer (KBr disc). SEM images are taken with a JEOL JSM-6300 microscope. TEM images are performed with a JEOL JEM-2100 microscope. Solid fluorescence are recorded by FL3-TCSPC Fluorescence Spectrometer, with exciting laser $\lambda = 382$ nm (for TiO$_2$) and $\lambda = 386$ nm (for PMA/TiO$_2$ composite), respectively. UV–vis spectra are performed on Braic UV-1201 spectrophotometer.

RESULTS AND DISCUSSION

Sedimentation test

Sedimentation test has been used for a visual comparison between the nano TiO$_2$ before and after modification, as shown in Figure 2. Most normal TiO$_2$ has rapidly settled down within 1 h, whereas the modified TiO$_2$ still remains suspending after 12 h. This obvious contrast strongly indicates that OA surface-grafting can significantly improve the dispersion status of nano TiO$_2$ in organic phase.

IR spectral studies

The oleic acid-modified TiO$_2$ shows two sharp bands of medium intensity at 2920 and 2854 cm^{-1}, which are assigned to (^{v}CH$_3$—, ^{v}CH$_2$—). The weak peaks at 1716, 1638, 1514, and 1405 cm^{-1} are attributed to (^{v}COOTi—). Wide peak at 3400–3200 is due to the vibrations of hydroxyls in TiO$_2$ surface. In the spectrum of PMA/TiO$_2$, the wide band of medium intensity at 2932 cm^{-1} confirms the variation from C=C to C—C in MA addition polymerization.

50 nm [Fig. 4(b)] and they are distributed all over the matrix. In another composite particle of 0.5 μm, the amount of blended TiO_2 is smaller but their distribution is still well. Particularly, in these composites, no TiO_2 particles are separated to PMA matrix,
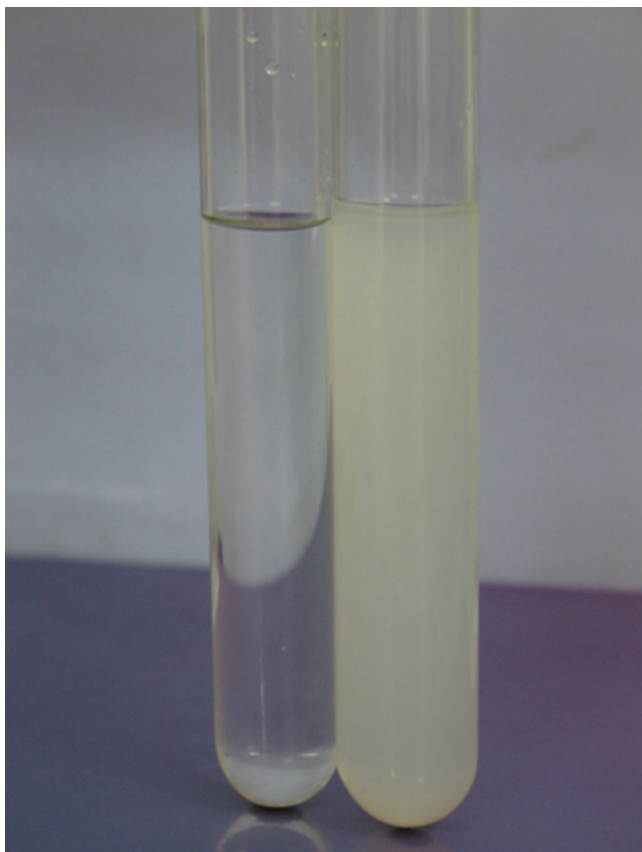

Figure 2 Sedimentation test results (after 12 h, in DMF): left tube is the normal TiO_2 and right is the modified TiO_2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

SEM studies

SEM images of the prepared composite are presented in Figure 3. From the section view [Fig. 3(a)], it can be seen that the composite are constructed by many thin lamellas via layer-by-layer deposition and this information can be further confirmed by the following TEM experiments [Fig. 4(b)]. In the front view Fig. 3(b), some particles can be clearly observed embedded within the PMA substrate. After EDS analysis [Fig. 3(c)] focusing on one particle demonstrates the existence of C, O, Ti elements, which suggests that these particles are TiO_2.

TEM and XRD studies

Figure 4(a) is the TEM image of a composite particle, whose diameter is 5–6 μm. Thousands of TiO_2 nanoparticles can be clearly seen homogeneously dispersed in matrix. Although there are some big agglomerates, whose size is about 1.0 μm, their amount is relatively few. In a smaller composite particle [Fig. 4(b)], the dispersion status of nano TiO_2 is more definite. Most nanoparticles are smaller than
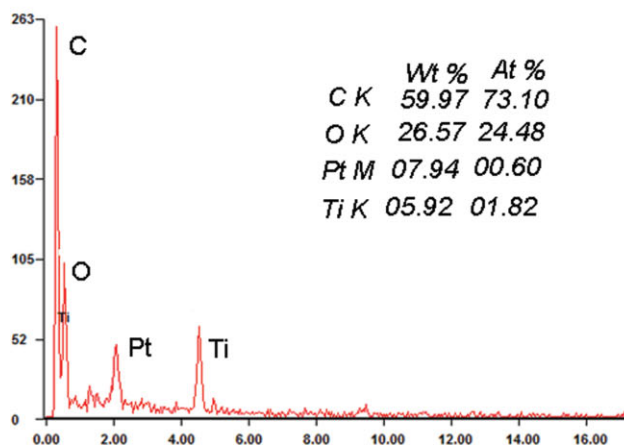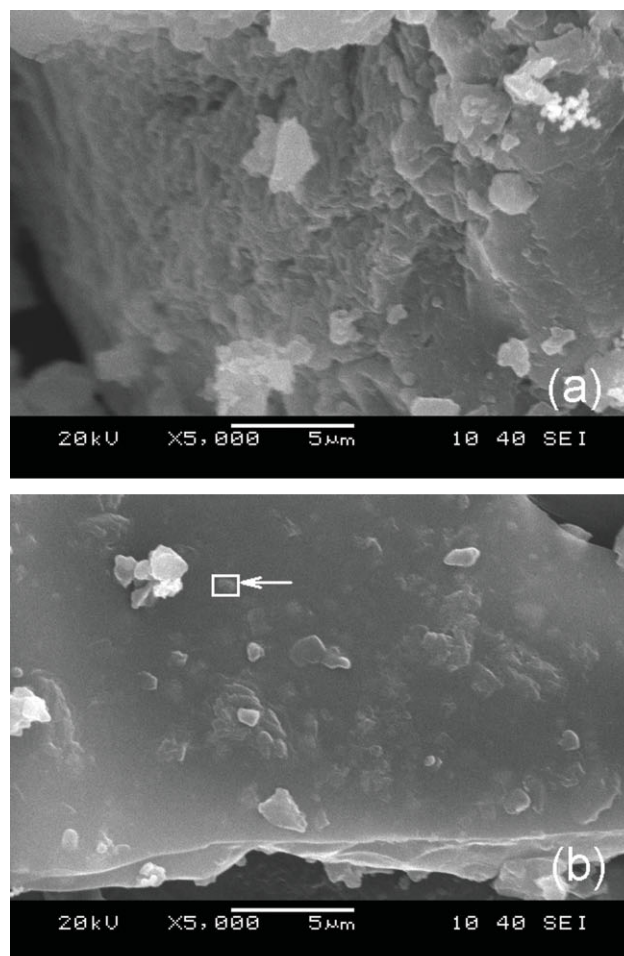

Figure 3 SEM photos of PMA/TiO_2 composite: (a) section view; (b) front view; (c) EDS analysis focusing on the area highlighted by square in (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
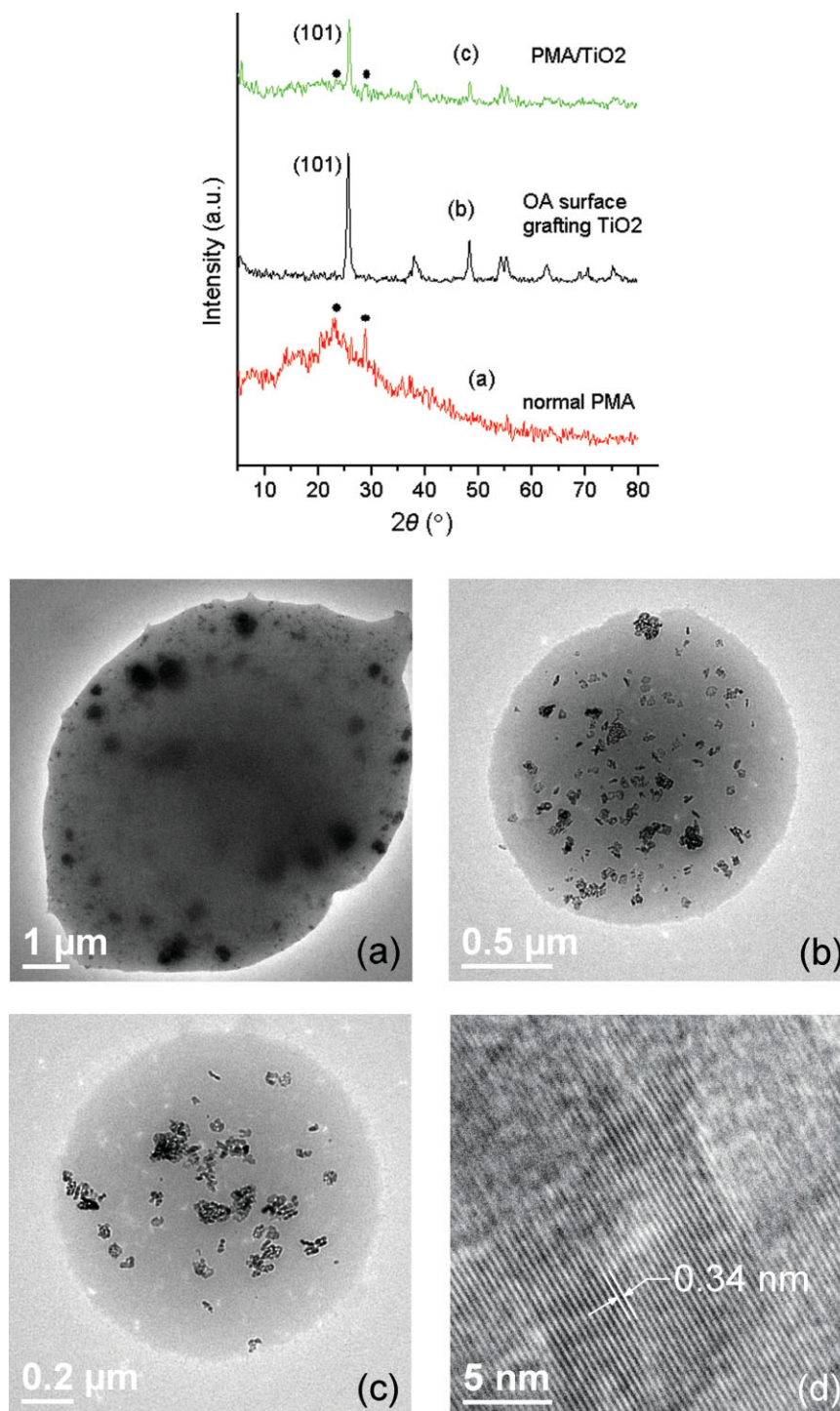
Figure 4 TEM images and XRD of composite: (a) PMA/TiO$_2$ composite of 5–6 μm; (b) PMA/TiO$_2$ composite of 1 μm; (c) PMA/TiO$_2$ composite of 0.5 μm; (d) HRTEM of nano TiO$_2$ in PMA. In composites of different size, TiO$_2$ are homogeneously dispersed in matrix. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

which demonstrates that the inorganic fillers have been fully coated by polymers. Finally, Figure 4(d) is the high-resolution TEM (HRTEM) image of nano TiO$_2$. The measured interplanar spacing is 0.34 nm, which can be assigned as the (101) plane of anatase TiO$_2$.

The XRD experiment has been carried out as the supplementary studies for TEM. In the XRD pattern of PMA/TiO$_2$ composite (Fig. 4), except for the characteristic peaks of anatase TiO$_2$ (i.e., $2\theta = 25.8°$), two weak signals from PMA, respectively, at 24.3° and 28.6° (indicated by black spots) also can be found.
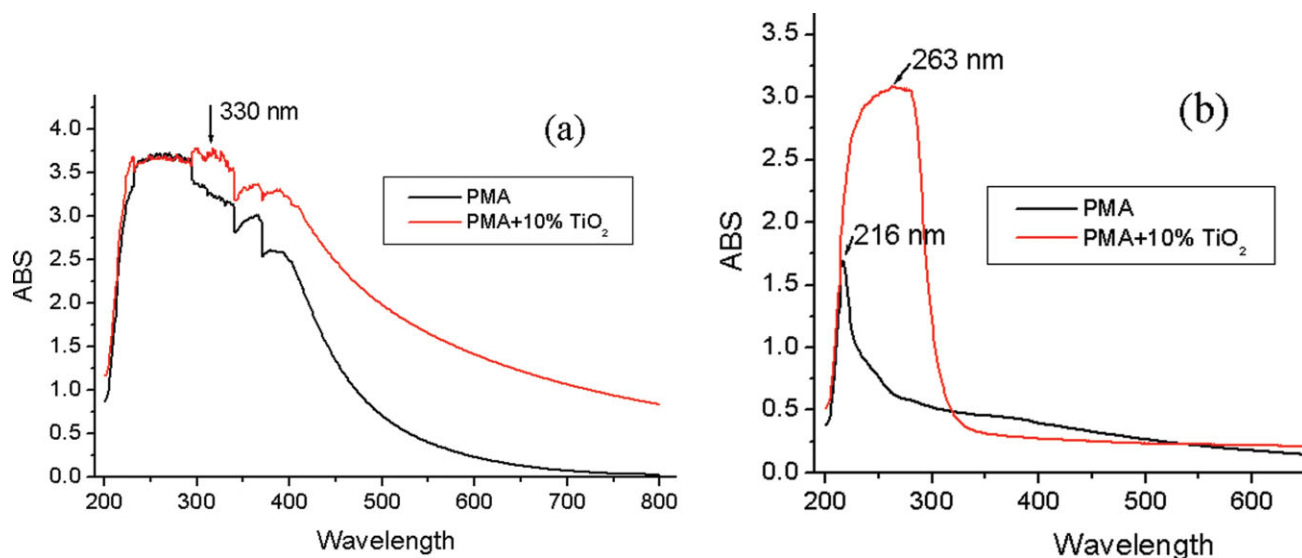
Figure 5 UV–vis spectra of normal PMA and PMA/TiO$_2$ composite: (a) aqueous, (b) solid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

UV–vis spectral studies

UV–vis spectra of normal PMA and the as-prepared PMA/TiO$_2$ (aqueous, 0.05M) are depicted in Figure 5(a). In comparison with normal PMA, the composites present an additional absorption peak at 330 nm, which is safely assigned as the characteristic signal of anatase TiO$_2$.[15] This phenomenon can be properly attributed to the division between matrix and the nanofillers because PMA is water-soluble. As a result, PMA and TiO$_2$ that suspended in water, respectively, presents absorption peaks.

In their solid state UV–vis spectra [Fig. 5(b)], contrastive changes can be found. Normal PMA gives only one sharp signal with the maximum absorption wavelength λ_{max} = 216 nm, which can be due to the $\pi \rightarrow \pi^*$ transition associated with C=O linkages. However, in PMA/TiO$_2$ composite it has been broadened covering the area from 200 to 320 nm and the λ_{max} has been red-shifted from 216 to 263 nm. This interesting phenomenon can be due to the change of aggregation states of PMA when TiO$_2$ nanoparticles are homogeneously blended into matrix.[16]
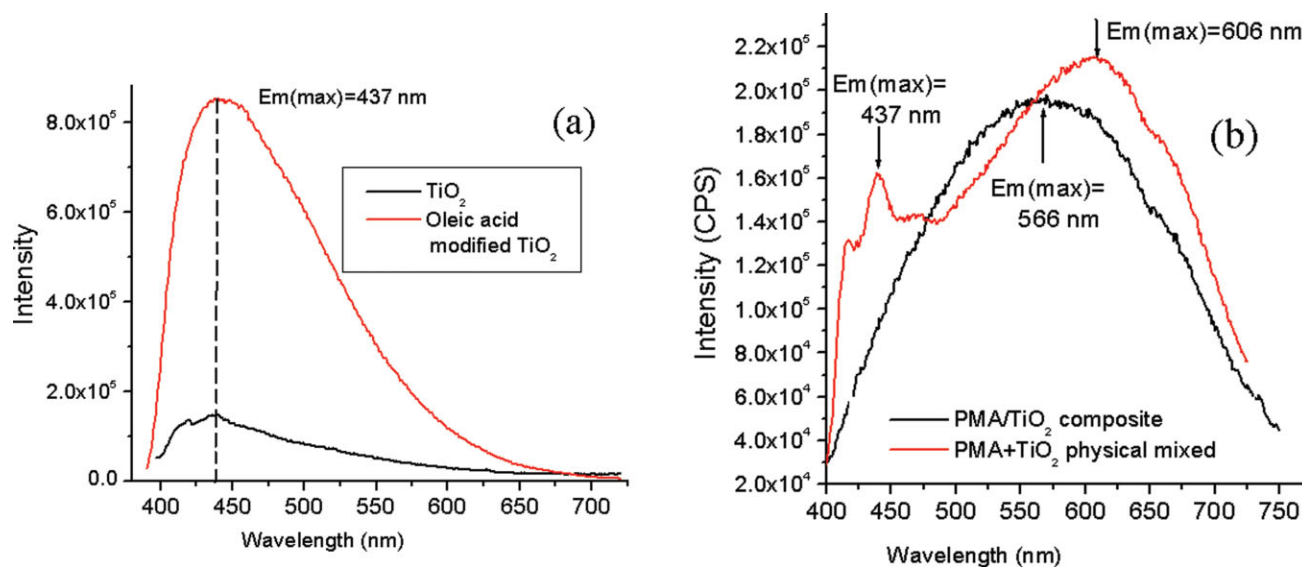

Figure 6 Solid fluorescence emission spectrum of: (a) modified TiO$_2$ and normal TiO$_2$, (b) PMA/TiO$_2$ composite and PMA+TiO$_2$ (10 wt%) mixture. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

(a) stable homogeneous system   **(b) in situ anionic polymerization**   **(c) PMA/TiO₂ composite**

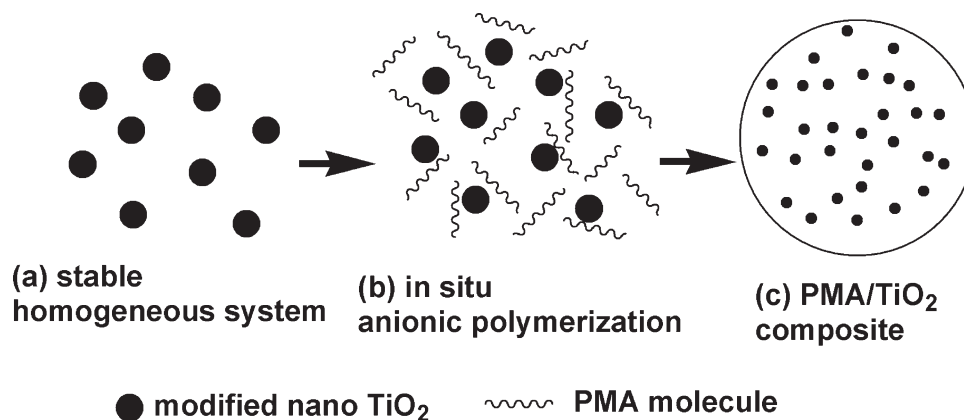● modified nano TiO₂   ～～ PMA molecule

Figure 7 Possible formation mechanism for PMA/TiO₂: (a) prepare stable homogeneous gel before polymerization; (b) *in situ* anionic polymerization initiated by modified TiO₂; (c) TiO₂ coated by PMA to form composite.

Solid fluorescence spectrum

From Figure 6(a), it can be found that the emission intensity of nano TiO₂ has been significantly increased by ∼5 folders after the surface modification, but the location of the maximum emission remains unchanged (E_m(max) = 437 nm). This information can be attributed to the division of big TiO₂ agglomerates, which not only increases the surface area for receiving laser excitation but also reduces the probability of self-quenching. This fluorescence enhancement is in good agreement with the sedimentation test result. Namely, the agglomeration of nano TiO₂ has been effectively prevented via OA surface-grafting.

Figure 6(b) is the contrast scheme of fluorescence spectrum of PMA/TiO₂ composite and PMA+TiO₂ (10 wt%) mixture. This mixture is made by grinding TiO₂ powders and normal PMA together. Clearly, the mixture gives two independent emission peaks. One at 437 nm can be properly assigned as the characteristic signal of anatase TiO₂ and the other wide peak with the maximum emission wavelength E_m(max) = 606 nm is tentatively attributed to the intermolecular $\pi \rightarrow \pi^*$ transition[17] given by PMA. Oppositely, the composite presents an unique emission with E_m(max) = 566 nm from PMA substrate, while the TiO₂ emission has disappeared. This result further confirms the TEM observation in Figure 6(b). Namely, all TiO₂ nanoparticles have been fully coated by PMA, which shields the excitation of nano TiO₂ by laser beam.

Formation mechanism of PMA/TiO₂

Based on the experimental results, the possible formation mechanism of PMA/TiO₂ composite is also proposed. Before the polymerization, the modified nano TiO₂ powders have been added into MA solution and a stable homogeneous system [Fig. 7(a)] is consequently formed. However, the nanomaterials also play the roll as the initiators for MA monomers. After rising the reaction temperature to 150°C, the *in situ* anionic polymerization takes place without influencing the system homogeneity. During the polymerization, OA tails in TiO₂ surface can significantly improve the consistency between nanofillers and polymer matrix [Fig. 7(b)]. Finally, TiO₂ nanoparticles are fully coated by PMA substrate and PMA/TiO₂ composites are prepared [Fig. 7(c)].

CONCLUSIONS

In this work, we make an attempt to develop an easy-to-operate method for preparing nanocomposites. Bare TiO₂ nanoparticles that treated by a combined modification process can be utilized as both the anionic initiators for monomers and the nanofiller for the prepared matrix. The homogeneous dispersion of TiO₂ in PMA matrix is well supported by TEM and SEM. Therefore, this approach can properly solve the problem of reclaiming nanoinitiators from polymer products. We propose this simple approach is also applicable to prepare other nanocomposites.

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