Deposition of Poly(acrylic acid) Films by Electrohydrodynamic Atomization in Postdischarge at Atmospheric Pressure in Air

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Deposition of poly(acrylic acid) films has been carried out in air by electrohydrodynamic atomization in post dielectric barrier discharge at atmospheric pressure. The topmost surface layer of the coatings has been analyzed by X-ray photoelectron spectroscopy, revealing a high level of retention of the carboxylic acid functionality, up to 80%. These films are found to exhibit a low water contact angle and a high resistance to washing.

1. Introduction

Low-pressure glow discharges are well-known processes to produce well-adhered, thin coatings (a few tens of nanometers) with a wide range of surface functionalities.[1−8] The plasma polymerization of acrylic acid ($CH_2{=}CHCO_2H$) at low pressure has been extensively studied since the carboxylic acid groups are suitable for many technological applications such as adhesion and biotechnology. However, some of the drawbacks of this technology are the requirement for expensive vacuum pumping systems, the restriction of the use of vacuum-compatible materials, and low deposition rates of a few tens of nanometers per minute. Nowadays, great effort is made to develop new processes for surface treatment or deposition in air at atmospheric pressure. In the past, the limitation for development of atmospheric pressure electrical discharges (APEDs) for surface treatment of polymers was due to a relatively high gas temperature in the spot of the filamentary discharge, a limited production of chemically active species restricted to excited oxygen and nitrogen species, and the difficulty to get a homogeneous discharge. Indeed, dielectric barrier discharges (DBDs) are usually filamentary ones and lead to heterogeneous treatments.[9] Some works have been carried out in the past to produce homogeneous DBDs without filaments in helium or N_2,[10,11] referred to as atmospheric pressure glow discharges (APGDs). APGDs offer an alternative homogeneous cold plasma source, ideal for film deposition.[12,13] Recently, Badyal et al. have combined a droplet production device and an APGD to deposit well-defined poly(acrylic acid) (PAA) films[14] and silicon-containing films.[15] In that case, the polymeric precursor was injected into the APGD from an ultrasonic atomizing nozzle, presenting the advantage to limit the extent of the monomer fragmentation and to give rise to rapid deposition of a highly functionalized plasma polymer layer. The other important advantage of such a system is the control of the introduction of the liquid precursor; the deposition rate is not limited by the vapor pressure of the organic precursor, making possible the use of even nonvolatile precursors. In our experimental setup, the production of acrylic acid droplets has been done by electrohydrodynamic atomization (EHDA). The advantages of EHDA in cone−jet mode are (i) the possible monodispersity of the aerosol, which favors the reproducibility of the deposition conditions of the polymer that will be formed, (ii) the presence of droplets charged with similar polarity, avoiding their coalescence, and finally (iii) a high level of charges that favors the orientation of the droplets toward the grounded electrode and increases the deposition rate. In this paper, we will present results on PAA films which have been obtained in postdischarge at atmospheric pressure after a DBD treatment of the films in air. The overall film composition of the PAA

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(1) Denes, F. *Trends Polym. Sci.* **1997**, *5*, 23.
(2) Fye, G.; Roucoules, V.; Cameron, A. M.; Oates, L. J.; Cameron, N. R.; Steel, P. G.; Badyal, J. P. S.; Davis, B. G.; Coe, D.; Cox R. *Langmuir* **2002**, *18*, 8996.
(3) Van Ooij, W. J.; Chityala, A. *Polymer Surface Modification: Relevance to Adhesion*; VSP: Zeist, The Netherlands, 2000; Vol. 2, p 243.
(4) Karches, M.; Bayer, C.; Rudolf von Rohr, Ph. *Surf. Coat. Technol.* **1999**, *879*, 116−119.
(5) Inagaki, N., Tasaka, S., Ishii, K. *J. Appl. Polym. Sci.* **1993**, *48*, 1433.
(6) Friedrich, J.; Kühn, G.; Mix, R.; Unger, W. *Plasma Processes Polym.* **2004**, *1*, 28.
(7) Schönherr, H.; van Os, M. T.; Förch, R.; Timmons, R. B.; Knoll, W.; Vancso, G. J. *Chem. Mater.* **2000**, *12*, 3689.
(8) Tatoulian, M.; Brétagnol, F.; Arefi-Khonsari, F.; Amouroux, J.; Bouloussa, O.; Rondelez, F.; Paul, A. J.; Mitchell, R. *Plasma Processes Polym.* **2005**, *2* (1), 38−44.
(9) Borra, J. P. *J. Phys. D: Appl. Phys.* **2006**, *39*, R19−R54.
(10) Kogoma, M.; Okazaki, S. *J. Phys. D: Appl. Phys.* **1994**, *27*, 1985.
(11) Massines, F.; Rabehi, A.; Decomps, P.; Ben Gadri, R.; Ségur, P.; Mayoux, C. *J. Appl. Phys.* **1998**, *83*, 2950.
(12) Kanazawa, S.; Kogoma, M.; Okazaki, S.; Moriwaki, T. *Nucl. Instrum. Methods Phys. Res.* **1989**, *B37/38*, 842.
(13) Prat, R.; Koh, Y. J.; Babukkutty, Y.; Kogoma, M.; Okazaki, S.; Kodama, M. *Polymer* **2000**, *41*, 7355.
(14) Ward, L. J.; Scofield, W. C. E.; Badyal, J. P. S.; Goodwin, A. J.; Merlin, P. J. *Chem. Mater.* **2003**, *15*, 1466.
(15) Ward, L. J.; Scofield, W. C. E.; Badyal, J. P. S.; Goodwin, A. J.; Merlin, P. J. *Langmuir* **2003**, *19*, 2110.

10.1021/cm060066e CCC: $33.50

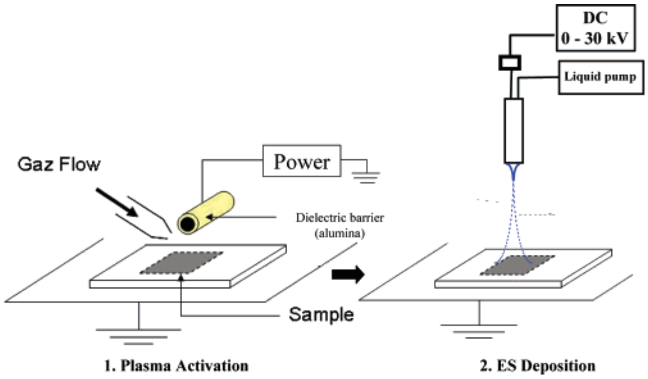

Figure 1. Schematic of the apparatus used for the plasma surface modification of polymer films and for electrospray deposition

film will be characterized by X-ray photoelectron spectroscopy (XPS). Special attention will be paid to the level of retention of the carboxylic acid functionality and to the stability of the coating upon washing.

2. Experimental Section

Setup. A Plexiglas reactor was used for the plasma surface modification of polymer films and for electrospray (ES) deposition (Figure 1). The polymer film to be treated is placed on a grounded plane electrode (10×10 cm^2) which can move under a fixed cylinder electrode (1.5 cm diameter) at a speed of 1.0 mm/s. Acrylic acid monomer (Aldrich, 99%) was introduced into the reactor through a stainless steel needle with an inside diameter of 0.5 mm. The substrate to be coated is placed on a stainless steel grounded flat electrode, several centimeters away from the tip of the needle. With this configuration, the diameter of the spray of droplets is around 4 cm. For electrospray deposition, an electrical field is used to electrically stress the liquid at the tip of the needle. The voltage applied to the nozzle is around 6 kV dc, and the current measured by an oscilloscope ranges from 50 to 200 nA, depending on the conductivity and the flow rate of the precursor. EHDA, also called electrospraying, refers to a process where a liquid jet breaks up into droplets under the influence of electrical forces. Depending on the kinetic energy of the liquid jet leaving the nozzle, the capillary pressure of the liquid, and the electric pressure normal to the liquid surface, different spraying modes can be obtained. One of these spraying modes is the cone−jet mode, sometimes referred to as the Taylor cone. In this mode, the charge carriers (mainly ions present as impurities in the liquid) are accelerated by the tangential electric field and collide with the surrounding liquid molecules which are dragged toward the cone apex. Due to the acceleration of these charges at the liquid surface, the liquid takes a conical shape which ends in a filament of liquid (also referred as the jet). This jet breaks up into small droplets in the micrometer range with narrow size, charge, and velocity distribution. The liquid flow rate can be regulated by a syringe pump feeding the nozzle from 0.1 to 100 mL/h. To obtain stable electrospraying conditions, the liquid flow rate and the deposition time have been, respectively, fixed at 1 mL/h and 40 s. The mean deposition rate has been estimated by measuring the scanning electron microscopy (SEM) images of the cross section of the AA films deposited on a polyethylene (PE) sheet. The measurements have been carried out at different positions, from the center to the edge of the spray. Under our experimental conditions, we have estimated a mean value ranging, respectively, from 300 to 65 nm/min. The grounded plate is on runners so that the sample can be placed on the plate, ensuring its movement beneath the electrospray, giving rise to a large coverage of the substrate. For industrial applications, the homogeneity of the thickness could be easily ensured by multiplying the number of spray nozzles.

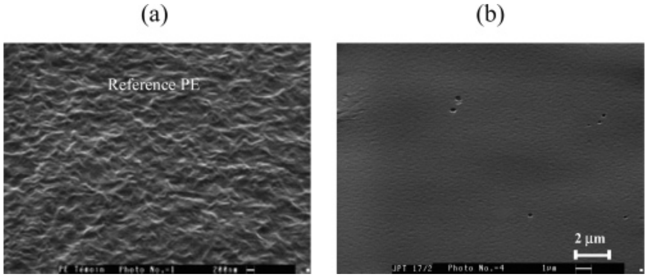

Figure 2. SEM analyses of a noncovered, nontreated PE film (a) and a PAA-covered film (b).

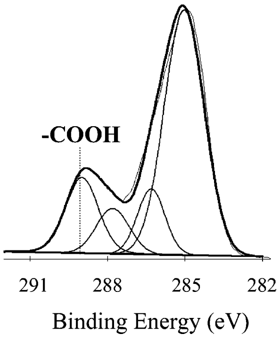

Figure 3. C_{1s} XPS spectrum of PAA coatings deposited on a DBD-pretreated PE film ($Q_{AA} = 1$ mL/h, deposition time 40 s).

About 10 cm upstream from the electrospray is placed a strip electrode generating a DBD plasma. The high-voltage electrode is covered with a thin layer of alumina (Al_2O_3) around 2 mm thick which opposes the same grounded metal plate so that the substrate can be passed first through the plasma and then through the electrospray in a single pass. The number of passages of the polymer film through the DBD plasma ranges between 1 and 3, leading to different surface energies of the substrate. The high voltage was applied to the electrode with the help of a low-frequency (45 kHz) generator. The gap between the electrodes was fixed to 1 mm, and the DBD was carried out in ambient air.

Surface Characterization. XPS measurements were performed with a Surface Science Instruments (SSI) M-Probe spectrometer. The samples were irradiated with monochromatic Al Kα X-rays (1486.6 eV) using a spot size of 150 μm and 40 W power. For each sample, two survey spectra were recorded with a pass energy of 150 eV, from which the surface chemical compositions were determined. In addition, one set of high-resolution spectra (C_{1s}, O_{1s}, N_{1s}) were recorded with a pass energy of 25 eV, from which the chemical states were determined. Charge compensation for these electrically insulating specimens was achieved using a beam of ca. 4−9 eV electrons at a flood gun current of ca. 0.1 mA with an electrically grounded 90% transmission nickel mesh screen positioned ca. 1 mm above the sample surface.

Contact angle measurements of water sessile drops were performed using a home-built profile projector, equipped with an automatic image processing system. The advancing contact angle was measured five times on different parts of the sample, and typical deviations of ±3° with respect to the mean value were observed. The reported value corresponds to the average of these five measurements.

3. Results and Discussion

PAA films have been deposited by electrospray on a PE film which has been pretreated with a DBD plasma in air to

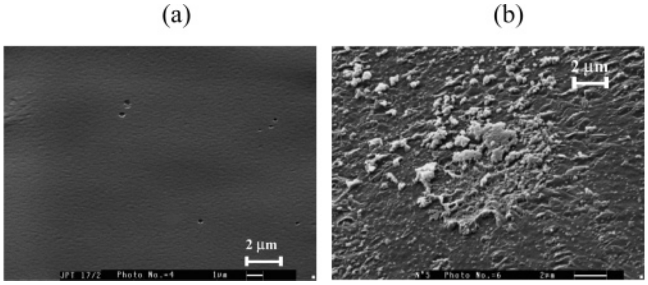

Figure 4. SEM pictures of PAA coatings deposited on a plasma-activated PE film, (a) before and (b) after Soxhlet extraction in ethanol (12 h) (Q_{AA} = 1 mL/h, deposition time 40 s).

get a highly wettable surface (water contact angle (WCA) <20°). SEM analyses show that the electrospray technology can produce a homogeneous and pinhole-free coating (Figure 2). The chemical composition of the PAA films has been studied by XPS. Figure 3 shows the peak-fitted spectrum for the C_{1s} core level. The high binding energy structure is indicative of the existence of carbon−oxygen bonds.

The spectrum can be satisfactorily fitted by a combination of four distinct peaks: the peak at 285 eV corresponds to *C*−C and *C*−H moieties, the peak at 286.5 eV to *C*−O functional groups, the peak at 287.9 eV to *C*═O or −O−*C*−O groups, and the peak at 289.4 eV to COOH groups. The well-resolved feature at 289.2 eV is indicative of a high carboxylic acid group retention: the COOH/C_{1s} ratio is around 26.0% compared to a theoretical maximum of 33% for a conventional poly(acrylic acid), which corresponds to a COOH retention rate of around 80%. The WCA measurement of the PAA film also provides evidence for a high content of hydrophilic groups such as COOH functions since its value is less than 15°. These contact angle measurements have also confirmed the presence of a homogeneous coating since measurements carried out on different locations of the sample (2 cm × 10 cm) were similar.

Since the stability of the polymerized coating to solvents is essential for its application, we have therefore investigated the resistance of the films to Soxhlet extraction in ethanol. SEM analyses show that the PAA coatings deposited on highly wettable DBD-pretreated PE resist severe washing conditions performed in Soxhlet extraction in ethanol (Figure 4). The coating still remains on the substrate, and porous zones appear due to the swelling effect of the deposited polymer by ethanol. Figure 5c shows the XPS peak-fitted spectrum of a washed sample which is quite the same as the unwashed PAA coating; upon washing, the carboxylic acid group retention decreases slightly from 26.3% to 23.4%.

Table 1. Influence of the Surface Wettability of PE[a] on the Film Properties of PAA Coatings Deposited by Electrospray Followed by Washing (Q_{AA} = 1 mL/h, Deposition Time 40 s)

	90° (nontreated PE)	65−70°	45−50°	20−25°
COOH/C_{1s} (%)	0	1.6	10.4	23.4
COOH retention (%)	0	4.8	31.2	70.3
water contact angle (deg)	85−90	30−55	20−40	<15

[a] The surface wettability of the PE substrate is given in the column heads.

However, parts a and b of Figure 5 also show that carboxylic group retention depends on the level of wettability of the polyethylene films. In the case of a non-pre-treated PE film (Figure 5a), no COOH groups can be retained on the surface after the samples are washed with Soxhlet extraction in ethanol, revealing a complete loss of the PAA coating. In the case of the latter, the absence of polar groups on the PE films prevents the formation of covalent bonds with the PAA coatings, which favors the delamination and the elimination of the organic coating. Parts b and c of Figure 5 correspond, respectively, to a PAA coating deposited on a moderately (WCA = 50°) and a highly (WCA = 20°) wettable substrate; the increase of the component at 289 eV assigned essentially to COOH groups shows that the resistance to washing of the PAA coatings increases with the wettability and the density of polar groups grafted by the DBD treatment on the underlying PE.

Table 1summarizes the data of the COOH retention rate after washing of the PAA coatings deposited on different activated PE films but also the resulting WCA of the washed PAA coating: both data are strongly dependent on the initial wettability of the plasma-pretreated PE film. For nonactivated PE films, XPS and WCA confirm the absence of PAA coatings after washing. For activated PE films, the higher the wettability, the stronger the resistance to washing of the PAA coatings; the wettability probably favors the spreading of the PAA coatings and strengthens its adhesion to the substrate through the formation of covalent bonds via the presence of functional groups such as alcohol/carboxyl groups.

Furthermore, our results also suggest that the COOH content is correlated with the density of reactive groups.

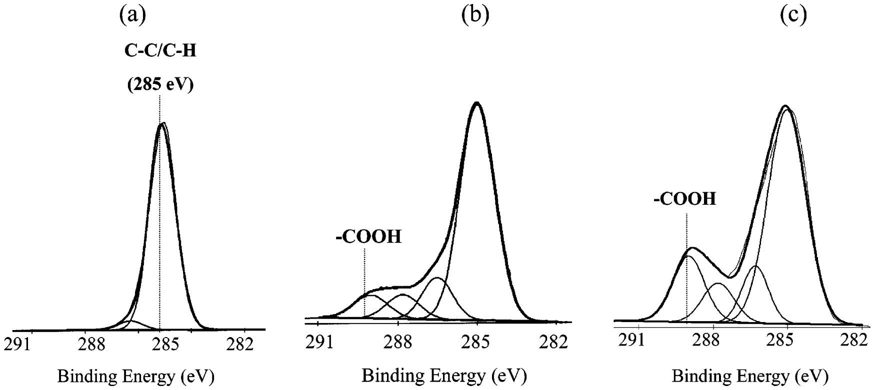

Figure 5. C_{1s} XPS spectra of PAA coatings deposited on different DBD-pretreated PE films after being washed: (a) non-pre-treated PE films (90°); (b) moderately wettable surface (50°); (c) highly wettable surface (20°) (Q_{AA} = 1 mL/h, deposition time 40 s).

Some authors have shown an interrelationship between the amount of peroxide moieties grafted to the surface and the carboxylic concentration.[16,17] It is well-known that most polymer radicals produced after plasma activation are rapidly converted into the corresponding peroxy radicals upon exposure to air. Kuzuya et al. have used electron spin resonance (ESR) to study the formation and the dissipation of the peroxy radicals after plasma irradiation.[18] They have reported that the formation of peroxy radicals was maximum at a very early stage (several minutes after the treatment) and then decreased exponentially with prolongation of the standing time in air through the formation of hydroperoxide. After 1 h, the rate of decay of the radicals is around 0.60, and after 6 h, 10% of the peroxy radicals are still present at the plasma-treated PE. This is an important point, since in our experimental conditions, the electrospray deposition of AA is carried out a few seconds after the DBD treatment, so the peroxy or the hydroperoxy radicals present at the surface of the DBD-pretreated PE could initiate a graft polymerization of acrylic acid. Moreover, the coverage of AA is reinforced by the use of ES, which forms unipolar micrometer-size droplets from the liquid, which increases considerably the surface area of the liquid by volume unit and, as a result, heterogeneous interactions between the liquid monomer and the reactive species formed in the treated PE surface. Moreover, the liquid monomer is injected in the form of charged droplets that are accelerated and easily dragged toward the substrate, which decreases the evaporation rate and leads to high deposition rates of a few hundred nanometers per minute; the charged droplets strike the surface at a mean speed of 4 m/s, flatten, and form a thin film of controlled thickness, well adherent to the substrate.

4. Conclusion

EHDA coupled with a dielectric barrier discharge is a promising technology for polymerization of unsaturated organic precursors at atmospheric pressure: the DBD generates reactive groups that will initiate the grafting polymerization of vinyl monomers and the interlocking between the coating and the substrate, whereas the ES leads to the formation of charged micrometer-size droplets, which avoids their coalescence and reduces their transient time from the nozzle to the substrate. This process presents different features such as (i) the possibility to obtain a homogeneous covering of AA with a controlled thickness, (ii) a high retention of the monomer functionality, and (iii) an excellent stability to washing in water, which render them ideal for biotechnological applications among others.

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(16) Alexander, M. R.; Whittle, J. D.; Barton, D.; Short, R. D. *J. Mater. Chem.* **2004**, *14*, 408−412.

(17) Gupta, B.; Hilborn, J. G.; Bisson, I.; Frey, P. *J. Appl. Polym. Sci*. **2001**, *81*, 2993−3001.

(18) Kuzuya, M.; Kondo, S. I.; Sugito, M.; Yamashiro, T. *Macromolecules* **1998**, *31*, 3230−3234.