

Enhanced adherence of ALD TiO₂ nanocoatings in polymeric substrates

O. Prieto, J. Feroso, I. Segura, I. Lungoci, M. Acebes, R. Irusta and A. Lorenzana

Fundación CARTIF, Parque Tecnológico de Boecillo Par. 205, Boecillo (Valladolid), España.
olgpri@cartif.es

TiO₂ self-cleaning coatings are finding increasing applications in several fields, i.e. windows' glasses, buildings' materials, pavements of roads, automobiles' components, etc. Such an interest is due to the capability of those coatings, to add decontamination and self-cleaning properties to the substrates in which are deposited. The coatings are generally layers of around 200 nm thickness, which can be obtained by several techniques. Atomic layer deposition (ALD) is a method for thin film deposition where the solid material is formed as a result of subsequent self-limited surface reactions [1]. The deposition occurs sub-monolayer by sub-monolayer, giving an accurate control over film thickness and composition. Furthermore, the self-limiting growth mechanism enables the deposition of uniform films on large areas and complex-shaped surfaces. ALD nucleation usually requires that the substrate has reactive surface groups with which the precursor molecules can react to initiate ALD growth. Hydroxyl groups on oxide surfaces are typical examples of such reactive groups. In that case, the deposited thin film is chemically bonded to the underlying substrate, and will therefore usually have a good adhesion.

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, plasma modification, laser treatment, UV irradiation and chemical treatment [2]. Increasing surface energy enhances the wettability and improves coating uniformity and adhesion [3].

This work presents the results of a thorough study which main objective was the surface modification of polymer substrates to enhance the adherence of TiO₂ nanocoatings obtained by ALD tool (figure 1) Two polymeric substrates were considered (PMMA and PC), and were subjected to physical (UV irradiation) and chemical (immersion under sulphocromic solution). These methods cause the C–C chains to break down and form polar groups such as carbonyl, carboxyl and alkoxy, thus changing the wettability characteristic of the surface from hydrophobic to hydrophilic. The samples were characterised to evaluate the characteristics of the modified surfaces, by conducting FT-IR, and surface energy measurements. Spectroscopic results allow to monitor photochemical changes in PMMA surface. ATR-FTIR spectra of unirradiated and UV-irradiated PMMA are shown in figure 2. The hydroxyl/hydroperoxide (absorbing at 3000–3600 cm⁻¹ range) and carbonyl groups (absorbing at 1600–1800 cm⁻¹) are mainly responsible for the increase of sample wettability upon UV. The broadening of the whole carbonyl band indicates that new oxidized groups are formed resulting of photochemical reactions. Furthermore, the roughness of the surfaces was measured by nanoindentation. Samples from the surface-treated and sound polymers were TiO₂ coated by ALD (5000 cycles, 100°C). The adherence of the coatings was measured by using the cross-sectional nanoindentation technique, as well as scratch analyses [4], obtaining both quantitative and qualitative measurements of the coatings adherence.

References

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Figures



Figure 1. Atomic Layer Deposition equipment used to obtain nanocoatings

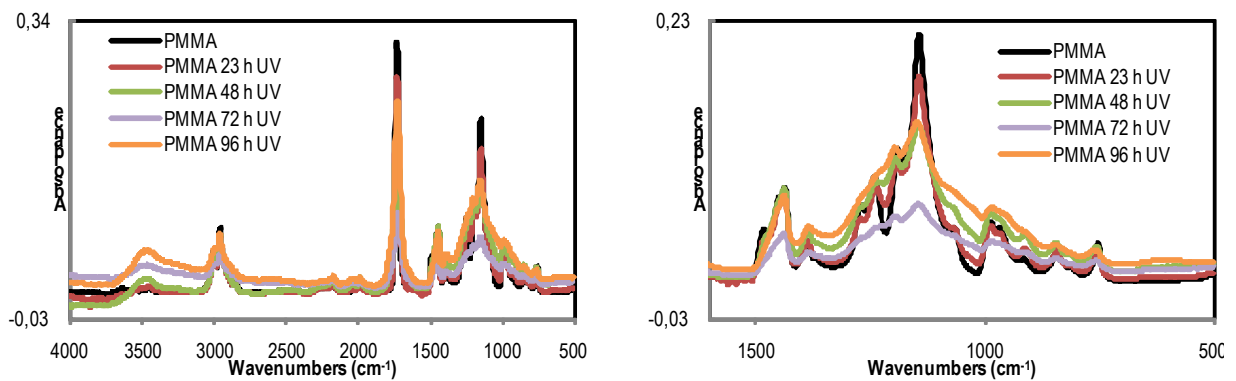


Figure 2. ATR- FTIR spectra of PMMA with UV treatment.