X-ray Scattering Experiments on Sputtered Titanium Dioxide Coatings onto PVDF Polymers for Self-Cleaning Applications

S. M. Marques,[1] C. J. Tavares,[1] S. Lanceros-Méndez,[1] Z. Denchev[2]

[1]Centre of Physics - GRF, University of Minho, Guimarães 4800-058, Portugal
[2]i3N Associated Laboratory, IPC – Institute for Polymers and Composites, University of Minho, Guimarães 4800-058, Portugal

ABSTRACT: The performance of active polymer substrates used in sensor and actuator or tactile display applications can be hindered by the inevitable soiling of their surface. A possible approach to overcome this problem is to deposit a self-cleaning coating onto the polymer surface, taking care that the layer underneath withholds its intrinsic properties. In this work, titanium dioxide, TiO_2, was naturally chosen for coating material due to its inherent photocatalytic properties. Thus, TiO_2 thin films were deposited by reactive magnetron sputtering on poly(vinilydene fluoride) - (PVDF) substrates, in its α- (nonelectroactive) and β- (electroactive) phases. Wide angle x-ray scattering (WAXS) experiments in a synchrotron were performed to monitor the crystalline structure of the polymer substrates upon thin film deposition and also to assess the crystalline structure of the TiO_2 coating at different temperatures. In the WAXS patterns of the coated α-PVDF, the TiO_2 polymorph anatase phase can be distinguished. At the same time, no explicit diffraction peaks for anatase were detected in the coated β-PVDF. Fourier transform infrared spectroscopy evidenced that the chemical structure of PVDF is unaffected by the coating deposition process. These structural results have been correlated with the photocatalytic properties of the TiO_2 coatings. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 726–731, 2011

Key words: photocatalysis; self-cleaning; sputtering; titanium dioxide; WAXS; PVDF

INTRODUCTION

Active polymers have become very popular in the flexible electronics industry for applications in sensors and actuators.[1–3] In particular, electroactive polymers are capable of generating an electric field when their shape is modified, hence being used as actuators, sensors, or tactile displays. As actuators, they are characterized by being able to undergo a large amount of deformation while sustaining moderate forces. Consequently, the performance of these systems can be hindered by inevitable soiling of the surface, which can also instigate the degradation of the polymer. By depositing a self-cleaning coating onto the polymer surface one can control pollution adsorption on the active surface, taking also care in ensuring that under layer withholds its intrinsic properties. With this in mind, titanium dioxide, TiO_2 was chosen due to its excellent photocatalytic properties.[4–6] These thin films have been deposited by reactive magnetron sputtering on poly(vinilidene fluoride) polymer (PVDF) substrates. It has been previously reported that these polymer substrates act synergistically with the overlying coating to actively promote a higher efficiency in photocatalysis.[7] Further reports have shown that the photocatalytic efficiency of the TiO_2 coatings has been improved by anionic doping of the crystalline anatase structure with nitrogen.[8,9] This effect has been achieved by depositing TiO_2 thin films by unbalanced reactive magnetron sputtering on PVDF in its α (nonelectroactive) and β (electroactive) phases. The latter phase has been obtained by uniaxially stretching the α-phase material[10] and has been deposited in a poled form. The main effect of the poling process, necessary to optimize the electroactive properties of PVDF in its β-phase, is the alignment of the randomly organized dipolar moments against an applied electric field. The β-PVDF is an electroactive polymer with many applications as sensors and actuators. Furthermore, α-PVDF is also used in wires, cables, and tubes. The possibility of a photocatalytic self-cleaning will improve the performance of PVDF in many of these applications and open possibilities for new ones. Enhancing the photocatalytic efficiency of TiO_2 has become a major concern bearing in mind industrial applications for general purpose plastics.

In this study, the photocatalytic behavior of TiO_2 coatings was determined by combined ultra-violet

irradiation and absorption measurements of a particular dye (Red 41, acting as an organic pollutant). The observed photo-decomposition of the dye was measured in the UV/visible spectrum by the decrease of the maximum absorbance of the dye with irradiation time. Wide angle x-ray scattering (WAXS) experiments were performed to monitor the crystalline structure of the polymer substrates upon thin film deposition and also to assess the degree of crystallinity of TiO_2 coating in its as-deposited and upon thermal annealing at varying temperature state. Subsequent Fourier transform infrared spectroscopy (FTIR) analysis was used to determine if the polymer structure was affected by the coating deposition process.

EXPERIMENTAL

TiO_2 deposition

The TiO_2 thin films were deposited at room temperature on ~30 μm thick PVDF substrate 14 mm × 10 mm strips, by unbalanced pulsed d.c. reactive magnetron sputtering, from a high purity Ti target in an Ar/O_2 atmosphere; the particular deposition conditions have been already reported elsewhere.[7] No external substrate heating was used during the deposition, to prevent polymer structural damage.

Characterization of photocatalytic performance

To study the photocatalytic performance of the TiO_2 thin films, an organic dye (Red 41 - used as organic pollutant) with a concentration of $10^{-5}M$ was prepared by dilution in water. The TiO_2 thin films on the polymer substrates were immersed in this solution in an open-top quartz cell with the irradiation perpendicular to the coating surface. No oxygen was artificially introduced in the solution during the irradiation experiments. A 150 W xenon discharge lamp was used as the UV source. A UV-broadband filter (UG11) was mounted between the lamp and cell to select the spectral range between 280–380 nm, the total irradiance being 2.0 mW/cm². After the irradiation experiments, performed for a particular period of time, the solution concentration was monitored using a Shimadzu UV-2501 spectrophotometer, by recording the maximum absorbance of the Red 41 dye. Previous irradiation tests of the same dye in the absence of the TiO_2 catalyst proved that its decomposition decays less than 2% after a 6 h exposure in the same conditions as the ordinary photocatalysis tests.

The concentration of the dye (c) was monitored as a function of time by the Beer-Lambert's law:

$$A = \varepsilon \ell c, \qquad (1)$$

where ε is the molar absorbance coefficient, A is the absorbance (optical density) of the dye and ℓ is the optical length of the quartz cell in which the catalyst is immersed in the dye. Thus the absorbance decay is proportional to the concentration decay (c_0 being the initial concentration of the dye), and the rate of the dye degradation (k) can de calculated from the first order equation:

$$\ln(c/c_0) = -kt. \qquad (2)$$

Structural characterization

All WAXS patterns in this study were registered at the Soft Condensed Matter Beamline (A2) of the Hamburger Synchrotronstrahlungslabor (HASYLAB, Hamburg, Germany) with synchrotron radiation
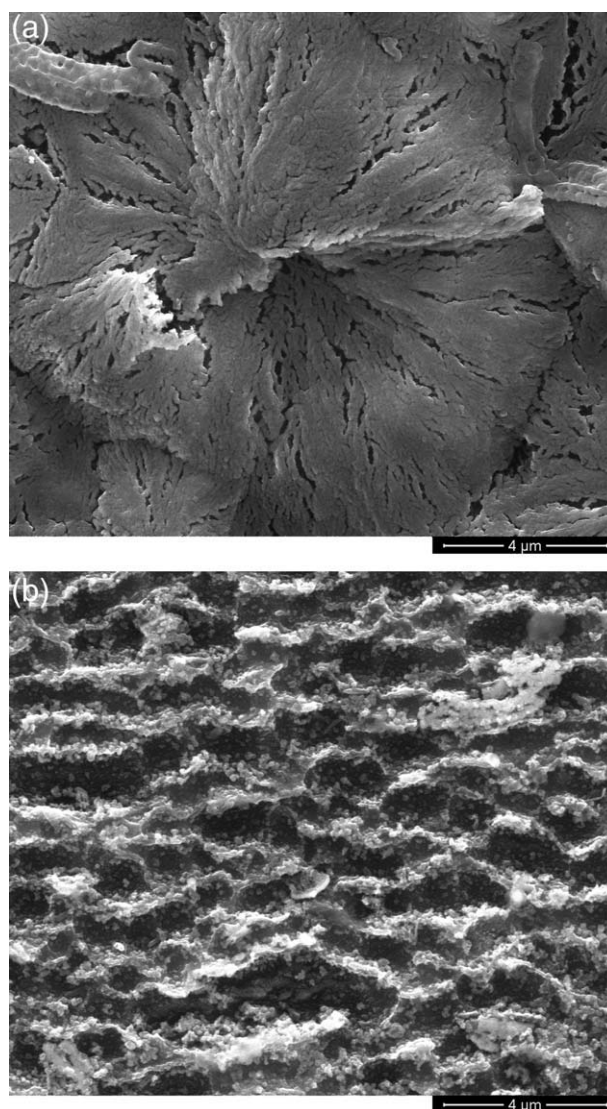

Figure 1 SEM micrographs of the TiO_2 thin films deposited on PVDF polymers, in its (a) α- and (b) β- phase.
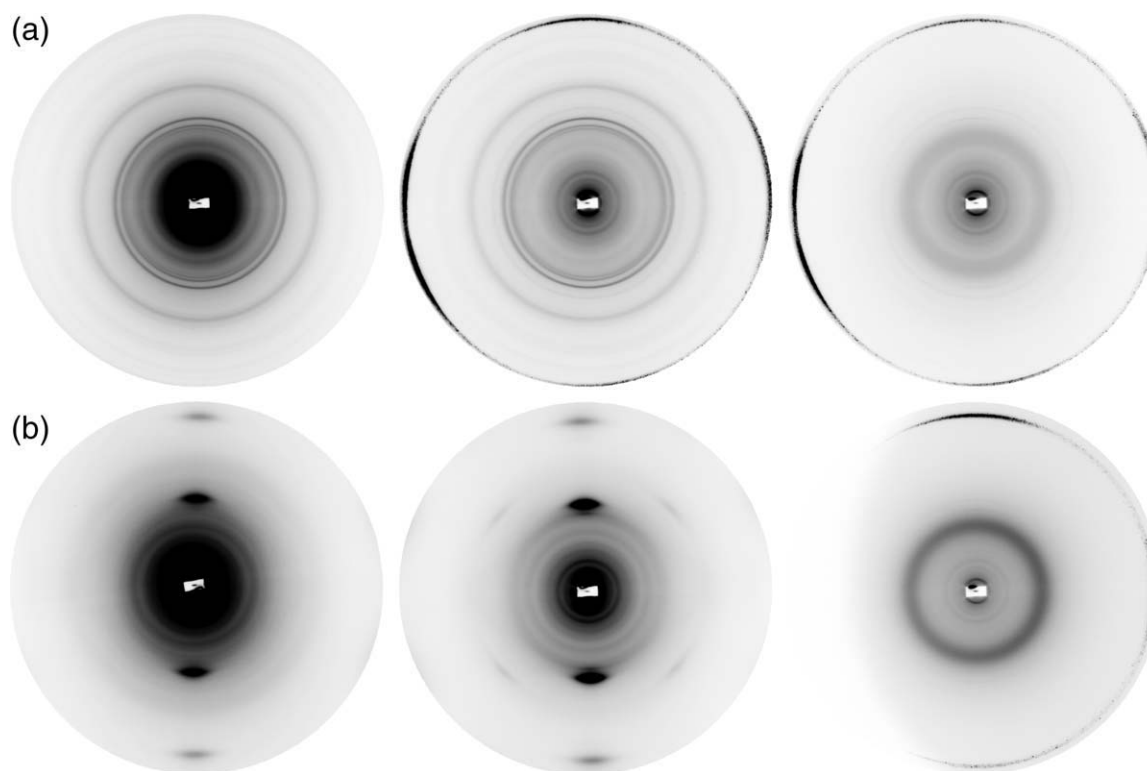
Figure 2 2D WAXS patterns of: (a) α-PVDF and (b) β-PVDF polymers uncoated (1) and coated with TiO$_2$ taken at annealing temperature of 30°C (2) and 200°C (3). For the sake of comparison, patterns of the uncoated polymers are also shown.

with the wavelength fixed at 0.15 nm. The sample-to-detector distance was set at 90 mm, being the diffraction patterns registered with an MAR two-dimensional CCD with an exposure time of 30 s. Scattering patterns were obtained at certain temperatures reached at a typical heating/cooling rate of 20°C/min. A specially designed sample holder was used to allow controlled heating/cooling of the sample in the range of 30–300°C. An Imago multichannel process and program controller from JUMO GmbH & Co. KG were used to regulate the sample temperature during heating or cooling at various rates. The difference between the readout and real temperature of the sample was found to be 3–4°C for the heating/cooling rate used.

The IR spectroscopy measurements were performed with a Perkin Elmer Spectrum 100 equipment in transmission mode analyzing the wave number range between 4000–500 cm^{-1}. For the scanning electron microscopy analysis a FEI Nova 200 FEG-SEM was used in high vacuum mode.

RESULTS AND DISCUSSION

Morphology and structural studies

In Figure 1 scanning electron microscopy (SEM) micrographs of TiO$_2$ thin films deposited on (a) α-

PVDF and (b) β-PVDF substrates can be observed. The characteristic isotropic spherulites of the α-phase are replicated with the TiO$_2$ layer deposition. Conversely, for the anisotropic β-phase polymer, the TiO$_2$ crystalline grains coalesce in the crests of the longitudinal polymer chains, surrendering a larger surface area for the deposited thin film, thus providing expectations for a higher dye adsorption and subsequent superior photocatalytic yield, as it will be shown later in this manuscript. The morphology of the TiO$_2$ thin films clearly replicates that of the underlying substrate, either isotropically or anisotropically, depending if deposited on α-PVDF or β-PVDF, respectively.

To study the crystalline structure of the as-deposited TiO$_2$ thin films, on both types of α- and β-PVDF polymorphs, and to monitor as well the phase evolution within the polymer itself, 2D WAXS patterns were obtained for both uncoated polymers and after deposition of TiO$_2$ (patterns taken at 30°C and at 200° C); this is represented in Figure 2. From the visual inspection of these 2D patterns one can conclude that the crystalline portion of TiO$_2$ that is deposited on the PVDF polymers is very small, owing to the low deposition temperatures, which inevitably inhibits thermodynamic equilibrium conditions for the TiO$_2$ prominent phases to crystallize in a regular structure, i.e., the thin TiO$_2$ coatings could be mostly

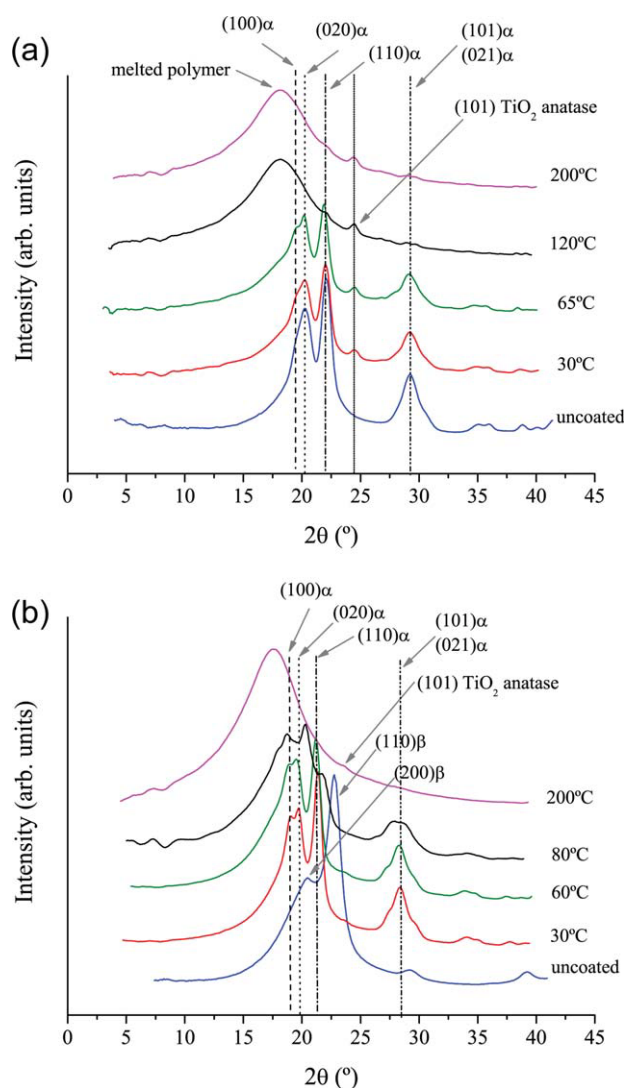**Figure 3** 1D WAXS profiles taken from the 2D patterns in Figures 2 for: (a) α-PVDF and (b) β-PVDF polymers coated with TiO₂ taken at various annealing temperatures. For sake of comparison, patterns of the uncoated polymers are also shown. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amorphous. Thus, the 2D plots in Figure 2 represent the crystallinity of the underlying polymer substrate. In the case of α-PVDF, isotropic Debye rings are observed, with no visual difference between the uncoated and coated samples. The β-PVDF samples are highly oriented with clear point-like WAXS reflections, which are extinguished at 200°C when this phase melts completely. No peaks attributable to the crystalline structure of TiO₂ polymorphs can be discerned, most probably due to overlapping by the polymer's intrinsic crystalline texture.

When retrieving 1D profiles obtained by sectioning of the 2D patterns in Figure 2, a clear peak of the anatase polymorph phase is detected for the α-PVDF, as it is evidenced in Figure 3. The α-PVDF

crystalline structure is visible up to 65°C, where the (020), (110), and (101) reflections are most prominent. In all 1D profiles of the coated α-PVDF the (101) anatase reflection is present indicating that, despite the low temperature deposition, TiO₂ crystals coalesce in an ordered way, giving rise to the mentioned structure. In the case of the deposition on β-PVDF substrates, the masking of the anatase (101) is stronger due to the polymer's intrinsic crystalline (110) texture; a very low anatase peak can only be discerned at 200°C as a shoulder to the amorphous halo of the molten polymer. As the temperature increases, a phase transformation from the PVDFβ-phase to the α-phase is observed. By peak fitting the 1D plots it was possible to determine the crystalline grain size of the anatase grains. For the case of deposition on α-PVDF substrates, the average grain size was determined to be ∼25 nm. Whereas for the case of deposition on β-PVDF substrates, the crystalline order is very weak and the grain size could not be accurately assessed due to the superposition of the polymer's texture. The reason for this can be attributed to the more isotropic nature of the α-PVDF substrate, which enhances the nucleation over a larger surface area; conversely, when depositing on β-PVDF, the crystalline grains tend to coalesce on the top of the longitudinal polymer chains, in detriment of the lower surface regions, as can be seen from Figure 1. Moreover, from a previous report[11] it was concluded that in the initial stages of film growth, substrate bias polarization induces coulombic forces between the deposited atoms and the surface charge induced by the electric dipoles within the β-PVDF poled substrates. This external electric field from the negative bias will induce a partial reorientation of
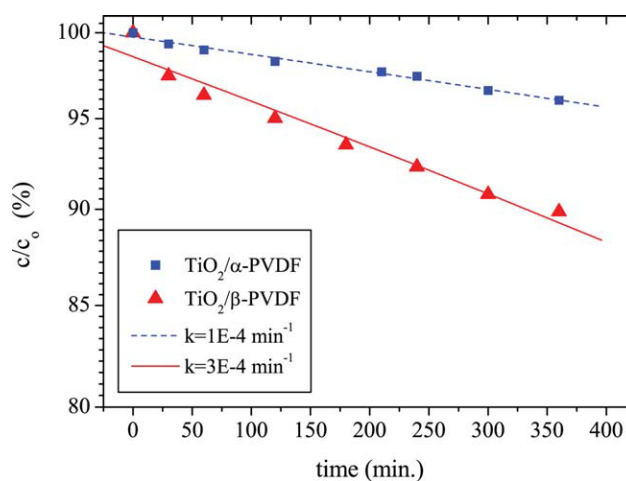

Figure 4 Relative decrease in RED 41 dye concentration (log scale) as a function of time for two TiO₂ coatings deposited on the different PVDF polymer substrates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
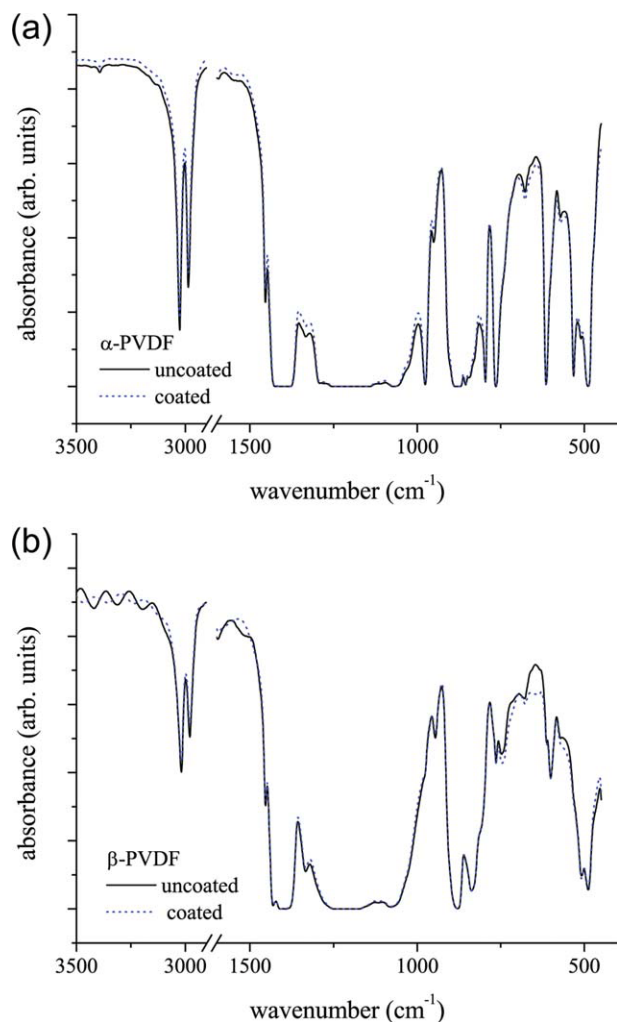
Figure 5 FTIR spectra comparison of (a) α-PVDF and (b) β-PVDF polymer uncoated and coated with TiO_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the dipolar moments of the polymer, causing a modification of the surface electrical charge density, which can affect the deposition of the TiO_2 molecules and inherently inhibit adatom mobility and subsequently deteriorate crystalline long-range order.

Photocatalytic activity

From irradiation tests shown in Figure 4 one can see that the electroactive β-PVDF poled substrates actively promote higher photocatalytic efficiency in comparison with the nonelectroactive α-PVDF, being the dye's first order degradation rate 3 times higher in the former case. The explanation for this resides in the fact that the poled β-phase shows preferential orientation of the dipolar moments and therefore a well defined surface charge is established on the polymer surface.[12] Hence, as the surface electric

charge is increased within the PVDF substrate, depending on phase and poling state, the photo-oxidation and reduction mechanisms on the dye are enhanced, since there is a larger carrier density and mobility, thus providing a pathway for a more efficient photocatalysis.

From the FTIR scans presented in Figure 5, it was possible to conclude that the deposition process, in particular the deposition flux and ionic bombardment of the growing film, of the TiO_2 thin films on both α- and β-PVDF substrates did not alter significantly the polymeric structural bonding characteristics, hence yielding evidence that the intrinsic electroactive nature of β-PVDF is preserved after deposition of the photocatalytic film.

CONCLUSIONS

Titanium dioxide thin films have been deposited by sputtering onto electroactive PVDF polymers at room temperature conditions. Due to the lack of substrate heating, to preserve the polymer crystalline structure, the as-deposited films were found to be mostly amorphous. The WAXS 2D patterns yielded information on the evolution of the crystalline structure of both polymer substrates with varying temperature. Their 1D sections, taken at various temperatures, evidenced the TiO_2 anatase polymorph phase, in particular its main (101) reflection. The anatase crystalline fraction is lower when depositing on β-PVDF since the topography of this anisotropic polymer tends to enhance a preferred nucleation of the TiO_2 on the longitudinal crests of its polymeric chains, as it was observed in the SEM micrographs. The photocatalytic performance of the same TiO_2 coating was improved when deposited on poled β-PVDF polymer, since the photo-oxidation and reduction mechanisms on the dye are enhanced by the surface charge that is established on the polymer surface; hence, β-PVDF contributes actively and with synergy to the photocatalytic process. FTIR analysis confirmed that the deposition process does not alter significantly the chemical structure within the polymeric substrate, thus not affecting its inherent electroactive properties.

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