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Factors affecting the interfacial adsorption of stabilisers on to titanium dioxide particles (flow microcalorimetry, modelling, oxidation and FTIR studies): Nano versus pigmentary grades

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Abstract

A series of nano and micron particle size anatase and rutile titanium dioxide (TiO_2) were prepared with various densities of surface treatments in order to examine the influence of the particle size on the photoactivity of the titania particle surface and their degree and nature of interfacial interaction with polymer stabilisers namely, Irganox 1010 (Phenolic type) and Tinuvin 770 (hindered piperidine type). The surface characteristics of the synthesized powders were studied by Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS). The surface area was determined using the Brunauer Emmett Teller (N_2 BET) method, and particle size measurements using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The photochemical activities of the titania particles have been examined by monitoring the oxygen consumption during photo-oxidation of 2-propanol. Surface activity of the titania with stabilisers has also been examined by flow microcalorimetry (FMC) and DRIFTS in order to determine the nature of the interfacial interactions with different polymer stabilisers. Photoactivity assessment verified the higher activity of the nanoparticles. Hydroxyl groups were also found to be accountable for the higher photoactivity of the nanoparticles. The rutile crystal form conferred an inherent photostabilising effect that was further improved by surface coating with alumina. FMC studies revealed that the calcination of nanoanatase increased adsorption activity of hindered phenol and hindered amine probes, with the latter being more strongly adsorbed due to the higher basicity of the amine functionality. DRIFTS indicated adsorption may also occur through the ester functionalities. Calcination of the titania causes a reduction in the surface concentration of Ti–OH and hence a reduction in the amount of strongly adsorbed water blocking the adsorption sites and possibly bridging the amorphous primary particles on the uncalcined sample. With the calcined samples the adsorption activity was proportional to surface area. The physical and chemical nature of these intermolecular forces are assessed and discussed in relation to the potential effects on polymer stabilisation processes.

Keywords: Titanium dioxide; Pigments; Nanoparticles; Degradation; Oxidation; Microcalorimetry; Interfacial adsorption

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1. Introduction

The effect of titanium dioxide surface chemistry on interfacial interactions with stabilisers has not been studied in detail. In thermoplastics, the adsorption of stabilisers onto fillers is a recognised problem that is solved by using additives which sacrificially adsorb on to the filler surfaces thereby blocking the adsorption of the stabilisers [1]. Previous studies on silicas for example, indicated that the adsorption of stabilisers is not necessarily a negative feature and this can be used to provide what can be considered as a reservoir of stabilisers for controlled activity [2]. In order to understand how stabilisers are adsorbed and under which conditions they can be released, the interactions between pigments (fillers) and polymer additives must be well understood. Flow microcalorimetry (FMC) has proved to be a useful technique for studying such interactions and has become an established method for characterising filler surfaces in terms of their surface chemistry and their interactions with surface treatments etc. The technique was initially used for this purpose by Fowkes [3] and later refined by Ashton and Briggs [4]. FMC enables heats of adsorption and desorption to be measured and, with added concentration detectors, amounts adsorbed/desorbed can be obtained. The latter enables calculation of molar heats of adsorption–desorption. Knowledge of the microstructure of pigments and fillers is of great importance in understanding what processes limit the efficiency of the powders. It is important to recognise that the bulk properties of the materials such as mechanical, electronic and optical properties depend on the atomic and molecular structure of the materials.

The science of ultrafine particles on a nanometric scale has attracted considerable attention in recent years. Varieties of techniques and characterisation tools have been developed to prepare and study these particles. A unique property of nanoparticles is their extremely high surface area: they have many more sites for achieving property enhancements, making them ideal for a wide variety of applications. In recent years extensive studies have been undertaken on characterising interfacial interactions on carbon black particles of varying manufacturing types and polymer stabilisers [5–7] as an example. Here the nature of surface functional groups on the carbon blacks and acid–base characteristics were thoroughly characterised and measured. Both stabiliser adsorption and desorption properties were also measured and related in many cases to their interactive performance in the polymer during thermal and photo-oxidation processes. The presence of impurities such as sulphur compounds and adsorbed water were also found to cause further complications in the surface analysis of carbon black and so influence the adsorption properties of the stabilisers and their performance. Similar studies have also been undertaken on silica fillers [2].

Presently there is a rapidly growing interest in nanoscale TiO_2 materials in research activities. Catalysis by TiO_2 has become a very active field of research and it can be designed with a high efficacy by combining the physical properties of TiO_2 as a photocatalytic semiconductor and/or by doping the TiO_2 with various transition metal oxide systems. On the other hand the absorption of UV light by TiO_2 may be utilised for solar radiation panels. In all these applications, the morphology, average particle size and size distribution, phase composition and porosity of titania powders are important factors to be controlled. Nanoparticles show a great tendency to aggregate due to high surface energy combined with their high surface area to volume ratio. This aggregation tendency impedes their use in a variety of applications. For these reasons the synthesis of ultrafine particles with controlled size and surface chemistry is of technological interest.

In recent work we examined the role of uncoated ultrafine titanium dioxide pigments in alkyd and acrylic based paint films [8,9]. This work highlighted a very clear difference in behaviour between nanoparticle and pigmentary grade titanium dioxide with the former being more active in its uncoated form. Surface modifications of the TiO_2 particles with inorganic hydrates were found to reduce the photochemical reactivity of titanium pigments. This can reduce the generation of free radicals by physically inhibiting the diffusion of oxygen and preventing release of free radicals. The photosensivity of titanium dioxide is considered to arise from localized sites on the crystal surface, and occupation of these sites by surface treatments inhibits photo-reduction of the pigment by ultraviolet radiation and hence the destructive oxidation of the binder is inhibited. However, because such pigment particles are so small, their specific surface area is very high and therefore, important to the pigment's chemical performance. Thus, surface characteristics have profound impact on interactions of pigments with all the other components of polymer materials on the substrate. Titanium dioxide particles on the surface contain both basic terminal and acidic bridged-hydroxyl groups and these may be associated with the titania or a hydrous oxide coating. It will also possess labile Ti–O–Ti bonds, water molecules adsorbed at Lewis acid sites or surface hydroxyl groups as well as adsorbed anions such as sulphate and chloride process residues. All these species can exhibit strong interactions with polymer additives, in particular stabilisers, causing often antagonistic effects as reported recently [8,9]. Thus, hindered piperidine light stabilisers being basic in character have been found to exhibit little stabilisation effect in the presence of photocatalytic grade anatase nanoparticles.

This study aims to correlate the surface properties and particle size with the interfacial interactions of a range of pigmentary and nanoparticle titania pigments