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Transition metal-doped titanium(IV) dioxide: Characterisation and influence on photodegradation of poly(vinyl chloride)

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Abstract

The effects of transition metal dopants (V(IV), V(V), Mn(II), Cr(III), Mo(V), and W(V)), introduced into TiO_2, upon the rate of photodegradation of poly(vinyl chloride) (PVC) films containing TiO_2 have been measured. The rates were determined mainly by monitoring carbonyl group formation. In another set of experiments, the rates of chloride ion release from irradiated PVC particles suspended in water undergoing agitation with air or O_2 in the presence of particles of doped TiO_2 were measured electrochemically. The doping of TiO_2 (rutile) with Cr(III), V(V) or Mn(II) reduces the photoactivity of the pigment, while doping by Mo(V) or W(V) enhances its photoactivity; the results obtained from carbonyl index measurements are paralleled closely by those from chloride ion release. Even the most aggressive doped pigments were less reactive than Degussa P25 pigment, while the greatest protection to PVC film was offered by TiO_2 particles coated with Al_2O_3 or SiO_2. Overall, the photoactivity of doped TiO_2 is a complex function of dopant concentration, the energy levels of the dopants in the TiO_2 lattice, their d electronic configuration and their local distribution. Photoactivity is also linked to other factors such as crystal type, particle size distribution and surface area. There is a clear relationship between the tendency of the dopant to induce the rutile-to-anatase transition and its effect in enhancing the photoactivity of the pigment. The characterisation of the doped pigments was achieved using X-ray powder diffraction, EPR spectroscopy, diffuse reflectance UV–vis spectrophotometry, scanning optical and electron microscopy and particle size analysis using LALLS.

Keywords: Anatase; Chromium; EPR; Manganese; Molybdenum; Poly(vinyl chloride); Photodegradation; Rutile; Titanium dioxide; Tungsten; Vanadium; X-ray powder diffraction

1. Introduction

The photodegradation of poly(vinyl chloride) (PVC) has been the subject of intensive study and has been extensively reviewed [1–10]. The principal pathways involve dehydrochlorination to give polyene structures and oxidative degradation to give a variety of carbonyl compounds as end-products. The photodegradation of PVC containing varying amounts of titanium dioxide has also received much attention [3,7,10–16] because of the role this composite material occupies in the building industry in the form of doors, window profile, and fascia boards, etc. The weathering of this composite causes such effects as ‘chalking’ (loss of gloss and development of a powdery appearance), and coloration effects called ‘greying’, ‘pinking’ or ‘yellowing’ [10].

There have been various approaches towards preventing or diminishing these undesirable effects of which the most widely used is that of coating the TiO_2 with silica or alumina to reduce the photoactivity of the TiO_2 particles [10,17–22]. This activity derives from the semiconductor nature of the particles: illumination with

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near-UV light causes the development of a hole–electron pair in the particle which are the precursors, respectively, of the highly reactive hydroxyl radical and the superoxide ion [10,17–20,23]:

$$TiO_2 \xrightarrow{UV} h^+ + e^- \quad (1)$$

$$h^+ + H_2O\ (\text{surface}) \rightarrow {}^{\bullet}OH + H^+ \quad (2)$$

$$e^- + O_2\ (\text{surface}) \rightarrow O_2^{-\bullet} \quad (3)$$

Reactions (1)–(3) represent a simplified version of a more complex scheme, but the key radical products are the same [10,23–27].

An alternative approach to modifying the photoreactivity of the TiO_2 particle is to dope it with metal ions of at least different, and preferably variable, oxidation state, with the view to either promoting or reducing electron–hole recombination, i.e. the thermal reverse of Reaction (1). This approach has also been investigated extensively [26,28,29] using a range of transition metal ions, in connection with the use of TiO_2 particles (often immobilised on a support) to effect the photomineralisation of toxic organic pollutants in water [23,24,26,27,30,31].

In the present paper is described the application of such transition metal-doped TiO_2 particles to the problem of photodegradation of PVC–TiO_2 composites. The first part of the paper deals with the details of preparation and characterisation of the doped particles, noting the importance of reproducibility in this field, the second with their photochemical behaviour in a PVC matrix. The latter sets of experiments were directed towards defining the reactivity of variously modified TiO_2 particles towards a single polymer system, i.e. PVC is used as a trialling system for testing new modifications of TiO_2.

2. Experimental

2.1. Materials

Chemicals were commercial materials of the highest available purity. Brands and suppliers of TiO_2 are given in Table 1.

2.2. Preparation of samples

2.2.1. Preparation of doped TiO_2

2.2.1.1. Coprecipitation method. The coprecipitation method has been adapted from the method of Gopal [32], Iwasaki et al. [33] and Ying et al. [34]. Distilled water (170 cm^3), conc. HCl (12 cm^3) and propan-2-ol (12 cm^3) were mixed together at room temperature by stirring. The appropriate metal salt at the calculated percentage loading was added to the solution. After thorough mixing, titanium isopropoxide (10.4 cm^3) was gradually added using a pipette. A gelatinous precipitate was formed instantly. After the solution became clear it was heated in a water bath. The water bath temperature was slowly increased from room temperature to 328 K over a period of a few hours. The solutions were left overnight. The resulting precipitate was decanted and dried at 353 K and then placed in an oven for a few hours at 373 K. The samples were then calcined at either 873 K or 1273 K in air for 3 h (heating regime 298 K – chosen temperature at 200 K/h, dwell time = 3 h followed by cooling to 298 K at 200 K/h).

2.2.1.2. Absorption method. The appropriate metal salt was dissolved in methanol along with Degussa P25 (0.05 mol). The solution was stirred for a few hours and then the solvent was evaporated to leave TiO_2 powder. The powder was placed in an oven at 423 K for 2–3 h and later calcined in air at 873 K using the same heating regime as for the coprecipitation method.

2.2.2. Preparation of PVC films

PVC (1 g) was dissolved in HPLC grade tetrahydrofuran (20 cm^3) and the corresponding amount of modified TiO_2 pigment was added. The solution was then sonicated/stirred for approximately 1 h. Thin films (100–150 μm) were prepared by pouring the solution into disposable circular aluminium trays (area = 8.55 cm^2) and allowing the solvent to evaporate. Film thickness was calculated from the dimensions and weight of the film and confirmed by microscopy of a cross-section. The IR spectra were recorded and samples chosen for size according to their relative absorbances at 2913 cm^{-1}. The films were then irradiated in a QUV Weatherometer (Q Panel Company) equipped with 8 UV_B 300 W bulbs (for intensity see Section 2.5.1), at a temperature of 318 K.

2.3. Electrochemical measurements

Following Fonseca [35], the chloride ion content of photolysed aqueous PVC suspensions was estimated by electrochemical measurement using an Ag/AgCl electrode calibrated with a range of standard KCl solutions.

Table 1
Titanium dioxide brands and suppliers

Titanium dioxide brand	Anatase: rutile	Supplier
Degussa P25	70:30	Degusssa AG
PC500	Anatase	Millennium Chemicals
K2220, K2222	Coated rutile	Kronos