

NOTES

Grafting Polystyrene onto Sorbate-Modified Titanium Dioxide

INTRODUCTION

Modifications have been studied of titanium dioxide surfaces with various organic substances to improve the interfacial compatibility between the oxides and organic matrices in composite materials. In the pigments industry, many macromolecular or low molecular weight surfactants have been used to make the oxide surface more hydrophobic.

Grafting polymers onto the oxide was reported in the literature. Benson¹ and Platé et al.² used mechanochemical methods; Papirer et al.³ reacted polymer cations with surface hydroxy groups on the oxide; and Petrik et al.⁴ grafted to polymers by a chain transfer reaction. Te Grotenhuis⁵ introduced an unsaturated compound onto the surface through the reaction of hydroxy groups with vinyl isocyanate, subsequently grafting olefinic monomers or unsaturated polymers with the vinyl group. Nollen et al.⁶ also grafted polystyrene topochemically onto titanium dioxide the surface of which had been previously treated with nonreversible adsorption of acrylic or methacrylic acid.

The graft bond nature of silane was not described in the graft polymerization of styrene onto the functional silane modified clay.⁷ The existence of an adsorbed water layer on the surface in ambient conditions complicated the matter. One of the approaches to elucidate the graft bond is to prepare a model oxide with well-characterized bonds. In this paper, the modified titanium dioxide powder was prepared using an interfacial technique for the hydrolysis of the reaction mixture of titanium tetraisopropoxide and sorbic acid. Styrene was then graft polymerized onto the modified surface.

EXPERIMENTAL

The sorbate-modified titanium dioxide was prepared through the interfacial hydrolysis for partially acidolyzed titanium alkoxide. A typical procedure is illustrated as follows:

All reagents except styrene monomer and sorbic acid were reagent grade and used without further purification. Styrene monomer was distilled at 45°C under 27 Torr just prior to use. Sorbic acid was recrystallized from water. One ml (3.36 mmol) titanium tetraisopropoxide was partially acidolyzed by 0.302-g (2.69 mmol) sorbic acid in 20-ml hexane under nitrogen atmosphere and continually stirred at room temperature for 30 min. The resulting mixture was poured into 100-ml water while stirring to yield a pale-yellow particle-associated solid in the organic phase. After 2 hr of stirring, the solid was filtered, washed with ethyl ether, dried *in vacuo*, and weighed.

The content of the acid in the modified oxide was determined. The oxide was decomposed by dilute sulfuric acid-ethyl ether solution, and the organic acid was extracted with ethyl ether. Then the extract was washed with several portions of water and treated with sodium methoxide in methanol, the excess of which was back-titrated with 0.1N hydrochloric acid using phenolphthalein as indicator.

In the presence of the modified titanium dioxide, styrene was polymerized in bulk at 80°C using benzoyl peroxide as catalyst. The reaction mixture was poured into hexane, and the precipitate was filtered and dried *in vacuo* until a constant weight was reached. The product was then extracted with hot benzene by Soxhlet extraction apparatus for 6 hr to remove nongrafted polymer from the grafted polymer-titanium dioxide composition. The residual solid was submitted to pyrolysis gas chromatography to determine the grafted polystyrene (pyrolysis temperature 570°C).

RESULTS AND DISCUSSION

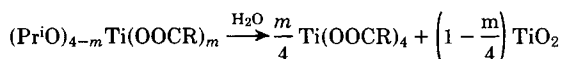
The hydrophobic titanium dioxides obtained are summarized in Table I. X-Ray analysis and electronmicrography revealed the oxides to be amorphous and to be 1–5 μm in diameter. IR spectroscopy revealed the presence of titanium sorbate and the absence of free carboxylic acid (IR: diene group, 1640, 1610 cm^{-1} ; carboxylate group, 1520, 1402 cm^{-1}).

TABLE I
Preparation of Modified Titanium Dioxide with Various Amounts of Sorbic Acid^a

Oxide	1	2	3	4	5
Titanium tetraisopropoxide					
g	1.03	1.03	0.97	0.99	0.84
mmol	3.6	3.6	3.4	3.5	3.0
Sorbic acid					
g	0.60	0.30	0.15	0.08	0
mmol	5.4	2.7	1.3	0.71	0
Molar ratio of sorbic acid and Ti(OPr ⁱ) ₄	1.5	0.74	0.39	0.20	0
Yield ^b of oxide, %	84	98	104	110	126
Acid content, mmol/g	4.9	3.5	1.9	0.8	0.1

^a Hexane was used as acidolysis solvent.

^b Yields were calculated on the basis of the stoichiometric reaction



where R is CH₃CH=CHCH=CH—, 0 ≤ m ≤ 3.

When more polar solvents were used for acidolysis, the modified titanium dioxides were larger in particle size and more hydrophilic than those obtained through hexane. Stirring affected the fineness of the modified oxide.

The formation of small particles may be explained as follows: acidolysis of titanium tetraisopropoxide with sorbic acid in hexane gives partially acidolyzed titanium isopropoxide,⁸ (PrⁱO)_{4-m}Ti(OOCR)_m, where R is 1,3-pentadienyl group and *m* is a fixed integer between 0 and 3.⁹ On hydrolysis the remaining titanium alkoxide structure is hydrolyzed and condensed at the interface between hexane and water, then a two-dimensional polytitanoxane film is formed. The film is broken into hydrophobic particles under stirring. This transformation is due to either hydrogen bond formation or condensation among the hydroxy groups pendent to the polytitanoxane film.¹⁰ The structure of the hydrolyzed oxide would depend upon the relative amounts of each component of partially acidolyzed titanium isopropoxide. One of the possible schemes for the reaction is illustrated in Figure 1.

Although titanium sorbate structure is thought to be more hydrolytically stable than the titanium isopropoxide structure,⁹ the carboxyl group was, in the case of titanium butoxide tristearate, easily hydrolyzed.¹¹ When oxide 1 was agitated in water at room temperature for 16 hr, the suspension was gradually converted into a colloidal solution. Hydrolyzed sorbic acid was extracted with ethyl ether and determined to be 33% of the acid. However, grafting polystyrene onto the sorbate-modified titanium dioxide resulted in excellent hydrolytic stability.

Styrene was polymerized in the presence of the modified titanium dioxide using benzoyl peroxide as a catalyst (Table I). For graft efficiency, the weight ratio of graft polystyrene to the graft polymer-titanium dioxide composition (Table II) indicates that the modification of the oxide surface is most important.

The grafted polystyrene is covalently bonded to the titanium sorbate on the titanium dioxide surface. IR spectra of the polystyrene-oxide 2 compositions, measured at several stages in the course of polymerization, showed that the peak height ratio of the diene group (1640 cm⁻¹) to the carboxylate group (1402 cm⁻¹) decreased as monomer conversion increased. The polystyrene-grafted titanium dioxide was decomposed by a solution of dilute sulfuric acid and methyl ethyl ketone, and the graft polymer was precipitated in hexane. The polymer obtained was not soluble in benzene and exhibited carboxylic acid peaks in addition to polystyrene peaks on the IR spectra. These results are consistent in that the grafted polymer is a copolymer of styrene and sorbic acid, and the grafting sites of the polystyrene are the diene group of titanium sorbate on the oxide surface.

This conclusion is further supported by the adsorption-desorption test: the sorbate-modified titanium dioxide 2 was suspended in benzene containing dissolved polystyrene (0.072 g/ml, $\bar{M}_w = 3.04 \times 10^5$); the solvent was evaporated to dryness. Then, benzene was added to the polystyrene-titanium dioxide mixed solid to dissolve desorbable polymer. The resulting solid was extracted with hot benzene for 6 hr. The graft efficiency of the polystyrene adsorbed nonreversibly on the

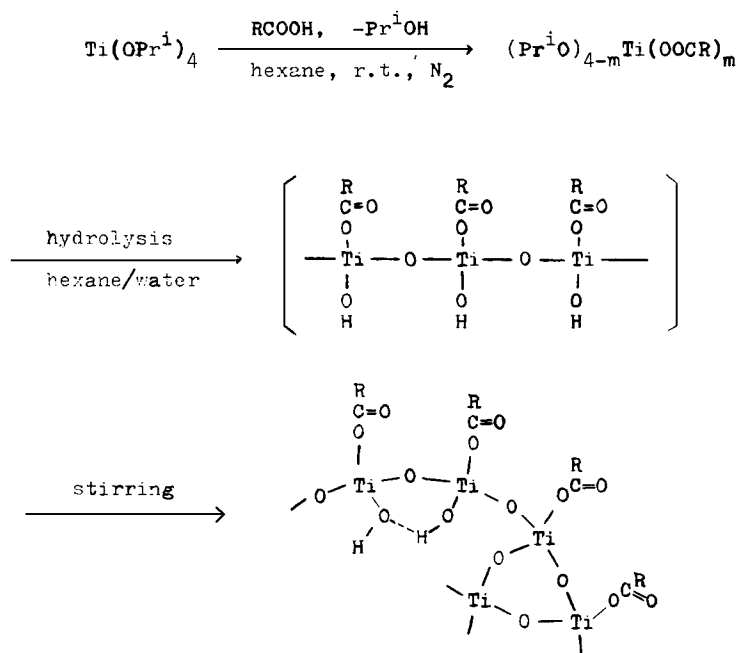


Fig. 1. Scheme for formation of sorbate-modified titanium dioxide powder; R is $\text{CH}_3\text{-CH=CHCH=CH-}$, $0 \leq m \leq 3$.

TABLE II
Graft Polymerization^a of Styrene onto Sorbate Modified Titanium Dioxide

Oxide, g	Styrene Monomer, ml	BPO, mg	Monomer Conversion, %	Graft Efficiency
1 0.10	1.0	22	50	0.033
2 0.10	1.0	22	45	0.013
3 0.10	1.0	21	57	0.007
4 0.10	1.0	21	48	0.005
5 0.10	1.0	23	54	0.004

^a Polymerization conditions: 80°C, 2 hr, under nitrogen.

oxide was determined to be 0.001. It is clearly indicated that the portion of adsorbed polymer (0.013) in the grafted polymer is small (Table II) and that the majority of the grafted polymers are covalently bonded to the oxide surface. Hydrolyzed sorbic acid from the grafted polystyrene-titanium dioxide 2 composition was not detected by chemical analysis.

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