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Effect of shape and surface chemistry of TiO_2 colloidal nanocrystals on the organic vapor absorption capacity of TiO_2/PMMA composite

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ABSTRACT

The organic vapor absorption capacity of poly(methyl metacrylate) (PMMA), filled with oleic acid (OLEA) capped TiO_2 nanocrystals (NCs) with curved shape, rod-like and spherical, is studied. The NC shape combined with the nature of the capping molecules can be used to enhance or reduce the PMMA ability to absorb different solvent molecules in a controlled way. Indeed, the arrangement of the ligands at the NC surface demonstrates an effective tool to control the extent of the interaction between the penetrating molecules and the embedded NCs from the outer to the inner specific chemical functionality of the coordinating ligand molecules.

1. Introduction

Polymer networks exposed to solvent vapors absorb the organic molecules and swell to an equilibrium state, where the tendency to absorb solvent molecules is balanced by the elastic response of the network [1]. After desorbing the solvent molecules, the polymer then shrinks and returns to its initial volume. The swelling and shrinking properties of polymers are currently being exploited in a large number of important industrial applications including chemical sensing [2–5], controlled drug delivery [6], muscle-like actuators [7], and metal extraction and separation applications [8]. On the other hand, in many technological fields the swelling is considered detrimental and needs to be avoided. Indeed, the penetration of molecules from outer environment into polymers can have disastrous effects, as in the case of water or gases molecules diffusion into food and beverage packaging. In this scenario the ability to enhance or reduce/inhibit the gas or vapor diffusion into a polymer material, according to the needs of the final applications, would have tremendous technological fallout.

Recent studies have shown that the ability of a polymer to absorb solvent molecules can be modified by filling the polymer with inorganic nanoparticles [9–15]. In particular, the interaction between the active sites on the surface of the nanoparticles and the penetrating molecules can control the selectivity, rate and efficiency of the absorption capability of the host polymer, thus offering a powerful tool to quantitatively vary the swelling/shrinking behavior in the polymer composite.

In this perspective curved nanofillers, rod-like and sphere shaped, present specific advantages due to their high surface-to-volume ratio, which can dramatically increase the number of active sites available for interaction with analyte molecules. Furthermore the use of colloidal nanocrystals (NCs) as nanofillers would offer further remarkable advantages afforded by the ease in both manipulating the shape and tailoring the chemical characteristics of the surface by using versatile functional groups, including biocompatible ones, able to effectively and selectively interact with different analytes.

In this work, we highlight on how the shape, rod-like or spherical, combined with surface chemical properties of the nanofillers can influence the swelling behavior of a polymer. This is a fundamental technical issue that needs to be fully clarified for possible exploitation of the potential offered by polymer composites for suitably controlled vapor/gas absorption properties as well as for all those applications where the interaction between capped nanoparticles and analyte molecules plays a fundamental role.

Here we demonstrate that the dispersion of TiO_2 colloidal NCs, capped by oleic acid (OLEA), in poly(methyl metacrylate) (PMMA) results in a degree of swelling upon exposure to the same solvent, that can be increased or reduced by simply varying the geometry,

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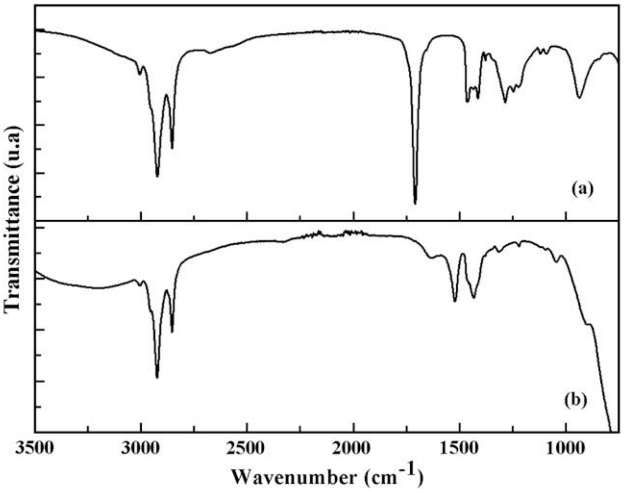

Fig. 1. FT-IR spectra in the 3500–400 cm^{-1} region of: (a) OLEA and (b) OLEA capped TiO_2 nanorods.

rod-like or spherical, of the nanofiller involved. The comparison between spherical and rod shaped TiO_2 NCs has been made possible thanks to an effective colloidal synthetic route [16] that allows to manipulate the NC shape, providing gram-scale quantities of organic-capped spherical or rod shaped NCs dispersed in chloroform solution by simply controlling the NC growth kinetics.

The swelling of the PMMA nanocomposite films was investigated at room temperature by measuring vis–IR reflectance spectra of the samples, deposited on Si substrates, in the presence of solvent vapors. Different solvents, like acetone, ethanol, propan-2-ol and water, were carefully chosen for their difference in polarity, number of C–H bonds, and pure PMMA swelling ability.

Then the swelling results were related to atomic force microscopy (AFM) observations and glass transition temperature, T_g, measurements performed on the PMMA nanocomposite samples to clarify fully the critical role played by the nanoscale curvature and the organic capping of the fillers in controlling the absorption capacity of the host polymer.

2. Experimental section

Titanium tetraisopropoxide ($Ti(OPr^i)_4$ or TTIP, 99.999%), trimethylamino-*N*-oxide dihydrate ($(CH_3)_3NO \cdot 2H_2O$ or TMAO, 98%, water solution), anhydrous ethyleneglycol ($HO(CH_2)_2OH$ or EG, 99.8%), and oleic acid ($C_{18}H_{33}CO_2H$ or OLEA, 90%) were purchased from Aldrich and were used as-received without further purification or distillation. All solvents used were of analytical grade and purchased from Aldrich.

Organic-capped anatase TiO_2 NCs were synthesized by hydrolysis of TTIP using technical grade OLEA as surfactant at low temperatures (80–100 °C) [16]. Briefly, hydrolysis of TTIP was carried out by an excess of aqueous base solution in the presence of TMAO as catalyst for polycondensation. The morphology of the resulting TiO_2 NCs was modulated by varying the rate of water supply in the reaction mixture. One-dimensional growth was guaranteed by direct injection of large aqueous base volumes in OLEA: TTIP mixtures, while nearly spherical particles were obtained upon in situ water release (from the slow esterification reaction of OLEA and added EG).

The extraction procedures were subsequently performed in air: TiO_2 NCs were readily precipitated upon addition of an excess of ethanol (or methanol) to the reaction mixture at room temperature. The resulting precipitate was isolated by centrifugation and repeatedly washed (three times) with ethanol to remove surfactant residuals. The resulting OLEA capped rod-like and dot-like TiO_2 NCs were homogeneously dispersed in chloroform solutions. By this way, highly concentrated transparent solution of TiO_2 NCs was obtained, stable over months.

Nanocomposite materials were prepared by incorporation of pre-made nanoparticles in organic polymers with the use of a common blending solvent by adding high molecular weight PMMA to a $CHCl_3$ solution of TiO_2 nanorods and nanospheres at increasing nanofillers concentration (from 0.025 M to 0.2 M), corresponding to an NC load percentage in polymer ranging from 4 wt% to 36 wt%. Prior to the incorporation, the NCs were repeatedly washed (three times) with ethanol to remove surfactant excess. A polymer concentration of 0.05 g/ml was selected to achieve optically clear nanocomposite solutions. The NC/polymer blend was gently stirred until the complete polymer dissolution in $CHCl_3$. Thin films were prepared depositing by spin-coating (using an EC101DT Photo Resist Spinners, Headway Research Inc.) few drops of the NC–polymer mixture onto properly cleaned glass and silicon substrates at 3000 rpm for 30 s. The film thickness, measured by means of Alpha-Step 500 surface profiler, was found in the range from 400 nm up to 1 μm, strongly depending on the NC concentration and surface ligand compositions.

Fourier transform infrared (FT-IR) spectroscopy was used to investigate the nature of the organic coating on the surface of the TiO_2 NCs. TiO_2 powders for FT-IR analysis were prepared by washing the extracted precipitate repeatedly (three times) in order to remove physisorbed surfactant molecules, and then evaporating the residual solvent under vacuum at room temperature.

In Fig. 1 the typical IR spectra in the region 3500–400 cm^{-1} of the OLEA capped TiO_2 nanorods (Fig. 1b) are reported and compared with that of the pure acid (Fig. 1a). A similar spectrum was obtained for the OLEA capped TiO_2 dots. Above 2000 cm^{-1} the

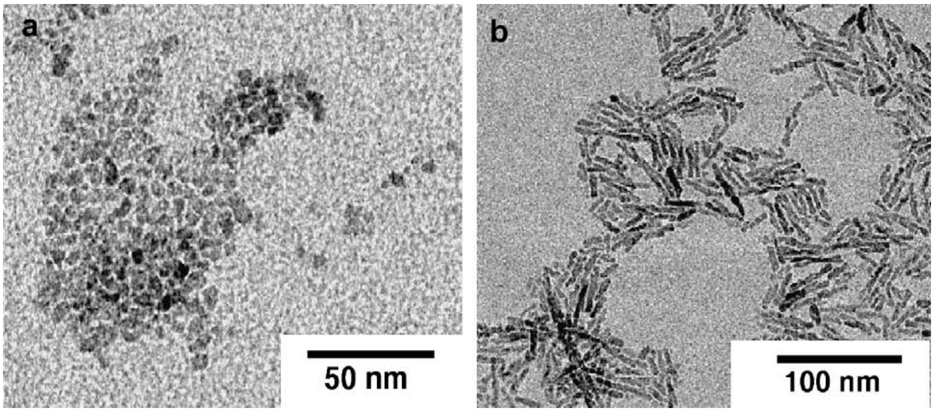

Fig. 2. TEM image of TiO_2 (a) nanospheres–PMMA nanocomposite and (b) nanorods–PMMA thin films deposited on a carbon-coated 400 mesh copper grids by spin coating.