Applied Surface Science 305 (2014) 292–300

Contents lists available at ScienceDirect

Applied Surface Science

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

Surface modification of cellulosic substrates via atmospheric pressure plasma polymerization of acrylic acid: Structure and properties

Jose Garcia-Torres[a,*], Dioulde Sylla[b], Laura Molina[a], Eulalia Crespo[a], Jordi Mota[a], Llorenç Bautista[a]

[a] Advanced Materials group, R&D Department, Leitat Technological Center, c/Innovacio 2, 08225 Terrassa, Barcelona, Spain
[b] Electrodep, Physical Chemistry Department, University of Barcelona, c/Marti i Franques, 1, 08028 Barcelona, Spain

ARTICLE INFO

Article history:
Received 4 December 2013
Received in revised form 19 February 2014
Accepted 8 March 2014
Available online 19 March 2014

Keywords:
Acrylic acid
Cellulose-based substrates
Atmospheric pressure plasma enhanced chemical vapor deposition
Poly(acrylic acid) films
Hydrophilic character

ABSTRACT

Surface chemical modification of cellulose-based substrates has been carried out by atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) of acrylic acid. The structure/properties relationship of the samples was studied as a function of the plasma experimental conditions. Acrylic acid monomer/helium ratio and treatment speed clearly influences the wettability properties of the paper substrate: advancing contact angle values were reduced to the half if compare to non-treated paper. Surface morphology of the films did not greatly vary at short polymerization times but fibers were covered by a poly(acrylic acid) film at longer times. FTIR and XPS techniques allowed detecting the retention of carboxylic acid groups/moieties. The possibility to quickly design architectures with tunable carboxylic functions by modifying the plasma processing parameters is shown.

1. Introduction

The nature of the surface of bulk materials has a high impact on their final properties because of the vast majority of phenomena take place at the interface level. Therefore, controlling the surface state of the material may widen their application window [1,2]. In this sense, the preparation of coatings different than the bulk material or the nanostructuration/patterning of the materials surface are commonly ways to modify surface characteristics. The introduction of chemical groups of complementary polarity (as in Lewis acid–base chemistry) or reactivity (electrophilic or nucleophilic characters) is attracting more and more interest because it allows tuning material surface functionality which opens the door to new technological applications (i.e. sensor technology, life sciences, etc.) [3,4].

A number of surface functionalization procedures are currently available like covalent bonding, adsorption, electrostatic interaction, oxidation, etc. [5]. Among those, plasma processes have received increase attention because they allow surface modification of materials attributing to different properties but without affecting their bulk. Up to this day, plasma deposition has been successfully used to obtain coatings with different chemically reactive moieties (primary amine (–NH_2), carboxyl (–COOH), hydroxyl (–OH) groups, etc.) [6–9]. Moreover, this technique allows not only the deposition on a wide variety of substrates [7,10] but also tuning the surface properties by varying the experimental conditions [11,12]. All these characteristics together with the unique properties of the obtained coatings (i.e. the films are generally amorphous, free from pinholes, highly cross-linked, resistant to heat and corrosion and very adhesive to a variety of substrates) makes them ideal candidates to be applied in a wide number of fields: mechanics, optics, electronics, biotechnology, biomedicine, etc. [13,14] by providing with new functionalities such as hydrophilicity, adhesion, biocompatibility, conductivity, anti-fogging, anti-fouling, and lubrication [15].

Besides these well-known examples, state-of-the-art applications are continuously being developed especially in the industrial domain. In the framework of these industrial applications, plasma polymerization of acrylic acid has been studied in order to obtain coatings with a high density of carboxylic acid (–COOH) groups [16,17]. Such COOH-dense surfaces can have important industrial applications: (1) improve adhesion and aging resistance of bonded components in the automotive industry [18] and (2) activate polyolefin surfaces and thus replace conventional treatments in the

---

* Corresponding author. Tel.: +34 699813563.
E-mail address: garcia.torres.jm@gmail.com (J. Garcia-Torres).

http://dx.doi.org/10.1016/j.apsusc.2014.03.065
0169-4332/

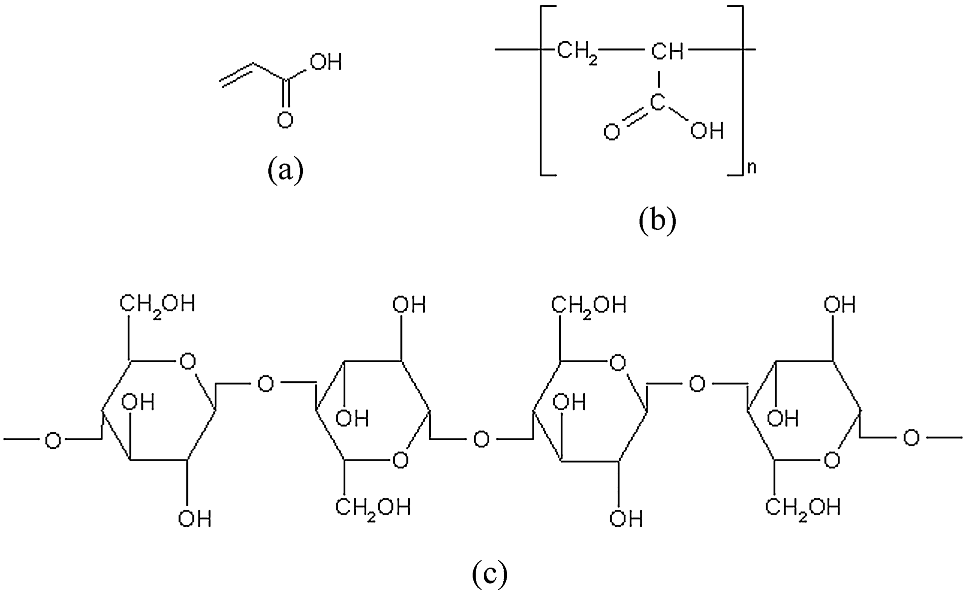

Fig. 1. Chemical structures of (a) acrylic acid monomer, (b) poly(acrylic acid) and (c) cellulose.

packaging sector [19]. Acrylic acid has been selected because its feasibility to give COOH-rich surfaces after plasma polymerization [16]. Different plasma techniques have been used to grow poly(acrylic acid) films, the most common which enables a good control of the surface chemistry is radiofrequency low pressure glow discharge [20,21]. The main drawbacks of these plasmas are the need for expensive vacuum systems and the low deposition rates. For all these reasons, atmospheric pressure plasma-enhanced chemical vapor deposition (AP-PECVD) is receiving increasing attention not only from a scientific but also from a technological and industrial point of view as an alternative to grow such plasma-polymer films [22].

Poly(acrylic acid) coatings prepared by plasma polymerization have been studied over a variety of substrates (glass, metals or polymers) [16]. However, cellulose has never been used to polymerize acrylic acid by AP-PECVD. Our interest resides on the use of cellulose because of the excellent properties it shows: biocompatiblity, biodegradability, high modulus and high strength, flexibility and good stability, low cost and abundance in nature. All these properties make this biopolymer an excellent candidate to find potential applications in optics [23], electronics [24], magnetic [25], mechanics [26], catalysts [27], packaging [28] and biomedicine [29–31]. Moreover and in the context of a sustainable society, there is strong motivation to replace petroleum-based polymers with polymers from renewable resources like cellulose.

Therefore, the objective of the present work is the surface chemical modification of cellulose-based substrates (Fig. 1) by plasma polymerization with carboxyl groups in order to modify their surface chemical structure and thus their properties (i.e. wettability properties). Acrylic acid (Fig. 2) is used as a monomer to prepare plasma polymerized films on paper substrate using atmospheric pressure-plasma enhanced chemical vapor deposition (AP-PECVD) technique. AP-PECVD method was selected attending the high-treatment speeds and the lack of vacuum conditions in order to evaluate the feasibility of this work to be applied at industrial scale. Acrylic acid was chosen for this study because it is known that this monomer can be easily polymerized by conventional polymerization processes [16]. Different deposition conditions (applied potential, treatment speed, monomer/carrier gas ratio, etc.) have been employed. The resulting film structure and properties have been characterized: morphology (FE-SEM), chemical structure (XPS, ATR-FTIR) and wettability (dynamic contact angle).

2. Materials and methods

2.1. Materials

Acrylic acid (AA) (with a 99% purity) was purchased from Sigma–Aldrich and used without further purification. Helium was used as a carrier and was purchased from Air Liquid. Premium Office paper 100% recyclable, 80 g/m^2, EU Ecolabel PT/11/02 was used as substrate.

2.2. Plasma treatments

Paper samples were coated in continuous mode using an Atmospheric Pressure Glow Discharge (APGD) equipment, model PLATEX 600 – LAB VERSION, from the Italian company Grinp, S.r.l. The two-planar electrode equipment operates at low frequency (20–45 kHz) to partially ionize gases and/or vapors of precursors. To obtain plasma-polymerized acrylic acid coatings, the discharge is fed with helium loaded with acrylic acid vapor. The gas mixture is introduced in the electrode gap through the upper and lower electrodes (electrodes distance = 1.2 mm) allowing the treatment of both sides of the substrate. In this work the monomer/gas carrier ratio (0.1/0, 0.1/1 and 0.1/3 l/min), power of discharge (1–2 kW) and treatment speed (1–10 m/min) have been investigated. Occasionally, the treatment speed was zero in order to have a thicker continuous film with the objective to compare the properties of the cellulosic-based substrate under the different treatments. On the other hand, the electrode temperature (160 °C) and distance between electrodes (1.2 mm) were kept constant throughout the experiments. The deposition was carried out at atmospheric pressure and at room temperature.

2.3. Characterization

Wettability properties have been analyzed using water contact angle (WCA) measurements. In order to measure the dynamic