Surface & Coatings Technology 217 (2013) 51–57

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Morphology, photocleaning and water wetting properties of cotton fabrics, modified with titanium dioxide coatings synthesized with plasma enhanced chemical vapor deposition technique

Anna Sobczyk-Guzenda [a,*], Hieronim Szymanowski [a], Witold Jakubowski [a], Anna Błasińska [b], Jacek Kowalski [a], Maciej Gazicki-Lipman [a]

[a] Lodz University of Technology, Institute of Materials Science and Engineering, Stefanowskiego 1/15, 90-924 Lodz, Poland
[b] Lodz University of Technology, Department of Material and Commodity Sciences and Textile Metrology, Żeromskiego 116, 90-924 Lodz, Poland

ARTICLE INFO

Article history:
Received 10 July 2012
Accepted in revised form 27 November 2012
Available online 5 December 2012

Keywords:
Cotton fabric
RF PECVD technique
TiO_2 coating
Surface morphology
Self-cleaning
Superhydrophilic effect

ABSTRACT

A modification of textile material with a titanium dioxide coating, applied with the help of radio frequency plasma enhanced chemical vapor deposition (RF PECVD) technique, is reported. In this procedure, titanium (IV) chloride was used as a source of titanium, oxygen was supplied in the form of O_2 gas, and a cotton fabric served as a substrate. Coating morphology was studied using scanning electron microscopy (SEM), with images of each sample being recorded three times: directly after deposition (a), following routine washing with a detergent solution (b) and after eighteen month long storage under ambient conditions (c). SEM studies reveal a strong dependence of the coating quality on the RF power of deposition. This parameter of plasma-chemical modification of the fabric also substantially affects its mechanical properties.

The photocleaning effect of the coatings was studied by following the changes of color intensity of stain spots of red wine, red beet juice and methylene blue dye on the fabrics, during their illumination with ultraviolet (UV) light. Similarly to the coating morphology, the intensity of this effect substantially depends on the RF power of deposition.

Finally, water wettability of the investigated materials was studied using a qualitative contact angle analysis. The results show that, following its deposition with a TiO_2 film, a hydrophilic cotton fabric becomes strongly hydrophobic. However, when illuminated with UV light, the water wetting properties of the TiO_2 coated material return to highly hydrophilic (superhydrophilic effect).

1. Introduction

First products making use of a photocleaning effect were self-cleaning paints, designed for both building interior and exterior, and commercialized over a decade ago [1–3]. Today, there are numerous reports dealing with self-cleaning surfaces, but the majority of these publications still concern materials used in the construction industry [4–7]. On the other hand, an excellent potential target for photocleaning, UV protection and antimicrobial effects is comprised of textile materials [7,8]. Special purpose clothing, especially that endangered by staining with heavy contaminants such as soot, oils or lubricants, is a good example. This is particularly important in the case of textile products that are either exploited outdoors or are not capable of washing (due to their size or water and/or detergent sensitivity). The latter case primarily concerns textiles (knitted, woven or rarely nonwoven) used in the public interior design in the form of curtains, blinds, roller blinds or external sunshades [8,9].

A way to self-cleaning textiles, perceived by many researchers, is an application of a titanium dioxide (TiO_2) coating [10–12]. Among many useful properties, TiO_2 is characterized by high refraction coefficient [13], absorption in the UV range [14], strong photocatalytic effect [15] and biological inertness [16]. Therefore, it is used in numerous applications ranging from food additives and white paint pigments to antireflective coatings and MOSFET dielectric layers [16].

The photocatalytic effect, exhibited by titanium dioxide, is a consequence of its semiconductor nature. The bandgap width of TiO_2 crystallographic form of anatase amounts to 3.2 eV and it is somewhat lower for rutile (3.0 eV) [17]. Both polymorphs show a bactericidal effect [18–21], an oxidizing effect [22–25], and a superhydrophilic effect [26–29], all having strong potential for commercial applications. Recently, we have demonstrated that the above phenomena are also exhibited by amorphous TiO_2 coatings, deposited on flat surfaces from $TiCl_4$ using the RF PECVD technique [30–32].

As far as processing textile materials with titanium dioxide is concerned, it has been shown that a coating of TiO_2 nanoparticles substantially improves the UV protective properties of polyamide and wool fabrics [9,33]. A manufacture of functional textile products

* Corresponding author. Tel.: +48 42 631 32 64; fax: +48 42 636 67 90.
E-mail address: anna.sobczyk-guzenda@p.lodz.pl (A. Sobczyk-Guzenda).

0257-8972/$ – see front matter
http://dx.doi.org/10.1016/j.surfcoat.2012.11.071

by an application of nanoparticles is usually carried out in a two-stage process. First, a substance of nanoparticles of a desired size, protected from their aggregation, has to be prepared. In the second stage the so formed nanosubstance is deposited onto a textile product (knitted, woven or nonwoven) in the form of emulsion, dispersion or foil, with the use of such fabric finishing techniques as spraying or coating. An introduction of nanoparticles at the formation stage of chemical fibers is also practiced [34,35]. However, although TiO_2 itself is known to be biologically inert, there is a serious risk that nanoparticles of dimensions between 10 and 100 nm may be harmful to human organisms, independent of their composition [36]. Therefore, the introduction of such nanosubstances onto textile surfaces could be considered hazardous, particularly in view of the fact that over 50% of the nanoparticles disappear after the first cycle of washing. This is the reason why the above technologies are possibly better suited for the manufacture of disposable products such as self-adhesive dressing, for example.

Another possibility is the deposition of a thin TiO_2 film. For that purpose, the sol–gel method is most frequently used [4,6,10]. Unfortunately, this technique requires thermal treatment of the pre-deposited sol, which in the case of textile substrates often leads to the degradation of the fiber. In addition, a problem of a coating thickness and composition inhomogeneity arises and this affects the product quality. Another limitation of the sol–gel method is a requirement of a good adhesion of a coating to the fiber.

A thin film technique, which enables deposition at nearly ambient temperatures, and assures both high quality and excellent adhesion of the coating, is a radio frequency plasma enhanced chemical vapor deposition (RF PECVD) method. However, this method is not very frequently used in the case of fiber or textile substrates. Low temperature plasma techniques are more often applied for fiber surface modification by means of grafting functional groups [37]. The aim of the present work is to use the RF PECVD method to place a titanium dioxide coating onto the surface of a cotton woven fabric. In particular, such conditions of the deposition process are sought which assure deposition of a good quality coating withstanding washing, and a storage over a prolonged period of time.

2. Materials and methods

2.1. Materials

Raw, non-colored cotton fabric, of a plain weave, was used as a substrate. Materials used in the PECVD process comprised liquid titanium (IV) chloride $TiCl_4$ (Aldrich, high grade purity) as a source of titanium and gaseous O_2 (Linde Gas, purity 99,999) as a source of oxygen. In addition, argon (Linde Gas, purity 99,999) was used as a carrier gas for the $TiCl_4$ vapors.

As far as the of titanium source is concerned, $TiCl_4$ was selected for two reasons. First, it is its high value of saturated vapor pressure which makes supply and dosing of this precursor relatively easy and controllable. Secondly, our own experience has shown that high quality thin films of very good photocatalytic properties can be synthesized using this compound [30–32].

2.2. PECVD reactor and process parameters

The deposition of thin TiO_2 films onto cotton fabric was realized in a parallel plate plasma reactor, described in detail elsewhere [30]. The main part of this reactor is the deposition chamber comprised of two parallel plate electrodes, separated with a ring of glass. The upper electrode remains on the ground potential and forms the chamber's cover. It is through the shower construction of this electrode that the mixture of working gasses (argon carried $TiCl_4$ vapor and oxygen) is introduced into the deposition chamber. The input flow rates of gaseous species (oxygen and argon) are controlled using MKS Baratron type 1179A flow controllers while the flow rate of $TiCl_4$ vapors is regulated indirectly, by adjusting the flow rate of the argon carrier gas and the temperature of the bubbler. The lower electrode is electrically isolated from the rest of the equipment and it is powered with an RF field of 13.56 MHz, supplied from the RF generator (RFPP 13.56 MHz Power Supplies model RF 5S) through a self-designed matching network. Cotton fabric substrates are placed directly on the surface of this electrode. Gaseous byproducts of the deposition process are removed by the equipment pumping system and collected in this system's liquid nitrogen cold trap.

Before deposition of a TiO_2 coating, the surface of the fabric had been etched with oxygen plasma for 3 min at 100 W of RF power. The subsequent deposition process lasted 45 min and was performed at one of the three different power levels of 100, 200 and 300 W. As far as the input rates of the working species are concerned, the empirically established flow rate of oxygen amounted to 40 sccm, with the criterion being the quality of the coatings. At oxygen flow rates higher than 50 sccm no solid films were formed. Coatings deposited at 50 sccm of O_2 had in their composition far removed from that of TiO_2, while those synthesized at flow rates lower than 40 sccm were loose and contaminated with powder products. The empirically established flow rate of argon carrier gas amounted to 2 sccm, while temperature of the $TiCl_4$ container was kept at 0°. With the input rates of working media established at the above levels, the system pressure during the deposition was equal to approximately 400 mTorr.

2.3. Color change assessment

The color assessment was carried out in accordance with the following standard: PN-EN 20105-A03:1996 Textiles – Tests for color fastness – Part A03: Gray scale for assessing staining. A contrast between a sample of non-modified textile and that of a TiO_2 coated textile was measured. For that purpose, both samples were positioned in the same plane and in the same direction with respect to their weave. In the same plane, stain assessing gray scale was placed. The scale has five levels and consists of five couples of neighboring fields. The highest level 5 corresponds to a couple of identical fields (no contrast). Contrast observations between textile samples were performed under standard conditions.

2.4. Microscopic investigations

Morphology of the coatings was investigated with the scanning electron microscopy (SEM) technique, using a Hitachi S 3000N electron microscope. Each sample was subjected to observation for three times: first directly after deposition, then following routine washing and finally after 18 months of storage in ambient conditions. Washing was performed in a commercial Ariston AVG-12 washer of an A class and a maximum load of 5 kg. For this purpose, 2 g of each textile sample together with 4.5 kg of cotton textiles as adjacent fabrics were washed at 40 °C for 30 min using approximately 80 ml of a commercial washing powder. As far as textile storage is concerned, in this study ambient storage conditions indicate temperature in the range 21–25 °C, humidity in the range 30–60% and average day sun exposure, depending on the season of the year.

2.5. Mechanical properties

Textile samples of 25 × 120 mm, cut in a direction perpendicular to the factory edge, were subjected to tensile strength measurements according to the PN-EN ISO 13934-1 standard. The testing was performed using an INSTRON model 4204 tensile test machine working at a rate of 100 mm/min with the initial distance between the clamps equal to 100 mm. Maximum load and elongation at break were determined for a non-modified sample and for samples TiO_2 coated at 100, 200 and 300 W of RF power, respectively.