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TiO_2/PDMS nanocomposites for use on self-cleaning surfaces

M.T.S. Tavares [a,*], A.S.F. Santos [b], I.M.G. Santos [c], M.R.S. Silva [c], M.R.D. Bomio [a], E. Longo [d], C.A. Paskocimas [a], F.V. Motta [a]

[a] Department of Materials Engineering, Federal University of Rio Grande do Norte, Campus Lagoa Nova, CEP 59078-900, Natal/RN, Brazil
[b] Department of Materials Engineering, Federal University of Paraíba, Cidade Universitária, CEP 58051-900, João Pessoa/PB, Brazil
[c] Department of Chemistry, Federal University of Paraíba, Cidade Universitária, CEP 58051-900, João Pessoa/PB, Brazil
[d] Interdisciplinary Laboratory of Electrochemistry and Ceramics, São Paulo State University, Rua Francisco Degni s/n, CEP 14801-907, Araraquara/SP, Brazil

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ABSTRACT

In this study, polydimethylsiloxane (PDMS)/TiO_2 nanocomposite was processed by the spray method. TiO_2 nanoparticles were synthesized by microwave-assisted hydrothermal method. Varying the proportion of nanoparticles in 0%, 0.5% and 1% by weight, commercial TiO_2 (P25) was used for comparison purposes. The photocatalytic activity of nanocomposites impregnated with methylene blue was assessed by means of UV–visible spectroscopy. Changes in contact angle were analyzed before and after UV degradation tests. The effect of ultraviolet radiation on the chemical structure of the PDMS matrix was evaluated by Fourier transform infrared spectroscopy (FTIR). The results indicated that the addition of TiO_2 nanoparticles in PDMS provides good photocatalytic properties in the decomposition of methylene blue, which is an important characteristic for the development of coatings for self-cleaning. For comparison purposes, commercial P25 was also used to investigate the photocatalytic activity.

1. Introduction

Titanium dioxide nanoparticles (TiO_2) have received special attention in several areas of materials engineering for enabling various applications such as solar cells, photocatalysis, photoelectrochemical applications, and treatment of water and wastewater [1–5]. The physicochemical properties of TiO_2 have been studied in order to obtain satisfactory results. The coating of glasses, mirrors or surgical devices with thin titanium dioxide films enables the production of anti-fog or self-cleaning materials [6,7]. Besides glasses, there are also self-cleaning coatings for application on the outside of buildings. The use of this material is already a reality in developed countries. The goal is similar to self-cleaning glasses, that is, to reduce maintenance costs.

Currently, the development of chemical methods suitable for the production of ceramic powders has attracted the attention of the scientific community [8–12]. Among numerous synthesis methods to obtain TiO_2, the microwave-assisted hydrothermal method has unique advantages of uniform, fast and volumetric heating compared to other methods, and has been efficiently used for the preparation of inorganic materials [13–16]. Furthermore, the method can significantly reduce the reaction time and the use of high temperatures, leading to rapid crystallization and simplifying the process of preparing nanoparticles [17].

Some of the materials most widely used in literature as reinforcement for nanocomposites are TiO_2 nanoparticles industrially applied in coatings and paints [18] and SiO_2 nanoparticles, which may provide great mechanical strength or flame retardant characteristics to nanocomposites [19]. One of the characteristics to be considered when inorganic charges are used in nanocomposites is the reduced chemical affinity between charges (hydrophilic nature) and the polymer (predominantly hydrophobic). Nanocomposites formed from different polymer matrices reinforced with TiO_2 nanoparticles have been studied for the analysis of the photocatalytic activity [20–22]; however, no synthesis of silicone nanocomposites (PDMS) with TiO_2 nanoparticles with photocatalytic properties for application in self-cleaning surfaces is found in the literature.

Silicones with methyl groups are hydrophobic and therefore good water repellents [23]. Silicones have high resistance to degradation by exposure to ultraviolet radiation and are resistant to heat generally from −45 °C to +145 °C [23,24]. This polymer is chemically inert and resistant to decomposition by heat, water or oxidizing agents, and is characterized by having high longevity with useful life of at least 10 years, being compatible with application means [24]. In addition, silicones have high gas permeability in thin films, are resistant to aging, sunlight, humidity and exposure to chemicals and have low mechanical strength [25].

This work was carried out due to the advantages that introducing nanoparticles in polymer matrices presented for use in self-cleaning coatings. In the first step, nanoparticles (TiO_2) were obtained by microwave-assisted hydrothermal method in order to reduce the time

* Corresponding author. Tel.: +55 84 3342 2512; fax: +55 84 3342 2406.
E-mail address: maratatianest@gmail.com (M.T.S. Tavares).

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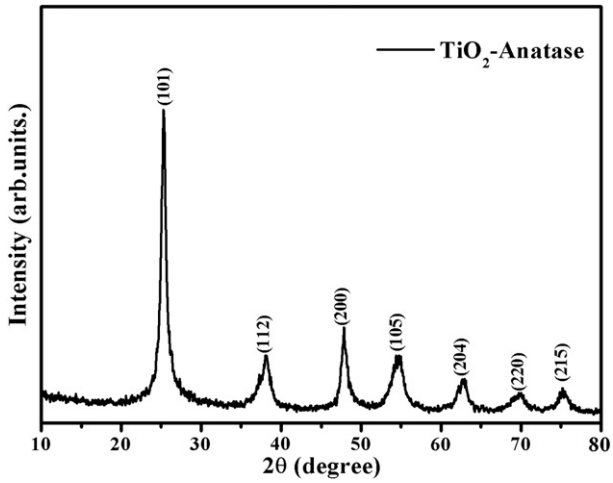

Fig. 1. Diffractogram of TiO_2 nanoparticles obtained by microwave-assisted hydrothermal method.

and temperature of treatment, then by the method of simply mixing, the nanocomposite was synthesized (PDMS/TiO_2) for further application in spraying for obtaining thin film with photocatalytic and self-cleaning properties.

2. Experimental method

2.1. Materials

The chemical reagents used in the present study were as follows: titanium IV isopropoxide (Aldrich, $C_{12}H_{28}O_4Ti$) as titanium precursor reagent, ethyl alcohol (Vetec, C_2H_2OH), glacial acetic acid (Vetec, $C_2H_4O_2$), and sulfuric acid (Vetec, H_2SO_4). The materials used to prepare the nanocomposites were as follows: poly (dimethylsiloxane) (PDMS) (Dow Corning Ltd.), polymerizing agent (Dow Corning Ltd.) and hexane (Dinâmica C_6H_{14}).

2.2. Synthesis of TiO_2 nanoparticles

The synthesis was initiated by diluting 10 ml of titanium IV isopropoxide in 30 ml of ethanol under stirring for 5 min at room temperature. Then, 20 ml of acetic acid was added dropwise, followed by the addition of 1 ml of sulfuric acid under constant stirring for 20 min [10]. Subsequently, the clear solution obtained was sonicated at 60 °C for 1 h, resulting in the formation of a milky colloidal solution, which was transferred to a Teflon-lined autoclave for hydrothermal treatment irradiated by microwave (2.45 GHz, maximum power of 800 W) at 120 °C for 2 h (heating rate fixed at 25 °C/min). After cooling, the precipitate formed was centrifuged and washed with distilled water and ethanol; this procedure was repeated three times to decrease the solution acidity, and then dried at room temperature. The samples were characterized by XRD and FEG-SEM.

2.3. Preparation of the PDMS/TiO_2 nanocomposite

Nanocomposites were prepared by simple mixing, without any pretreatment in the materials used as matrix and load. Polydimethylsiloxane (PDMS) was mixed with the polymerizing agent at a ratio of 10:1. Then, the mixture was diluted with hexane at a ratio of 1:2 (PDMS: hexane) with subsequent dispersion of TiO_2 nanoparticles in proportions of 0%, 0.5% and 1%; the mixture was sprayed on glass slides previously cleaned with commercial ethanol. The spraying process used a commercial airbrush coupled to a static deposition system similar to that used by Choonee et al. [26], but without the option of rotating the base. Subsequently nanocomposites were placed in an oven with air circulation for 30 min at 60 °C for polymerization.

2.4. Degradation by ultraviolet radiation (UV)

To analyze the photocatalytic activity of nanocomposites, the samples were immersed in aqueous solution of methylene blue in a concentration of $1.0 \cdot 10^{-3}$ mol/L for 48 h and were submitted to UV aging for 3 h in a reactor with dimensions of $h = 10$ cm, $l = 1$ m and $w = 20$ cm, with UVC lamps (254 nm ≈ 4.9 eV) SuperNiko brand, model ZG-30 T8. With intermediate measurements of UV–vis in wavelength 400–900 nm every 30 min.

2.5. Characterizations

TiO_2 nanoparticles were characterized for their crystalline phase by XRD and measurements were performed on a Shimadzu diffractometer/XRD-7000, CuKα radiation (λ = 1.54 Å), 40 kV and 30 mA and 2θ from 5° to 80°, and for their morphology by high resolution electron microscope (FEG), dispersing samples in acetone and then deposited on a monocrystalline silicon substrate. For characterization and study of the photocatalytic activity of nanocomposites (PDMS/TiO_2), samples were exposed to UV radiation and characterized before and after degradation by characterization techniques: UV–visible spectroscopy (model UV-2550, Shimadzu), Fourier transform infrared spectrophotometry (FTIR, model IR-Prestige-21, Shimadzu, using 32 scans, resolution of 4 cm^{-1} and range of 2 cm^{-1}) and wettability test (images were captured by a camera and stored by the Pinacle Studio 8 software and subsequently the contact angle was obtained through the Stuffens software).

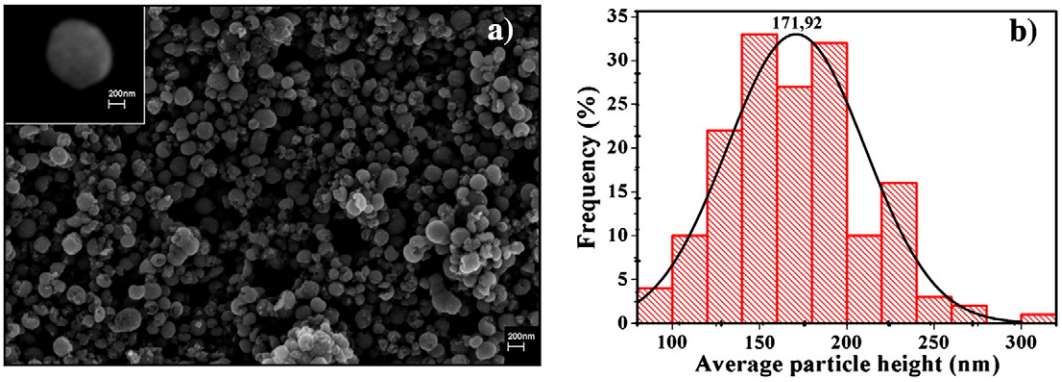

Fig. 2. (a) Micrograph of TiO_2 nanoparticles obtained by microwave-assisted hydrothermal method. (b) Particle size distribution.

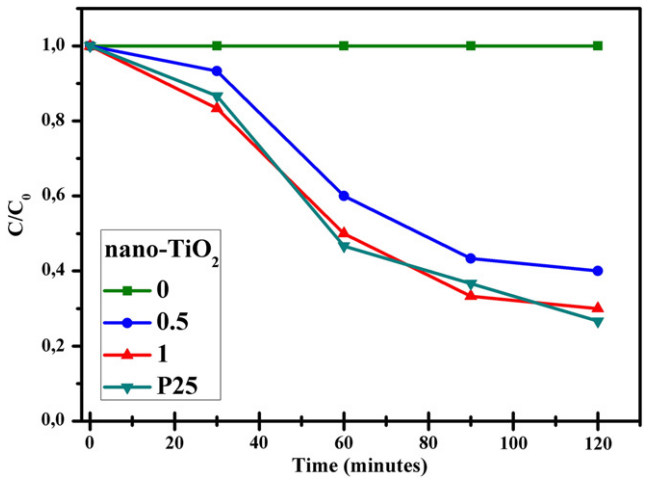

Fig. 3. Variation in the methylene blue concentration in nanocomposites after UV degradation.

3. Results and discussion

3.1. Characterization of nanoparticles

Fig. 1 shows the X-ray diffractogram of TiO_2 nanoparticles obtained by microwave-assisted hydrothermal method. According to XRD, it was observed that all the diffraction peaks are related to the crystalline anatase phase and were indexed according to PDF letter No. 01-071-1166. The anatase structure of nanocrystals is confirmed by the diffraction peaks at 2θ angles of 25.3°, 37.8°, 47.9°, 54.8°, 62.6° and 68.7° [27], with crystallite size of 4.6 nm. No peak of rutile and brookite phases was observed in the diffractogram.

Huang et al. [14] analyzed TiO_2 samples by XRD and found that the crystalline form of samples prepared by microwave-assisted hydrothermal method at temperatures above those used in this study, 150 °C and 180 °C, 120 min and landing, also forms the anatase crystalline phase with the main peak with $2\theta = 25.3°$.

Fig. 2a shows a scanning electron microscopy by field emission of TiO_2 nanoparticles, which presents the morphology of spherical particles with different sizes from 70 to 300 nm (Fig. 2b). The literature shows results of the strong influence of morphology on the photocatalytic activity. This is due to differences in the surface of the material, with possible different crystallographic planes [28,29]. According to Nakata and Fujishima [30], the spherical morphology of TiO_2 nanoparticles is the most commonly studied because they have high specific surface area and high pore volume, increasing the contact surface between particles, consequently increasing the mass transfer rates for the adsorption of organic pollutants, making them good candidates for use in photocatalysis.

3.2. Study of the photocatalytic activity of nanocomposites

The relative values of the variation in the methylene blue concentration were used to study the degradation by UV irradiation of PDMS/TiO_2 nanocomposites; the dye concentration as a function of irradiation time is illustrated in Fig. 3. During this process, it was observed that the methylene blue concentration in the nanocomposites decreases rapidly when exposed to UV radiation. Furthermore, coating with 1% TiO_2 shows degradation rate slightly higher than nanocomposite with 0.5% wt TiO_2; this is due to better dispersion of nanoparticles in the polymer matrix as can be seen in SEM images (Fig. 4). This shows that the amount of TiO_2 influences the photodegradation of methylene blue ($C_{16}H_{18}ClN_3S.3H_2O$) as well as the manner in which these nanoparticles are dispersed in to the matrix. P25 and 1% TiO_2 coating exhibits similar behavior. In PDMS films with 0% TiO_2, only a small reduction of the dye was observed, as described in the literature [20], demonstrating the effect of TiO_2 in the nanocomposite of the polymer matrix after UV irradiation.

PDMS/TiO_2 films were analyzed by infrared spectrophotometry before and after exposure to UV radiation to verify the behavior of the polymer after UV degradation; a film with pure PDMS was used for comparison. Fig. 5 shows that the absorption bands at 2962 cm^{-1} are attributed to the vibration mode of the C–H stretching. At 1411 cm^{-1}, there is an absorption band characteristic of the deformation of the $–CH_3$ radical, confirming the previous grouping [31]. The strong absorption band at 1256 cm^{-1} is attributed to the vibration mode of the –Si–C stretching. The strong absorption bands at 1072 and 1013 cm^{-1} are attributed to the vibration mode of the Si–O–Si stretching. The absorption band at 782 cm^{-1} is attributed to the vibration mode of the asymmetric Si–O–Si stretching, while the absorption band at 689 cm^{-1} is attributed to the deformation of the Si–O–Si bonding [32], where similar peaks can be observed, indicating that UV radiation did not influence the formation of new products in the chemical structure of samples, confirming the good stability of PDMS under UV degradation.

Fig. 6 shows the measurements of the contact angle formed between the water drop and the surface of nanocomposites before and after aging in UV chamber during 60 s. It was found that all coatings exhibit hydrophobic characteristics with angles above 80°. Exposure to

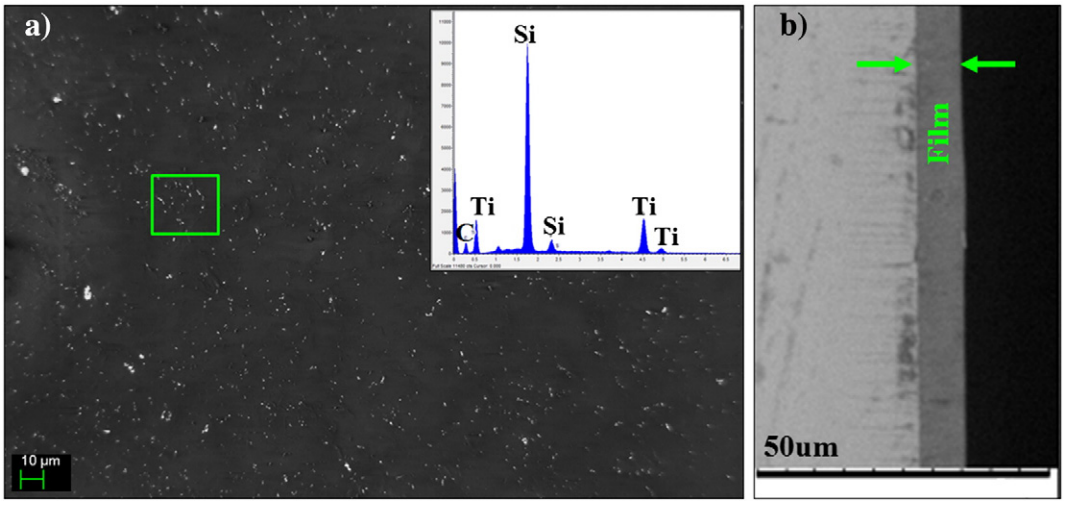

Fig. 4. (a) Micrograph of TiO_2 nanoparticles dispersed in the PDMS. (b) Transversal cross-section SEM micrographs of the films.

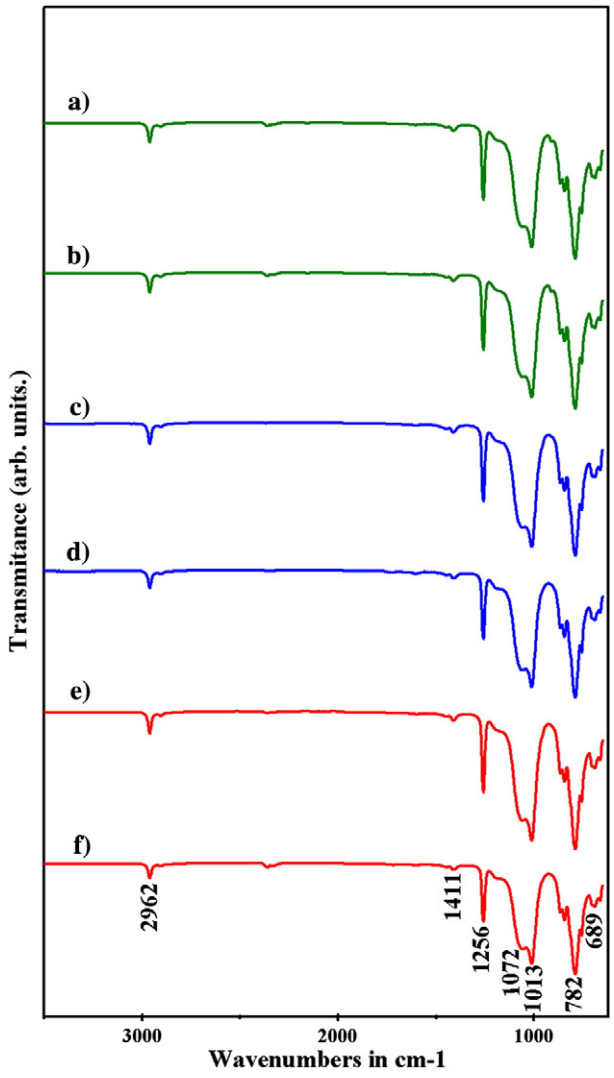

Fig. 5. FTIR spectrum/ATR composite PDMS/TiO_2. (a) 0% TiO_2 before degradation, (b) 0% TiO_2 after degradation, (c) 0.5% TiO_2 before degradation, (d) 0.5% TiO_2 after degradation, (e) 1% TiO_2 before degradation and (f) 1% TiO_2 after degradation.

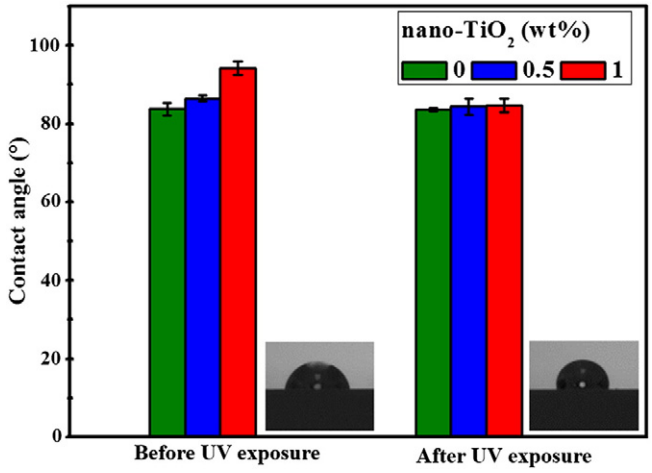

Fig. 6. Measurements of the contact angle of nanocomposites before and after UV degradation.

ultraviolet radiation only reduced the contact angle of samples containing TiO_2, confirming the likely hydrophilic characteristics of coatings containing these nanoparticles. Ding et al. [20] analyzed the contact angle of nanocomposites reinforced with TiO_2 nanoparticles; the contact angle with water decreases with increasing sun exposure for all coatings with different TiO_2 contents.

4. Conclusions

TiO_2 nanoparticles were efficiently obtained in their crystalline phase using the MAH method at 120 °C for 2 h. As shown in the FEG-SEM image, TiO_2 nanoparticles have spherical shape and uniform size, showing good dispersibility in the polymer matrix. The results indicated that the addition of TiO_2 nanoparticles to PDMS provided coating with good photocatalytic activity in the decomposition of methylene blue dye. PDMS/TiO_2 nanocomposites prepared by spray showed good chemical stability to UV radiation, as can be seen in the FTIR results. Both characteristics are important for the development of self-cleaning coatings.

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