

# Improvement of polyacrylate coating by filling modified nano-TiO<sub>2</sub>

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## Abstract

Nano-TiO<sub>2</sub> is modified by a method, by which nano-TiO<sub>2</sub> first reacts with silane coupling agent WD-70 with double bond group which subsequently copolymerizes with methyl methacrylate and butyl acrylate to produce a thin polymer shell on the nanoparticles. The modified nanoparticles have stable organophilicity. They are applied to polyacrylate coating and performances of the coating are measured by different methods. The modification of nano-TiO<sub>2</sub> particles can improve their dispersibility in coating, enhance hardness of coating and reduce water absorption and permeability of polyacrylate coating. The mechanism has been analyzed in this paper.

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*Keywords:* Nano-TiO<sub>2</sub>; Modification; Polyacrylate coating; Water absorption; Permeability

## 1. Introduction

Organic coatings are widely applied for decoration and protection of metals and fillers are usually added in application. With the development of nanotechnology, nanoparticles have been increasingly applied to organic coatings [1–3]. Titanium dioxide is one of the fillers which are usually used, and nano-TiO<sub>2</sub> is also often used as a filler because of its excellent performance. Nanoparticles can be directly added in organic resin. However, because of their incompatibility with organic resin and aggregation, the advantages of nanoparticles do not exhibit themselves to the full. Therefore, nanoparticles need some modification to turn their surface from hydrophilic to organophilic [4,5].

A lot of methods can be used to modify nanoparticles, for example, surface-active agent, coupling agent, fatty acid and alcohol have been studied to modify nanoparticles [6–10]. We design a scheme in which nanoparticles first react with coupling agent, a silane with active double bond (WD-70), and then the coupling agent copolymerizes with monomers. Effects of the modified nano-TiO<sub>2</sub> on polyacrylate coating have been investigated and their mechanism has been analyzed.

## 2. Experiment

### 2.1. Materials

Nano-TiO<sub>2</sub> powder was provided by ZhouShan Ming-Ri Co. Ltd., ZheJiang; polyacrylate resin provided by ShuangHu Coating Co., China; curing agent N75, a product of Deggusa company, Germany; coupling agent WD-70 [ $\gamma$ -(methacryloxy) propyltrimethoxy silane] provided by Organosilicon New Material Co. Ltd., Wuhan University. Other chemical agents were commercial product (untreated).

### 2.2. Surface modification of nanoparticles and evaluation of modification

First, the surface of TiO<sub>2</sub> nanoparticles was functionalized by treatment with WD-70. 40.00 g nano-TiO<sub>2</sub> was added in solution (6.0 ml WD-70 dissolved in 200.0 ml dimethyl benzene) and stirred for 12 h. Then grafting copolymerization was produced at 70 °C under N<sub>2</sub> atmosphere. The monomers of 24.0 ml methyl methacrylate and 16.0 ml butyl acrylate dissolved in 30.0 ml dimethyl benzene were dripped in for about 4 h and the polymerization continued for 2 h.

The organic groups on surface of modified particles were examined by infrared spectra and weight-loss in calcination at 800 °C. Their organophilicity was evaluated by distribution of modified nanopowders in water and organic phase after ultrasonic treatment for about 10 min.

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### 2.3. Preparation of coating film and evaluation of its performance

First, a paint was prepared by dispersing nano-TiO<sub>2</sub> particles into polyacrylate resin in a certain proportion with a high-speed mechanical stirrer. Scanning electron microscope (SEM) was used to observe the dispersity of nanoparticles in the paint. The paint and varnish without fillers were brushed on tinplate according to the national standard of China GB1727-79. The adhesivity of coating was determined according to GB1720-79, the impact strength determined according to GB1732-79, the flexibility determined according to GB1731-79 and the hardness tested by pencil according to GB6739-86. In addition, free-standing coating membranes were prepared, brushing the paint and varnish on a Teflon board and separating them from the board when they were cured and dried. For absolute volatilization of the solvent and dehydration of the coating, the membranes were put aside for 20 days and then transferred in a dryer for 10 days.

#### 2.3.1. Water absorption

The free-standing varnish and paint membranes were tailored in square with a certain area and stored in distilled water at 25 °C and then weighed on an analytical scale at intervals.

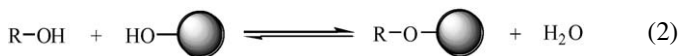
#### 2.3.2. Permeation

The varnish and paint membranes were tested by permeation of water vapor and NaCl in solution. A vessel in which some water was sealed with the membrane was placed in a dryer and taken to weigh on an analytical scale at regular intervals. Another method was also employed to measure the permeability of Cl<sup>-</sup>, a membrane was used to separate 0.50 mol/l NaCl solution from distilled water. With the permeation of NaCl through the membrane, electrical conductivity of the distilled water increased, which could be measured with DDS-11 electrical conductivity analyzer.

## 3. Results and discussion

### 3.1. Evaluation of the modification

Because a tiny amount of water and residual surface OH groups unavoidably exist on nanoparticles, it is easy for nano-TiO<sub>2</sub> particles to heavily agglomerate in organic solvent and resin. Surface-active agent molecule can be adsorbed on nanoparticles by its hydrophilic end and organic acid and alcohol can react with the surface OH groups on particles.



When a tiny amount of water and surface OH groups on nanoparticles react with coupling agent WD-70

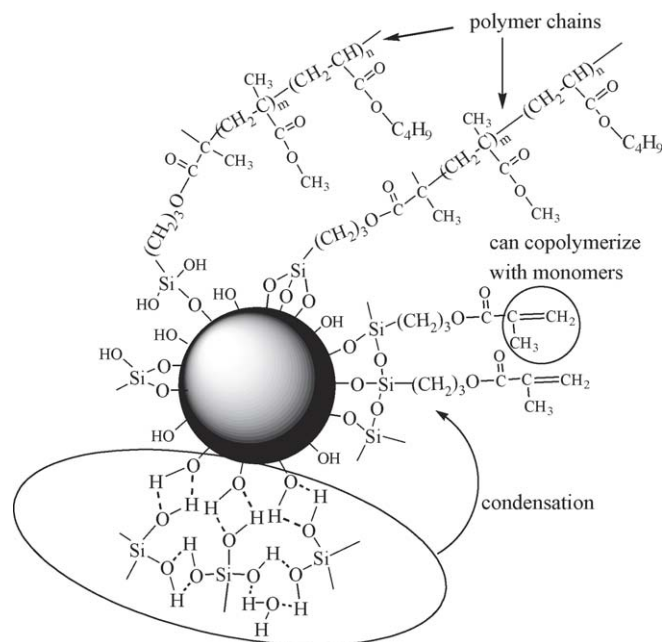


Fig. 1. Schematic structure of modified particles.

[CH<sub>2</sub>=CHCH<sub>3</sub>-COO-(CH<sub>2</sub>)<sub>3</sub>-Si-(OCH<sub>3</sub>)<sub>3</sub>], the functional groups with double bond are introduced onto nanoparticles and they can copolymerize with monomers to produce a thin polymer shell on nanoparticles (Fig. 1).

In Fig. 2, (a) is the infrared spectrum of nano-TiO<sub>2</sub> modified with WD-70 and (b) is the infrared spectrum of nano-TiO<sub>2</sub> modified by copolymerization after treatment with WD-70. The main characteristic band of Ti-O is in the range of 500–780 cm<sup>-1</sup>. The strong absorption at 3428 cm<sup>-1</sup> results from -OH vibration. The absorption at 1060 cm<sup>-1</sup> reflects Si-O-Si structure that is produced by hydrolysis and polycondensation of the coupling agent. The absorption peaks near 2900 cm<sup>-1</sup>, 1455 cm<sup>-1</sup> and 1400 cm<sup>-1</sup> are ascribed to CH<sub>3</sub>- and -(CH<sub>2</sub>)<sub>n</sub>- groups. These peaks are visibly enhanced by subsequent copolymerization for more introduced CH<sub>3</sub>- and -(CH<sub>2</sub>)<sub>n</sub>- groups and their location shifted a little because of the effect of CH<sub>3</sub>-O- and C<sub>4</sub>H<sub>9</sub>-O- groups, which come from monomers of methyl methacrylate and butyl acrylate. The absorption peak around 1290 cm<sup>-1</sup> is attributed to C-O group, which also is enhanced and shifted in location because of the conjoint atoms. Significantly, the absorption at 1635 cm<sup>-1</sup> that reflects C=C double bond groups almost disappears after copolymerization and the strong absorption at 1719 cm<sup>-1</sup> which characterizes the structure of ester is dramatically enhanced. From the spectra, it can be deduced that the coupling agent WD-70 has been grafted on nano-TiO<sub>2</sub> particles and copolymerized with monomers to produce a layer of polyacrylate connecting with nano-TiO<sub>2</sub> particle via coupling agent.

We compared this modification method with the methods using surface-active agent, fatty acid and fatty alcohol to modify nano-TiO<sub>2</sub>. Table 1 is the evaluation of modification results, which indicated that the combination of coupling agent and copolymerization had adsorbed more organic materials on

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