



Original Research Paper

Fluoroalkylsilane treatment of TiO₂ nanoparticles in difference pH values: Characterization and mechanismS. Pazokifard^{a,b}, S.M. Mirabedini^a, M. Esfandeh^a, S. Farrokhpay^{b,c,*}^a Colour, Resin & Surface Coatings Department, Iran Polymer and Petrochemical Institute, P.O. Box 14965-115, Tehran, Iran^b Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia^c JKMR, University of Queensland, 40 Isles Road, Indooroopilly, Qld 4068, Australia

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ABSTRACT

In this research, TiO₂ nanoparticles were treated with hydrophobic 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (fluorosilane) in acidic, neutral and alkaline conditions. The treated nanoparticles were characterized using FTIR spectroscopy, thermal gravimetric analysis, X-ray photoelectron spectroscopy, transmission electron microscopy and X-ray diffraction spectroscopy. Reflectance spectra were obtained using UV–vis diffuse reflectance spectroscopy and band gap energy of the various nanoparticles was determined. Zeta potential measurements were used to evaluate colloidal stability of nanoparticles in aqueous media. The mechanism of fluorosilane adsorption on the surface of TiO₂ nanoparticles was investigated using ATR-FTIR spectroscopy and turbidimetric technique.

The characterization results revealed that the amorphous fluorosilane adsorbs on the surface of TiO₂ nanoparticles in both neutral (pH 6) and alkaline (pH 11) solutions. The values of the band gap energy for all treated nanoparticles were almost the same, in the range of 3.10–3.18 eV. Zeta potential measurements showed that isoelectric point of the TiO₂ nanoparticles shifts from 6.8 for untreated TiO₂ to 4.4 for treated one. Based on the zeta potential measurement results, it is expected that treated TiO₂ nanoparticles in neutral or alkaline conditions have higher colloidal stability and better dispersion in the aqueous solutions. Hydrophobic character of fluoro species on the surface of nanoparticles leads the treated nanoparticles migrate towards the suspension surface. Therefore, these treated nanoparticles may be useful for developing self-cleaning coatings with minimal destructive effect on the polymeric matrix.

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1. Introduction

Titanium dioxide in anatase crystalline form has many applications in water waste treatment, self-cleaning, self-sterilizing, antireflective, air-cleaning, anti-fogging and antifouling coatings, basically due to its photocatalytic activity [1,2]. However, incorporation of photoactive particles into or deposited on the surface of organic coatings has many limitations, due to possible oxidation or degradation of the host polymer matrix [3–5]. Therefore, surface modification of these particles can be used to adjust their photocatalytic properties [6–8]. Fluoro-organic, fluorosilane, and silicone compounds are well known as low energy, hydrophobic or/and lipophobic materials [9]. When fluorosilane treated TiO₂ nanoparticles are dispersed in an aqueous solution, hydrophobic particles tend to migrate to the solution–air interface as a result of incompatibility with hydrophilic solution and also the thermodynamic drive to minimize the surface energy [10]. It is expected that

hydrophobic TiO₂ nanoparticles in water-base organic coatings tend to migrate to the coating/air interface during the film formation and drying, therefore, destructive effect of the photocatalytic nanoparticles on the polymeric matrix can be minimized.

Silanisation of metal oxides such as TiO₂ and SiO₂ particles is usually performed through a sol–gel route. This process involves hydrolysis of silane alkoxy groups and condensation with functional groups of the metal oxides. Different parameters such as mole ratio of reactants, water content, temperature, time and pH of hydrolysis and condensation steps affect the reaction process. Silane grafting of metal oxides primarily depends on the surface charges of metal oxide and this in turn is affected by the pH of the solution in which the metal oxide is suspended [11]. Therefore, pH of the media plays an important role in the surface treatment of TiO₂ nanoparticles. However, many researchers have focused on the acidic conditions, based on a common thought of fast hydrolysis of the ethoxysilanes at low pH, and only a few studies are available about the hydrolysis and condensation of different substituted ethoxysilanes under basic-catalyzed conditions [12,13].

In this work, TiO₂ nanoparticle was chosen because of its high photocatalytic activity; 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane

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