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ORIGINAL CONTRIBUTION

Mingjiao Yang
Yi Dan

Preparation and characterization of poly(methyl methacrylate)/titanium oxide composite particles

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M. Yang (✉) · Y. Dan
State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute, Sichuan University, Chengdu,
610065 Sichuan, P. R. China
E-mail: heatheryang@tom.com
Tel.: +86-28-85407286

Abstract Before polymerization, the introduction of double bonds onto the surface of the TiO_2 particles was achieved by the treatment of the TiO_2 particles with the silane-coupling agent. Via in-situ emulsion polymerization, the poly(methyl methacrylate) (PMMA)/titanium oxide (TiO_2) composite particles were prepared by graft polymerization of MMA from the surface of the modified TiO_2 particles. The structure of the obtained PMMA/TiO_2 composite particles was characterized using fourier transform infrared spectra (FT-IR), thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC) and size excluding chromatography (SEC). The morphology of the obtained PMMA/TiO_2 composite particles was observed by transmission electron microscope (TEM). The results of FT-IR and TGA measurements show that PMMA is successfully grafted from the surface of the TiO_2 particles and that the percentage of grafting and the grafting efficiency can reach 208.3% and 96.6%, respectively. At the same time, the TGA and DSC measurements indicate an enhancement of thermal stability. TEM images demonstrate a better dispersion of the TiO_2 particles in the composite latex. In addition, UV-visible absorption measurements show that the PMMA/TiO_2 composite particles can absorb over 95% UV light at 210–400 nm wavelength.

Keywords In-situ emulsion polymerization · Graft polymerization · Poly(methyl methacrylate) · Titanium oxide · Composite particles

Introduction

Inorganic–organic composite materials are increasingly important and have gained much interest due to the remarkable change in properties, such as mechanical, thermal, electrical and magnetic properties, compared to pure organic polymers. The combination of inorganic particles with polymers is accomplished by the means of surface encapsulation or surface grafting. Surface encapsulation, belonging to simple physical mixture, may lead to separation in discrete phases; whereas, surface grafting can endue a strong interaction between polymer and inorganic particle. The surface grafting of inorganic particles was widely investigated to improve surface properties of inorganic particles.

There are two methods of surface grafting: one is “grafting to" [1], i.e., end-functionalized polymers are grafted to the surface of inorganic particles, the other is “grafting from" [2], i.e., the polymer is grafted in situ from the surface of inorganic particles. As far as the “grafting to” method is concerned, the reaction should be carried out by solution polymerization or bulk polymerization. Since ultrafine silica, ferrite, and titanium oxide have reactive hydroxyl groups on the surfaces, surface grafting by the reaction of reactive polymers having isocyanate [3] (alkoxy silane [4], etc.,) with hydroxyl groups has been reported. It is possible to control the molecular weight and the number of grafted polymer chains on the surface. As far as the "grafting from" method is concerned, there are two ideas: (1) reactive groups such as azo groups [5] or peroxyester groups [6] or introduced onto the surface of inorganic particles can initiate the polymerization of vinyl monomers; (2) double bonds [7] introduced onto the surface of inorganic particles can react with the other vinyl monomers. The introduction of the initiating groups, such as azo groups or peroxyester groups, onto the surface of the inorganic particles usually need multi-step synthesis, while the introduction of the double bonds can be achieved by one-step synthesis using silane coupling agent (CA) containing double bonds to modify the surface of the inorganic particles. In the present work, the second method is employed.

Owing to its unique advantages, such as environmental friendliness, high reaction rate, and relative simple engineering technology in industrialization, the emulsion polymerization has attracted extensive interest. In the literature, relative to this work, preparation of inorganic/polymer composite by in-situ emulsion polymerization was reported by Hasegawa et al. [8], Jesionowski [9], Wang et al. [10] among others, but the polymerization mechanism all belong to surface encapsulation without covalent bond bindings. There have also been some reports on the preparation of inorganic/polymer composite particles based on covalent bond binds via in-situ emulsion polymerization by Yang and Dan [11], Jiang and Dan [12], among others, and much progress has been made. But, there still exist some problems that should be solved as soon as possible, e.g., the percentage of grafting and the grafting efficiency of polymerization system were relatively lower and the system obtained was less stable. Nevertheless, the percentage of grafting and the grafting affect the structure and performance of the inorganic/polymer composite particles to a great degree.

Due to its broad UV-absorption spectrum, the ultrafine TiO_2 particles are widely used in cosmetic, plastic and dope fields. However, the application of the TiO_2 particles is restricted to a great degree by its poor dispersibility. Hence, the surface modification of the TiO_2 particles with various chemical agents is the subject of much current research. In this paper, the PMMA/TiO_2 system was chosen as a model to prepare inorganic/polymer composite particles via emulsion polymerization. Preparation and characterization of the PMMA/TiO_2 composite particles will be described. The structural and thermal analyses provide the proof of the graft polymerization of MMA from the surface of the TiO_2 particles. Further, the morphologies of the particles and its UV-light-absorbing properties will be studied.

Experimental

Materials

The methyl methacrylate (MMA), purchased from Rongfeng Chemical Reagents Factory (China), was distilled under reduced pressure prior to use for removing the inhibitor. The titanium dioxide particle (TiO_2) was from Materials College of Sichuan University (China). [γ-(methacryloxy)-propyl]trimethoxysilane (γ-MPS), used for modifying surface of the TiO_2, came from Ha'erbin Chemical Research Institute (China). The sodium lauryl sulfate (SLS, AR) and the potassium persulfate (KPS) were obtained from Wuhan Chemical Reagents Factory (China) and Beijing Chemical Reagents Factory (China), respectively, and used without further treatment, acting as emulsifier agent and an initiator, respectively. The calcium chloride ($CaCl_2$) came from Tianjin Tanggudeng Chemical Factory (China). Deionized water was used throughout the experiments. Trichloromethane ($CHCl_3$, AR) was purchased from Kelong Chemical Reagents Factory (China).

Modification of the TiO_2 particles

The TiO_2 particles were dispersed in 95% ethanol solution under ultrasonic vibrations for 5 min. Then, the TiO_2 slurry (note that the TiO_2 particles is manufactured by vitriol method, the TiO_2 slurry is slightly acidic) was diverted into 125 ml three-neck flask (TNF) equipped with mechanical stirrer, thermometer, and 5% CA (based on the content of TiO_2) was added. Treatment was continued for 6 h at 60°C, keeping the stirring rate at 300 rpm. Subsequently, the TiO_2 slurry was dried, and extracted with ethanol to remove the CA adsorbed physically on the surface of the TiO_2 particles.

Preparation and purification of the PMMA/TiO_2 composite particles

In order to obtain the PMMA/TiO_2 composite particles, the PMMA/TiO_2 composite latex was prepared first via in-situ emulsion polymerization of MMA in the presence of the modified TiO_2 particles. Firstly, 3 g of the modified TiO_2 was dispersed in 30 ml of 1% SLS (based on the amount of deionized water) aqueous solution under ultrasonic vibrations for 5 min; then, the modified TiO_2 slurry was diverted into 125 ml TNF equipped with mechanical stirrer, thermometer and drop funnel. When the temperature rose to 70°C, a proper amount of 0.5% KPS (based on the amount of MMA) aqueous solution was charged in the TNF and 7 g of the purified MMA monomer was trickled slowly into the TNF. Polymerization was continued for 3 h at 70°C, keeping the stirring rate at 300 rpm. In the end, the system was cooled naturally and the PMMA/TiO_2 composite latex was obtained. The conversion of MMA is 92.37%.

By precipitating the latex with the 5 mass% $CaCl_2$ aqueous solution, filtering, washing, drying at 60°C, and pulverizing, the PMMA/TiO_2 composite particles were obtained.

The PMMA/TiO_2 composite particles were Soxhlet extracted with refluxing $CHCl_3$ at water-bath 70°C for 72 h to remove the homopolymer PMMA. In order to ensure that the homopolymer PMMA was extracted completely, the PMMA/TiO_2 mixture, obtained by directly mixing the PMMA particles with the modified TiO_2 particles was Soxhlet extracted at the same time.

Measurements and characterization

FT-IR measurements of all the purified samples were carried out on Nicolet 560 FT-IR spectrometer. The KBr pellet method was used.

Before measurement of the solid content ($S\%$), the latex was filtered to remove the gel. The solid content of the composite latex was measured by gravity method, and calculated by the Eq. (1):

$$S\% = \frac{M_2 - M_3}{M_1} \times 100\% \tag{1}$$

where M_1 is mass of the composite latex sample; M_2 is mass of the solid after dried; M_3 is mass of the inhibitor.

The conversion of MMA ($C\%$) was calculated by the Eq. (2):

$$C\% = \frac{(M_4 - M_5) \times S\% + M_5 - M_4 Y}{M_4 X} \times 100\% \tag{2}$$

where M_4 is mass of the total materials charged; M_5 is mass of the filtered gel; X is mass percentage of the MMA based on total materials charged; Y is mass percentage of the SLS, KPS and modified TiO_2 based on total materials charged.

The amount of grafted polymer was estimated by measuring thermogravimetrically, the weight loss of the extracted composite particles. A Dupont 2100 Thermogravimetric Analyzer (TGA) was used. The extracted samples were heated up to 500°C at the heating rate of 10°C/min under a nitrogen atmosphere. The percentage of grafting was determined by the following equation [13]:

$$\text{Percentage of grafting (\%)} = \frac{\text{Polymer grafted (g)}}{\text{Modified TiO}_2\text{ charged (g)}} \times 100\% \tag{3}$$

where the mass of polymer grafted and modified TiO_2 charged were determined by the results of TGA measurement of PMMA/TiO_2 composite particles. The grafting efficiency was defined as the mass percentage of PMMA grafted on TiO_2 particles based on the total PMMA, and was determined by the following equation:

$$\text{Grafting efficiency (\%)} = \frac{\text{Modified TiO}_2\text{ charged} \times \text{percentage of grafting}}{\text{MMA charged} \times \text{conversion of MMA}} \times 100\% \tag{4}$$

The DSC measurements were carried out on a NETZSCH DSC 204 apparatus by heating 5 mg of extracted sample (or PMMA particles) to 250°C at a heating rate of 20°C/min under a nitrogen atmosphere. The data obtained from the second scanning were accepted.

The SEC measurements were taken was performed on an Agilent 1100 apparatus, and the mobile phase was tetrahydrofuran (THF) at an elution rate of 1 mL/min.

UV-visible spectra was taken with a TU-1901 spectrophotometer in the range of 210–850 nm.

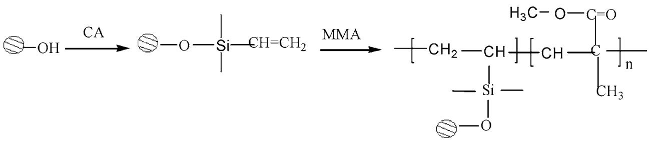
The morphologies of the latex particles were observed on a Hitachi H-600 Transmission electron microscope (TEM). Before measurements, the latexes were diluted with 1% SLS aqueous solution, followed by staining with phosphorus tungsten acid.

Results and discussion

It is well known that, in general, inorganic particles have hydroxyl groups on their surface, which can react with alkoxy silanes. Therefore, alkoxy silanes with reactive functional groups, the so-called coupling agent, are suitable for the introduction of functional groups onto the surface of inorganic particles. In the present article, the grafting of PMMA from the surface of TiO_2 particles by the reaction of vinyl groups introduced onto the surfaces using the CA with MMA monomers was investigated (Scheme 1).

Introduction of vinyl groups onto the surface of the TiO_2 particles

In the present article, [γ-(methacryloxy)-propyl]trimethoxysilane (γ-MPS) was used to surface treatment of



Scheme 1 The scheme of preparation of PMMA/TiO_2 composite particles

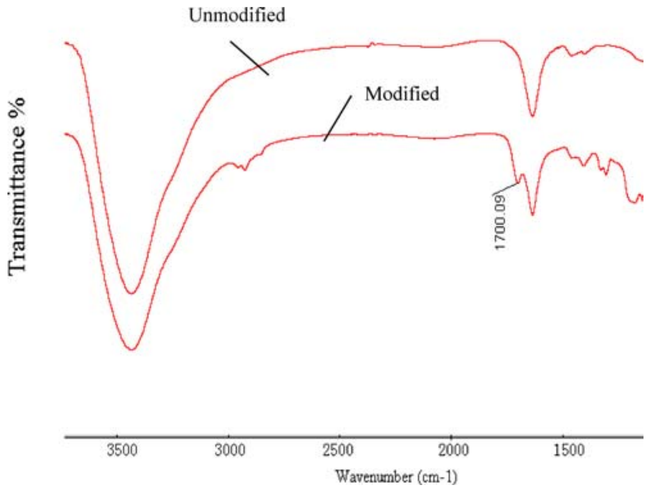


Fig. 1 FT-IR spectra of modified TiO_2 particles and unmodified TiO_2 particles

TiO₂ particles. For, there are chemisorbed and physisorbed silane CAs on the surface of TiO_2 particles. Attempt was made to remove the physisorbed silane CAs by Soxhlet extraction with refluxing ethanol at water-bath 80°C for 72 h. Figure 1 is FT-IR spectra of unmodified TiO_2 particles and modified TiO_2 particles. It can be seen that FT-IR spectrum of the modified TiO_2 appears absorption band at 1,700 cm^{-1}, resulting from the carbonyl group stretching mode in γ-MPS. However, the FT-IR spectrum of the unmodified TiO_2 particles does not appear absorption at 1,700 cm^{-1} . This suggests that γ-MPS is chemisorbed on the surface of TiO_2 particles. Thus, vinyl groups are introduced onto the surface of TiO_2 particles successfully.

How much is the silane chemisorbed on the surface of the TiO_2 particles is important for the following polymerization? In the present article, it is quantitatively analyzed by FT-IR. The degree of chemical and physical adsorption of the silane can be examined by extraction in a good solvent for γ-MPS. The chemisorbed layers may be defined as those that cannot be removed by the solvent, while the physisorbed layers can be removed by the solvent. In this analysis, the carbonyl group band in γ-MPS has a large specific absorption, allowing for high sensitivity measurements. Figure 2 shows the FT-IR spectra of the extracted and the unextracted modified TiO_2 particles. By calculating the ratio of integral area of the carbonyl group band of the extracted modified TiO_2 particles (0.661) to that of the unextracted modified TiO_2 particles (0.922), it is deduced that 72% of the silane is chemisorbed on the surface of TiO_2 particles.

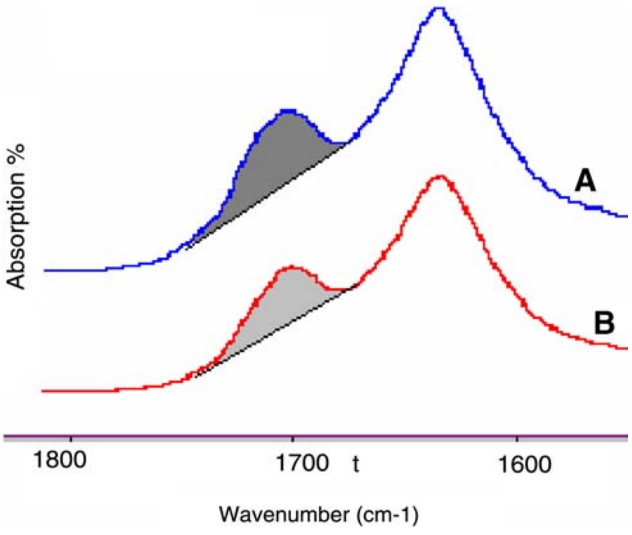
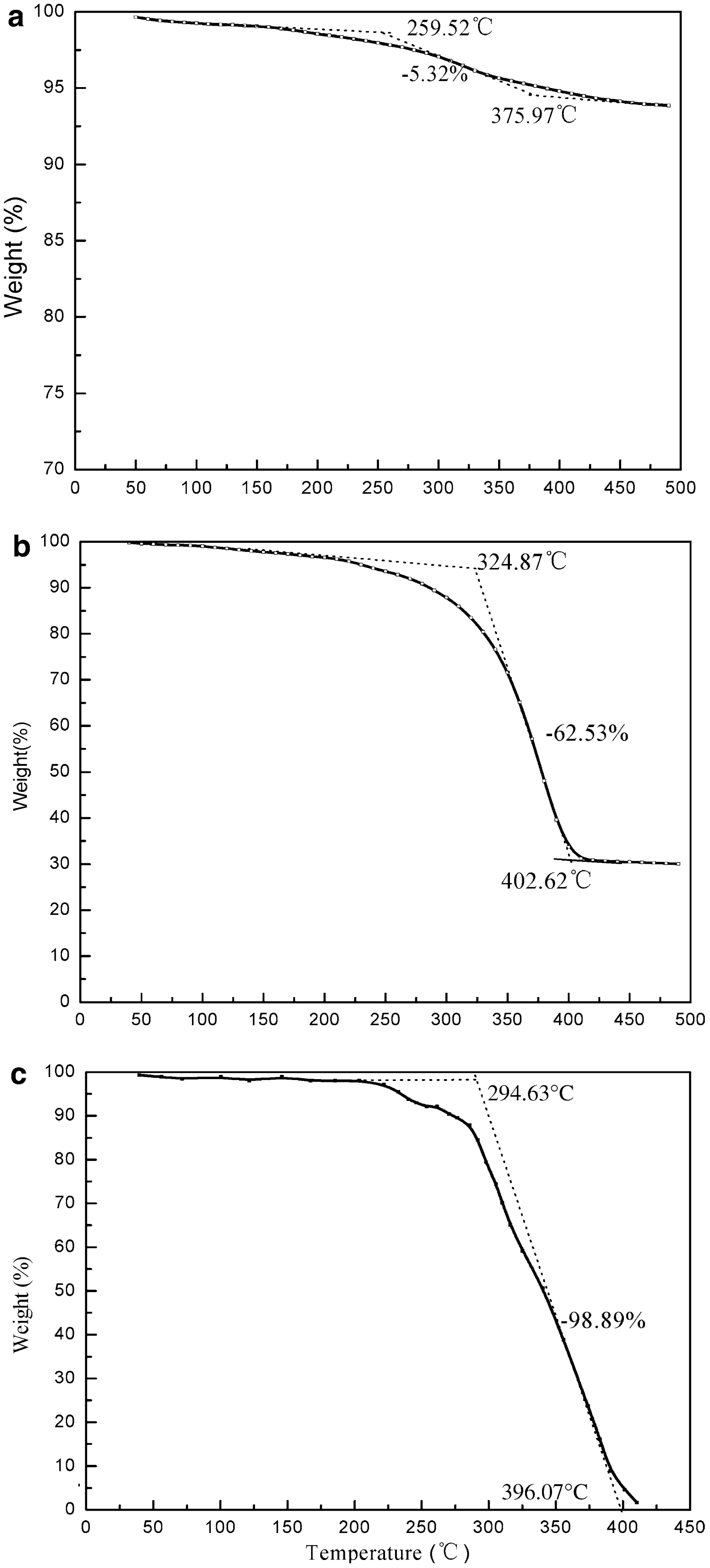


Fig. 2 FT-IR spectra of modified TiO_2 particles: **a** unextracted; **b** extracted

Polymerization of MMA from the surface of the modified TiO_2 particles

How much is the polymer grafted from the surface of the inorganic particles is always attended in the field of inorganic–organic composite? In the present article, the degree of the grafted and ungrafted PMMA can be examined by extraction in a good solvent for PMMA. The grafted PMMA may be defined as those that cannot be removed by the solvent, while the ungrafted PMMA can be removed by the solvent. The percentage of grafting and the grafting efficiency of the composite were determined by means of TGA. Before TGA measurement, the PMMA/TiO_2 composite was extracted by $CHCl_3$ at water-bath 70°C for 72 h. In order to prove that the ungrafted PMMA in the composite system can be extracted completely, PMMA/TiO_2 mixture with 10:1 mass ratio of the PMMA to the modified TiO_2 and PMMA/TiO_2 composite particles were extracted by $CHCl_3$ at the same temperature and the same time. Hence, the mass of polymer grafted and the mass of TiO_2 particles are corresponding to the weight loss and the remains of the sample during TGA measurement, respectively. Figure 3 is the TGA curve of (a) the PMMA/TiO_2 mixture, (b) the PMMA/TiO_2 composite and (c) the pure PMMA. In the Fig. 3a, the weight loss

Fig. 3 TGA curve of **a** PMMA/TiO_2 mixture, **b** PMMA/TiO_2 composite and **c** pure PMMA



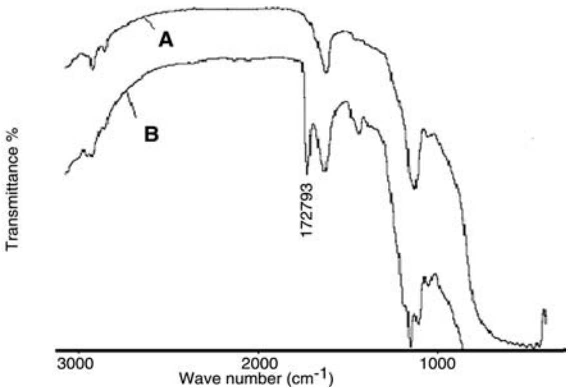


Fig. 4 FT-IR spectra of **a** the PMMA/TiO_2 mixture and **b** the PMMA/TiO_2 composite

was 5.32%. Considering that the TiO_2 particles were modified with 5% CA before polymerization, we can infer that the ungrafted PMMA was extracted completely. Weight loss and remains of the PMMA/TiO_2 composite PMMA/TiO_2 are 62.53% and 30.02% (see Fig. 3b), respectively. Namely, 0.6253 g of the PMMA is grafted from the surface of 0.3002 g TiO_2, in addition, according to the recipe (MMA:TiO_2 is 7:3), 0.7004 g MMA is corresponding to 0.3002 g TiO_2. The conversion of MMA, measured by gravity method, is 92.37%. The percentage of grafting and the grafting efficiency, which are calculated by Eqs. (3) and (4), are 208.3% and 96.6%, respectively. Hence, the PMMA/TiO_2 composite particles with higher grafting efficiency are prepared successfully.

Structural characterization

In order to ensure that the scheme of preparation of PMMA/TiO_2 composite particle is viable, the CA without carbonyl groups was selected and the structure of the composite particles was studied by FT-IR. Figure 4 illustrates FT-IR spectra of the PMMA/TiO_2 composite particles and the PMMA/TiO_2 mixture. As for the PMMA/TiO_2 mixture, the mass ratio of the PMMA particles to the modified TiO_2 particles is higher than that of the MMA monomer to the modified TiO_2 in the recipe of preparation of the PMMA/TiO_2 composite latex. The two samples were treated and extracted under the same conditions, which can make sure that the ungrafted PMMA can be removed completely. From Fig. 4, it can be seen that FT-IR spectrum of the PMMA/TiO_2 composite particles exhibits characteristic absorption band of carbonyl groups in PMMA at 1,727 cm^{-1}, while that of the PMMA/TiO_2 mixture does not appear absorption at 1,727 cm^{-1}, indicating that PMMA has successfully grafted from the surface of the TiO_2 particles.

Table 1 Molecular weight and molecular weight distribution of the (a) PMMA and (b) PMMA grafted from the surface of TiO_2 particles

	a	b
$\overline{M_n}$	3.1555e5	2.3936e5
$\overline{M_w}$	1.0043e6	6.5222e5
$\overline{M_z}$	1.6501e6	1.1248e6
$\overline{M_v}$	1.0043e6	6.5222e5
D	3.1827	2.7248

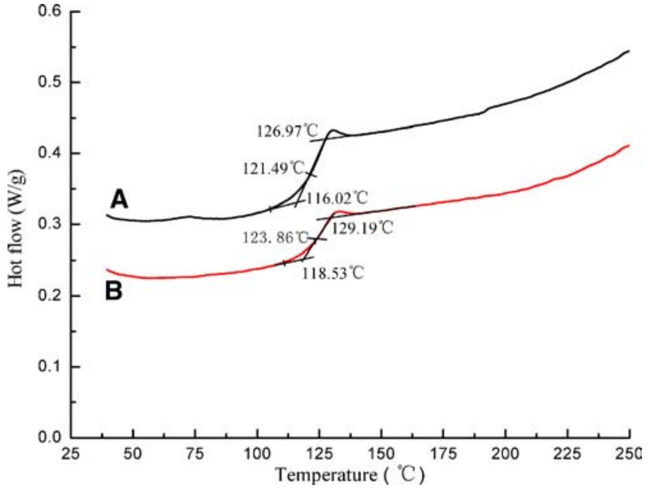


Fig. 5 DSC thermograms of **a** the pure PMMA and **b** the extracted composite particles

The molecular weight and molecular weight distribution were obtained by SEC measurements. Before the measurements, the extracted PMMA/TiO_2 composite was treated with hydrofluoric acid (HF) to remove the TiO_2 particles. The molecular weight and molecular weight distribution are summed up in Table 1. The molecular weight of PMMA grafted from the surface of TiO_2 particles is lower than that of the pure PMMA, and the distribution index (*D*) of the former (2.72) is smaller than that of the latter (3.18).

Thermal characterization

The DSC thermograms of pure PMMA and the extracted composite particles are compared in Fig. 5, which provide additional proof of graft polymerization of MMA from the surface of the TiO_2 particles. The pure PMMA exhibit an endothermic conversion at round 116–126 °C; while, the extracted PMMA/TiO_2 composite exhibit an endothermic conversion at around 118–129°C, which indicate that the T_g of the extracted PMMA/TiO_2 composite is higher than that of the pure

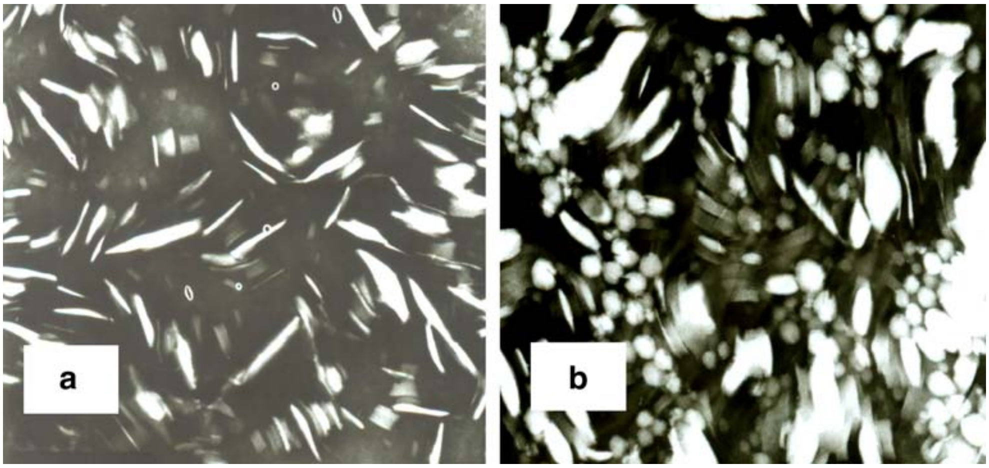


Fig. 6 TEM images of **a** the modified TiO_2 particles (amplified 80,000 times) and **b** PMMA/TiO_2 composite particles (amplified 80,000 times)

PMMA. Undoubtedly, the addition of the TiO_2 particles is responsible for the T_g elevation.

In addition, it can be seen from Fig. 3, that the onset temperature of polymer decomposition for the PMMA/TiO_2 composite is shifted to a higher temperature range, compared with that of pure PMMA, which indicates the enhancement of thermal stability of the composite. This thermal behavior of the composite, together with the SEC results, provided a strong support for graft polymerization of MMA from the surface of the TiO_2 particles. It is the TiO_2 particles' cross-linked role in polymerization process that leads to a higher decomposition temperature. This is an interesting result and it will be researched with emphasis in our following work.

Morphologies

The PMMA/TiO_2 composite particles in the latex were observed through TEM. Before observation, the modified TiO_2 particles were dispersed in 1% SLS aqueous solution and the PMMA/TiO_2 composite latex was diluted with 1% SLS aqueous solution, followed by staining with phosphorus tungsten acid. The TEM images of the modified TiO_2 particles and the PMMA/TiO_2 composite latex are shown in Fig. 6. It can be observed that both the modified TiO_2 and the PMMA/TiO_2 composite particles are dispersed at a nanoscale level. The TiO_2 particles are needle shaped, and the surface of the particles is smooth (see Fig. 6a). After polymerization of MMA was carried out in its presence, the surface of the TiO_2 particles becomes rough (see Fig. 6b), resulting from the grafting of PMMA from the surface of the TiO_2 particles. Inevitably, there exist still some ungrafted PMMA particles in the composite latex.

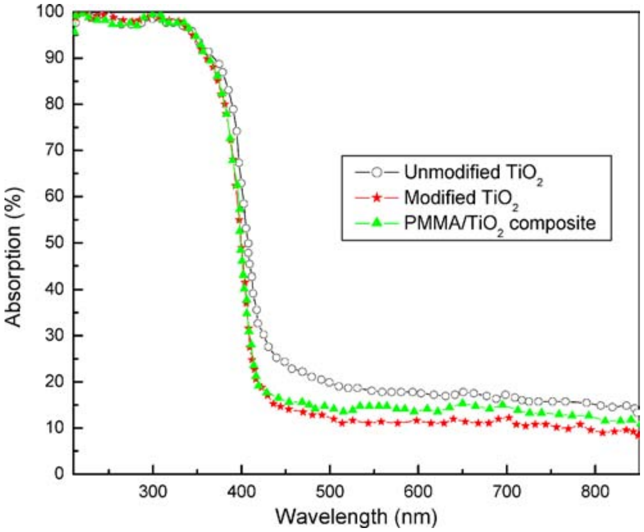


Fig. 7 UV-visible spectra of the unmodified TiO_2 particles, the modified TiO_2 particles and the PMMA/TiO_2 composite particles

UV light absorbing property

The UV light absorbing properties of the unmodified TiO_2 particles, the modified TiO_2 particles and the PMMA/TiO_2 composite were detected by UV-visible spectrometer, respectively, and the results are shown in Fig. 7. The results show that whether the unmodified TiO_2 particles, or the modified TiO_2 particles, or the PMMA/TiO_2 composite, over 95% UV light at 210–400 nm wavelength is absorbed. The UV light absorbing property of the TiO_2 particles is little affected by the modification of the silane, or the graft polymerization of MMA. Thus, the TiO_2 particles still retain their typical optical properties in the polymers. The absorption spectra indicate that the PMMA/TiO_2 composite will be a promising one for weather-resistant materials.

Conclusions

The PMMA/TiO_2 composite particles have been prepared via in-situ emulsion polymerization. FT-IR characterizations confirm PMMA is successfully grafted from the surface of the TiO_2 particles. It can be calculated from TGA measurements that the percentage of grafting and the grafting efficiency of PMMA reach 208.3% and 96.6% respectively. At the same time, the TGA and DSC measurements indicate an enhancement of thermal stability. TEM images demonstrate a better dispersion of the TiO_2 particles in the composite latex (Figs 8 and 9). UV-visible absorption measurements show the PMMA/TiO_2 composite particles can absorb over 95% UV light at 210–400 nm wavelength. The PMMA/TiO_2 composite will be a promising one for weather-resistant materials.

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