Surface & Coatings Technology 234 (2013) 33–41

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Synthesis and characterization of di(ethylene glycol) vinyl ether films deposited by atmospheric pressure corona discharge plasma

Ibrahim Al-Hamarneh [a,*], Patrick Pedrow [b], Asma Eskhan [c], Nehal Abu-Lail [c]

[a] Department of Physics, Faculty of Science, Al-Balqa Applied University, Salt 19117, Jordan
[b] School of Electrical Engineering and Computer Science, Washington State University, Pullman, WA 99164, USA
[c] Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, USA

ARTICLE INFO

Available online 4 July 2013

Keywords:
Atmospheric pressure corona discharge plasma
EO2V
SS 316L

ABSTRACT

This study concerns plasma deposition by atmospheric-pressure corona discharge processing of di(ethylene glycol) vinyl ether (EO2V) as vaporized precursor. Plasma polymerized EO2V (pp-EO2V) thin films were coated using mixed $Ar–O_2$ plasma as carrier gas onto plasma pre-treated surfaces of surgical-grade 316L stainless steel (SS 316L) coupons. The influence of plasma operating conditions on physical and chemical properties of pp-EO2V films was evaluated by contact angle measurements, Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). It was found that surface hydrophilic properties of the deposited film could be controlled by varying plasma deposition time, the carrier gas mixture and the applied plasma voltage. Spectral analyses of FT-IR and XPS affirm compositional changes occurred on the synthesized surface due to plasma activation of new polar and hydrophilic functional groups. There was a good correlation between the FT-IR results and the contact angle measurements. AFM images were used to investigate surface roughness and morphological aspects of the film. Rough estimate of the coating thickness was also provided based on AFM measurements. Stability of the film was evaluated by AFM before and after soaking in phosphate buffer saline solution.

1. Introduction

Atmospheric-pressure corona discharge plasma is produced when a gas is ionized by a high electric field. Often, corona discharge plasma systems are cost effective and can be used for generation, treatment and surface oxidation of thin films on various substrates [1]. Physical and chemical natures of the modification are often difficult to control due to variations in ambient conditions such as temperature, humidity and contaminations [2]. Plasma deposition and treatment conditions have important influence on the nature of corona discharge coatings [3]. Several researchers, e.g. [4,5], reported on how various monomers and power levels influence the composition of such films. For example, Wu et al. [6] showed that the non-fouling properties of the PEO-like films containing two ethylene oxide (EO) units are strongly related to the plasma power employed during film synthesis.

Surgical-grade 316L stainless steel (SS 316L) is widely used in the medical device industry due to its desirable mechanical properties, low carbon content and high corrosion resistance. In a previous study [7], we have presented the results of a surface modification of SS 316L coupons using a corona discharge plasma generated in atmospheric pressure $Ar–O_2$ gas. That work was dedicated to enhancing the surface hydrophilicity of the stainless steel to improve adhesion for a plasma polymer layer. We described optimization of the surface modification in association with the plasma reactor system and some of the plasma operating conditions. Plasma treatment and surface modification techniques of stainless steel applied for various applications are widely used by many workers. Examples from literature are found in [8,9].

Ultimately, a thin film of polyethylene glycol (PEG) will be coated on the SS 316L surface to control bacterial adhesion that afflicts biomedical implants, as will be presented in our next publication. PEG is used because its surface resists cell and protein adhesion and concomitant biofouling [10]. Unfortunately, direct coupling of PEG to stainless steel (SS) is difficult due to the lack of chemical reactivity of the metal oxides and hydroxides on the ambient SS surface [11]. To mitigate this problem, plasma polymerization of volatile low-molecular weight EO containing monomers can be used as an intermediate layer or primer coat between the SS substrate and the PEG layer [12]. In an earlier study conducted in 2007 [13] we attached a PEG polymer film synthesized using a dip-coating procedure onto SS 316L substrate precoated with a primer film of plasma polymerized di(ethylene glycol) vinyl ether (pp-EO2V) that was applied with a low pressure radiofrequency inductively coupled.

In the present study, we supplement our previous works and conduct an experimental study on the synthesis and surface characterization of a

* Corresponding author. Tel.: +962 777489677.
E-mail addresses: hamarnehibrahim@yahoo.com, hamarneh@bau.edu.jo (I. Al-Hamarneh).

0257-8972/$ – see front matter
http://dx.doi.org/10.1016/j.surfcoat.2013.06.112

pp-EO2V thin film coated onto SS 316L coupons. Herein, a process and a material to cover the steel are described. To this end, a home-built corona discharge plasma reactor has been designed, constructed and characterized. As mentioned previously, the reactor was first used to treat the SS 316L coupons and then to coat the treated surfaces with a pp-EO2V film. In the present work, the physical and chemical properties of the plasma polymerized film on the stainless steel surface were studied. The effects of plasma conditions, namely monomer deposition time, working gas mixture and applied voltage were investigated in order to optimize the plasma process. The plasma processed film has been studied at different deposition conditions using FT-IR absorption spectroscopy and the results have been analyzed and compared with the contact angle measurements. In this paper, we describe fabrication of a hydrophilic thin film on SS 316L and present measured polar and non-polar contact angles along with calculated surface free energy (SFE) values that confirm the hydrophilic nature of the film. The surface composition and elemental concentrations were determined by XPS. The surface morphology and roughness of the deposited films were studied using AFM images. Stability of the films was studied by AFM examination of the surface roughness before and after soaking the coated coupons in a flask containing Dulbecco's phosphate-buffered-saline (DPBS) liquid without calcium [14] at room temperature for 24 h.

2. Experimental

2.1. Materials

The monomer di(ethylene glycol) vinyl ether (EO2V) [$CH_2=CH(OCH_2CH_2)_2OH$] purchased from Aldrich Chemical was the highest purity available (>98%) and used as received. High purity feed gases of Ar and O_2 were used. Coupons of surgical-grade 316L stainless steel of diameter of 12.5 mm and 2.25 mm thick were used as substrates in this study using the polishing and washing procedures described elsewhere [7,13].

2.2. Corona discharge plasma processing

Corona discharge plasma polymerization of film onto the surface of SS 316L coupons was carried out at atmospheric-pressure from the precursor EO2V using Ar and O_2 as carrier and reactive gases.

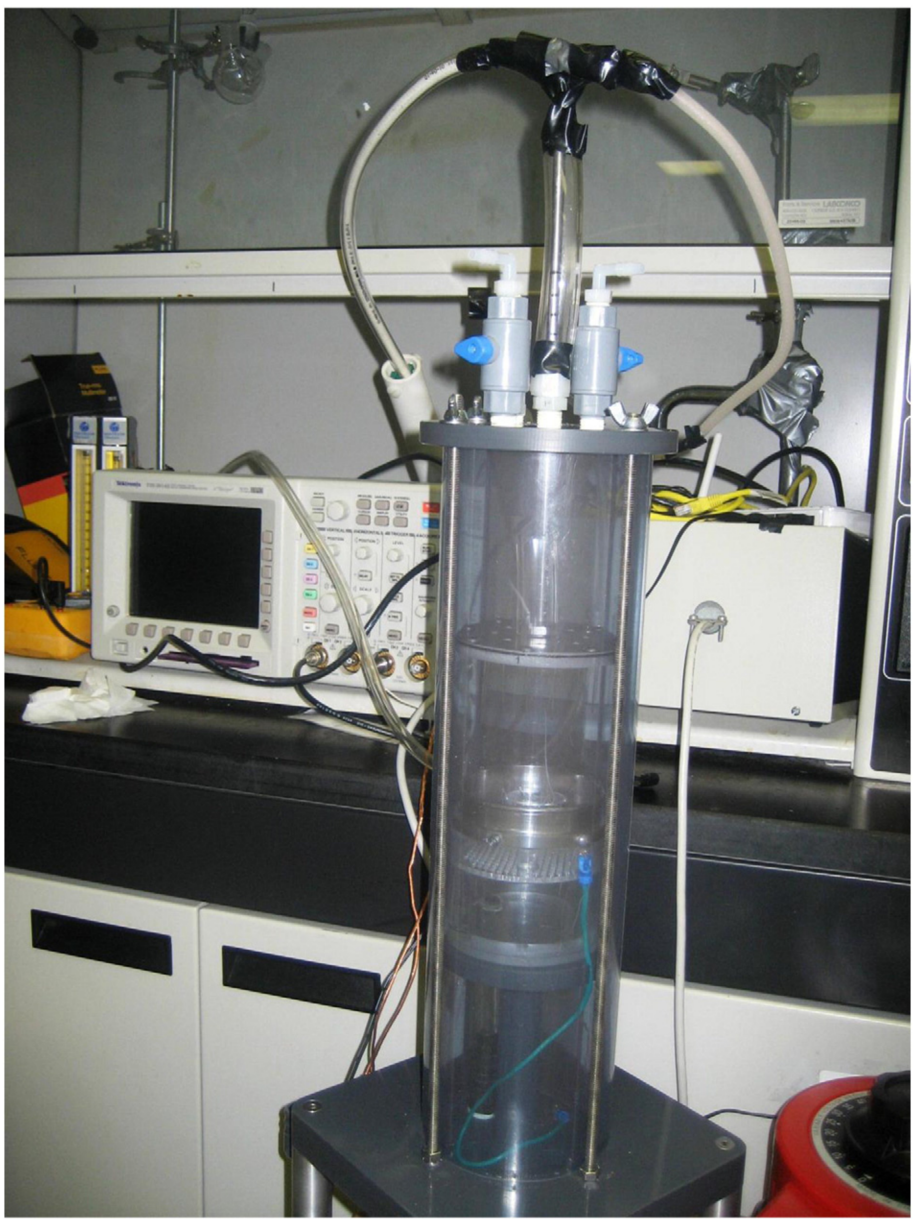

Fig. 1. A photo and cross-sectional schematic diagram of the corona discharge plasma reactor.