



Surface characterization and stability of an epoxy resin surface modified with polyamines grafted on polydopamine

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ARTICLE INFO

Article history:

Received 29 November 2013

Received in revised form 19 February 2014

Accepted 3 March 2014

Available online 12 March 2014

Keywords:

Polydopamine

Polyamine

TOF-SIMS

Surface characterization

ABSTRACT

This paper reports on polydopamine and polyamine surface modifications of an etched epoxy cresol novolac (ECN) resin using the 'grafting to' method. Three different polyamines are used for the grafting reactions: branched polyethyleneimine (B-PEI), linear polyethyleneimine (L-PEI) and diethylenetriamine (DETA). These modifications are compared to control materials prepared via direct deposition of polyamines. The stability of the modifications toward a concentrated hydrochloric acid (HCl) environment is evaluated. The modified surfaces are characterized with scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and time-of-flight static secondary ion mass spectroscopy (TOF-SIMS).

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1. Introduction

During the past decades, the need to tailor the chemistry of polymer surfaces has increased significantly. Especially in the field of biomaterials [1–3], bioelectronics [4,5] and microelectronics [6,7], a large amount of examples can be coined up in which specific (covalently bonded) chemical functional groups are required. In this paper, the introduction of primary amine groups on polymer surfaces is emphasized. Primary amine groups can be used to increase the adhesion toward electroless deposited metals which is vital in the production of (flexible) electronic devices [8,9]. On the other hand, surface amine groups have a positive influence on cell adhesion and spreading due to changes of the surface properties like hydrophilicity, surface charge and surface free energy [10–12]. Moreover, immobilization of bioactive molecules can be performed on surfaces which contain positively charged protonated amine groups. These positive charges can attract negatively charged molecules like proteins from the extra cellular matrix [12,13].

Different surface modification techniques like plasma [2,14], plasma-induced graft polymerization [15,16], plasma

polymerization [8,17] and wet-chemical modifications [13,18] have been developed for the above mentioned purposes. Due to the simplicity of wet-chemical modifications performed in aqueous media, it still attracts a lot of interest from both the scientific and technological research areas. Indeed, surface modification techniques using plasma still require advanced and expensive equipment compared to wet-chemical modifications. Furthermore, plasma surface treatment of 3D structures is still under development while wet-chemical modifications can overcome this drawback.

In the past, coupling molecules such as cyanuric chloride have been used to introduce amine groups on the surface through wet-chemical modifications [18,19]. However, this reaction requires the use of organic solvents and the presence of nucleophilic groups on the initial surface. In 2007, Messersmith et al. reported on surface modification of wide range of materials ranging like metals, metal oxides, silicon to polymers with polydopamine [20]. This polydopamine modification was inspired by the chemical structure of mussel adhesive proteins (MAPs). Important here is that all kinds of polymer surfaces can be modified with polydopamine, independent of their surface properties and functional groups. Surfaces can be modified by simply introducing them in an aqueous dopamine solution at pH 8.5 (marine conditions). In general, this polydopamine layer has a thickness of 5–50 nm [21]. A lot of discussion is still going on concerning the chemical structure of this

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polydopamine layer. The most recent progress on this specific topic can be found in literature [22]. Nevertheless, it is assumed that catechol, quinone, amine and 5,6-dihydroxyindole moieties are present on the surface of a polydopamine modified substrate.

Polydopamine modified surfaces can also be used as a versatile platform for secondary modifications which can further tailor the surface chemical properties [20,23–25]. An important secondary modification consists of introducing (bio)macromolecules which contain a nucleophilic group (R-N-H, R-S-H) through Michael addition or Schiff base reaction using the 'grafting to' approach. This strategy will be applied here to introduce polyamines on polydopamine modified surfaces.

Surface modifications with polydopamine or polyamines potentially increase the adhesion toward electroless deposited metals. Therefore, they can be used in the processing of sequential build-up layers in the printed circuit board industry [14,18,26]. During the electroless deposition process, the substrates are immersed in different wet-chemical aqueous solutions. One of these steps is the catalytic activation in a highly acidic Pd colloid suspension [26]. Therefore, the stability of the polydopamine and subsequent polyamine modifications toward 1 M HCl solution is investigated. It is known that polydopamine coated substrates are quite stable against a HCl medium [27,28]. However, the stability of the grafted polyamines has not been investigated until now.

In this work, the epoxy surfaces are modified with polydopamine. Next, polyamines such as branched polyethyleneimine (B-PEI), linear polyethyleneimine (L-PEI) and diethylenetriamine (DETA) are grafted to the polydopamine layer. All samples have been tested on their stability toward a 1 M HCl solution. The modified substrates have been subjected to a thorough chemical surface analysis using XPS and TOF-S-SIMS. Moreover, the surface topography is analyzed with SEM. New insights are provided on the stability, chemical structure and surface topography of these specific modifications.

2. Experimental

2.1. Materials

Branched PEI (M_w 25,000 g/mol), DETA, linear PEI (50 wt% in water, M_w 1200 g/mol), TRIS (trisaminol) and dopamine. HCl are purchased from Sigma–Aldrich and used as received. MilliQ water is used for solution preparation and rinsing steps.

Probelec XB 7081TM is provided by HuntsmanTM. Probelec XB 7081 is a liquid photo imageable dielectric. It contains an epoxy cresol novolak (ECN) prepolymer dissolved in 1-methoxy-2-propylacetate, a cationic photo-initiator and different types of filler materials [19].

2.2. Preparation of a mildly roughened ECN resin on FR4

FR4 is used as a base substrate (10 cm × 10 cm; 1.2 mm thick). FR4 is by far the most commonly used material for printed circuits. It is constructed of woven fiber glass cloths impregnated with a flame retardant epoxy resin [29]. Probelec XB 7071 is dip coated on FR4. Next, this substrate is submitted to different drying, illumination and curing steps as described previously [19]. The final layer has a uniform thickness of about 40 μm. Roughness is introduced by 10 min swelling followed by chemical etching at 80 °C (1, 1.5 or 2 min) in Circuposit Hole Prep 4425 and KMnO₄/NaOH (Circuposit 3310) solutions, respectively [19].

2.3. Surface modifications of a mildly roughened ECN resin

The surfaces of the ECN resins are modified with polydopamine using the procedure described by Messersmith et al. [27]. A TRIS-HCl

buffer solution is prepared at pH 8.5. Next, the substrates are inserted in this solution. Finally, 2 g/ml of dopamine is added and the reaction mixture is stirred slowly under ambient air for 24 h.

Branched and linear PEI are grafted on the polydopamine by inserting the polydopamine modified substrates in a PEI aqueous solution for 1 or 24 h. This solution contains 5 g/L of PEI and 10 mmol/L of TRIS. Prior to the modification reaction, the pH is adjusted to 8.0 using a 0.1 M HCl solution.

DETA is grafted on the polydopamine by inserting the polydopamine modified substrates in a DETA aqueous solution for 24 h. This solution contains 5 g/L of DETA and 10 mmol/L of TRIS. Prior to the modification reaction, the pH is adjusted to 8.0 using a 0.1 M HCl solution.

The modifications using only polyamines in aqueous environment are performed in a solution containing 5 g/L of polyamine (B-PEI, L-PEI or DETA) and 10 mmol/L of TRIS for 24 h. Prior to the modification reaction, the pH is adjusted to 8.0 using a 0.1 M HCl solution.

After all modification reactions, the modified samples are rinsed twice for 2 min in water followed by drying using nitrogen blowing.

2.4. SEM and SEM-EDS analysis

Scanning electron microscope (SEM) analysis is performed on a JEOL JSM-5600 instrument. The SEM analysis is performed using a secondary electron detector. Prior to analysis, all samples are coated with a thin gold layer (circa 20 nm) using a plasma magnetron sputter coater.

2.5. Chemical surface analysis

XPS analysis of the substrate surfaces before and after modification is performed on an ESCA S-probe VG monochromatic spectrometer with an Al K α X-ray source (1486 eV). Survey scan spectra of at least 3 random locations are recorded using a spot size of 250 μm × 1000 μm. In all spectra, the aliphatic carbon 1s peak is set at 285 eV to calibrate the spectrum. After calibration, the peak areas from other elements in the observed spectra are defined after a Shirley background fitting. Next, all elemental peaks are integrated and the atomic concentrations are determined using the Casa XPS software package (Casa Software Ltd, UK).

TOF-S-SIMS analyses are carried out on a TOF-SIMS V instrument (IONTOF, Germany) equipped with a Bi_n^{q+} ($n = 1-5$, $q = 1, 2$) liquid metal ion gun (LMIG). Mass spectra are recorded by bombarding areas typically of 500 μm × 500 μm with 25 keV Bi₃⁺ ions using the so-called 'high current bunched mode', featuring high mass resolution and a beam spot diameter of about 2 μm. The acquisition time of typically 100 s results in a total ion-dose density of 2.5×10^{11} ions cm⁻². The bunched pulse length of 1 ns allows a mass resolution of 5000 (FWHM) to be achieved at m/z 15, while the mass accuracy is better than 100 ppm up to m/z 850. Mass spectra are recorded for three different spots on each sample. Positive ion mass calibration is performed using the ion signals at m/z 1 (H⁺), 15 (CH₃⁺), 29 (C₂H₅⁺) and 43 (C₃H₇⁺). For the negative ion mass calibration, the ions at m/z 1 (H⁻), 12 (C⁻), 17 (OH⁻) and 42 (CNO⁻) are used. Charge compensation is performed using low-energy electrons from a flood gun. Static secondary ion mass spectrometry is widely recognized as the method of choice for molecular surface analysis with an information depth of essentially one monolayer.

3. Results and discussion

In order to introduce polyamines on the surface of rough epoxy resins, polyamines are grafted to polydopamine modified epoxy surfaces. The reaction conditions are based on the work of Lee et al. [30]. However, in this work, the goal is to investigate the chemical

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