



Self cleaning TiO₂ coating on polycarbonate: Surface treatment, photocatalytic and nanomechanical properties

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ABSTRACT

A developed route to form TiO₂ self cleaning coatings on polycarbonate substrates is reported. TiO₂ coatings on plastics may find widespread application in auto and construction industries if possess desired photocatalytic and mechanical properties. A chemical surface treatment method was used to create hydrophilic groups on the surface. X-ray photoelectron spectroscopy showed the treatment led to the oxidation of surface groups. TiO₂ deposition was based on wet coating using an anatase sol of TiO₂ nanoparticles of 30 nm size. The sol was synthesized using a sol–gel route. A pre-coat of peroxotitanium complex was employed to improve adhesion and inhibit the substrate degradation. The coating reduced the transparency for 10–15%. The photocatalytic activity was found linearly dependent on the thickness. The reaction rate constant for methylene blue degradation was estimated 0.024 s⁻¹ for films of 150 nm thickness. The mechanical properties were also improved after coating, as demonstrated by nano-indentation and nano-scratch tests. The hardness and scratch resistance were improved by 2.5 and ~6.4 folds.

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1. Introduction

TiO₂ self cleaning coatings are finding increasing applications in buildings, public furniture and auto industry. The self cleaning mechanism is mainly based on TiO₂ photocatalysis, where photo-induced electron–holes catalyze reaction on the surface [1–3]. The coatings are generally layers of around 200 nm thickness, which are deposited using various possible techniques. Methods such as sputtering [4–7], electrophoretic deposition [8], spray pyrolysis [9], thermal oxidation [10], chemical vapor deposition [11] and wet coating [12–15] are among the reported methods. Among these methods wet coatings, such as spray or dip coating of a nanocrystalline sol are practically preferred due to the ease of applying the coating and low price.

Polymers are very important as substrate materials for self cleaning coatings. Polymeric substrates include paints, plastic sheets and laminates. A problem in coating polymers by oxide materials is the low surface energy of polymers, and the lack of proper binding sites on the surface, which result in low adhesion and weak mechanical properties. Various surface treatments have been suggested for increasing the surface energy of polymers, including ion-beam irradiation [16–18], plasma modification [19–24], laser treatment [25,26], UV

irradiation [27] and chemical treatment [28]. Increasing surface energy enhances the wettability and improves coating uniformity and adhesion [28,29].

In this work, we report the route that we developed to create self cleaning TiO₂ coatings on polycarbonate (PC) substrates. PC is an engineering plastic with unique properties such as light weight, high chemical resistance, good heat resistance, high impact strength and transparency [30]. PC with a self cleaning TiO₂ layer exhibits better hardness and scratch resistance, as we show using nano-indentation and nano-scratch tests. Good mechanical properties for the self cleaning coatings are vital to make these coatings attractive in auto and construction industries. To our knowledge this is the first report to cover the complete process including the surface treatment and coating, as well as photocatalytic and mechanical properties.

2. Experimental

2.1. Materials and synthesis

The plastic substrates were polycarbonate (PC) sheets with 1 mm thickness cut into 35 mm × 25 mm pieces. The substrates were washed first by water and detergent and rinsed with de-ionized (DI) water. They were further cleaned in 2-propanol (Merck, Purity ≥ 99.5%) ultrasonically and again rinsed with DI water and dried. The surface of PC sheets were treated in a chemical solution made by dropwise adding 37.5 ml H₂SO₄ (Merck, 95%–97%) to 4 g K₂Cr₂O₇ (Panreac Co., Purity: 99%) followed by

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addition of 12.5 ml DI water. The substrates were immersed in the solution at different times, after the solution was cooled down to room temperature.

A peroxotitanium complex solution was prepared by mixing titanium tetraisopropoxide (TTIP) (Merck, purity $\geq 99.5\%$), H_2O_2 (Merck, 30%) and H_2O , with volume proportions of 12:90:200, respectively. The pH was then raised to 7.0. The resulting solution was refluxed for 10 h to obtain crystalline anatase sol. TiO_2 layers were coated on PC substrates using dip coating at 3 mm/s. For all the samples, a pre-coat of the peroxotitanium complex solution was applied initially on the surface of PC substrates to enhance the adhesion and act as a barrier for photocatalytic degradation of PC. Subsequent layers of crystalline TiO_2 were deposited by 1 to 4 times dip coating. The samples were dried after each dip in a furnace at $90^\circ C$ for 15 min.

2.2. Characterization

Contact angle (CA) measurements were performed using 1 μ l water drops and a CCD camera connected to a computer (Dataphysics, OCA 15 plus). To investigate the chemical bonds on the surface of PC substrate, X-ray photoelectron spectroscopy (XPS) was carried out using a monochromatized Al K_{α} X-ray source and a Spec energy analyzer model EA10+. The topography of the surface was evaluated by atomic force microscopy (AFM) (Park Scientific Instruments, AUTOPROBE CP). Optical absorbance and transmittance measurements were carried out using Jasco V-530 UV/VIS spectrophotometer. The size of nanoparticles in the aqueous sol was measured using dynamic light scattering (DLS) (Malvern, ZEN1600 Nano S (633 nm)). The Zeta potential of nanoparticles surface was measured using Malvern Zetasizer. X-ray diffraction (XRD) measurements were performed using a Bruker model D4ENDEAVOR machine at 1.54 \AA Cu K_{α} . The photocatalytic activity was evaluated by monitoring the degradation of methylene blue (MB) solution ($5 \mu M$) under UV illumination. The samples were placed in 7 ml aqueous MB solution and were kept in dark for 2 h. They were then irradiated from top using a UV lamp (Philips TUV 4 W, main spectral peak: 254 nm) at 11 mW/cm^2 . The intensity of the absorption peak at 663 nm was measured using UV-Vis spectrophotometry at 10 min intervals to probe the degradation process.

A Hysitron Inc. TriboScope® nanomechanical test instrument with a two dimensional transducer and commercial diamond cube corner indenter (three-sided pyramid geometry) with a tip radius of ~ 50 – 55 nm was used for nano-indentation and scratch tests. The calibration was performed using fused silica samples. Mechanical tests were performed in conjunction with atomic force microscopy (AFM) imaging (NanoScope III).

3. Results and discussion

3.1. Surface modification

The cleaning process as described in the experimental section acts as the preliminary treatment that removes contaminants and increases the adhesion between the substrate and coating [31]. We employed a chemical method for activating the surface of PC substrates to increase their surface energy. Chemical treatments are available, easy and low-priced compared to other methods of surface treatment, such as ion-assisted treatments, plasma treatments, laser and UV irradiation. All these methods cause the C–C chains to break down and form polar groups such as carbonyl, carboxyl and alkoxy which change the wetting characteristic of the surface from hydrophobic to hydrophilic [32,33].

The surface of substrates was treated by immersing them into the treatment solution. Fig. 1 shows the variation of the CA for different immersion times. The initial CA of PC surface was 88° , which decreased substantially after treatment. While the CA has a decreasing

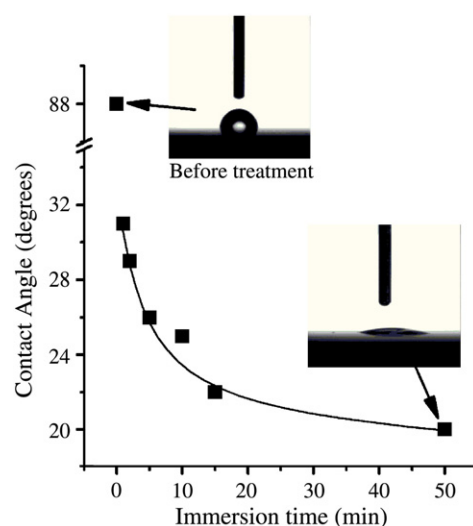


Fig. 1. Decreasing trend of CA in terms of immersion time, in the treatment solution.

trend with immersion time, one notes that the rate of decrease after 15 min is very slow. This implies that 15 min immersion time is an optimum. The final CA was about 20° .

The surface treatment introduces an increase in the intensity of $-(C-O)-$ groups on the surface, as revealed by XPS data. Fig. 2 shows the XPS spectra of C 1s region of the untreated (a) and the chemically treated surface (b). The $-(C-C)-$ and $-(C-O)-$ binding energies were observed at 285 eV and 286.6 eV, respectively. The $-(C-O)-$ peak has considerably increased after treatment, in expense of decreasing the $-(C-C)-$ peak. The $(C-O)/(C-C)$ ratio has increased from 0.07 for untreated surface to 0.20 for treated surface. This demonstrates that chemical treatment results in oxidation of the surface groups, leading to $-(C-O)-$ functional groups with hydrophilic property. Our experience with plasma surface treatment (to be published later) shows that plasma treatment creates more divergent oxygen containing groups, such as $-(C-O)-$, $-(C=O)-$ and $-(O-C=O)-$, as also reported by others [19–24]. This is because the plasma treatment provides numerous surface reaction routes compared to the chemical route.

The ageing and optical properties of the treated substrates are illustrated in Fig. 3. An important issue in surface modifications is their stability in time. Fig. 3(a) illustrates how the CA of a treated sample changes during a few days ageing. One observes that after one day the CA increased for about 10° – 15° , while later the rate of change considerably decreased. The ageing experiments were performed at $28^\circ C$ as well as $-5^\circ C$. Qualitatively, ageing is slower at lower temperatures, as both the rate of initial CA increase and the final CA are smaller for $-5^\circ C$. At $28^\circ C$ the CA has reached to almost 50° in 15 days, from the initial value of 22° . This rate of ageing is slower than what was reported for ion-beam treated surface, which changed from 16° to 78° in 15 days [16]. Dependence of CA values on storage time after treatment is explained as a reversing or the migration of oxidation products [34]. It seems that reversing or the migration rate of oxidation products in chemical treatment method is slower than ion-beam method.

Fig. 3(b) shows the optical transmittance of the surface treated and untreated PC substrates. One observes that chemical treatment makes no effect on the transparency of the substrate, as the transmittance spectra are identical. It has been reported that UV treated substrates change slightly in transmittance, in particular for samples with long UV irradiation [35,36]. A slight decrease of 1%–5% and sometimes even more, in the optical transmittance of plasma treated and ion-beam treated polymeric substrates has been reported [16,17,31]. The reduction in UV treated substrates is even more.

Surface morphology of a PC substrate before and after chemical treatment was observed using AFM (Fig. 4). The morphologies are almost similar. The rms roughness values before and after treatment were 2.0 nm

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