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Superhydrophilicity and durability of fluoropolymer-TiO_2 coatings

Katarzyna R. Arturi*, Henrik Jepsen, Jesper N. Callsen, Erik G. Søgaard, Morten E. Simonsen

Section of Chemical Engineering, Department of Chemistry and Bioscience, Aalborg University Esbjerg, Niels Bohrs Vej 8, 6700 Esbjerg, Denmark

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ABSTRACT

Self-cleaning fluoropolymer-TiO_2 coatings have been in focus as a promising group of materials for a number of years due to their favorable combination of photo-activated hydrophilicity and chemical resistivity of the Teflon-based material. The technology incorporates photocatalysis, which results in oxidation of organic compounds absorbed to a surface, with its superhydrophilic nature, which hinders further absorption of any non-polar substances. The main practical challenge concerning this subject is optimization of the coatings composition without compromising its stability and durability. The aim of this study was to characterize the superhydrophilicity (SHP) of a fluoropolymer-TiO_2 coatings as a function of their composition, namely the amounts of polymer, type of the applied curing agent, and the amounts of the titania particles. The hydrophilicity of the coatings was compared to their surface structure and durability to withstand UV-light exposure. In this study, 24 combinations of coatings were studied with contact angle measurements, Fourier transform infra red spectroscopy (FTIR), and scanning electron microscopy (SEM). The results were analyzed statistically with general linear models (GLM) and multivariate data analysis (MDA). The contact angle measurements have shown that time was the most important variable influencing the surface properties of self-cleaning coatings. In terms of composition, the amount of polymer was of significance. Neither the curing agent, nor the amount of titanium dioxide seemed to have any lasting effect on SHP. The analysis of surface structure indicated that illumination influenced the organic polymer, and at long exposure times it led to the degradation of the polymer. This was confirmed by SEM analysis.

1. Introduction

Self-cleaning coatings represent a relatively new type of materials that through a combined effect of photocatalytic activity and superhydrophilicity (SHP) [1–3] ensure an easy maintenance of any object's surface, resulting in environmental and economical benefits [4]. The photoactivity entails oxidation of any organic contaminants, while the superhydrophilicity ensures that it remains clean through the surfaces' lack of affinity to the organic compounds. Some of the first methods for the production of self-cleaning coatings involved spraying the surface of a subject with photoactive particles of e.g. TiO_2, at elevated temperatures, typically over 400 °C. This method limited the range of possibilities for practical application of the technology to relatively small, temperature resistant substrates, thus excluding plastics, one of the fastest growing industry of materials. Degradation due to temperature can be avoided by application of innovative deposition methods, e.g. electrodeposition [5] or atomic layer deposition (ALD) [6]. Beside the application of pure TiO_2 particles, a combination of photo-activated particles with chemically resistant organic coatings have been increasingly popular in the resent years [7–12]. One of the standing challenges in this method is preservation of the substrates integrity, as there is a risk for degradation due to photo-activated oxidation. Application of additional inorganic or organic protective layers of the organic coating has come a long way for resolving this problem. An example of such coating is Teflon-based fluoropolymer matrix supporting active TiO_2 particles. Self-cleaning surfaces have many possible applications within purification, sterilization, anti-fouling, anti-fogging, and anti-beading methods [13]. Some of the more practical examples of applications include coating of stone facades [14], windows [15], and car mirrors [16].

Despite the huge advancements within the field of the self-cleaning polymer containing coatings, numerous challenges are still to overcome. The lack of knowledge about the mechanisms behind SHP has been one of the deterrents, but the biggest challenge is optimizing the composition of the coatings, i.e. maximizing

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* Corresponding author at: Section of Chemical Engineering, Department of Chemistry and Bioscience, Aalborg University Esbjerg, Niels Bohrs Vej 8, 6700 Esbjerg, Denmark.

E-mail address: kra@bio.aau.dk (K.R. Arturi).

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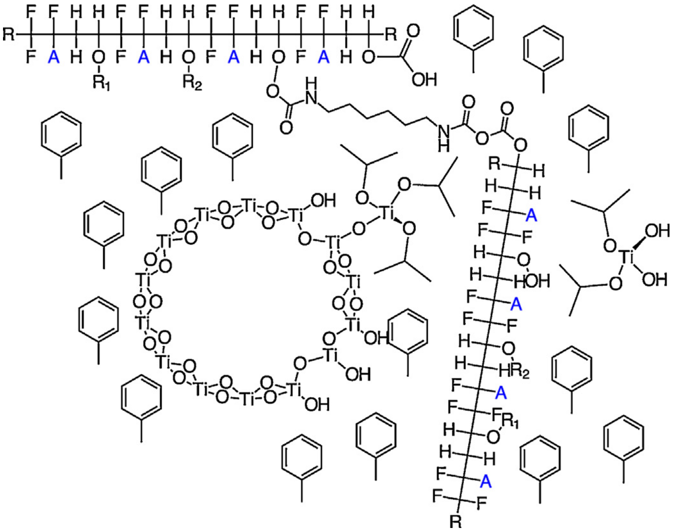

Fig. 1. Cross-linking during formation of fluoropolymer-TiO_2 self-cleaning coatings. The free molecules represent the remains of solvent, e.g. toluene. On the surface, TiO_2 particles are modified according to pH value as follows (low pH–high pH) $-TiOH_2^+ \leftrightarrow -TiOH \leftrightarrow -TiO^-$.

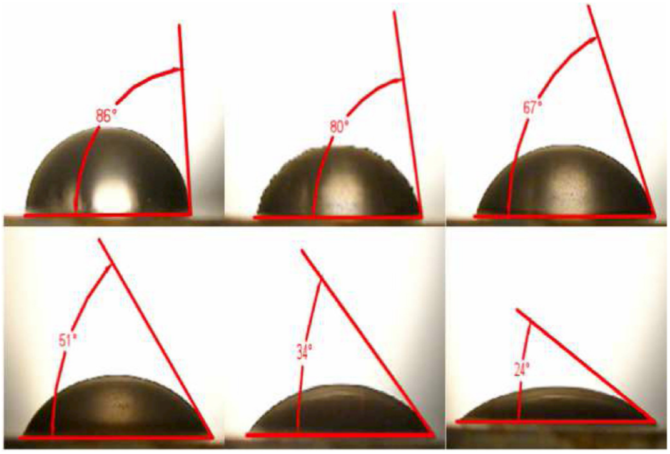

Fig. 2. Achievement of superhydrophilicity by fluoropolymer-TiO_2 coatings due to UV-C illumination.

the self-cleaning properties without compromising the structural stability of the polymer material. This lack of the durability, which can be attributed to the degradation of the polymer material by the active particles, limits the practical application of these materials immensely. This study focuses on investigation of superhydrophilicity of organic fluoropolymer-TiO_2 coatings as a function of their composition, and to assess the durability with regard to UV exposure. Design of more effective and stable coatings is essential for the development of these materials, and yet, the scientific knowledge about these subjects is rather limited. Hydrophilicity of the coatings is studied with contact angle measurements, while the structure, morphology, and durability of the coatings are investigated with Fourier transform infra red spectroscopy (FT-IR) and scanning electron microscopy (SEM). In both instances powerful statistical tools, general linear models (GLM) and multivariate data analysis (MDA) are employed in order to develop effective tools for description of the desired quantities.

2. Materials and methods

2.1. Coatings composition

Fluoropolymer-TiO_2 coatings were produced by curing a mixture of photoactive TiO_2 particles, fluoropolymer continuous phase, and an organotitanium compound, with an isocyanate or hexamethoxymethylmelamine based curing agent. A number of coating was prepared without titania, in order to uncover the influence of titania on SHP. This method is based on a patent (EP 1 157 741 A1) [17]. The coatings used in this study consisted of P-25 Degussa TiO_2 (anatase/rutile ratio – 3:1, particle size 21 nm, surface area 50 m^2/g), Lumiflon® 200, two types of curing agents (BL 3175 and Cymel 303), and titanium tetraisopropoxid (TTIP), as an organotitanium binder. The applied TiO_2 is one of the most photoactive TiO_2 mixtures available on the market [18,19]. Lumiflon® 200 is a teflon based, fluorine rich material, in which a number of reactive chains is added to achieve certain properties and to enable the curing. Cross linking involves a reaction between N=C=O and COOH or OH groups, which results in formation of an urethan bridge between different chains of the fluoropolymer. Fig. 1 show the principle behind formation of the superhydrophilic, self-cleaning, fluoropolymer-TiO_2 coatings used in this study. This study is based on a full experimental design of the described variables: exposure time *t*, type of curing agent *H*, amount of polymer *P*, and titania *T*.

2.2. Coatings preparation

The coatings were produced by dispersing different amounts of Degussa-25 (1 g, 1.5 g, 2.0 g. 2.5 g) in 25 ml of toluene (Sigma–Aldrich, 99 vol%), followed by addition of Lumiflon® 200 (1 g, 1.5 g. 2.0 g), and the organotitatnium (2 ml). Lastly, 1 g of one of the two curing agents was added. A summary of the levels for each factor is presented in Table 1. Mixing was performed with ultrasound (sonification for 10 s with a frequency of 60 kHz). The mixtures were used immediately after preparation to coat microscope slides glass substrates. The glass substrates were degreased, cleaned, and dried prior to the procedure. The substrates were coated by an automatic device with a single coating layer (≈50 nm thickness) with a velocity of 2.5 cm/s. The substrates were then dried shortly at room temperature, followed by drying at the temperature optimal for the curing agent (3 h at 160 °C for BL 3175 and 140 °C for Cymel 303), and stored in dark in order to minimize an accidental activation. The cross-linking time should normally be achieved in ≈15–60 min. The specified levels of coatings' composition have given rise to 24 different mixtures, each of which was produced and analyzed in duplicate and in random sequence in order to achieve statistical independence of the data. For each repetition, 8 substrates were coated: 2 blank (coated and not illuminated) and 6 treated (UV illuminated).

Table 1
Nomenclature used in the statistical analysis of Θ, and the levels of factors.

t: time = 0, t_0 + 10, t_0 + 20, . . ., 90 (min)	H: Curing agent	T: TiO_2 (g)	P: Polymer (g)
Level 1	BL3175	1.0	1.0
Level 2	Cymel 303	1.5	1.5
Level 3		2.0	2.0
Level 4		2.5	