

POLY(ACRYLIC) NANOCOATINGS DEPOSITED BY AP-PECVD PROCESSES ON PAPER SUBSTRATES FOR PACKAGING APPLICATIONS

José Manuel García, Jordi Mota, Laia Crespo, Meritxell Martínez, Laurent Aubouy, Llorenç Bautista

R&D Department, Leitat Technological Center, C/Innovació 2, 08225, Terrassa, Spain.

Abstract

Poly(acrylic acid) coatings on paper substrates have been prepared by atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD). The structure/properties relationships of the samples were studied in dependence 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 (around 60 °) if compare to non-treated paper (120 ° approximately). The surface morphology of the films did not greatly vary with the plasma polymerization treatment.

Keywords: acrylic acid, atmospheric pressure plasma enhanced chemical vapor deposition, paper substrate, hydrophilic character

1. Introduction

In the last decades, thin functionalized plasma-polymerized films has received increased attention because plasma processes allows surface modification of materials attributing different properties but without affecting their bulk. On the other hand, this technique allows not only the deposition on a wide variety of substrates [1,2] but also tuning the surface properties by varying the experimental conditions [3,4]. 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 variety of fields: mechanics, optics, electronics, biotechnology or biomedicine [5,6]

Up to day, plasma deposition has been revealed successful to obtain coatings with different chemically reactive moieties (primary amine (-NH₂), carboxyl (-COOH) or hydroxyl (-

OH) groups). Among those, carboxylic group containing films are one of the most studied layers [7,8]. Acrylic acid is typically used as a monomer to grow such films. Plasma-deposited acrylic acid thin films can be obtained using various plasma techniques. The most common which enables a good control of the surface chemistry is radiofrequency low pressure glow discharge fed with acrylic acid vapor [9,10]. However, the main drawbacks of these plasmas are the need for expensive vacuum systems and the low deposition rate. Atmospheric pressure plasma-enhanced chemical vapor deposition (AP-PECVD) has thus recently received increasing attention to grow plasma-polymer films [11].

In this paper, acrylic acid is used as a monomer to prepare plasma polymerized films on paper substrate using AP-PECVD technique. Acrylic acid was chosen for this study because it is known that this plasma polymer can served as an adhesion-promoting interlayer for packaging applications. Moreover, from a scientific point of view, acrylic acid can be easily polymerized by conventional polymerization processes. The influence of the preparation conditions (applied potential, speed, carrier gas/monomer ratio,...) on the final properties of the deposited coating will be reported.

2. Materials and Methods

2.1. Materials

Acrylic acid (AA) 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/m², 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. 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 varied while keeping constant the electrode temperature (160°C) and distance between electrodes (1.2 mm).

Surface morphology was examined with a Hitachi H-4100 FE field emission scanning electron microscope (FE-SEM) after depositing a carbon nanocoating to make the samples conductive.

Wettability properties have been analyzed using contact angle measurements. In order to measure the dynamic contact angle of plasma-treated fabrics, a Krüss K100 MK2 tensiometer was employed. Wilhelmy method has been applied on 20 mm x 20 mm samples. An average value of contact angle has been calculated by measuring four replicates of each sample. All measurements were determined at 65 ± 2 % of relative humidity and 20 ± 0.5 °C (ISO 139:2005).

Surface characterization of poly(acrylic acid) film-coated papers have been done by FTIR-ATR and XPS spectroscopies. FTIR-ATR (Nicolet 710 FTIR – Diamond crystal, Pike®, Miracle™) spectra were recorded between 500 and 4000 cm^{-1} . Mean spectra of 32 scans and normalization to the maximum peak have been carried out using IR solution software (Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI 5600 multitechnique system. The binding energies (BE) of the XPS signals of all species have been corrected by assuming C1s signal at 285.0 eV

3. Results and Discussion

3.1. Wettability properties

3.1.1. Influence of the acrylic acid/He ratio and power of discharge

The first step of this work was to study the influence of the discharge power in the wetting properties of the treated paper for the 3 different acrylic acid/helium ratios used. Figure 1

shows the variation of the advancing water contact angle with the applied power. As it can be observed, no influence of the power discharge on the contact angle is detected when no helium is used (Figure 1A). However, under the presence of a small proportion of helium contact angle decreases but only at high discharge powers (Figure 1B). A decrease in the contact angle was observed at lower discharge powers when the proportion of He in the fed mixture increased (Figure 1C). The reason could be an activation process of the gas carrier which made easier the polymerization of acrylic acid monomer on the substrate: the higher the He content, the higher the activation and the better the polymerization. On the other hand, no important differences were detected when discharge power increased up to 2 kW.

3.1.2. Influence of treatment speed

Other important parameter that may affect the wettability of the films is the treatment speed. Treatment speed influences on the time the substrates resides between the two electrodes, in other words, the lower the treatment speed is the higher the plasma treatment time is. Figure 2 shows how the treatment speed can influence on the contact angle of the tested films prepared with the higher He content. As it can be observed, the wettability of the paper decreases as the treatment speed increases, which could be attributed to a thinner deposited poly(acrylic acid) film.

Based on the previous results, the films with the better wettability properties were obtained from the mixture with the acrylic acid monomer/helium ratio 0.1/3 l/min at a treatment rate of 1 m/min. Power discharge slightly influenced the contact angle value: $60.3^\circ (\pm 5.5^\circ)$ at 1 kW and $72.5^\circ (\pm 4.1^\circ)$ at 2 kW.

3.2. Surface Characterization

The surface morphology of non-treated and plasma-polymerized paper substrates with the better wettability properties were analyzed FE-SEM microscope. Figure 3 the SEM images in which it can be observed cellulose fibers and the inorganic charge typical of printing papers. Looking specifically at the cellulosic fibers, no significant differences

were detected between treated and non-treated samples at low magnifications (Figure 3A-C). However, higher roughness seems to be observed after plasma polymerization at high magnifications (Figure 3D-E), results in agreement with those presented by Amorosi *et al.* [12].

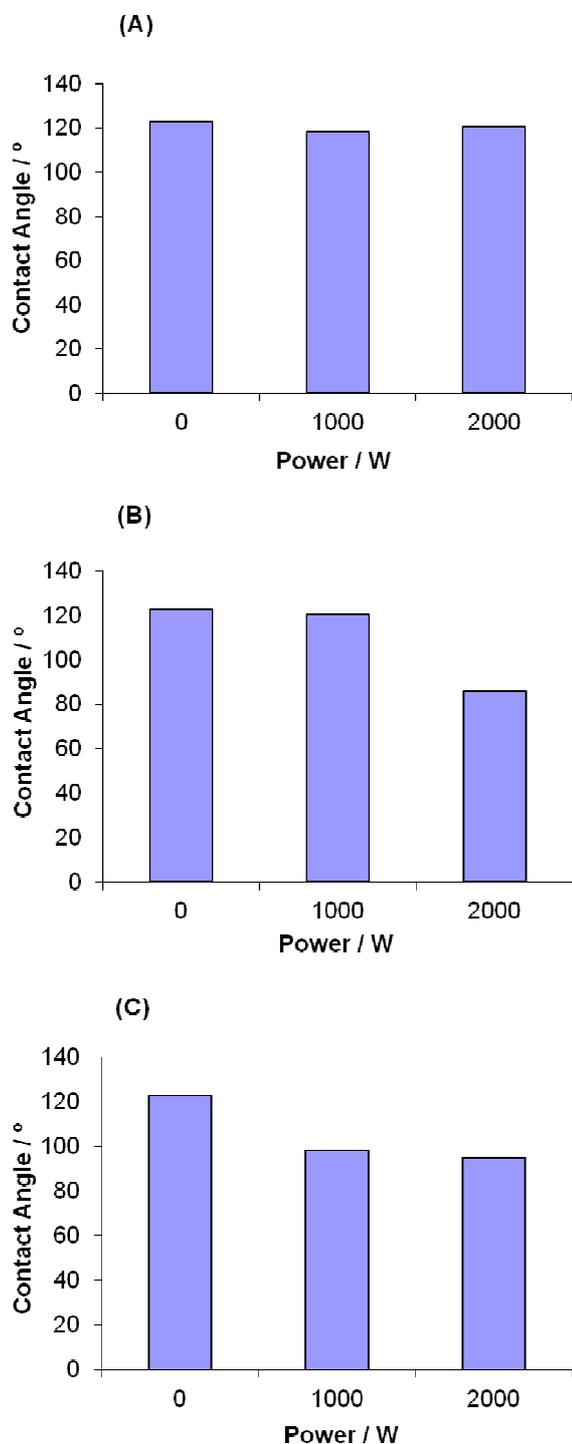


Figure 1. Influence of the power discharge on the contact angle for different acrylic acid/He ratios. A) Only Acrylic acid, B) 0.1/1 l/min and C) 0.1/3 l/min.

FTIR-ATR spectra of non-treated and plasma-treated samples confirm the cellulosic nature of the substrates studied in this work. However, FTIR-ATR technique is not able to differentiate surface modifications associated to plasma polymerization treatments. This suggests that the chemical modification on the paper surface is at nanometric level, not at micrometric level. On the other hand, preliminary XPS studies reveal the presence of carboxyl groups attributed to the polymerization of acrylic acid monomer by atmospheric pressure plasma.

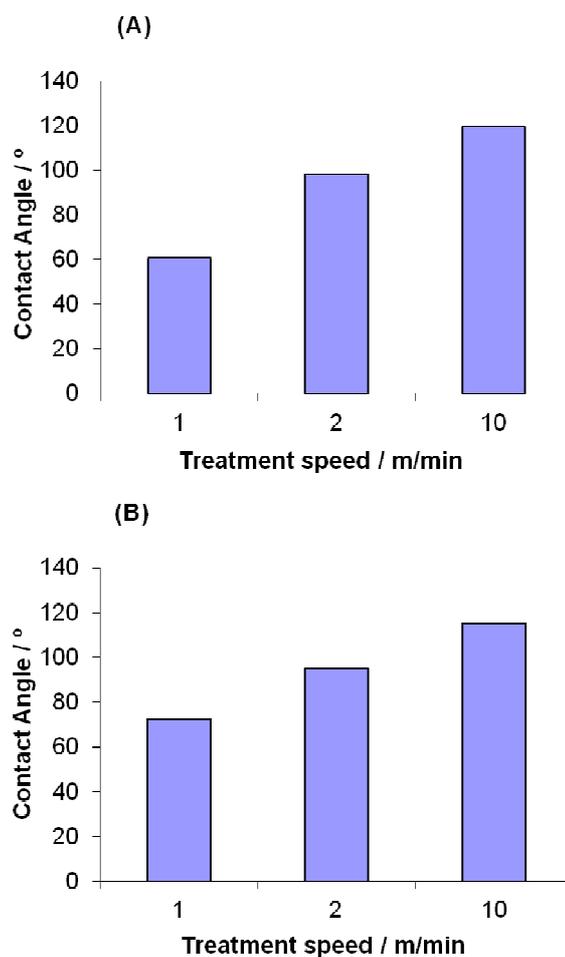


Figure 2. Influence of the treatment speed on the contact angle of the plasma-polymerized poly(acrylic acid) films obtained from the mixture with the higher He content at the different power discharges. A) 1000 W and B) 2000 W.

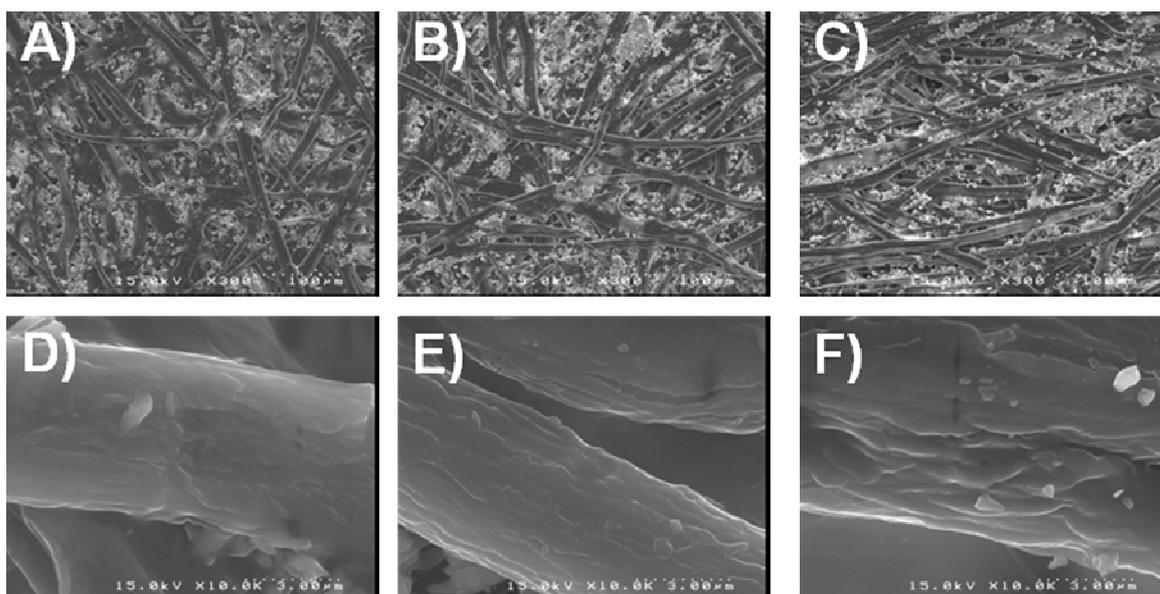


Figure 3. SEM images of non-treated (A,D) and treated samples with acrylic acid/He ratio 0.1/3 l/min at different treatment speed: 1 m/min (B,E) and 2 m/min (C,F).

4. Summary

In the present work, nanocoatings made from acrylic acid via AP-PECVD processes were prepared. Depending on the conditions of the process, the wettability properties were significantly modified: the helium content in the fed mixture as well as the treatment speed greatly influenced on the contact angle. Contact angle values of 60 ° approximately were obtained after plasma-polymerized paper substrates. Moreover, surface morphology of cellulosic fibers was slightly roughened by the plasma process. Summarizing, plasma polymerization parameters have to be carefully adjusted in order to control the film characteristics such as wettability or morphology.

Acknowledgements

This work has been achieved thanks to the support of ACCIO (Generalitat of Catalunya) in the framework of the BIP project TECCOL11-1-0001 co-financed by FEDER fundings.

References

- [1] M.R. Alexander, T.M. Duc, *J. Mater. Chem.* 8, 1998, 937.
- [2] F. Arefi, V. Andre, P. Montazerrahmati, J. Amoroux, *Pure and Applied Chemistry* 64, **1992**, 715.
- [3] T.P. Kasih, S.Kuroda, H. Kubota, *Plasma Process. Polym.* 4, **2007**, 648.
- [4] Y. Sawada, S.Ogawa, M. Kogoma, *J. Phys. D: Appl. Phys.* 28, **1995**, 1661.
- [5] K.S. Siow, L. Britcher, S. Kumar, H. J Griesser, *Plasma Process. Polym.* 3, **2006**, 392.
- [6] D.S Kumar, Y. Yoshida, *Surf. Coat. Technol.* 169-170, **2003**, 600.
- [7] A. Fahmy, R.Mix, A. Schönhals, J.F. Friedrich, *Plasma Process. Polym.* 8, **2011**, 545.
- [8] P.Hamerli, *Biomaterials*, 24, **2003**, 3989.
- [9] L. Detomaso, R. Gristina, R. d'Agostino, G.S. Senesi, P. Favia, *Surf. Coat. Technol.* 200, **2005**, 1022.
- [10] P.Rossini, P. Colpo, G. Ceccone, K. D. Jandt, F. Rossi, *Mater. Sci. Eng. C* 23, **2005**, 1022.
- [11] O. Carton, D.B. Salem, S. Bhatt, J. Pulpytel, F. Arefi-khonsari, *Plasma Process. Polym.* DOI: 10.1002/ppap. 201200044.
- [12] C. Amorosi, T. Fouquet, V. Toniazzo, D. Ruch, L. Averous, *Reactive&Funct. Polym.* 72, **2012**, 341.

