



Effects of UV irradiation treated polycarbonate substrates for nanocrystalline deposition of TiO₂ thin films

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ABSTRACT

In this study, in order to achieve effective coating of the homogeneous titanium dioxide (TiO₂) thin film, UV irradiation pre-treatment was carried out to activate PC surfaces before coating. Sol-gel-based nanocrystalline TiO₂ thin films were prepared by employing tetrabutyl-titanate as a precursor. Nanocrystalline TiO₂ thin films were deposited by sol-gel spin coating on the treated substrates. Some characterization techniques such as UV/Visible, FTIR spectroscopy, and contact angle measurement were used to study the induced changes on the properties of the treated substrates. FTIR and UV spectra obtained from substrates before and after UV irradiation treatment, showed that UV irradiation has induced some chemical and physical changes in surface properties. The initial contact angle of PC surface was 94°, which decreased substantially after treatment. The XRD pattern reveals that TiO₂ thin film has a crystalline structure, and it has been observed in two phases: (1) anatase and (2) rutile. According to UV/Vis spectra of samples, the prepared films have high transmission. AFM has been applied for morphology characterization of the films surface. The surface morphology results indicate that UV exposure time leads to alter the roughness of the nanoTiO₂ thin films.

1 Introduction

During the past decade, TiO₂ thin films have been studied because of their considerable influence on the structural, optical, chemical, and electrical properties from the viewpoint of applications, such as optical filter, dye sensitized solar cells, antireflective coatings, gas sensors, and planar waveguides [1]. At normal pressure and temperature, TiO₂ has three different crystalline forms in nature, brookite (orthorhombic), anatase (tetragonal), and rutile (tetragonal) [2]. Rutile is most stable of the three [3]. Usually TiO₂ thin films

can be synthesized by several techniques such as, chemical vapor deposition, physical vapor deposition, electrodeposition, pulsed laser deposition, and sol-gel method [4-5]. Sol-gel processes are a series of hydrolysis and condensations reactions of an alkoxy silane [6]. The reaction does not require high temperature. TiO₂ thin films are achievable from sol-gel process in the form of coatings [6]. The sol-gel method allows for the simple production of good uniformly thin films with low cost, produced at low temperatures, and easily reclaimed after reaction in

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addition to enabling chemical & mechanical stability of the films [7]. The most basic component of plastic materials is polymers. Polymers are large molecules comprised of many repeated units called monomers that have been chemically bonded into long chains. Polymeric materials usually have a low surface energy and high contact angle with polar liquids. Polymer surface modification is a method for generating functional polymer surface combined with the desirable attributes of bulk polymers. Key properties imparted by these technologies include wettability, adhesion to other polymers or metals, printability and resistance to glazing. Surface modification plays a very important role in many industrial end-use applications [8]. Polycarbonate is one of the most important engineering plastics due to its high toughness, clarity, high chemical resistance, good heat resistance, low light and high impact strength. It is used in many applications [9]. The desirable bulk properties of polycarbonate are often compromised by unfavorable surface characteristics such as low surface energy that generally leads to poor adhesion. Ultraviolet (UV) irradiation is one such surface modification for increasing the surface energy of polycarbonate. When light is absorbed by a polymer, photochemical reactions can occur as a result in activation of polymer surface and change the chemical composition of its surface [10]. During the UV irradiation, mainly excited molecules are formed before secondary reactions such as chain-scission and cross linking occur [11].

The effect of NaOH-etching and UVC-irradiation on the mechanical stability of TiO₂ nanoparticles on polycarbonate substrates was investigated by Sai Wei Lam et al [12]. The TiO₂ layers with self-cleaning properties were deposited on PC substrates by Yaghoubi et al. [9]. The chemical treatment carried out in their work was implemented to create oxidized species on the surface of the polymer. The mechanical properties and photocatalytic after coating were investigated by J. H. Yang et al. [13]. The transparent thin films on ABS and PC substrates were prepared by changing the ratio of acetylacetone in used TiO₂ sol, the number of dip coating cycle and TiO₂ concentration. TiO₂ thin film on the polymer substrates with good adhesion was fabricated. This work is continuation of our previous study on surface properties of UV irradiated polycarbonate- TiO₂

nanocomposite films [14]. In the present work, substrates with different irradiation times were analyzed using contact angle measurement, UV/Vis spectroscopy, and FTIR. After preparing TiO₂ thin films through sol-gel method, a systematic study of the effect of treated substrates by UV irradiation on optical and structural properties of thin films has been carried out. TiO₂ thin films were characterized by XRD, UV/Vis spectroscopy, and AFM.

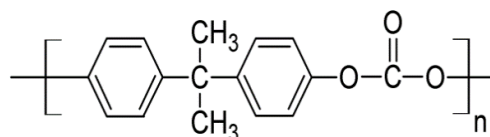
2 Experimental

2.1. Preparation of the coating solution

TiO₂ nanoparticles were prepared through modified sol-gel process using titanium-n-butoxide as the precursor. Ti(oBu)₄ diluted with PrOH as solvent where the resultant mixture was stirred at room temperature for 1 h. Acetylacetone was added dropwise to the mixed solution under a stirring as stabilizer where the solution was stirred for 2 h. Then the HNO₃ aqueous solution added under stirring ensures a pH of the sol-gel solution of about 2. Finally the solution was refluxed at 85 °C for 8 h to obtain crystalline TiO₂ sol [15].

2.2. Preparation of TiO₂ thin films

Polycarbonates samples, manufactured by General Electrical (GE) with the trade name of Lexan, were chosen. The chemical structure of Lexan is given as:



At first, one set of polycarbonate (PC) samples were chosen. The polycarbonate sheets with 250 μm thickness were cut into 30×20 mm pieces. A low pressure mercury vapor lamp (TUV 30W, Philips, Holland), which emits radiation at 254 nm, was used. The intensity of the incident light was 24 Wm⁻². UV irradiation, typically of wavelength between 250-400 nm, produces photons that can result in activation of polymer surfaces. In the photo-Fries reaction, the PC substrates were irradiated with UV lamp by wavelengths below 310 nm [16]. Samples were placed at a 15 cm distance from the light source. Irradiation times were for 0, 4, 6, 8 and 10 h. All irradiations were performed at room temperature in air. Finally, the sol

was deposited on treated substrates three times by spin-coating technique. Five samples were prepared for each group. Spin coating was performed at room temperature. During the entire coating process, a spinning speed of 1000 rpm was controlled accurately for 30 s. After each coating, films were dried at room temperature.

2.3. Characterization

The crystallization behaviour of the TiO₂ films was examined using X-ray diffraction (Philips Powder Diffractometer Type PW 1373 goniometer). The XRD was equipped with a graphite monochromator crystal. The X-ray wavelength was 1.5405 Å and the diffraction patterns were recorded over the 2θ range 4° to 80° with a scanning speed of 2° min⁻¹.

The hydrophobicity / hydrophilicity of a solid surface is usually expressed in terms of wettability that can be quantified by measuring the static contact angle formed between water drops and the surface of the modified substrates. Static contact angles were measured using the sessile drop method with a contact angle measurement equipment (Kruss G10). The water droplet is formed on the equilibrium dome shape on the horizontal sample surface and imaged by a system containing the CCD camera connected to a computer. The size of water droplets was 5 μl that transported on the surfaces from a zero falling height. Measurements should be done repeatedly in order to determine a mean arithmetic value. For substrates, the contact angle were measured at five different places on the surface of substrates, each value of contact angle is an average of 5 measurements.

To study the structural changes including the alteration in position and intensity of the characteristic bands, the Fourier transform infrared (FTIR, Shimadzu FTIR spectrophotometer 8300) with 550–4000 cm⁻¹ wave number were used. Photochemical changes in substrates and thin films were recorded by UV/Vis absorption spectroscopy using the PG Instrument model T80. The morphology of the surface thin films was studied by Atomic Force Microscopy (Park Scientific Instruments, AUTOPROBE CP).

3 Results and discussion

3.1. Surface modification

The short wavelength UV irradiation emitted by UV

lamp have enough energy to break chemical bonds in polymers, leading to chain scission of the polymer [16]. The wettability of material surfaces are influenced by two major factors: chemical functionality and/or surface roughness [17]. Figure 1 shows the change of the water contact angle for the PC substrate as a function of UV treatment time. The lower values of the water contact angle for the UV irradiation treated surfaces explains their hydrophilicity. It shows that the contact angle on the untreated surface is 94°. Figure 1 shows that the contact angle decreases with increasing treatment time. The water contact angle decreased significantly until 6 h before decreasing slightly thereafter. The UV/Vis spectroscopy of pristine sample and treated substrates in the wavelength range 200-900 nm is shown in Fig. 2.

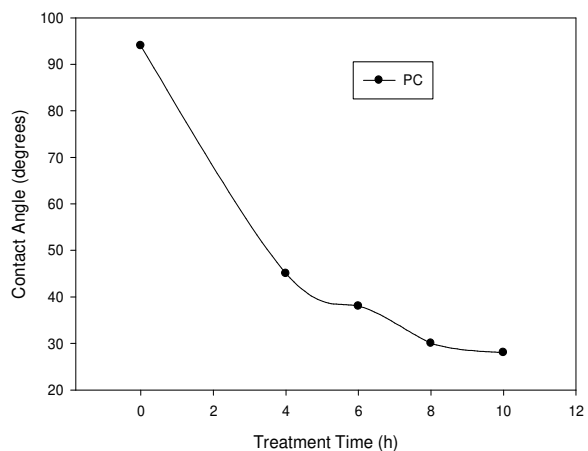


Fig. 1. Changes of the water contact angle on PC as a function of UV irradiation times.

From Fig. 2, it is evident that the pristine PC has no absorption bands in the studied wavelength range. On the other hand, absorption bands at 315 and 355 nm correspond to phenylsalicylate and dihydroxybenzophenone respectively [18]. A shift in absorption edge towards longer wavelength with increasing irradiation time can be readily observed. This behavior may be attributed to the formation of extended systems of conjugate bonds as a result of the UV irradiation induced bond cleavage and reconstruction [19].

FTIR spectroscopy has been found to be an important technique in the examination of physical and chemical characteristics taking place in the polymeric material

due to irradiation. The FTIR spectra of PC substrates, for pristine and exposed for 4, 6, 8 and 10 h are shown in Fig. 3.

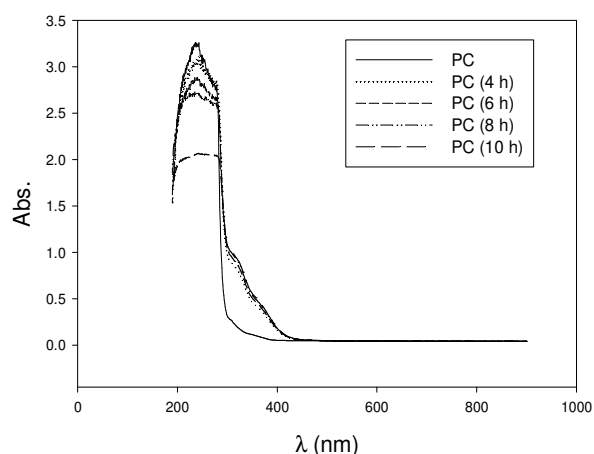


Fig. 2. The absorption spectra for the pristine and UV irradiated PC substrates.

The relative changes in the bonds have been estimated from the relative increase or decrease in the intensity of the peak associated to the functional groups present in the polymers. In the present study, the characteristic absorption bands of PC, observed in the region 1600–1800 cm^{-1} , appear to belong to the overtones of C=O stretching vibration of carbonate groups, the intensity of the peak corresponding to 1654 cm^{-1} representing C=O stretch decrease with the UV irradiation time. The decrease in the intensity is associated with chain scission which may take place at the carbonate site where hydroxyl groups are formed [11]. It seems likely that reduction in the contact angle attributed to the increase in the proportion of oxygen containing groups affects the hydrophilicity [20].

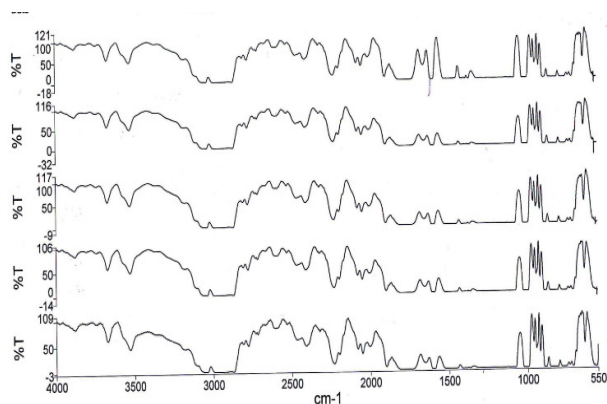


Fig. 3. FTIR spectra of pristine and irradiated substrates.

3.2. Characterization of the TiO_2 thin films

3.2.1. XRD characterization

Figure 4a shows the X-ray diffraction pattern of the PC sample. The pattern is characterized by the appearance of halos extending over the 2θ range from 12° to 26° , due to the diffuse scattering of amorphous PC. Halos show that the amorphous phase is dominant in the compound [21]. X-ray diffraction pattern of the TiO_2 thin film was shown in Fig. 4b. XRD patterns revealed that the TiO_2 film was the most crystalline one, containing both rutile and anatase phases. The pattern clearly presents one main peak at $2\theta = 25.4^\circ$, which corresponds to the (1 0 1) reflection of the crystalline anatase phase, in addition to the dispersion peak of amorphous PC. Other diffraction angles of the samples are 37.7° , 55.2° , 27.4° , 36.0° , 41.1° which correspond to the anatase (1 1 2), (2 1 1), rutile (1 1 0), (1 0 1) and (1 1 1), respectively [22, 23].

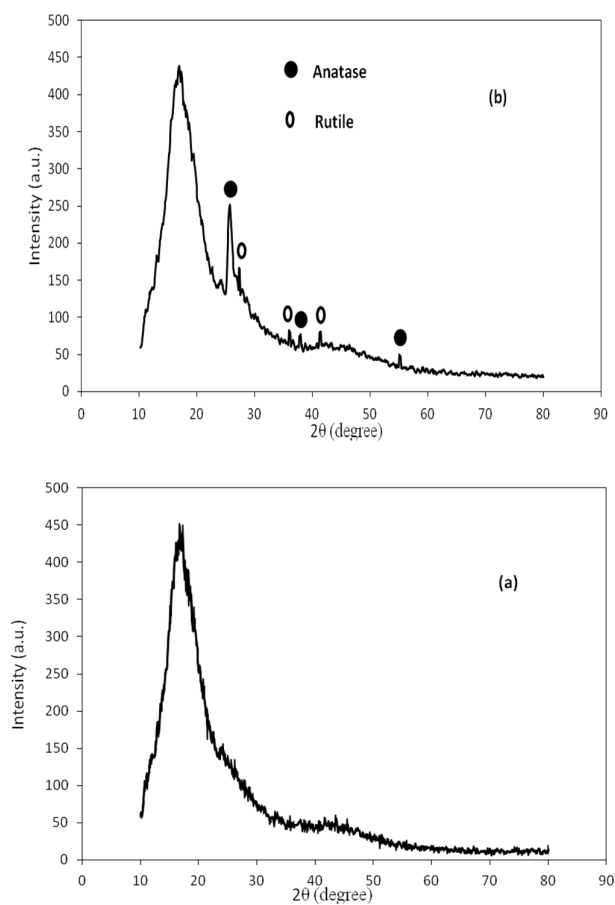


Fig. 4. XRD diffraction patterns of (a): PC, (b): TiO_2 film.

3.2.2. UV/Vis spectroscopy

It is well known that TiO₂ has strong absorption in the ultraviolet region [25]. The optical absorbance spectrum of nanoTiO₂ thin films over the wavelength (λ) range 200-900 nm are shown in Fig. 5. TiO₂ thin films represent high transparency in the visible range of 400-800 nm. The absorption edge of the films shifted towards longer wavelengths with increasing the UV irradiation time. The transmittance of the TiO₂ thin films is slightly less than that of the uncoated substrates. The optical transmittance of the PC substrate and TiO₂ thin films is measured by UV/Vis spectrometer and transmittance spectra and shown in Fig. 6. The TiO₂ coating slightly reduces the transmittance of the PC. Decrease in transmittance in the 400-700 nm range can be associated with the band gap absorption of TiO₂.

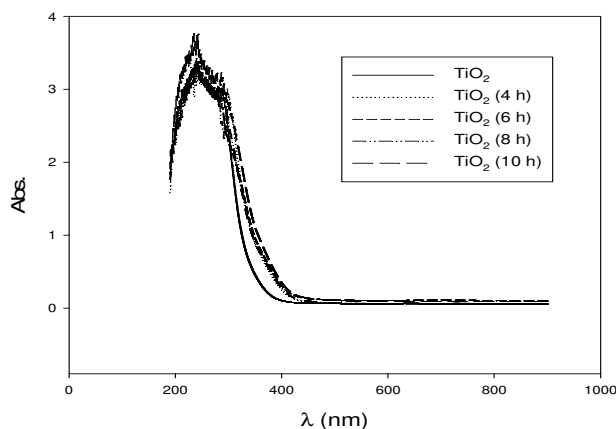


Fig. 5. The absorption spectra for TiO₂ thin films.

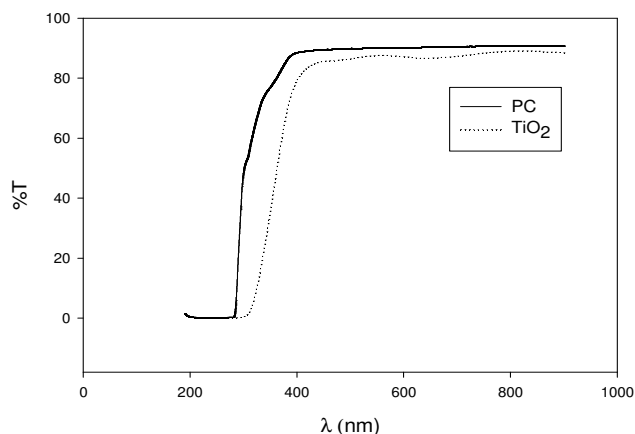


Fig. 6. UV/Vis transmission spectra of the substrate and TiO₂ thin film.

3.2.3. Atomic force microscopy

The influence of the treatment time on the surface morphologies of the films were studied by Atomic Force Microscopy. As it can be seen from the 3D topographic image in Fig. 7a, the surface of the PC is smooth and uniform. In this case the root mean square (RMS) roughness of its surface is 1.7 nm. Figure 7b shows the surface morphology of TiO₂ film on untreated PC. The TiO₂ film was not homogeneous which could be due to the relatively hydrophobic property of the PC surface where the value of the RMS roughness increases to 3.1 nm. UV irradiation possesses comparatively a hydrophilic surface which

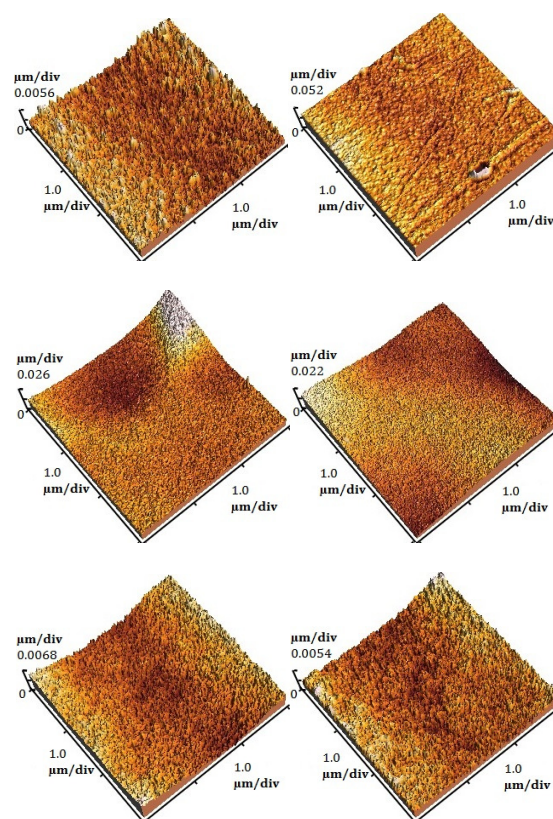


Fig. 7. AFM images (a): polycarbonate and thin films (b): TiO₂, (c): TiO₂ (4 h), (d): TiO₂ (6 h), (e): TiO₂ (8 h), (f): TiO₂ (10 h).

enhances the adhesion of the TiO₂ films to the substrates. The average surface roughness value increases for the irradiated samples [11]. Figure 7c-f shows the changes in the AFM images of thin films as a function of the treatment time. An increase in the mean roughness of the films to 6.7 was observed when the treatment time of substrates is increased from 0 to 4 h. By treating PC surface with UV irradiation for 6 h, surface chemistry may be modified resulting in a

surface energy increases. The roughness of the film depends on a major factor: surface energy and which causes the RMS surface roughness of the film to decrease down to 4.9 nm. The corresponding RMS roughness of films obtained from AFM images reveals that the surface roughness decreases from 4.9 nm to 1.5 nm as the treatment time increases from 6 to 10 h (Fig.8). The lower roughness value represents good homogeneity of the TiO₂ particles on the surface [25].

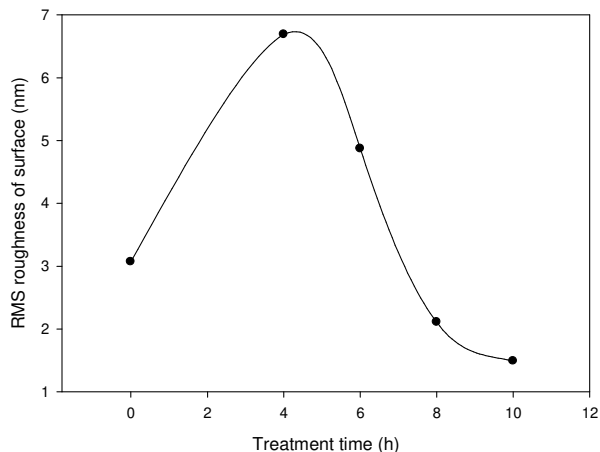


Fig. 8. RMS roughness of TiO₂ thin films.

4 Conclusions

Substrates at different treatment times were analyzed using contact angle measurement, FTIR and UV/Vis spectroscopy. For the UV irradiation-treated PC, the improved surface hydrophilic property and the increased surface roughness are the advantages favoring the effective coating of TiO₂ film. The formation of photostabilized groups was confirmed from the UV/Vis spectroscopy results. In this study, we have successfully fabricated TiO₂ thin films with desired structural and optical properties by sol-gel and spin coating method. X-ray diffraction shows that it is a nanocrystalline structure. The deposited TiO₂ thin films reveal a high transparency in the visible range.

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