Progress in Organic Coatings 53 (2005) 225–234

PROGRESS IN ORGANIC COATINGS

www.elsevier.com/locate/porgcoat

Influence of the RF plasma polymerization process on the barrier properties of coil-coating

R. Serra [a], M.L. Zheludkevich [a,*], M.G.S. Ferreira [a,b]

[a] Universidade de Aveiro, Dep. Eng. Cerâmica e do Vidro, 3810-193 Aveiro, Portugal
[b] Instituto Superior Técnico, ICEMS, Departamento de Engenharia Química, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Received 15 November 2004; accepted 1 March 2005

Abstract

The work is devoted to the investigation of the influence of silica-based plasma polymer films deposition on the protective properties of polyurethane coil-coating. Different locations and different deposition stages were investigated for radio frequency (rf) plasma deposition reactor to establish relations between deposition stages and coating properties. The surface evolution of the plasma treated samples was assessed by atomic force microscopy (AFM). Energy dispersive spectroscopy (EDS) was used to study the coating composition and electrochemical impedance spectroscopy (EIS) was used to evaluate the barrier properties and water uptake rate of the different samples. Transmission electron microscopy (TEM) was used to obtain information regarding the polymer structure.

The results show that plasma deposition of thin silica-based layer leads to degradation of the barrier properties of the coil-coating. The degree of the coating degradation strongly depends on the electrode location during plasma polymer deposition. The coil-coatings with plasma films deposited on the ground electrode demonstrated higher corrosion protection than the ones prepared on the powered electrode. The oxygen plasma activation of the coil-coatings before silica deposition leads to delamination of the top layer from the surface of the coil-coating during immersion in aqueous solutions. However, oxygen plasma post-treatment of the silica-based top layer tends to improve the barrier properties of the final system.

Keywords: Plasma polymer; Coil-coating; AFM; EIS; Corrosion protection

1. Introduction

Coil-coating is a continuous deposition process for flat metallic sheet. This technology consists of several stages: metal cleaning followed by chemical pre-treatment of the surface, priming and deposition of one or several polymer layers by roller application. The layers composition can range from polyesters, polyurethanes, epoxies, vinyls, plastisols, acrylics and fluorocarbons. These coil-coated systems offer good durability, formability, corrosion resistance and a wide range of colours. This is also an environmentally friendly technology for metal finishing, since coil coaters are able to capture and regenerate volatile organic compounds (VOCs) and solvents to minimize water and air pollution [1,2].

For current applications, the coil-coated product need enhanced properties: superior hardness, scratch resistance, modified surface hydrophobicity and easy to clean properties [3,4]. Plasma deposition of a thin top layer with tailored properties can help to solve these problems [5]. Different methods can be used to initiate the plasma polymerization including microwave [6] and radio frequency (rf) [7] plasma processes, cathodic dc [8] plasma deposition and hollow cathode [7] plasma polymerization techniques. Each method has its own optimal range of operational parameters and can offer films with different properties.

In several works [9–14], it was shown that thin plasma polymer films confer good protective properties to metallic substrates. Moreover these properties can be sharply influenced by the operational parameters of the plasma polymerization process and the chemical composition of the precursors. The advantage of plasma polymerization is achieved in

* Corresponding author. Tel.: +351 234 378146; fax: +351 234 425300.
E-mail address: mzheludkevich@cv.ua.pt (M.L. Zheludkevich).

0300-9440/$ – see front matter
doi:10.1016/j.porgcoat.2005.03.006

ultra thin film applications (e.g., thickness of 100–5000 Å, particularly, the 100–500 Å) [15]. It is well known that both barrier and adhesion properties of a protective layer are crucial in metal corrosion protection. Plasma polymers are generally formed in an extremely tight and three-dimensional network, which behaves more like a low-permeability sieve than a solution-diffusion type of normal polymer. Increase of the operational pressure helps to the formation of nanoparticles incorporated into the growing film but also the formation of nanopores or nanoscale holes in the substrate/coating interface. The introduction of oxygen leads to slower growth of the nanoparticles in the polymer matrix, and increase of the oxygen pressure facilitates the formation of a smoother and porousless film with higher hydrophilicity [16–18]. Another important feature with plasma polymer deposition is that surface cleaning and/or surface treatment can be performed directly before polymer deposition without breaking the vacuum. With good adhesion and in situ vacuum process characteristics together with the excellent barrier characteristics the plasma polymerization entitled itself to provide remarkable levels of corrosion protection for metal surfaces.

Despite the above, so far, only plasma polymers deposited on metal substrates as protective coating or pretreatment were investigated, no investigation has been performed to study the modification of the protective properties of coil-coated systems by deposition of a tailored plasma polymer film on their surface as a top coating.

The plasma polymerization process has different stages of preparation, initial activation of the coil-coating surface, polymer coating deposition and final surface treatment. This work investigates the influence of different stages on the protective properties of polyurethane coil-coating. Another factor to take in account is to which electrode is connected the substrate inside the plasma reactor, ground electrode or powered electrode. The aim of this work is to know the influence of the different stages on the system barrier properties in order to obtain an optimal coating system. Both the barrier properties and the structure evolution of the plasma polymer modified coil-coating were investigated using atomic force microscopy (AFM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), electrochemical impedance spectroscopy (EIS) and transmission electron microscopy (TEM). Impedance measurements data were correlated with the evolution of the morphology and the chemical composition evolution of the coatings.

2. Experimental

2.1. Substrates

Polyurethane coil-coating for automotive application was applied on all the substrates used for the experimental work. The coil-coating was applied on electro chromium coated steel substrate with a fine stone finish. The applied coil-coating system contains four layers: polyurethane-based primer (13–15 μm); polyurethane-based coating (15 μm); polyurethane clear coating (15–18 μm); polyurethane/fluoropolymer clear coating (15–16 μm). The polyurethane coating was protected with a strippable film that was removed before the plasma treatment. The systems studied were tested in its as-received conditions.

2.2. Plasma polymer deposition

The substrate to be coated can be attached either to the ground electrode at the top of the chamber or to the powered electrode at the base of the chamber closer to the gas outlet. The ground electrode is free to move, although it is constrained by the vacuum system. Fig. 1 shows a schematic diagram for the rf plasma discharge chamber.

Before plasma polymer deposition, all substrates were activated in oxygen plasma (50 mTorr O_2, 20 W power, 5 min exposure, electrode gap 75 mm and gas flow 20 sccm). The activation parameters were kept constant for all the coatings produced. The substrates were then coated using the hexamethyldisiloxane (HMDSO) precursor and oxygen carrier gas in ratio 1:19 at 20 mTorr and 100 W during 80 s. Further oxygen plasma post-treatment was performed for some coatings during 1 min at same conditions as in the case of the activation procedure. Coatings prepared after different stages of plasma deposition procedure were investigated in order to reveal the influence of the different steps on the barrier properties of coatings. As reference was used the metallic substrate coated with the coil-coating only—untreated coil-coating.

2.3. Experimental tests

The polyurethane coil-coated metallic substrates were used as reference—untreated coating. The coil-coated sam-

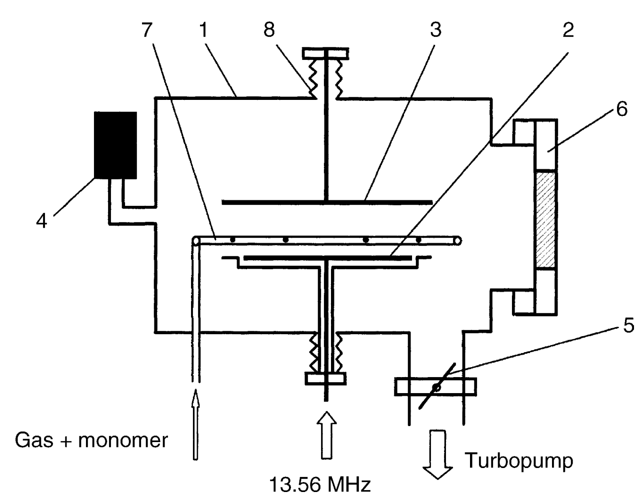

Fig. 1. Schema of the plasma discharge chamber, where (1) vacuum chamber; (2) powered electrode; (3) grounded electrode; (4) capacitive pressure gauge (baratron); (5) butterfly valve; (6) vacuum door with viewport; (7) gas shower ring; (8) bellows translational stage.