Preparation of Poly(methyl methacrylate)/Titanium Oxide Composite Particles via *in-situ* Emulsion Polymerization

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ABSTRACT: Poly(methyl methacrylate) (PMMA)/Titanium oxide (TiO_2) composite particles were prepared via *in-situ* emulsion polymerization of MMA in the presence of TiO_2 particles. Before polymerization, the TiO_2 particles was modified by the silane coupling agent, which is crucial to ensure that PMMA reacts with TiO_2 via covalent bond bindings. The structure of the obtained PMMA/TiO_2 composite particles was characterized using Fourier transform infrared spectra (FTIR) and thermogravimetric analysis (TGA). The results indicate that there are covalent bond bindings between PMMA macromolecules and TiO_2 particles. Based on these facts, several factors affecting the resulting PMMA/TiO_2 composite system, such as the type of coupling agents, the mass ratio of the MMA to the modified TiO_2, the emulsifier concentration, and the initiator concentration, etc., were examined by the measurement of conversion of monomers, the gel content of polymers, the percentage of grafting, and the grafting efficiency, using gravity method or TGA method. As a result, the optimized recipe was achieved, and the percentage of grafting and the grafting efficiency could reach 216.86 and 96.64%, respectively. In addition, the obtained PMMA/TiO_2 composite particles were found to a stable colloidal dispersion in good solvent for PMMA. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4056–4063, 2006

Key words: *in-situ* emulsion polymerization; graft polymerization; poly(methyl methacrylate); titanium oxide; composite particles

INTRODUCTION

Owing to their extraordinary properties based on the combination of the merits of polymers, e.g., elasticity, easy-processing, and transparency, with the better properties of inorganic materials, e.g., specific absorption of light, heat resistance, stability in performance, and catalysis, the inorganic/polymer composite particles are promising system in the materials area. These materials have gained much interest due to the remarkable change in properties such as thermal, electrical, and magnetic,[1] compared to pure organic polymers. For example, poly(maleic anhydride–styrene)/silicon dioxide was applicable to preparation of titania photocatalyst systems, which exhibited photo-induced electron-transfer catalysis by visible light.[2] Polyvinyl carbazole/cadmium sulfide nanocrystal polymer composite could be used as photoconducting materials. The resulting materials allowed the tuning of the band-gap of the sensitizing nanocrystals, so that their spectral response was adjusted to suit a particular wavelength of operation.[3] The enhancement of mechanical and thermal properties of polymers by inclusion of inorganic materials, especially in the form of nanocomposites, offered the possibility for these materials to substitute classical compounds based on metals or on traditional composites in the transportation industry.[4] Solid-state lithium batteries or supercapacitors had been produced using organic–inorganic polymeric systems.[5]

The combination of inorganic particles with polymers is accomplished by means of surface encapsulation or surface grafting. Surface encapsulation, belonging to simple physical mixture, may lead to separation in discrete phases, resulting in poor mechanical optical properties of the resulting materials, whereas surface grafting can endue a strong interaction between polymer and inorganic particle. As to surface grafting, there are two methods: one is "grafting to"[6] (i.e., end-functionalized polymers are grafted to the surface of inorganic particles) the other is "grafting from"[7] (i.e., the polymer is grafted *in situ* from the surface of inorganic particles). As far as "grafting to" method is concerned, the reaction should be carried out by solution polymerization or bulk polymerization. However, the "grafting from" method is not

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limited to these, i.e., surface grafting from the surface of inorganic particles can be carried out in aqueous medium through emulsion polymerization process.

Owing to its unique advantages, such as environment friendliness, high reaction rate, and relative simple engineering technology in industrialization, the emulsion polymerization has attracted extensive interests. In the literature, the relative work, preparation of inorganic/polymer composite by *in situ* emulsion polymerization was reported by Hasegawa et al., [8] Jesionowski et al., [9] Wang et al.,[10] etc., but the polymerization mechanism all belong to surface encapsulation without covalent bond bindings. There have been also some reports on 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] etc., and much progress have been made. But, there still exists 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 obtained system was less stable. Nevertheless, the percentage of grafting and the grafting affects the structure and performance of the inorganic/polymer composite particles to a great degree. At present, how to improve the percentage of grafting and the grafting efficiency and to enhance the stability of polymerization system is still focus of attention, which also is the objective of our research.

Owing 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 study, PMMA/TiO_2 system was chosen as a model to prepare inorganic/polymer composite particles via emulsion polymerization. The structure of the obtained PMMA/TiO_2 composite particles was characterized using FTIR and TGA. Several factors affecting the resulting PMMA/TiO_2 composite system, such as the type of coupling agents, the mass ratio of the MMA to the modified TiO_2, the emulsifier concentration, the initiator concentration, etc., were examined by the measurement of conversion of monomers, the gel content of polymers, the percentage of grafting, and the grafting efficiency using gravity method or TGA method. Especially, the factors affecting the percentage of grafting and the grafting efficiency were investigated with emphasis. As a result, the optimized recipe was achieved, and the percentage of grafting and the grafting efficiency could reach 216.86 and 96.64%, respectively. In addition, the obtained PMMA/TiO_2 composite particles were found to a stable colloidal dispersion in good solvent for PMMA.

EXPERIMENTAL

Materials

The methyl methacrylate (MMA), purchased from Rongfeng Chemical Reagents Factory (China), was distilled under reduced pressure prior to use, to remove the inhibitor. The titanium dioxide particles (TiO_2) with specific surface of ~130 m^2/g were from Materials College of Sichuan University (China). The coupling agents, used for modifying the surface of the TiO_2 particles, were 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 purification, acting as emulsifier agent and initiator, respectively. The calcium chloride ($CaCl_2$) was obtained 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 modified by 5% coupling agent (based on the content of the TiO_2 particles) that was diluted by 95% ethanol. Before polymerization, the modified TiO_2 particles were Soxhlet extracted with refluxing ethanol at water bath (80°C) for 72 h, to remove the coupling agent physically adsorbed on the surface of TiO_2 particles.

Preparation of the PMMA/TiO_2 composite particles

To obtain PMMA/TiO_2 composite particles, the PMMA/TiO_2 composite lattices were prepared first by grafting PMMA from the surface of TiO_2 via *in-situ* emulsion polymerization. First, 0.08−0.4 g SLS was dissolved in 31–35 g deionized water, and then 1–5 g modified TiO_2 was dispersed in SLS aqueous solution under ultrasonic vibrations for 5 min. Under vigorous stirring, the modified TiO_2 slurry was diverted into 125-mL three-necked flask (TNF) equipped with mechanical stirrer, thermometer, and drop funnel. When temperature rose to 60−70°C, 5–9 g 0.5 wt % (based on the mass of MMA) KPS aqueous solution was charged in the TNF. Five minutes later, the purified MMA monomer was trickled slowly into the TNF, and after an hour, the monomer was trickled completely. The reaction was continued for about an hour, then the system was cooled naturally, and the PMMA/TiO_2 composite latex was obtained. By precipitating the latex with the 5 wt % $CaCl_2$ aqueous solution, filtering, washing, drying, and pulverizing, the PMMA/TiO_2 composite particles were obtained.

Preparation of the PMMA/unmodified TiO_2 particles

The reaction procedure of preparation of the PMMA/unmodified TiO_2 particles are similar to that of the preparation of the PMMA/TiO_2 composite particles; only the modified TiO_2 particles were replaced with the unmodified TiO_2 particles.

Preparation of the PMMA particles

The PMMA particles were obtained through traditional emulsion polymerization of MMA. First, 20 g purified MMA monomer, 1.6 g SLS, 80 g water, and 0.1 g KPS were charged in the TNF with thermometer, reflux condenser, and stirrer. Then, polymerization was carried out at 80 ± 0.5 (°C) for 2 h with stirring. After cooling, the obtained PMMA latex was coagulated with the 5% $CaCl_2$ aqueous solution, and the precipitate was filtered, washed with water to remove emulsifier, dried at 60°C, and pulverized. After that, the PMMA particles were obtained.

Preparation of the PMMA/TiO_2 mixture

The PMMA/TiO_2 mixture was obtained by directly mixing the PMMA particles with the modified TiO_2 particles at the different mass ratio of PMMA to TiO_2 at ambient temperature.

Characterization

Solid content of the composite latex

Before measurement of the solid content ($S\%$), the latex was filtered to remove the gel. The solid content 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; and M_3 is mass of the inhibitor.

Conversion of MMA

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.

Gel content of the composite latex

The gel content ($G\%$) of the composite latex was calculated by the eq. (3)

$$G\% = \frac{M_5}{M_4 \times (X + Y)} \times 100\% \tag{3}$$

FTIR measurement

Before the FTIR measurement, both of the PMMA/TiO_2 composite particles, the unmodified PMMA/TiO_2 particles, and the PMMA/TiO_2 mixture were Soxhlet extracted with refluxing $CHCl_3$ at water bath (70°C) for 72 h, to remove the free PMMA. Then, the purified samples and the pure PMMA were prepared in the form of potassium bromide pellets. FTIR measurements of all the samples were carried out on Nicolet 560 FTIR spectrometer.

Tga measurement

Thermogravimetric analysis (TGA) was performed on a Dupont 2100 thermal analysis apparatus over the temperature range 30–500°C at a rate of 10°C/min. The samples were heated in nitrogen atmosphere, and the rate of N_2 was 50-mL/min. Before TGA measurements, both of the PMMA/TiO_2 composite particles and the PMMA/TiO_2 mixture were Soxhlet extracted with refluxing $CHCl_3$ at water bath (70°C) for 72 h, to remove the free PMMA.

Determination of the percentage of grafting and the grafting efficiency

The percentage of grafting was determined by the following equation[13]

$$\text{Percentage of grafting (\%)} = \frac{\text{Polymer grafted (g)}}{\text{Modified TiO}_2\text{ charged (g)}} \times 100\% \tag{4}$$

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 total PMMA, and was determined by the following equation

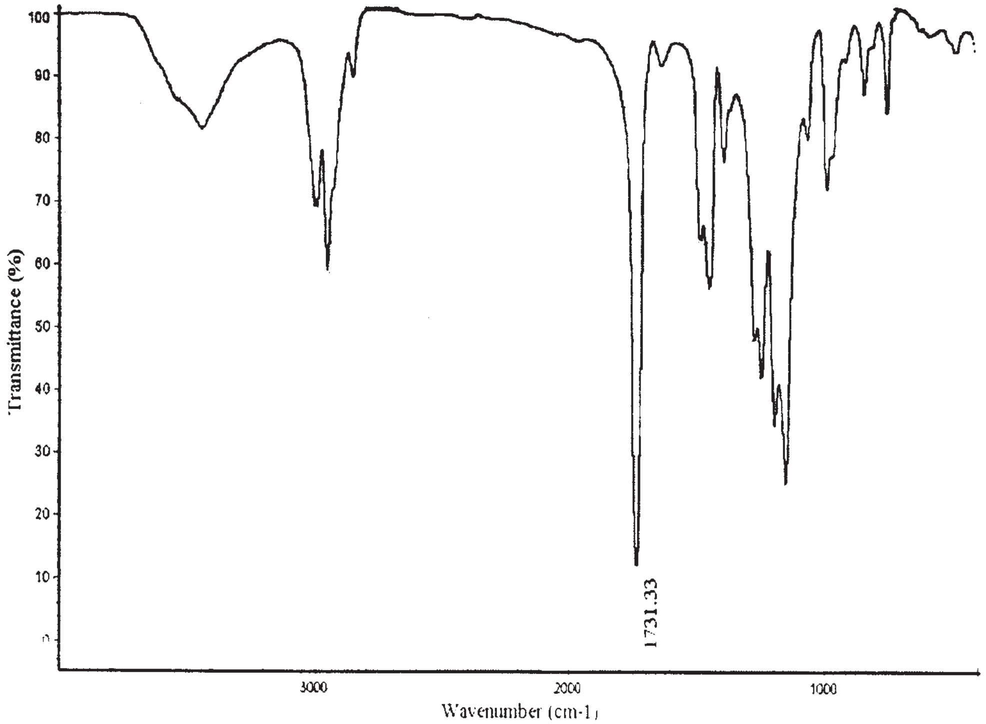

Figure 1 FTIR spectrum of the PMMA.

Grafting efficiency (%)

$$= \frac{\text{Modified TiO}_2\text{ charged} \times \text{percentage of grafting}}{\text{MMA charged} \times \text{conversion of MMA}} \times 100\% \quad (5)$$

RESULTS AND DISCUSSION

It is well-known that, in general, inorganic particles have hydroxyl groups on their surface, which can react with alkoxy silane. In the present article, the grafting of PMMA from the surface of TiO$_2$ particles was achieved by the reaction of double bonds groups introduced onto the surfaces using the coupling agent with MMA monomers. The structure of the obtained samples was characterized by FTIR. Several factors affecting the grafting of PMMA from the surface of the modified TiO$_2$ particles, such as the type of coupling agent, the mass ratio of the MMA monomer to the modified TiO$_2$, the emulsifier concentration, and the initiator concentration, were investigated. In the course of discussion, the percentage of grafting and the grafting efficiency were probed with emphasis.

Ftir analysis

To testify that silane coupling agent plays an important role in the formation of the covalent bond bindings between PMMA and the TiO$_2$ particles during the preparation of the PMMA/TiO$_2$ composite particles, the polymerization of MMA was achieved in the presence of (A) the unmodified TiO$_2$ particles and (B) the modified TiO$_2$ particles, respectively. The resulting products are signed as the PMMA/unmodified TiO$_2$ particles and the PMMA/TiO$_2$ composite particles. Attempts were made to remove the free PMMA by the Soxhlet extraction with the refluxing CHCl$_3$ at water bath (70°C) for 72 h. The structure of the composite particles was studied by FTIR. Figure 1 shows the FTIR spectrum of the PMMA, which exhibited characteristic absorptions of carbonyl groups at 1732 cm^{-1}. In this research system, absorption bands at about 1730 cm^{-1} can testify the existence of PMMA macromolecules. Figure 2 illustrates FTIR spectra of the PMMA/unmodified TiO$_2$ particles and the PMMA/TiO$_2$ composite particles. From Figure 2, it can be seen that FTIR spectrum of the extracted PMMA/TiO$_2$ composite particles exhibits characteristic absorption band of carbonyl groups in PMMA at 1727 cm^{-1}, while that of the extracted PMMA/unmodified TiO$_2$ particles does not appear absorption at 1727 cm^{-1}, indicating that the coupling agent plays a bridge role in connecting the TiO$_2$ particles with PMMA and that has successfully grafted from the surface of TiO$_2$ particles.

Effects of the type of coupling agent

The general formula of the coupling agent used in this research system is expressed as $CH_2{=}C(R_1)\ R_2$ Si

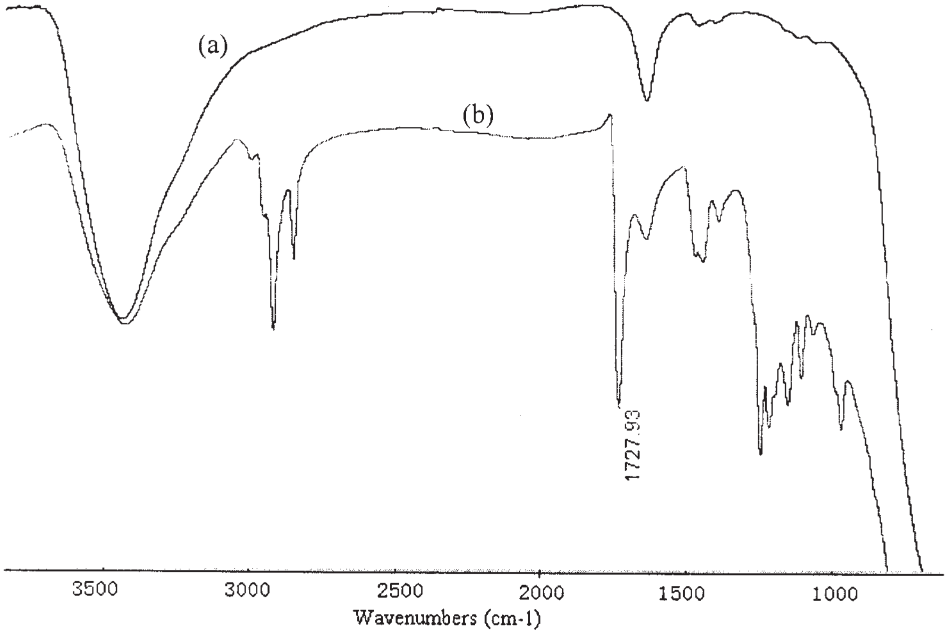

Figure 2 FTIR spectra of (a) the unmodified PMMA/TiO_2 particles and (b) the PMMA/TiO_2 composite particles.

$(OR_3)_3$, where, R_1 is CH_3 or H; R_2 is zero or $COO(CH_2)_3$; and R_3 is CH_3 or C_2H_5. Three PMMA/TiO_2 composite particles were obtained with the same recipe (except for the type of coupling agent) and the same polymerization process, and the three samples were treated and extracted under the same conditions. The results of the effects of the type of coupling agent on the grafting efficiency are shown in Table I. It can be seen that the grafting efficiency of PMMA from the surface of TiO_2 modified by the coupling agent A and the coupling agent B are by far smaller than that by the coupling agent C, which is in accordance with the fact that vinyl group of the coupling agent C is more reactive than that of the coupling agent A and B. On the basis of the above results, we select the coupling agent C to modify TiO_2 particles in the following experiments.

TABLE I
The Effect of Type of Coupling Agent on the Grafting Efficiency

Type of coupling agent	Grafting efficiency (%)
A	14.05
B	15.36
C	46.3

General formula of the coupling agent is A: R_1= H, R_2 = zero, R_3 = CH_3; B: R_1 = H, R_2 = zero, R_3 = C_2H_5; C: R_1 = CH_3, R_2 = COO $(CH_2)_3$, R_3 = CH_3 MMA: modified TiO_2 is 9:1; SLS concentration is 2%; KPS concentration is 0.5%.

Effects of the mass ratio of the MMA monomer to the modified TiO_2

The results of the conversion of the MMA monomer and the gel content of the products with different mass ratio of the MMA to the modified TiO_2 are illustrated in Figure 3. It can be seen that with increasing the content of the modified TiO_2, the conversion of MMA tends to decrease and the gel content of polymerization system tends to increase; when mass ratio of the MMA to the modified TiO_2 is at the range of 9.5:0.5–6:4, the change is slight, while when mass ratio of the

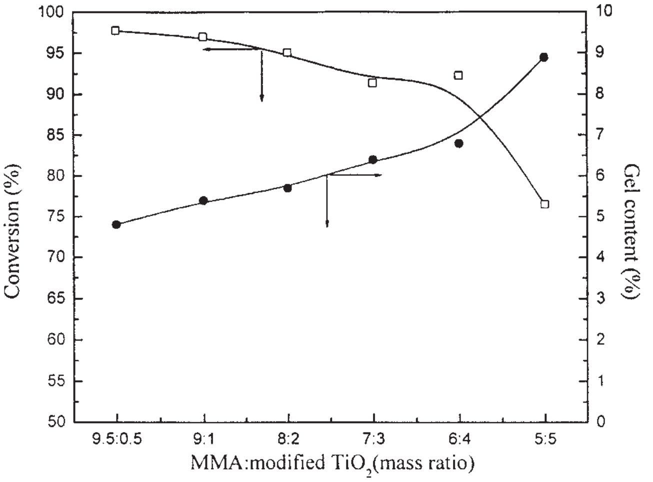

Figure 3 The conversion of MMA and the gel content of PMMA/TiO_2 composite system versus mass ratios of the MMA to the modified TiO_2. SLS concentration is 1% KPS concentration is 0.5%.

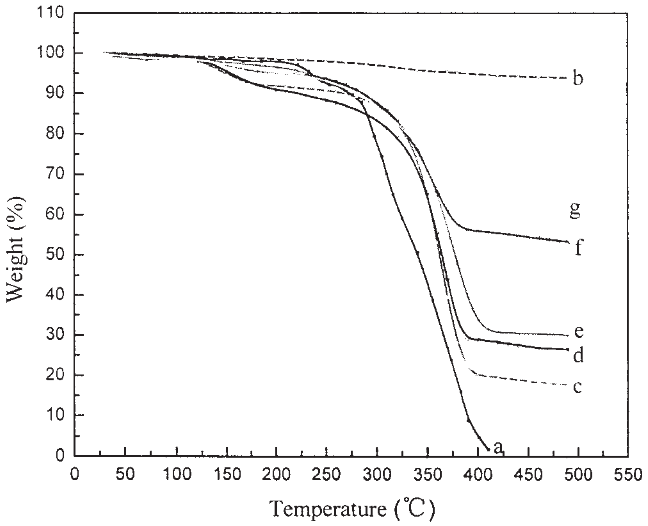

Figure 4 TGA curves of (a) PMMA, (b) PMMA/TiO$_2$ mixture, and (c–g) PMMA/TiO$_2$ composite with different mass ratio of the MMA to the modified TiO$_2$ particles. MMA: modified TiO$_2$: (c) 9:1, (d) 8:2, (e) 7:3, (f) 6:4, (g) 5:5.

MMA to the modified TiO$_2$ is 5:5, the change is obvious, relatively, which may result from more interparticle collision due to an increase of the content of modified TiO$_2$ particles.

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. To prove that the ungrafted PMMA in the composite system can be extracted completely, the PMMA/TiO$_2$ mixture with 10:1 mass ratio of the PMMA to the modified TiO$_2$ and PMMA/TiO$_2$ composite particles was extracted by $CHCl_3$ at the same temperature and 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. The TGA curve of (a) PMMA, (b) PMMA/TiO$_2$ mixture and (c–g) PMMA/TiO$_2$ composite particles with different mass ratio of the MMA to the modified TiO$_2$ is shown in Figure 4. In the Figure 4 (b), the weight loss was 5.32%. Considering that TiO$_2$ particles modified with 5% coupling agent before polymerization, we can infer that the ungrafted PMMA was extracted completely. Weight loss and remains of PMMA/TiO$_2$ composite with different mass ratio of the MMA to the modified TiO$_2$ are summarized in Table II, while the results of the percentage of grafting and the grafting efficiency calculated by eqs. (3) and (4) are shown in Table III. It can be seen that, with increasing of modified TiO$_2$ particles, the remains of PMMA/TiO$_2$ composite particles increase (Table II), and the percentage of grafting decreases (Table III); the grafting efficiency increases first and then decreases (Table III). When mass ratio of the MMA to the modified TiO$_2$ particles is 7:3, the grafting efficiency is the highest (Table III). Results of TGA measurements confirm again that the PMMA molecules are grafted from the surface of TiO$_2$ particles, and the grafting efficiency is higher, reaching 96.64%.

TABLE II
Weight Loss and Remains of the PMMA/TiO$_2$ Composite Particles with Different Mass Ratio of the MMA to the Modified TiO$_2$

	MMA:modified TiO$_2$ (mass ratio)				
	9:1	8:2	2:3	6:1	5:5
Weight loss (%)	71.81	61.1	62.53	39.15	30.74
Remains (%)	17.74	26.48	30.02	53.344	60.93

TABLE III
The Percentage of Grafting and the Grafting Efficiency of PMMA/TiO$_2$ Composite Particles with Different Mass Ratio of the MMA to the Modified TiO$_2$

	MMA:modified TiO$_2$ (mass ratio)				
	9:1	8:2	7:3	6:4	5:5
Percentage of grafting (%)	399.79	225.74	216.86	68.40	45.45
Grafting efficiency (%)	43.49	56.39	96.64	46.95	56.44

Further, from Figure 4, the decomposition temperatures of PMMA and PMMA/TiO$_2$ composite particles with different mass ratio of the MMA to the modified TiO$_2$ were obtained, and the data are listed in Table IV. The results show that the decomposition temperature of PMMA/TiO$_2$ composites is higher than that of PMMA generally. It is TiO$_2$ particles' crosslinked role in polymerization process that leads to the decomposition temperature rise. This is an interesting result and it will be researched with emphasis in our following work.

Effects of the emulsifier concentration

The emulsifier concentration of reaction system is directly relative to the stability of the latex. The function of emulsifier here is similar to that in the traditional

TABLE IV
Comparison of Decomposition Temperatures of PMMA and PMMA/TiO$_2$ Composite Particles with Different Mass Ratio of the MMA to the Modified TiO$_2$

		MMA:modified TiO$_2$ (mass ratio)				
	PMMA	9:1	8:2	7:3	6:4	5:5
Decomposition temperature (°C)	294.63	334.76	336.74	324.87	311.86	306.86

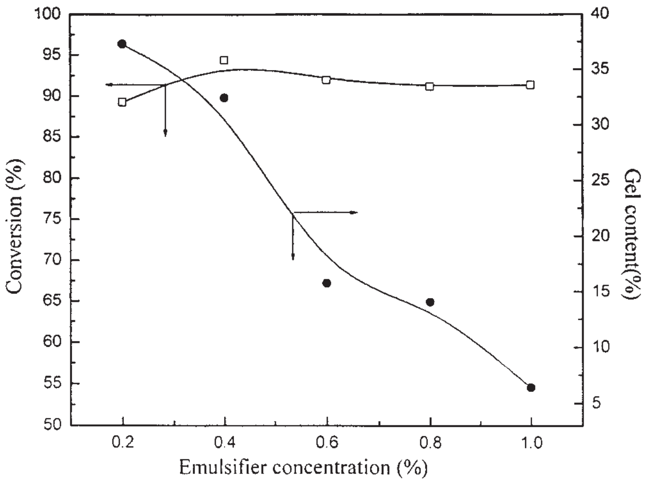

Figure 5 The conversion of MMA and the gel content of PMMA/TiO_2 system versus emulsifier concentrations. MMA: modified TiO_2 is 7:3; KPS concentration is 0.5%.

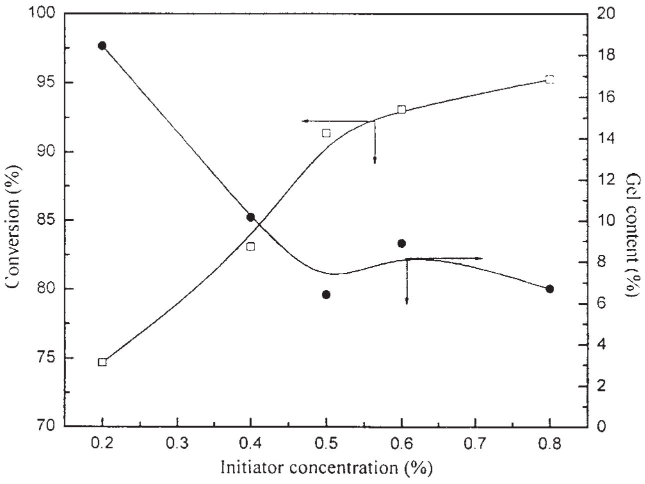

Figure 6 The conversion of MMA and the gel content of PMMA/TiO_2 composite system versus initiator concentrations. MMA: modified TiO_2 is 7:3; SLS concentration is 1%.

emulsion polymerization. When the composite particles are encapsulated by the emulsifier completely, the composite latex is stable; in reverse, the composite latex is instable. To obtain the stable latex and avoid producing more ungrafted PMMA, emulsifier concentration was selected from 0.2 to 1% based on mass of deionized water. Figure 5 shows the conversion of the MMA and the gel content of the PMMA/TiO_2 composite system with different emulsifier concentrations. From Figure 5, it can be seen that the conversion of the MMA is less pertinent to the emulsifier concentration, while to which the gel content of PMMA/TiO_2 system is closely pertinent. With increasing the emulsifier concentration, the gel content decreases sharply. When emulsifier concentration is 1%, the gel content is the lowest.

Effects of the initiator concentration

In the research system, the initiator can initiate both MMA to form the homopolymerized PMMA and vinyl group of modified particles to further form grafted PMMA, which is a competitive course. When the former is predominant, the percentage of grafting and the grafting efficiency will be lower; in reverse, the percentage of grafting and the grafting efficiency will be higher. The conversion of MMA and the gel content of PMMA/TiO_2 composite system with different initiator concentrations are illustrated in Figure 6. It can be seen that with increasing initiator concentration, the conversion increases and the gel content decreases. When the initiator concentration increases to 0.5%, not only the conversion but also the gel content tends to vary little. Table V lists the percentage of grafting and the grafting efficiency of PMMA/TiO_2 composite particles with different initiator concentration. When initiator concentration increases, the percentage of grafting and the grafting efficiency increase first, and then decrease. When initiator concentration is 0.5%, both the percentage of grafting and the grafting efficiency are the highest. In other words, a moderate increase of initiator concentration can promote more PMMA graft from the surface of TiO_2 particles. However, when initiator concentration increases ulteriorly, more ungrafted PMMA is formed.

Dispersibility of the PMMA/TiO_2 composite particles

In actual application, the dispersibility of the inorganic–organic composite in the polymer matrix or organic solvent is very important. The stability of the PMMA/TiO_2 composite particles in $CHCl_3$ was compared with that of unmodified TiO_2 particles and PMMA/TiO_2 mixture. The unmodified TiO_2 particles precipitated completely within several minutes. The modified TiO_2 particles precipitated completely after 12 h. The stability of the PMMA/TiO_2 mixture in

TABLE V
The Percentage of Grafting and the Grafting Efficiency of PMMA/TiO_2 Composite Particles with Different Initiator Concentrations

	Initiator concentration (%)				
	0.2	0.4	0.5	0.6	0.8
Percentage of grafting (%)	154.87	161.83	216.86[a]	109.58	121.43
Grafting efficiency (%)	79.89	92.87	96.64[a]	50.44	54.63

[a] Results from the TGA measurements.

$CHCl_3$ is hardly improved. However, the PMMA/TiO_2 composite particles were found to a stable colloidal dispersion in $CHCl_3$.

CONCLUSIONS

PMMA/TiO_2 composite particles based on covalent bond bindings can be prepared via *in-situ* emulsion polymerization of MMA in the presence of TiO_2 particles. The polymerization process is stable. Under the optimized recipe of the reaction system, the percentage of grafting and the grafting efficiency could reach 216.86 and 96.64%, respectively. The PMMA/TiO_2 composite particles exhibit a stable colloid dispersion in $CHCl_3$.

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