ORIGINAL CONTRIBUTION

Preparation and characterization of poly (MMA-M12-BPMA)/TiO₂ composite particles

Jiangpeng Zou · Yi Zhao · Mingjiao Yang · Yi Dan

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Abstract In this paper, poly(MMA-M12-BPMA)/TiO₂ composite particles were prepared by the copolymerization of a reactive surfactant sodium sulfopropyl-laurylmaleate (M12) and a reactive UV-stabilizer 2-hydroxy-4-(3methacryloxy-2-hydroxylpropoxy) benzophenone (BPMA) with methyl methacrylate (MMA) in the presence of TiO₂. The structure and performance of composite particles were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, X-ray photoelectron spectroscopy, gel permeation chromatography, ultraviolet-visible absorption spectroscopy, differential scanning calorimeter, and scanning electron microscope. The measurement results indicate that the percentage of grafting and the grafting efficiency can reach 336.87% and 36.38%, respectively, and the glass transition temperature of poly(MMA-M12-BPMA)/TiO₂ composite particles is higher than that of poly (MMA-M12-BPMA); the size of the composite particles is about 130-200 nm. The poly(MMA-M12-BPMA) grafted from the surface of TiO2 keeps the excellent characteristic of BPMA that possesses high absorbance of ultraviolet light, which is very important for improving UV-resistant performance of the polymethyl methacrylate. These research results are very useful for preparing polymethyl methacrylate with resistance to UV light.

Keywords Reactive surfactant · Reactive UV stabilizer · UV-resistant performance · Methyl methacrylate · Titanium dioxide

Introduction

Polymethyl methacrylate is a kind of thermoplastic material which is widely used as fluorescent solar collections, sheet glazing material, optical lenses, and coatings. Photolysis of polymethyl methacrylate by ultraviolet (190-400 nm) usually causes chain scission, crosslinking, and distinct discoloration. Adding the UV stabilizers into the matrix is a common method to protect polymethyl methacrylate from UV destroys. But organic UV stabilizer will decompose during processing or migrate from the polymethyl methacrylate. This results in the organic UV stabilizer being deposited on the polymer surfaces and decreases its photostabilization efficiency. For example, the organic UV stabilizer hydroxyl-benzophenone could vaporize and extract easily from the polymethyl methacrylate matrix. By using reactive UV stabilizer [1-5], the organic UV stabilizer can be introduced into the polymer chains by covalent bond. The problems of migration and evaporation will be solved, and the service life of the polymethyl methacrylate will be prolonged. Titanium dioxide is one of the inorganic UV stabilizers which are excellent in shielding ultraviolet [6–8]. To combine the UV-resistant performances of inorganic and organic UV stabilizers together, it is important to introduce the inorganic UV stabilizer TiO₂ into the polymer chains by covalent bond too, and then the UV-resistant performance of polymethyl methacrylate can be highly enhanced by the effects of organic UV stabilizers and inorganic UV stabilizer TiO2 together. The surface grafting

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of inorganic particles was widely investigated to introduce the inorganic UV stabilizer TiO_2 into the polymer chains by covalent bond. The inorganic/polymer particles are often obtained by solution polymerization or emulsion polymerization. In the recent years, there are some reports about the preparation of inorganic/polymer composite particles by many groups [9–14].

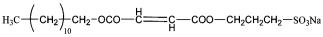
Compared with other polymerization such as solution polymerization, emulsion polymerization is a good method in preparing the composite particles for its advantage of high reaction rate and good heat dispersion. But there are some drawbacks of surfactant in emulsion polymerization. For example, the surfactant may cause foaming or migrate to the pigment phase and cause destabilization of latex particles when mixed with other products in paints. A way to reduce the negative effects of the surfactant is to use reactive surfactant [15–17] which contains a polymerizable double bond. When the surfactant is anchored onto the surface of the latex particles in emulsion polymerization, it cannot migrate in the water phase and can continue to stabilize the particles.

In this paper, a reactive surfactant sodium sulfopropyllaurylmaleate (M12), a reactive UV stabilizer 2-hydroxy-4-(3-methacryloxy-2-hydroxylpropoxy) benzophenone (BPMA), and methyl methacrylate are copolymerized with modified titanium dioxide via emulsion polymerization; then, the poly(MMA-M12-BPMA)/TiO₂ composite particles in which polymethyl methacrylate combines the organic UV stabilizers and the titanium dioxide with covalent bond can be obtained. It is important to enhance the UV-resistant performance of polymethyl methacrylate. Fourier transform infrared spectra (FTIR), thermogravimetric analysis (TGA) measurement, X-ray photoelectron spectroscopy (XPS) analysis, and gel permeation chromatography (GPC) measurement were performed to investigate the structure and the grafted results. Ultraviolet-visible absorption (UV-vis) spectrophotometry measurement and differential scanning calorimeter (DSC) were carried out to investigate the UV-resistant performance and thermal performance of the composite particles, respectively. The morphology of the raw TiO₂ particles and the composite particles were observed by scanning electron microscope (SEM).

Experimental

Materials

Methyl methacrylate (MMA), from Rongfeng Chemical Reagents Factory (China), was redistilled under reduced pressure. The initiator, potassium peroxydisulfate (KPS)



Scheme 1 The molecule structure of M12

was purchased from Beijing Chemical Reagent Factory (Beijing, China). TiO₂ with rutile form was from PanGang Group Corporation of China. The coupling agent, 3-(trimethoxysilyl) propylmethacrylate (γ-MPS), used for modifying the surface of the TiO2 was from Ha'erbin Chemical Research Institute (Ha'erbin, China). Sodium sulfopropyl-laurylmaleate (M12) and 2-hydroxy-4-(3methacryloxy-2-hydroxylpropoxy)benzophenone (BPMA) were synthesized according to the method reported elsewhere [18, 19], and the molecule structure of M12 and BPMA were shown in Schemes 1 and 2. Calcium chloride (CaCl₂) was purchased from Tianjin Tanggudeng Chemical Factory (Tianjin, China). Deionized water was used in the experiments. Trichloromethane (CHCl₃; AR) and tetrahydrofuran (THF; AR) purchased from Kelong Chemical Reagents Factory (Chengdu, China) were used without further purification.

Modification of TiO₂

The TiO_2 particles were dispersed in an ethanol solution of 5 wt% γ -MPS (based on the content of TiO_2) for 10 min via ultrasonic vibrations with an SC-I ultrasonic apparatus supplied by Chengdu Jiuzhou Ultrasonic Technology Co., Ltd. (Chengdu, China).Then, the mixture was maintained at 70–75 °C for 6 h. The TiO_2 slurry was dried at 70–80 °C and extracted with ethanol to remove the γ -MPS adsorbed physically on the surface of the TiO_2 particles. At last, the product was dried at 70–80 °C to remove the solvent.

Synthesis of the poly(MMA-M12-BPMA)

In a typical preparation of copolymer poly(MMA-M12-BPMA), firstly, 45 ml of M12 (1.5 mmol) aqueous solution was added into a 150-ml three-neck flask (TNF) equipped with N_2 flows, mechanical stirrer, and drop funnel. When temperature rose to 60–70 °C, 0.5% (based on the amount of MMA) KPS aqueous solution was added into the TNF. A few minutes later, MMA (89.9 mmol) and BPMA (1.3 mmol) mixture was trickled slowly into the

$$\begin{array}{c|c} & \text{HO} & \text{OH} & \text{O} \\ & & & \text{OCH}_2 & \text{CHCH}_2\text{OCC} \longrightarrow \text{CH}_2 \\ & & & \text{CH}_3 \\ \end{array}$$

Scheme 2 The molecule structure of BPMA



Scheme 3 Preparation of poly (MMA-M12-BPMA)/TiO₂ composite particles

$$M = \begin{pmatrix} \begin{pmatrix} & & \\ &$$

TNF. The polymerization was carried out at about 70–80 °C for about 3 h, and then, the poly(MMA-M12-BPMA) latex was obtained. The latex was precipitated with the water solution of CaCl₂, and the precipitation was filtered, washed, dried at 60 °C, and pulverized. After that, the poly(MMA-M12-BPMA) was obtained.

Preparation of the poly(MMA-M12-BPMA)/TiO $_2$ composite particles and the poly(MMA-M12)/TiO $_2$ composite particles

Poly(MMA-M12-BPMA)/TiO₂ composite particles were prepared by emulsion copolymerization of M12, BPMA,

and methyl methacrylate in the presence of TiO₂. Firstly, 1 g modified TiO₂ was dispersed in 45 ml of M12 (1.5 mmol) aqueous solution via ultrasonic vibrator under 150–200 W for 10 min. Then, the TiO₂ slurry was transferred into a 150-ml TNF equipped with N₂ flows, mechanical stirrer, and drop funnel. A 0.5% (based on the amount of MMA) KPS aqueous solution was added into the TNF with mechanical stirring when temperature reached 60–70 °C. After 10 min, MMA (89.9 mmol) and BPMA (1.3 mmol) mixture was added drop by drop into the TNF. Emulsion polymerization was carried out at 80 °C for 4 h. Then, the poly(MMA-M12-BPMA)/TiO₂ composite latex was coagulated by adding CaCl₂ aqueous solution, filtered,

Fig. 1 FTIR spectra of a chloroform (99.0%), b chloroform solution after extracting sample for 240 h

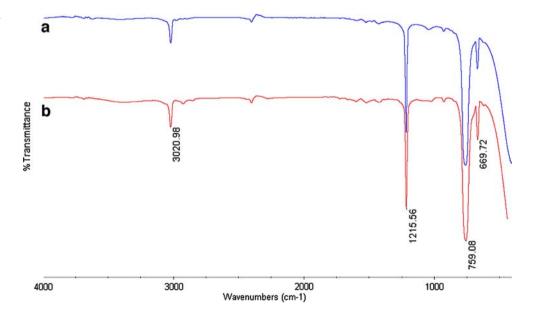
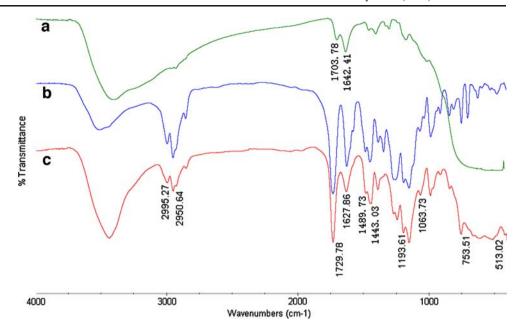




Fig. 2 FTIR spectra of **a** modified TiO₂, **b** poly(MMA-M12-BPMA), and **c** extracted poly (MMA-M12-BPMA)/TiO₂ composite particles



washed, dried at 60 °C, and pulverized to get the poly (MMA-M12-BPMA)/TiO₂ composite particles. The poly (MMA-M12)/TiO₂ composite particles were prepared in the same method without BPMA in the feed.

Measurements and characterization

Solid content of the composite latex

The solid content (S%) was measured by gravity method and calculated by the Eq. 1.

$$S\% = \frac{m_2 - m_3}{m_1} \times 100\% \tag{1}$$

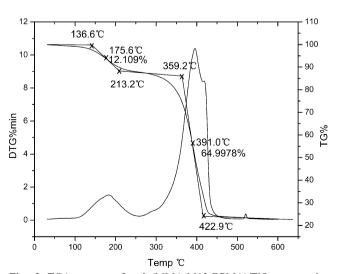


Fig. 3 TGA curves of poly(MMA-M12-BPMA)/TiO $_2$ composite particles

Where m_1 is mass of the composite latex sample, m_2 is mass of the solid after being dried, and m_3 is mass of the inhibitor.

Conversion of monomers

The conversion of monomers (C %) was calculated by Eq. 2.

$$C\% = \frac{m_4 \times S\% - m_{\rm T} - m_{\rm i}}{m_{\rm m}} \times 100\% \tag{2}$$

where m_4 is mass of the total composite latex, m_T and m_i are the weight of TiO₂ and initiator used, respectively, and m_m is mass of the monomers MMA, M12, and BPMA.

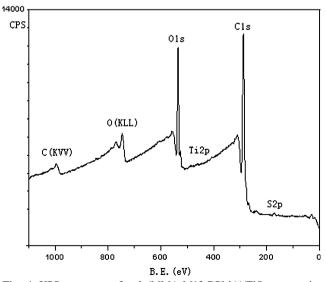
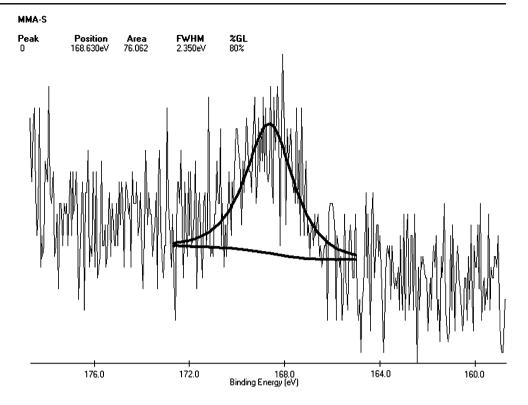


Fig. 4 XPS spectrum of poly(MMA-M12-BPMA)/ TiO_2 composite particles showing survey spectra



Fig. 5 XPS spectrum of poly (MMA-M12-BPMA)/TiO₂ composite particles showing S2p peak

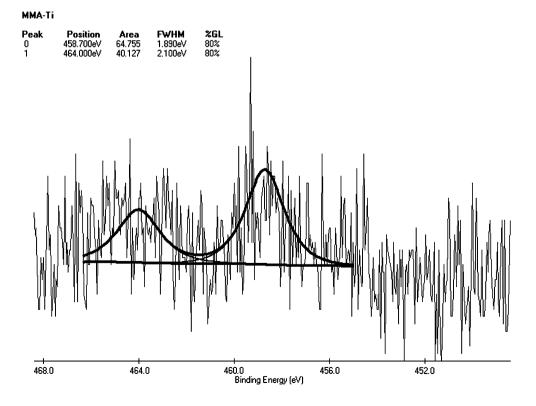


FTIR measurement

Before FTIR measurement, the poly(MMA-M12-BPMA) was Soxhlet extracted with refluxing deionized water for 72 h. The poly(MMA-M12-BPMA)/TiO₂ composite par-

ticles and the modified TiO_2 were Soxhlet extracted in a Soxhlet extractor by the use of deionized water for 72 h and then by the use of CHCl₃ for 10 days to remove the free M12, BPMA, poly(MMA-M12-BPMA), and γ -MPS. During the extracting period, the solvent of chloroform was

Fig. 6 XPS spectrum of poly (MMA-M12-BPMA)/TiO₂ composite particles showing ti2p peak





refreshed by the fresh chloroform (99.0%) after an interval time. The FTIR spectra of purified poly(MMA-M12-BPMA), poly(MMA-M12-BPMA)/TiO₂ composite particles, and modified TiO₂ were carried out on a Nicolet 560 FTIR spectrometer at room temperature.

TGA measurement

Thermogravimetric analysis measurement was performed on a Dupont 2100 thermal analysis apparatus over temperature ranging from 30 to 500 °C at a rate of 10 °C/min. The extracted samples were measured in nitrogen atmosphere at a flow of 50 ml/min.

Determination of the percentage of grafting and the grafting efficiency

According to the results of TGA measurement, the percentage of grafting was determined by the following equation.

$$\mbox{Percentage of grafting (\%)} = \frac{\mbox{Polymer grafted (g)}}{\mbox{Modified TiO}_2 \mbox{ used (g)}} \times 100\%$$

s the mass percentage

(4)

The grafting efficiency was defined as the mass percentage of poly(MMA-M12-BPMA) grafted on TiO₂ particles based on total poly(MMA-M12-BPMA) and was determined by the following equation.

Grafting efficiency (%)

$$= \frac{\text{Polymer grafted (g)}}{\text{Monomers used (g)} \times \text{Conversion of monomers}}$$
$$\times 100\%$$

X-ray photoelectron spectroscopy measurement

XPS analysis was performed on a XPS spectrometer with $CuK\alpha$ radiation (40 kV, 25 mA) at a scanning speed $0.03^{\circ}/s$.

Table 1 Element components on the surfaces of poly(MMA-M12-BPMA)/ TiO_2

Elements	Content/%
С	81.12
O	17.78
Ti	0.45
S	0.73

Table 2 Molecular weight and molecular weight distribution of poly (MMA-M12-BPMA) and poly(MMA-M12-BPMA) grafted from the surface of TiO₂ particles

	poly(MMA-M12-BPMA)	poly(MMA-M12-BPMA)
$M_{ m n}$ (g/mol)	1.2680×10 ⁵	9.2008×10 ⁴
$M_{ m w}$ (g/mol)	2.7093×10 ⁵	1.9963×10 ⁵
$M_{ m z}$ (g/mol)	3.5301×10 ⁵	2.6933×10 ⁵
$M_{ m v}$ (g/mol)	2.7093×10 ⁵	1.9963×10 ⁵
D	2.1367	2.1697

GPC measurement

Molecular weight and molecular weight distribution of polymer samples were measured at 35 °C by GPC on a Waters 2410 instrument using THF as the solvent (1.0 ml/min).

UV-vis spectrophotometer measurement

Before measurements, the poly(MMA-M12)/TiO₂ composite particles were extracted by the same method of extracting the poly(MMA-M12-BPMA)/TiO₂ composite particles mentioned above. The extracted poly(MMA-M12-BPMA)/TiO₂ and the extracted poly(MMA-M12)/TiO₂ composite particles were treated with hydrofluoric acid (HF) to remove the TiO₂ particles. The UV-vis absorption spectrum of the poly(MMA-M12-BPMA) grafted from the surface of TiO₂, the pure poly(MMA-M12-BPMA), the poly(MMA-M12) grafted from the surface of TiO₂ were characterized by a UV-240 UV-vis spectrophotometer (Shimadzu Company, Japan) in the range of 200–450 nm using THF as solvent.

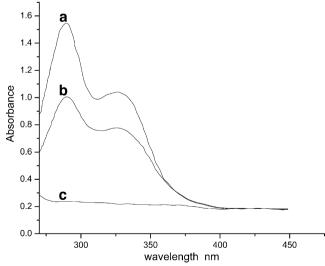


Fig. 7 The UV-vis absorption spectra of **a** poly(MMA-M12-BPMA), **b** poly(MMA-M12-BPMA) grafted from the surface of TiO₂, and **c** poly(MMA-M12) grafted from the surface of TiO₂ in THF



DSC measurement

The DSC measurements were carried out on a NETZSCH DSC 204 apparatus. Five milligrams of extracted sample was heated from 50 to 200 °C. The heating rate was 10 °C/min, and the test was under a nitrogen atmosphere. The data obtained from the second scanning were accepted.

SEM measurement

Morphology of the raw TiO₂ particles and the poly(MMA-M12-BPMA)/TiO₂ composite particles were observed by a JEOL JSM-5900LV scanning electron microscope.

Results and discussion

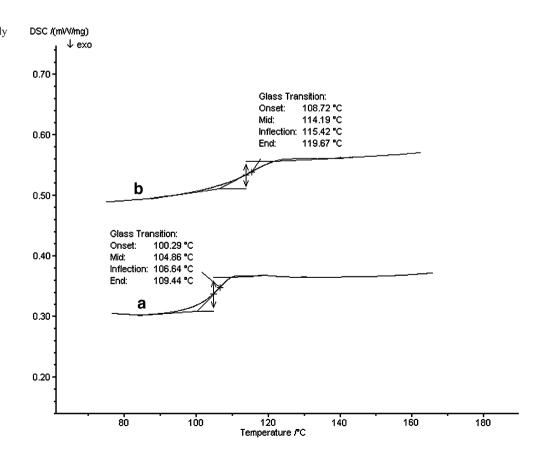
It is well known that there are lots of hydroxyl groups on the surface of TiO₂ which could react with organic compounds. In this paper, the poly(MMA-M12-BPMA)/TiO₂ composite latex was obtained through emulsion polymerization of M12 and BPMA with methyl methacrylate in the presence of TiO₂. The schematic procedure for the composite latex preparation is illustrated in Scheme 3. First, the surface-modified TiO₂ was prepared via the reaction between silane coupling

agent γ -MPS and TiO₂. And then, the modified TiO₂ containing carbon–carbon double bond reacted with methyl methacrylate, reactive UV stabilizer 2-hydroxy-4-(3-methacryloxy-2-hydroxylpropoxy) benzophenone (BPMA), and reactive surfactant sodium sulfopropyllaurylmaleate (M12) via emulsion copolymerization.

FTIR and TGA analysis of poly(MMA-M12-BPMA)/TiO₂ composite particles

To account for the polymerization of MMA, M12, and BPMA from the surface of TiO2, FTIR measurement was conducted. Before measurement, the products were extracted by the chloroform (99.0%) for 240 h firstly [the chloroform solution was replaced by the chloroform (99.0%) at the interval time during extraction of the products]. The free M12, BPMA, poly(MMA-M12-BPMA) and coupling agent can be removed. Figure 1 shows the FTIR spectra of chloroform (99.0%) and the chloroform solution after extracting the samples for 240 h. From Fig. 1a,b, it can be seen that there is no difference between the spectra of the chloroform solution after extracting 240 h and the chloroform (99.0%); only the characteristic absorption bands of >CH₂ at about 3,020 cm⁻¹ and that of C-Cl from chloroform at about 1,215 and 759 cm⁻¹ can be found, respectively. These results indicate that all the free M12,

Fig. 8 DSC curves of **a** poly (MMA-M12-BPMA) and **b** extracted poly(MMA-M12-BPMA)/TiO₂ composite particles





BPMA, poly(MMA-M12-BPMA), and coupling agent have been removed absolutely by extracting for 240 h.

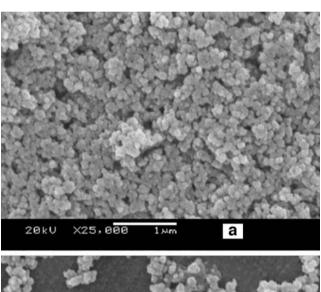
Figure 2 shows the FTIR spectra of (a) the modified TiO₂, (b) the poly(MMA-M12-BPMA), and (c) the extracted poly(MMA-M12-BPMA)/TiO2 composite particles. From Fig. 2a, it can be seen that there are characteristic absorptions at about 1,703 and 3,000 cm⁻¹, which are due to the stretching vibration of carbonyl group and >CH₂ in γ-MPS, respectively. Comparing the spectrum of the poly(MMA-M12-BPMA)/TiO₂ composite particles (Fig. 2c) with the modified TiO₂ (Fig. 2a), we can find the presence of absorption at 1,729 cm⁻¹, which is attributed to carbonyl group(>C=O) of methyl methacrylate. The absorption at 1,193 and 1,063 cm⁻¹ are attributed to sulfonic (>S-O) bands of M12. The appearance of absorption at 1,627 cm⁻¹ is attributed to ketone carbonyl group (>C=O) of BPMA. These characteristic absorptions discussed above are the same as the absorption of the poly(MMA-M12-BPMA; Fig. 2b). The absorption at 500–600 cm⁻¹ is characteristic of the Ti-O belonging to TiO2. The qualitative analysis of FTIR indicates that the poly(MMA-M12-BPMA) has been successfully grafted on the surface of TiO_2 .

TGA measurement is a quite helpful method to know how much polymer was grafted on the surface of the TiO2 particles. TGA measurement was conducted. The percentage of grafting and the grafting efficiency of the composite were determined by means of TGA. Figure 3 is the TGA curve of poly(MMA-M12-BPMA)/TiO₂ composite particles. In this figure, the weight loss is 77.11%, which attests that the poly(MMA-M12-BPMA) has grafted onto the TiO2 particles. The percentage of the remains is 22.89%, so the grafting percentage is 336.87% according to Eq. 3. As the conversion of monomers measured by gravity method is 93.54%, the grafting efficiency, calculated by Eq. 4, is 36.38%. Therefore, the poly(MMA-M12-BPMA)/TiO₂ composite particles with higher grafting percentage can be prepared. But the grafting efficiency is not high as expected; it might be ascribed to the low mass ratio of TiO₂ and MMA. The low mass ratio results in low reactive points density on the surface of the particle, so some of the monomers are copolymerized without TiO₂.

XPS analysis

X-ray photoelectron spectroscopy was used to determine surface elemental and chemical composition of the samples. Figure 4 is the XPS spectrum of the poly(MMA-M12-BPMA)/TiO₂ composite particles showing survey spectra. The XPS survey spectrum indicates the presence of titanium, oxygen, carbon, and sulfur. Figures 5 and 6 illustrate the XPS spectra of S2p and Ti2p in the poly (MMA-M12-BPMA)/TiO₂ composite particles, respective-

ly. The peak at about 169.0 eV is attributed to the sulfur. Further more, the element components on the surfaces of the poly(MMA-M12-BPMA)/TiO₂ composite particles were calculated by the method of atomic sensitivity factors [20]. The element components on the surfaces of poly (MMA-M12-BPMA)/TiO₂ are given in Table 1. The content of sulfur is 0.73%, which is attributed to the M12. Although KPS contains sulfur, the content is too low to be tested [21]. Therefore, the XPS spectrum of S2p further improves so that the M12 reacts with other monomers in the emulsion polymerization. The peak at about 458.5 eV is attributed to the titanium, and the content of titanium is 0.45%. But the grafting percentage is 336.87%, which is discussed above; the content of titanium must be much higher than 0.45%. Considering the depth of surface that the XPS method can measure, no more than 10 nm, the poly(MMA-M12-BPMA) must be coated on the surface of TiO₂. Most of the titanium cannot be tested by the XPS method. The results indicate that the shape of the Poly(MMA-M12-BPMA)/TiO₂ composite particles was core-shell.



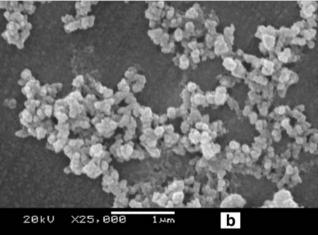


Fig. 9 SEM images of a raw TiO₂, b poly(MMA-M12-BPMA)/TiO₂ composite particles



GPC measurement

The molecular weight and molecular weight distribution were obtained by GPC measurements. Before the measurements, the extracted poly(MMA-M12-BPMA)/TiO₂ composite particles were treated with HF to remove the TiO₂ particles. The molecular weight and molecular weight distribution are summed up in Table 2. The molecular weight of the pure poly(MMA-M12-BPMA) is higher than that of poly(MMA-M12-BPMA) grafted from the surface of TiO₂ particles.

UV-vis spectrophotometer analysis

To enhance the UV-resistant performance of the polymethyl methacrylate, the reactive UV stabilizer BPMA was introduced into the polymethyl methacrylate chains by covalent bond. This way, UV stabilizer can be embedded in the polymer chains. The evaporation, migration, and distribution of the UV stabilizers will be settled and the service life of the polymethyl methacrylate will be prolonged. The ultraviolet absorption spectra of (a) the poly(MMA-M12-BPMA), (b) the poly(MMA-M12-BPMA) grafted from the surface of TiO₂, and (c) the poly (MMA-M12) grafted from the surface of TiO₂ are shown in Fig. 7. The curve c in Fig. 7 has no absorption band between 275 and 400 nm, which is ascribed to ultraviolet range. That might cause the polymethyl methacrylate to be easily destroyed under ultraviolet irradiation. The absorption band at 333 nm is due to the $\pi \rightarrow \pi^*$ transition and that at 285 nm is due to the $\pi \rightarrow \pi^*$ transition of BPMA [22] (curve a in Fig. 7). There are no differences between the ultraviolet absorption spectrum of poly(MMA-M12-BPMA) grafted from the surface of TiO₂ (curve b in Fig. 7) and that of poly(MMA-M12-BPMA; curve a in Fig. 7). It further indicates that BPMA has successfully reacted with MMA and M12 and grafted from TiO2. The poly(MMA-M12-BPMA) grafted from the surface of TiO₂ keeps the excellent character of BPMA that possesses high absorbance of ultraviolet light, which is very important for improving UV-resistant performance of the polymethyl methacrylate.

DSC analysis of poly(MMA-M12-BPMA)/TiO₂ composite particles

The DSC curves of copolymer poly(MMA-M12-BPMA) and poly(MMA-M12-BPMA)/TiO₂ composite particles are shown in Fig. 8. The copolymer poly(MMA-M12-BPMA) exhibits only one glass-transition temperature ($T_{\rm g}$) at 104.86 °C, which further proves that BPMA and M12 are copolymerized with methyl methacrylate. The glass-transition temperature of poly(MMA-M12-BPMA)/TiO₂ composite

particles was 114.19 °C. The increment of $T_{\rm g}$ was mainly ascribed to the confinement of the intercalated polymer chains within the ${\rm TiO_2}$ that prevent the segmental motions of the polymer chains. The DSC study also implied good thermal stability of the composite particles and successful bonding of the organic and inorganic component in the composite particles.

SEM measurement

The SEM images of the raw TiO₂ particles and the poly (MMA-M12-BPMA)/TiO₂ composite particles are shown in Fig. 9. The raw TiO₂ particles are elliptic in shape, and the surface of the particles are smooth (see Fig. 9a). The size of the TiO₂ particles is about 100 nm. After copolymerization with MMA, the surface of the TiO₂ particles becomes rough (see Fig. 9b) because of the grafting of poly(MMA-M12-BPMA) from the surface of the TiO₂ particles. The size of the composite particles is about 130–200 nm. According to the SEM images and the XPS analysis mentioned above, the poly(MMA-M12-BPMA) must be coated on the surface of TiO₂.

Conclusions

The poly(MMA-M12-BPMA)/TiO₂ composite particles are successfully prepared via in situ emulsion polymerization of a reactive surfactant sodium sulfopropyl-laurylmaleate (M12) and a reactive UV stabilizer 2-hydroxy-4-(3methacryloxy-2-hydroxylpropoxy) benzophenone (BPMA) with methyl methacrylate (MMA) in the presence of TiO₂. Furthermore, the percentage of grafting and the grafting efficiency are up to 336.87% and 36.38%, respectively. The glass-transition temperature (T_g) of composite particles is higher than that of copolymer poly(MMA-M12-BPMA), which implied good thermal stability of the composite particles. The size of the composite particles is about 130– 200 nm. The poly(MMA-M12-BPMA) grafted from the surface of TiO₂ keeps the excellent character of BPMA that possesses high absorbance of ultraviolet light. These research results are very important for preparing polymethyl methacrylate that can resists to UV light. The study on the UV-resistant performance of the poly(MMA-M12-BPMA)/TiO₂ composite particles is in process by our group and will be published in the near future.

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References

- Parmar RJ, Saxena S, Parmar JS (1998) Die Angewandte Makromolekulare Chemie 259:1–5
- Seliger H, Happa E, Cascaval A, Birsa L, Nicolaescu T, Poinescu I, Cojocariu C (1999) Eur Polym J 35:827–833
- 3. Liu N, Pan J, Lau WWY (1999) Polym Degrad Stab 63:71-77
- 4. Bojinov V, Grabchev I (2002) J Photochem Photobiol, A Chem 146:199–205
- 5. Liu X, Yang J, Chen Y (2002) Polym Adv Technol 13:247-253
- Allen NS, Edge M, Ortega A, Liauw CM, Stratton J, McIntyre RB (2002) Polym Degrad Stab 78:467–478
- Wang H, Xu P, Meng S, Zhong W, Du W, Du Q (2006) Polym Degrad Stab 91:1455–1461
- 8. Yang H, Zhu S, Pan N (2004) J Appl Polym Sci 92:3201-3210
- 9. Yang Y, Dan Y (2003) Colloid Polym Sci 281:794-799
- 10. Jiang L, Dan Y (2004) Colloid Polym Sci 282:1374-1380

- 11. Yang M, Dan Y (2005) Colloid Polym Sci 284:243-250
- Lee JY, Sung JH, Jung IB, Park BJ, Choi HJ (2005) Synth Met 153:221–224
- Jang IB, Sung JH, Choi HJ, Chin I (2005) J Mater Sci 40:3021– 3024
- Park JH, Lee MA, Park BJ, Choi HJ (2007) Current Applied Physics 7:349–351
- 15. Asua JM, Schoonbrood HAS (1998) Acta Polym 49:671-686
- 16. Guyot A, Tauer K, Asua JM et al (1999) Acta Polym 50:57-66
- 17. Guyot A (2002) Macromol Symp 179:105-132
- 18. Kozuka et al (1976) United States Patent 3,980,622
- 19. Goldberg AI et al (1964) United States Patent 3,162,676
- Wang J, Wu W, Feng D (1992) The introduction to electron spectroscopy (XPS/XAES/UPS). National Defense Industry Press, Beijing, pp 249–260
- Yang M (2006) Doctor dissertation of Sichuan University, Chengdu, pp 61–69
- 22. Zhao Y, Dan Y (2006) J Appl Polym Sci 102:2203-2211

