

Grafting modification on the surface of titanium dioxide by polystyrene

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Abstract: Based on the technology of titanium dioxide grafting modification with polystyrene (PS), the modification mechanisms are studied and the polystyrene-grafting states on the surface of titanium dioxide have been set up. Under the synergistic actions of mechanical force, chemistry and heat, macromolecular free radicals of PS are created, at the same time, the O—O bonds of titanium dioxide are broken and the oxide free radicals produced, and the numbers of oxygen atom are increased and crystal lattice defects rich electrons are formed on the surface of titanium dioxide. The radical polymerization is the main reaction between PS and titanium dioxide and C—O bonds form in the process of modification. Multi-sites chemical adsorption also exists besides grafting between PS and titanium dioxide.

Key words: titanium dioxide; polystyrene; grafting modification; characterization; radical polymerization reaction

1 Introduction

Applications on pigment and filler surface modification by mechano-chemistry have been studied for several years, most of which have been focusing on promoting the mineral filler surface modification that have reduced effects on the reactions between the modifying agent and filler [1-3].

The technology of polymer grafting on pigment surface by mechano-chemistry has been less studied. This method has two basic approaches [4-10]. One is the reaction between the mechano-chemistry activated pigment/filler surface and the macromolecule free radicals that was produced from the mechano-chemistry initiated polymer degradation. Another is the grafting of monomers on the surface and in-situ polymerization activated by mechano-chemistry process.

The merit of the technology is the effective modification of pigment/filler surfaces during preparation. Also, the modifying agent can function as grinding aids and can be synthesized selectively in-situ according to modifying needs. The drawbacks of the technology include the long modification time; weak mechano-chemical effects using existing apparatus (e.g. vibrating mill, ball mill, *etc.*); and an incomplete understanding of the heat and chemical effects. The modification mechanisms have not been made clear

entirely thus far.

Titanium dioxide is an important white pigment used extensively in paints, plastics, chemical fiber and makeup. Ultrafine grinding and surface modification are integral for its preparation and application. The typical modifying agents used for titanium dioxide includes various surfactants, silane coupling agents, titanate coupling agents *etc.* Polymeric materials are seldom as modifying agent.

In this study, the new technology involving polystyrene (PS) as modifying agent and the use of the stirring mill as modifying apparatus is used. Titanium dioxide is modified in the process of ultrafine preparation under the synergistic actions of heat, chemistry and mechano-chemistry, the mechanisms of modification are studied and important conclusions are made.

2 Experimental

2.1 Materials

Titanium dioxide was made in Hengyang, China. It is anatase morphology, its purity is 97% and its density is 3.84 g/cm³. Benzene with analytical purity, made in 9066 factory, China, was used as an extracting solvent. Benzoyl peroxide with chemical purity, made in Beijing Kehua Company, was used as an initiating agent. PS, its average relative molecular mass being 111860, was used as the modifying agent.

2.2 The experimental flow

The experimental flow is shown in **figure 1**.

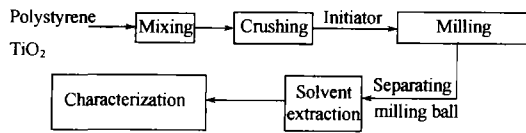


Figure 1 The technology flowsheet of titanium dioxide being modified by polystyrene.

2.3 Characterization

BRUKERIFS113V Fourier Transform Infrared Spectrometer, made in Germany, was used to analyze and measure the components on the particle surface. LCT-1 Differential Thermal Analyzer, made in Beijing Optical Instrument Factory, was used to measure and analyze the grafting and wrapping quantity on the particle surface and adsorption manner. MACROLB-MKII X Ray Photoelectron Spectrometer, made in England VG Company, was used to measure and analyze the bonding states between the polymer and the particle surface. WATERS150C Gel Permeation Chromatographer, made in American Waters Company, was used to measure the polymer molecular mass. SACP3 Centrifugal Sedimentation Apparatus was used to measure the particle size and specific surface area. S-250MK₂ Scanning Electron Microscope, made in England Cambridge Company, was used to measure the particle morphology before and after modification.

2.4 The calculation techniques of some parameters

Supposing that the PS is grafted in a single layer on the surface of particles, the wrapped rate is calculated by equation [11]:

$$n = \left(\frac{M}{q} N_A a_0 \right) / S_w .$$

where n is the wrapped rate, % ; M the wrapped quan-

ties, %, which is calculated by TG curve and supposed that the losing mass of modified sample above 300°C are PS grafted quantities; q the relative molecular mass of PS grafted on the surface of particles measured by experiment; N_A the Avogadro constant, 6.02×10^{23} ; a_0 the sectional area of PS, $3.688 \times 10^{-19} \text{ m}^2$, got from reference [12]; S_w the specific area of the grafted particles, m^2/kg , measured by experiment.

3 Results and discussion

3.1 The mechanism analysis in the process of modification

Table 1 is the changes of relative molecular mass of PS in the process of modification. **Figure 2** is the infrared spectrum of polystyrene fragment after crushing. Before titanium dioxide being modified in stirring mill, it was mixed and crushed in planet mill with polystyrene in order to mix well and activate the degradation of styrene. This created a small quantity of macromolecular free radicals grafting on the surface of titanium dioxide partly and also created double bond on the PS molecular itself. Moreover, the surface of titanium dioxide was also activated in some degree. When the titanium dioxide was modified in the stirring mill, under the actions of heat, chemistry and mechano-chemistry, besides the reaction of the activated titanium dioxide surface reacting with the double bond of polystyrene fragment, the polystyrene also created free radicals continuously. The main reactions are as follows (R-R instead for Polystyrene):

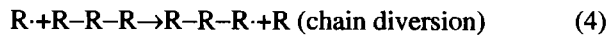
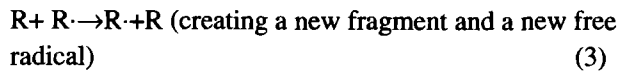
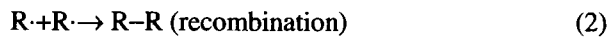
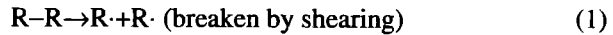


Table 1 The changes of relative molecular mass of PS in the process of modification

Samples	Peaks	q	distribution factor	q (10%PS)	q (90%PS)
PS original particle	Main peak	111860	2.35	575783	55284
	Second peak	—	—	—	—
PS fragments	Main peak	94499	2.23	486081	46560
	Second peak	—	—	—	—
Modified sample	Main peak	64179	2.45	359333	31978
	Second peak	171	1.10	284	130

The actions of benzoyl peroxide are in promoting the degradation of polystyrene and in reacting with the double bond of the polystyrene fragment to create free radicals. The macromolecular free radicals react with the electron deficient oxygen atoms created by

mechano-chemistry on the surface of titanium dioxide, the C–O bonds are created. They are also chemi-adsorbed in the defects created by mechano-chemistry on the surface of titanium dioxide, where is electron rich. The modification mechanism is free radical

polymerization mainly. The electrons deficient oxygen atoms and the electrons in the defects take on roles of terminating agents. The reactions belong to solid-solid reaction, in which thermodynamic equilibrium between the solid mixtures relies on diffusing velocity between them. One of the important functions of mechanical force is to improve mixture and collision between the titanium dioxide and the modifying agent.

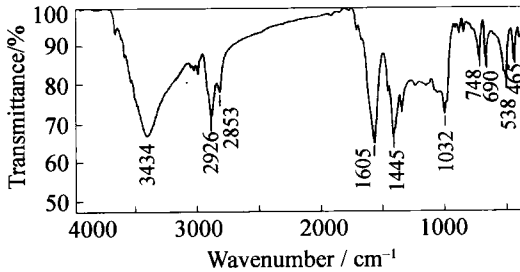


Figure 2 Infrared spectrum of the PS fragment.

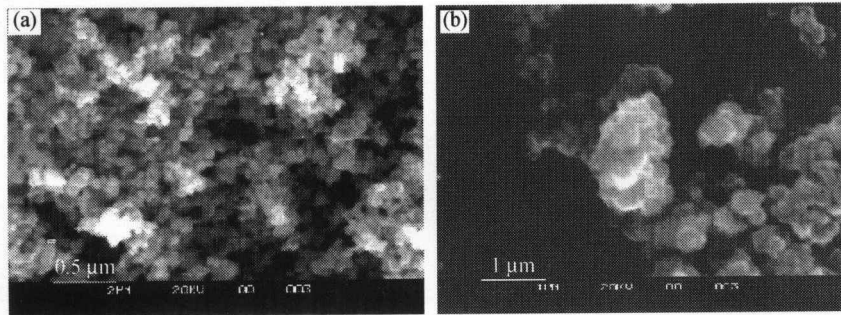


Figure 3 The SEM morphology of titanium dioxide before and after, (a) original sample of titanium dioxide; (b) titanium dioxide sample modified by PS.

Table 2 The changes of some characteristics of TiO_2 before and after modification

Samples	$M / \%$	$n / \%$	$d_{50} / \mu\text{m}$	$S_w / (\text{m}^2 \cdot \text{kg}^{-1})$
Original sample	0	0	0.40	5007
Modified sample	2.58	1.7	3.98	474

3.3 The study of infrared spectrum

Figure 4 is the infrared spectrum of the original TiO_2 sample and figure 5 is the infrared spectrum of the modified TiO_2 sample. Figure 5 has the absorption peaks of benzene ring at 1599, 1488, 1380, 2920, 2848 cm^{-1} , the absorption peaks of carbonyl group at 1750 cm^{-1} and the absorption peaks of C–O bond at 1100 cm^{-1} , but the absorption peak of hydroxyl group has less change after modification. It is verified that the C–O bond was created and the hydroxyl group on the surface of titanium dioxide was not reacted in the process of modification and there existed PS on the surface of titanium dioxide.

3.4 The XPS (X-ray photoelectron spectrum) study

Table 3 is the XPS results of the original sample and the modified sample of TiO_2 . The relative number of oxygen atoms increases after modification. The ratio of atoms reacting with the modifying agent to that

3.2 The analysis of titanium dioxide particles before and after modification

Figure 3 shows the SEM morphology of titanium dioxide before and after modification. The particles are loose aggregation before modification and grow up after modification. The M , n , d_{50} (particle sizes), and S_w before and after modification are given in table 2. The particle sizes agree well with the TEM measurements and the large particle size after modification is due to the aggregation caused by grinding. Based on assuming single layer grafting adsorption on the particle surface, the calculation result is that the wrapping rate is lower. However, the hydrophobicity is stronger according to the technology study [13]. It is thought that there exists multi-layers sorption and wrapping up on the surface of modified titanium dioxide.

not reacting with the modifying agent is 1:2. It is deduced that the wrapping rate is 33%, which is different from the results of table 2. This shows ulteriorly that multi-layer sorption exist on the surface of titanium dioxide. A substantial increment in oxygen chemical shift after modification shows that the chemical environments of oxygen atom have been changed and that the styrene fragments react with oxygen atoms on the surface of titanium dioxide.

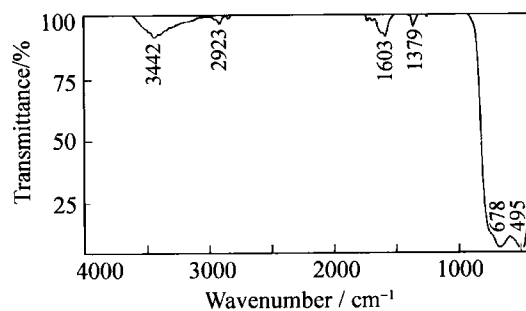


Figure 4 Infrared spectrum of original TiO_2 sample.

3.5 The bonding states between PS and the surface of titanium dioxide.

The surface states of titanium dioxide after modification are set up on the foundations of what have been studied previously. The followings are the analysis. (1) comparing with other oxides, the polarity of Ti–O bond in titanium dioxide is stronger and the adsorbent water dissociate easily to create hydroxyl due to the polarization. The hydroxyls do not change after modification, C–O bond and polystyrene exist on the surface of modified sample. (2) The crystal cells of anatase titanium dioxide appear on square double taper and rod shaped. The dissociation is mainly from [011] and [001] in the process of grinding. Because the O–O bond length is longer than that of Ti–O bond, the fracture is predominant between O–O bonds to form deficient electron oxygen atoms. (3) Because the relative quantities of oxygen atoms after modification increase, and the radius of oxygen is bigger than that of titanium atom, the surface of titanium dioxide is surrounded by oxygen atom primarily which carry negative charge. Moreover, it has been verified that the defects bearing electrons are easily created in the process of grinding for metals and metal oxide. In words, there

are electric charges existing on the surface of titanium dioxide. (4) **Figure 6** is the main surface characteristics of titanium dioxide introduced by J.R. Zheng [14], where the location 7 and location 8 stand for electron rich and electron deficient regions, respectively. (5) The macromolecular radicals with strong oxidizing property created by the initiating agent and mechanochemistry react easily with the electron deficient oxygen atom to form C–O bond, or adsorb chemically on the surface of titanium dioxide by receiving electron form. The bond energy of C–O bond is stronger than that of O–O bond, so the chemical shifts of oxygen atoms that react with the modifying agent increase after modification.

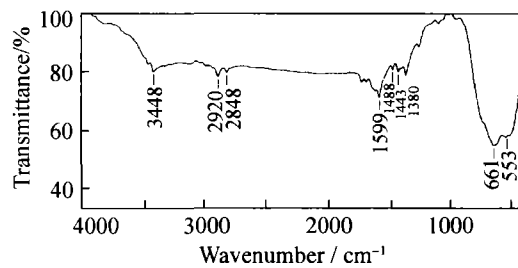


Figure 5 Infrared spectrum of modified TiO₂ sample.

Table 3 The XPS results of titanium dioxide samples

Sample	Element	Chemical shifts	Shifts change	Explaining	Remark
Original sample	C1s	284.68	—	C1s contaminated by organic substance	The ratio of atom numbers Ti:O being 1:2.66 before modification and 1:2.98 after modification and the ratio of molecular numbers grafted and non-grafted being approximately 1:2.
	O1s	529.90	—	—	
	Ti2p	458.49	—	—	
Modified sample	C1s	284.66	-0.06	C1s contaminated by organic substance and polymer	
	O1s	531.48	+1.58	Grafted O1s	
		529.90	0	Non-grafted O1s	
	Ti2p	458.49	0	Non-grafted Ti2p	
458.43		-0.06	Grafted Ti2p		

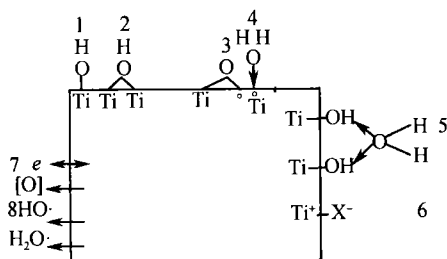


Figure 6 The main surface character of TiO₂, 1—alkalinescence end; 2—acidic hydroxide grope end; 3—unstable Ti–O–Ti bonds; 4—H₂O molecule absorbed by Lewis acid field; 5—H₂O molecule combined by surface hydroxide group; 6—adsorbed anion; 7—The supplying field and accepting field of latent electron; 8—adsorptive oxidant such as hydroxide, peroxide, or active oxygen formed by light catalysis.

From the above analysis and the technology of ti-

tanium dioxide modification by PS, the bonding states on the surface of titanium dioxide after modification is shown in **figure 7**, in which R stands for the grafted polymer. The theoretical fundamental of titanium dioxide grafting modification by PS is expressed fully in the figure.

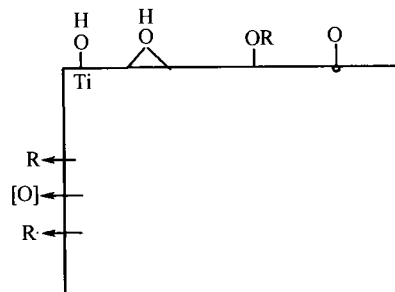


Figure 7 PS grafting model.

4 Conclusions

(1) The preconditions and substantial foundations of titanium dioxide solid phase grafting modification by PS are that polystyrene are broken to create macromolecular radicals by chemical, mechano-chemical and thermal action. The O–O bonds are broken down, the numbers of oxygen atom are increased and many defects bearing electron rich regions are also formed by mechanical force on the surface of titanium dioxide during modification. The mechano-chemistry is thought to be prerequisite for the technology.

(2) There exists multi-layer adsorption on the surface of titanium dioxide.

(3) The mechanism of titanium dioxide solid phase grafting modification by PS is free radical polymerization. The Ti–O free radicals and electrons are acceptors of PS macromolecular free radicals.

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