Plasma Induced Grafting of PSt onto Titanium Dioxide Powder. II

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ABSTRACT: Grafting of polystyrene (PSt) onto titanium dioxide powder was investigated in this study. The graft polymerization reaction was induced by N_2 plasma treatment of the surfaces of the titanium dioxide powder. IR and XPS results showed that PSt was grafted onto the titanium dioxide powder. The crystal structure of the titanium dioxide powder observed by XRD spectra was unchanged after plasma graft polymerization. In the grafting reaction, the grafting yield increased with the plasma power, the plasma treatment time, and the grafting reaction, but it increased first then decreased after reaching 50°C. The type of monomers also has an effect on the grafting yield. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2112–2117, 2005

Key words: graft polymerization; plasma; PSt; surface modification; titanium dioxide

INTRODUCTION

Titanium dioxide powder is a kind of typical ultrafine inorganic powder. Its unique physical chemistry properties and excellent pigmentary characteristics have been widely applied in solar cells, gas sensors, photocatalysts, and so forth.[1–10] The surface of titanium dioxide powder has to be treated to passivate its photocatalysis activity and improve its dispersion in organic media for application. So titanium dioxide powder usually needs surface modification coated by macromolecular surfactants or coupling reagents on its surface. The conventional way is to introduce surfactants or coupling reagents by physical adsorption or chemical reaction in solution.[8–29] This has some disadvantages. For instance, the pigment cannot be filled too much in the fibers, it costs too much, it pollutes the environment, and so forth.

Surface modification processes of low-temperature plasma were first developed in the 1960s.[30] They have been widely recognized during the last 20 years, and several successful applications have emerged. Low temperature plasma has many particularly appreciated advantages for surface modification applications. For instance, it has free radicals, charged particles, and, especially, energetic electrons. These particles not only have high enough energy to activate, ionize, or bond-break reactant molecules, but also cannot decompose or ablate the materials when disposing of them. They can only change the surface properties of the materials rather than the bulk properties. It does not pollute our environment. It can reduce energy consumption, and so on.[30,31]

It is well-known that radicals are formed not only on the surface of organic materials but also on the surface of inorganic materials during plasma treatment.[32–39] Some of the radicals on material surfaces produced by plasma treatment can initiate graft polymerization of vinyl monomers.[34–39] Most of these are about plasma-initiated graft polymerization of vinyl monomers on bulk materials, but few investigations have been reported about plasma-initiated graft polymerization of vinyl monomers on powder, especially inorganic powder.[40] It is difficult to handle powder in plasma because of its aggregation and large surface area per mass unit. In surface modification by plasma, it is necessary to touch the surface of the powder with plasma. The untouched regions of the particle surfaces are never modified. Therefore, the aggregation of the powder should be destroyed in plasma and all particle surfaces should coercively touch plasma.[41]

Low-temperature plasma can be obtained by dielectric barrier discharge, microwave discharge, radio frequency discharge, hollow cathode discharge, and so forth. The radio frequency discharge technique (13.56MHz) was introduced in this study, to form radical groups on the surface of titanium dioxide powder and then graft PSt on it. To prevent aggregation among the powder and make sure that the powder will be well treated, the reactor is a modified flask-rotation type, in which liquid monomers are introduced into the flask after plasma treatment of the powder without breaking the vacuum.[42] The surface structure of the powder was detected by IR and XPS.
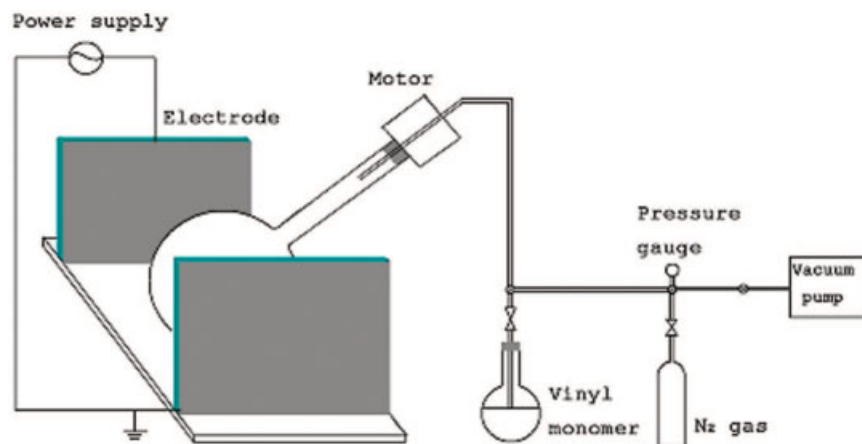
Figure 1 The scheme of the RF discharge plasma treatment instrument. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

XRD was also used to detect the crystal pattern before and after plasma treatment. The graft yield was determined by the weight difference of the titanium dioxide powder before and after the grafting reaction measured by TGA results. The effects of several factors on grafting have been studied, such as plasma power, plasma treatment time, grafting temperature, and so forth.

EXPERIMENTAL

Materials

Titanium dioxide (TiO$_2$) powder (4N, rutile) was obtained from Tianjin Delan Fine Chemical Factory, Tianjin, China. It was dried in vacuum at 110°C for 48 h before use. The styrene, provided by Shanghai Chemical Reagent CO. Ltd.(Shanghai, China), was purified by distillation at a reduced pressure. Nitrogen (N$_2$, 99.9%) was from Foshan Kedi Gas Chemical Industry CO., Ltd. Other reagents used were all analytical grade reagents.

Set-up and treatment

The power supply was fed into one electrode of 150 × 100 mm^2, and the other electrode was grounded. The electrical parameters were measured via a high-voltage attenuator (see Fig. 1). First, titanium dioxide powder (3g) was placed in the flask and evacuated to 5 × 10^{-3} torr and flashed with nitrogen gas, then evacuated to 1 × 10^{-2} torr. After flashing and evacuating three times, the titanium dioxide powder was treated under N$_2$ plasma (RF: 13.56MHz) of 5 × 10^{-2} torr. During plasma treatment, the flask was rotating. After treatment of 60 min, 20 mL styrene was introduced into the flask and the solution was stirred without breaking the vacuum.[42] After reaction, the mixture was centrifuged. The grafted TiO$_2$ was then extracted

three times with toluene to remove the excess monomer and PSt homopolymer. Then the product was dried under vacuum at 110°C and stored at room temperature in a dark place.[29,43]

The graft yield was determined by the weight difference of the titanium dioxide powder before and after the grafting reaction measured by TGA results. The degree of grafting was determined by the following equation:[44–46]

$$\text{Degree of grafting}(\%) = \frac{Wg - Wo}{Wo} \times 100$$

where Wg and Wo are the weights of the grafted and ungrafted titanium dioxide powder, respectively.

Measurements

IR spectra were obtained using a MAGNA IR 750 Spectrometer (USA). The sample for IR measurement is prepared by the KBr technique. Only the wavenumber region from 4000–400cm^{-1} is relevant to our discussion.

Wide angle X-ray diffraction measurements are taken on a Philip PW1700 X-ray automated powder diffractionmeter (Holand): Cu Kα radiation, 60KV voltage, 50MA current. The powder of the original and that of the grafted titanium dioxide were pressed into films at room temperature to prepare the samples for XRD measurement.

X-ray photoelectron spectroscopy (XPS) analysis was performed using an ESCALAB MK II spectrometer (UK), which utilizes Mg K-Al X-rays for excitation of the sample. The C1s spectra were decomposed by fitting the Gaussian function to the experimental curve, using a nonlinear, least-squares curve fitting program.

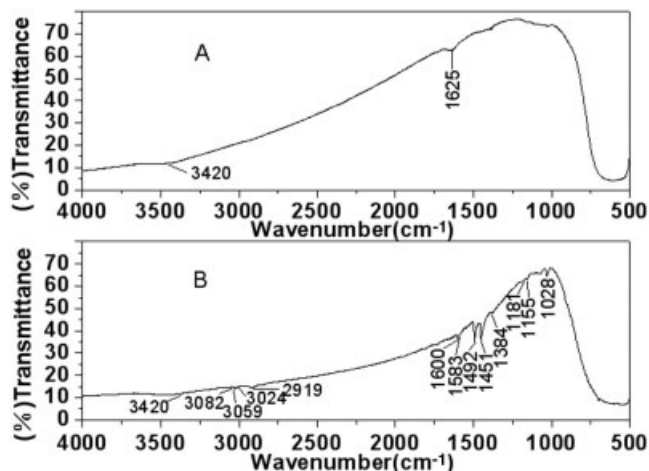**Figure 2** (A) IR spectra of the untreated TiO_2; (B) IR spectra of the grafted TiO_2.

Thermogravimetric analysis (TGA: TA-50, Shimadzu, Japan) was applied to estimate the quantity of polymer on the TiO_2 surface. The thermogravimetric analyzer operated between room temperature and 800°C in air flow with a heating rate of $10°Cmin^{-1}$.

RESULTS AND DISCUSSION

IR results

Grafted TiO_2, prepared by this process, was first examined by an infrared spectrum. The IR spectra of grafted TiO_2 after extraction by toluene and that of untreated TiO_2 particles are shown in Figure 2. From Figure 2A we can see that the untreated titanium dioxide sample only has absorbance peaks corresponding to hydroxyl or the adsorption water between $4000 \sim 1100cm^{-1}$. The broad peak at $3420cm^{-1}$ corresponds to the stretching motion of the surface hydroxyl or the adsorption water; the peak at 1620 cm^{-1} corresponds to the flexural vibration of the H-O-H bonds of the adsorbed water.[26] For the styrene grafted titanium dioxide (Fig. 2B), however, new absorbance peaks appear. The phenyl stretching bands are observed near $1600 \sim 1580cm^{-1}$. The C=C-H stretching bands are observed between 3082–3024 cm^{-1}. The -C-H stretching bands are observed near $2919cm^{-1}$. The –C-H bending bands are observed between $1492 \sim 1384cm^{-1}$. Also, the -O-C stretching bands are observed in the region of $1268 \sim 1119cm^{-1}$. According to Lin and coworkers,[25,26] polymer that is adsorbed on TiO_2 by physical adsorption can be completely desorbed from the surface by long time solvent extraction, leaving only grafted polymer unaffected. Therefore, the PSt on the surface is in connection with TiO_2 via chemical bonds.
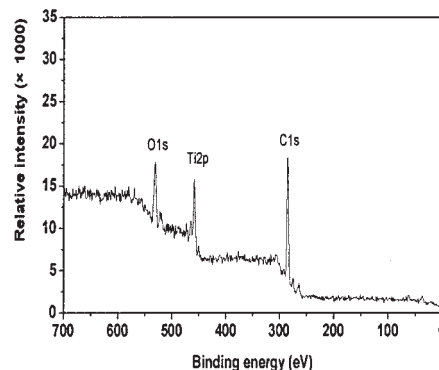

Figure 3 The survey spectra of the grafted TiO_2 after toluene extraction.

XPS spectra

The properties of the TiO_2 surface were further investigated by X-ray photoelectron spectroscopy (XPS). Figure 3 is the survey spectrum of the grafted TiO_2 after toluene extraction. It contains a C1s peak in addition to the Ti2p and O1s peaks, confirming the presence of the polymer in the sample. Figure 4 shows the high-resolution XPS spectra of the O1s peaks of the grafted TiO_2 after toluene extraction. The O1s region is decomposed into three contributions. The peaks at 530.0eV and 531.5eV correspond to Ti-O in TiO_2 and the hydroxyl groups(-OH), respectively. The peak at binding energy of 532.2eV corresponds to the oxygen species Ti-O-C, according to Beamson.[47] The chemical bond Ti-O-C shows that polystyrene was grafted onto the surface of the titanium dioxide powder.

XRD

As previously mentioned, active groups were formed on the surface of the titanium dioxide powder through N_2 plasma treatment and initiated the graft polymerization of styrene. Figure 5 shows the X-ray diffraction pattern of the original and the modified titanium dioxide powder. The crystals of titanium dioxide powder are rutile before and after graft polymerization,
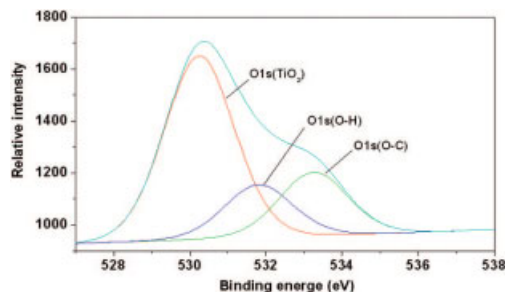

Figure 4 O1s spectra of the PSt-grafted TiO_2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
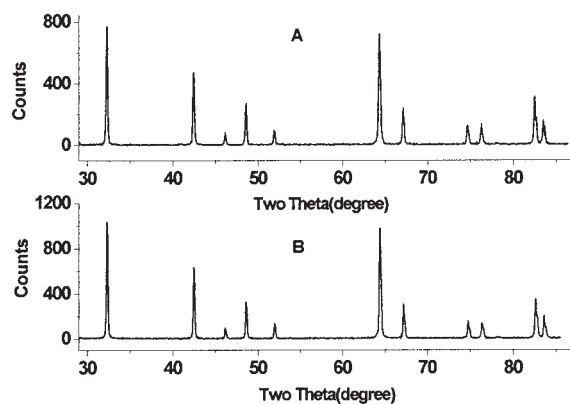
Figure 5 (A) The XRD spectra of the treated TiO$_2$; (B) the XRD spectra of the untreated TiO$_2$.

which means that the crystal pattern didn't change and the segment of PSt had not entered the crystal pattern of the titanium dioxide. The grafted PSt chains only covered the surface of the titanium dioxide powder.[48]

Plasma graft polymerization

Plasma graft polymerization is carried out by two successive processes, namely, the plasma surface activation of the substrate and the graft polymerization of monomers. The grafting is naturally dependent on the reaction factor derived from the processes.[49–56] In the plasma pretreatment, plasma power and plasma treatment time affect the concentration of radicals of the material surface. Several factors of postpolymerization, such as reaction time and grafting temperature, also have significant influence on the grafting yield.

Effect of plasma pretreatment on grafting yield. The grafting yield is plotted as a function of plasma power in Figure 6. The plasma treatment time was 60 min, and
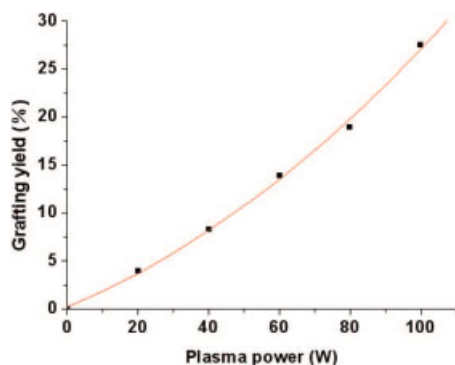

Figure 6 Relationship between grafting yield and plasma power. Plasma treatment time: 60 min; grafting time: 2 days; grafting temperature: 50°C. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Figure 7 Relationship between grafting yield and plasma treatment time. Plasma power: 100W; grafting time: 2 days; grafting temperature: 50°C. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]
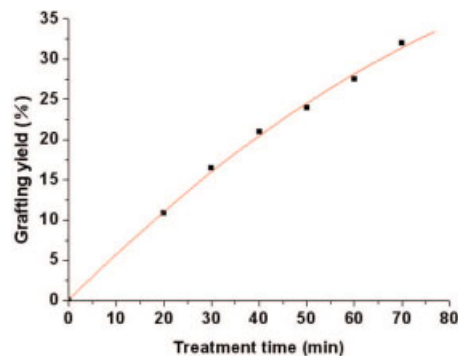
grafting time was 2 days at 50°C. Figure 6 shows that the grafting yield increased with the plasma power. The concentration of plasma induced radicals on the surface of the titanium dioxide powder increased with plasma power as indicated. Therefore, the grafting yield increased with the increasing of the plasma power. The relationship between the grafting yield and the plasma treatment time is shown in Figure 7, where plasma power was 100W and grafting time was 2 days at 50°C. It can be seen that the grafting yield was almost proportional to the plasma treatment time. The concentration of plasma induced radicals on the surface of the titanium dioxide increased with the increasing of the plasma treatment time. This caused the increase of the grafting yield with the increasing of the plasma treatment time. The relationship between the grafting yield versus the plasma power or the plasma treatment time in our experiment is different from that reported by Hirotsu and coworkers.[49–52] Hirotsu found that discharge power as low as 5W was quite effective and produced optimum effects on graft polymerization and grafting yield, followed by a decreasing trend for discharge power higher than 30W. The grafting yield increased at first with increase of the pretreatment time and reached a maximum around 60s at 10W. As the plasma pretreatment continued further, the grafting yield then leveled off.[50] This difference may be explained by the facts that the ratio of surface versus volume of small particles is very much larger than that of the film, and the formation of radicals never saturates.

Effect of postpolymerization condition on the grafting yield. Figure 8 shows the typical curves plotted of grafting yield versus reaction time for titanium dioxide, where plasma power was 100W and plasma treatment time was 60 min. The grafting reaction was carried out at 50°C. The grafting yield increased with the reaction time. The reaction temperature is one of the important factors controlling the grafting reaction. As shown in
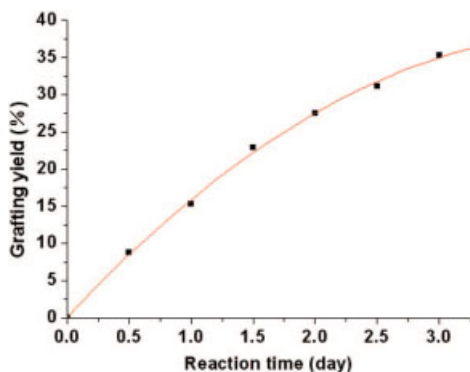
Figure 8 Relationship between grafting yield and grafting time. Plasma power: 100W; plasma treatment time: 60 min; grafting temperature: 50°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Effect of Different Types of Monomers on Grafting Yield. Plasma Power: 100W; Plasma Treatment Time: 60min

Samples	Reaction temp. (°C)	Reaction time (day)	Grafting yield (%)
MMA	30	3	38.12
	40	2	29.83
	50	1	17.57
styrene	30	3	34.78
	40	2	26.45
	50	1	15.34

Figure 9, the grafting yield increased at first with the temperature and reached a maximum at 50°C. As the reaction temperature increased further, the grafting yield decreased. This phenomenon was also observed by Hirotsu and coworkers.[49,50] It is considered that the fraction of decayed radicals and the termination rate constant increase at higher temperature, which causes the decrease in the grafting yield at elevated temperatures.[57]

Effect of different types of monomers on grafting yield. To investigate the effect of different types of monomers on grafting yield, styrene and methylic methacrylate (MMA) were introduced in the grafting reaction. Under the same plasma pretreatment condition and post-polymerization condition, the grafting yield of styrene was lower than that of MMA (see Table I). This result can be explained as follows: the grafting reaction is considered to be a polymer-chain propagating radical reaction. The polymer radicals produced fro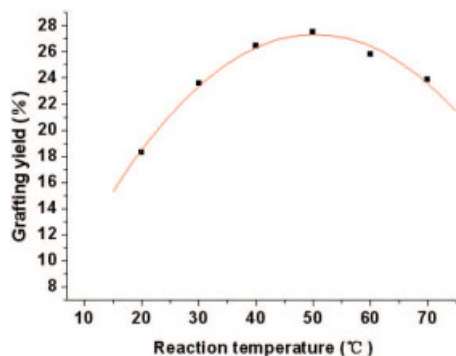m MMA are more active than those from styrene, which is passivated by the phenyl group. Moreover, the polarity of styrene is less than that of MMA. The affinity of styrene with TiO_2 powder is less than that of MMA with TiO_2 powder. The affinity between them may affect the graft polymerization rate. This phenomenon is the same as in plasma-induced polymerization. In plasma-induced polymerization, MMA is an active monomer, yet styrene can't be induced to polymerize.[58]

Reaction mechanism

As we all know, low temperature plasma contains free radicals, charged particles, and, especially, energetic electrons. These particles not only have high enough energy to activate, ionize, or bond-break reactant molecules, they also cannot decompose or ablate materials when disposing of them. They can only change the surface properties of the materials rather than the bulk properties.[30,31] The reaction mechanism may be as follows (Fig. 10):

Plasma contacted the surface of the titanium dioxide powder and activated the surface of it. Some radicals were formed on the surface. When the radicals reacted with styrene, polystyrene was grafted onto the surface of the titanium dioxide powder. However, it is still unknown how N_2 plasma created radicals on the TiO_2 surface and what kind of radicals are formed on the powder surface.

CONCLUSIONS

Polystyrene (PSt) was grafted onto titanium dioxide powder. The graft polymerization reaction was initi-

Figure 9 Relationship between grafting yield and grafting temperature. Plasma power: 100W; plasma treatment time: 60 min; grafting time: 2 days. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
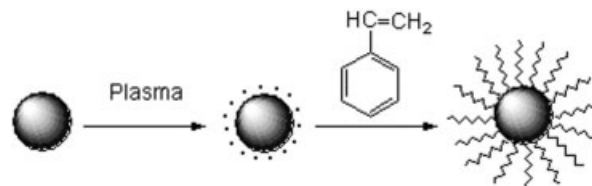

Figure 10 Reaction mechanism.

ated by N_2 plasma treatment of the surface of titanium dioxide. The crystal structure of the titanium dioxide powder observed by XRD spectra was unchanged after plasma graft polymerization. In the grafting reaction, the grafting yield on the powder versus treatment condition was different from the result of the bulk materials. That is: the grafting yield increased with plasma power, plasma treatment time, and the grafting reaction, but it increased first and then decreased after reaching 50°C. Moreover, the type of monomers has an effect on the grafting yield on powder.

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