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Short communication

# A novel approach to the preparation of powder coating—Manufacture of polyacrylate powder coatings via one step minisuspension polymerization

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**Abstract**

A novel method for manufacturing powder coating through one step minisuspension polymerization is described. The conventional production of powder coating includes six steps—synthesizing resins, mixing the raw material, extrusion, cooling, pre-crushing and pulverization. Comparatively, the present method can simplify the complicated processes, reduce equipment and save energy. Before polymerization, the $TiO_2$ particles were treated with a reactive silane coupling agent 3-methacryloxypropyltrimethoxysilane (MPTMS) to obtain enough compatibility with the monomers. The powder coating was directly synthesized through employing one step minisuspension polymerization in the presence of titanium dioxide white particles. The powder coating was characterized using Fourier transform infrared spectra (FT-IR) and thermogravimetric analysis (TGA). The results show that $TiO_2$ particles and polymer are successfully linked up via MPTMS in the powder particles. The morphology of powder coatings produced via different methods was observed by scanning electron microscope (SEM). The powder coatings obtained from minisuspension polymerization consist of regular spherical morphology particles with narrow particle size distribution. The powder flowability and surface film smoothness were enhanced compared to the pulverization powder coating.


*Keywords:* Powder coatings; Minisuspension polymerization; Particle morphology and size distribution; Powder flow; Film smoothness

## 1. Introduction

In coating application, pollution controls have become increasingly stringent, which forces to move away from the use of organic solvents towards alternative coating technologies. Volatile organic compound (VOC) emission limits are being reduced in many industrialized countries, for example new European Union (EU) legislation came into force in 2000. It has been estimated that *ca*. 6% of man-made VOC emissions across the EU emanate from coating operations [1]. Moves to reduce VOC emission have accelerated the development of environmentally-friendly coating systems such as aqueous and powder coatings. Although water is an attractive alternative, it does have drawbacks. The properties of waterborne polymers are often inferior to those of their solvent-borne analogues. Powder coating has almost no solvent emission during the course of coating preparation and application and overcomes the drawbacks of water-based coatings. Therefore, much interest has been focusing on powder coatings to eliminate VOC emission to the environment. Recently, the Big Three auto manufacturers, together with coating and application system suppliers, have been working to develop powder coatings systems [2–6]. However, the traditional production process of powder coatings includes synthesizing resins, blending resin and pigment, melting extrusion, cooling, pre-crushing and pulverization. It is evident that the production process is very complicated and employs a lot of energy and equipment. Thus, it is necessary to produce powder coatings by a novel method to simplify the complicated process and to save energy. In addition, the powder coatings obtained from the conventional pulverization normally possess irregular morphology and a wide size distribution, which gives rise to application problems such as poor flow, irregular feed rates and powder accumulation in transport hose and gun. From the results of application, they are not satisfactory in terms of the smoothness of finished films.

Powder coatings have a rather long history in automotive applications. However, for a long time all applications have been limited to underbody and interior trim components. For aesthetic

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reasons, related mainly to the poor flowability, the car producers were reluctant to use powder as a full-body coating for any of the layers [7]. To improve the appearance, it is necessary to produce powder coatings with fewer coarse particles and a regular morphology to improve both film appearance and powder flow [8,9].

There are a number of references [10–17] addressing the manufacture of powder coatings. One interesting example is the use of supercritical or liquid carbon dioxide as a medium for delivering powder coating system [18,19]. Nevertheless, nothing has been reported that employs the one step minisuspension process to directly synthesize powder coatings particles in the presence of titanium dioxide white particles. In this paper, a powder coating with spherical morphology was prepared via the minisuspension polymerization process in which the titanium dioxide white particles were encapsulated by polyacrylate. The suspension method was developed from a study of suspension polymerization. The production method was invented to obtain powder coating particles having a narrow particle size distribution by using a water-soluble polymer as the suspension stabilizer [20]. A surface chemical phenomenon was utilized in which the oil droplets were suspended in an aqueous solution of stabilizer. Using this process, we have tried to produce polyacrylate powder coating particles with spherical morphology and a narrow particle size distribution. In order to compare this preparation with the conventional method, the powder coating was also prepared through conventional pulverization with the same powder composition. Particle size distribution and powder flow were measured. Surface roughness of the films formed was also examined.

## 2. Experimental

### 2.1. Materials

Methyl methacrylate (MMA, CP), β-hydroxyethyl methacrylate (HEMA, CP) and butyl acrylate (BA, CP) were purified by distillation under nitrogen at reduced pressure. The initiator, 2,2′-azobis(isobutylonitrile) (AIBN, analytical grade), (Tianjin Chemical Co., Ltd., Tianjin, China) was re-crystallized in ethanol. Poly(vinyl alcohol) (PVA 1799) was purchased from Shijiazhuang Chemical Fibre Co., Ltd. (Hebei, China). 3-Methacryloxypropyltrimethoxysilane (MPTMS) and polyoxyethylene nonylphenyl ether (OP-10) were supplied by Tianjin Research Institute of Synthetic Material (China) without further purification. $TiO_2$ powder (R2310) was donated from Shijiazhuang GoldFish Coatings Co., Ltd. (Hebei, China). TEM images showed spherical particles of about 1 μm. Aerosil R-812 obtained commercially (from Nippon Aerosil Co.) was used as an external additive to improve flow of powder coatings.

### 2.2. Preparation of powder coating by minisuspension polymerization

#### 2.2.1. $TiO_2$ particle treated with MPTMS

$TiO_2$ particles were mixed with a mixture of water and methanol, and then MPTMS was added to the system. The mixture was first dispersed for 20 min through an ultrasonic instrument (HQ-50,100W, China) at room temperature and then the mixture was heated to reflux for at least 4 h. At the end of the reaction, the mixture was cooled down and diluted four or five times with *n*-propanol to improve the solubility of the homocondensates. This sample was centrifuged at 15,000 rpm for 2 h at room temperature. The clear supernatant, that contains the homocondensates and unreacted MPTMS, was decanted from the deposit composed of the particles with the grafted MPTMS. The deposit was dried at 50 °C in vacuum for at least 8 h.

#### 2.2.2. $TiO_2$/polymer powder coatings prepared through suspension polymerization

Initiator (AIBN) was dissolved in a monomer mixture solution of MMA, BA and HEMA. Then the treated $TiO_2$ particle was redispersed in the mixture of monomer and initiator. The sample was dispersed by ultrasonic instrument for 30 min at room temperature. An aqueous solution of non-ionic surfactant (OP-10, 0.3 g/l) was introduced to PVA aqueous solution. The $TiO_2$ particle dispersion in the mixed monomer solution was poured slowly into 2 wt% PVA aqueous solution and emulsified with a homogenizer at 5000 rpm for 20 min. Polymerization was then carried out under stirring in a four-neck glass reactor equipped with a stirrer, a reflux condenser and a nitrogen gas inlet system. The reactor was heated to 80 °C through a water bath and maintained for 6 h at this temperature. The particles produced were washed repeated by deionized water to remove PVA and dried under vacuum at ambient temperature.

### 2.3. Characterization

A Fourier transform infrared (FT-IR) analysis was performed using a spectrophotometer (Nicolet Co., NEXUS, USA). FT-IR was used to characterize the functional groups of the $TiO_2$, treated $TiO_2$ and $TiO_2$/coplymer composite powders.

The thermal characterization of powder coatings was determined by thermogravimetric analysis (TGA, TG 204, Netzsch Co., Germany). Samples were heated to 550 °C from room temperature at the speed of 10 °C/min

The mean size and size distribution of powder coatings particles were determined by particle size analyzer (Marwen Instruments Co., Mastersilersion, England).

The morphology of powder coatings particles was observed using scanning electron microscope (SEM, Phlilps Ltd. Co., XL30ESEM, Netherlands).

#### 2.3.1. Powder application

Powders were applied electrostatically using a corona charging gun and powder coating equipment (manufactured by Nihon Parkerizing Co.). Standard 1 mm × 100 mm × 300 mm steel test panels with an electrodeposited primer and a solvent-based primer surface were coated with powder coatings. A standard baking condition was controlled at 180 °C for 30 min.

#### 2.3.2. Powder flow

In this study, angle of repose was adopted as a representative value of powder flow and was measured using a Powder Tester