Polym. Bull. (2011) 66:277–288
DOI 10.1007/s00289-010-0318-6

ORIGINAL PAPER

Plasma treatment of polyacrylonitrile/vinyl acetate films obtained by the extrusion process

**R. R. Fleming · L. C. Pardini · C. A. R. Brito Jr. ·
M. S. Oliveira Jr. · N. P. Alves · M. Massi**

Received: 15 December 2009 / Revised: 9 March 2010 / Accepted: 7 June 2010 /

Abstract This work presents a study of superficial properties of polyacrylonitrile (PAN) films obtained by extrusion process. This innovative material was submitted to microwave plasma treatment generated at low pressure. The contact angle was measured with and without treatment in nitrogen and argon plasma, by the pendant drop technique. The work of adhesion was calculated by the Young–Dupré equation. The surface energy was calculated by the harmonic and geometric average methods, through the technique of two liquids proposed by Fowkes and Wu. The results showed an increase on the surface wetting, for films of plasma treat under nitrogen and argon, which indicated a modification in the surface of the PAN polymeric film.

Keywords Polyacrylonitrile · Extrusion · Contact angle · Surface energy · Plasma treatment

Introduction

Acrylonitrile was first synthesized by the French chemist Moureau at the end of the nineteenth century. All commercial acrylonitrile polymerization processes from precursors to acrylic fibers are free radical processes, and they are done mainly by

---

R. R. Fleming · L. C. Pardini · C. A. R. Brito Jr. · M. S. Oliveira Jr. · M. Massi
Technological Institute of Aeronautics - ITA, São José dos Campos, SP, Brazil

L. C. Pardini (✉)
General-Command Aerospace Technology, Aerospace and Aeronautical Institute – IAE,
São José dos Campos, SP, Brazil
e-mail: pardini@iae.cta.br

N. P. Alves
Quimlab Química Fina Ltda, Jacareí, SP, Brazil

anionic polymerization. Nearly all acrylic fibers are made from acrylonitrile copolymers containing one or more additional monomers that modify the properties of the fiber [1, 2]. For more than 50 years the use of polyacrylonitrile (PAN) polymer has been limited to use in the textile industry and in the aeronautical industry, as precursor of carbon fibers. Since then, the only way to process PAN was in the form of fibers by wet-spinning or dry-spinning methods. The PAN and its copolymers when heated at temperatures above its glass transition temperature starts the process of degradation before reaching the melt point, which is in the range of 317–330 °C [3–5]. Several attempts have been made along the years to process PAN by using conventional thermoplastic extrusion technology. In this way, some processes were patented, mainly from BASF and Dupont, but they were not commercially viable because the need for water at high temperature (200 °C) as a melt carrier [6–8]. Besides, the extrusion process has to be accomplished at high pressure (3–7 MPa), and as a consequence robust equipment is required for continuous extrusion.

Others attempts have been made trying to obtain meltable PAN copolymers for fiber manufacture, which were later patented under trade names of Barex and Amilon [9, 10]. In this case, the acrylonitrile polymerization was done by emulsion and the high cost of comonomers has threatened the economic viability of the products. In another work, Bortner [4] demonstrated the success of using supercritical carbon dioxide as a plastifier for PAN, which reduces the glass transition temperature, leading to a melt viscosity reduction. The result was a reduction in the PAN melting point, avoiding its degradation, but the injection process has to be done at high pressure (6 MPa) with liquid CO_2, in a pressure vessel (17.2 MPa), at 120 °C, to accomplish the saturation with acrylonitrile.

In 2006 after an experimental event, Alves demonstrated that 1,2,3-propanetriol, which melts at 17.8 °C and boils with decomposition at 290 °C, could be used as plastifier for PAN [11, 12]. In relation to acrylic fiber production this approach lead to a substantial cost reduction in relation to the traditional wet- and dry-spinning processes and its need of using solvents with low toxicity during spinning, which delayed the degradation process [1]. On the other hand, the possibility of melting PAN without degradation opened interesting perspectives in obtaining molded products, such as plates and films for example, by using traditional thermoplastic processes such as extrusion, injection, or blow molding.

Polymer films, whatever the process used to produce them, needs surface treatment for adhesion purposes. However, polymers surfaces are, in general, chemically inert, have low surface energy (<100 mN/m), and are characterized by a weak adhesion to other materials [13]. Commercially available surface treatment methods used for surface modification are oxidation, solvent, flame or thermal, ultraviolet, corona discharge, laser, and plasma treatment (radio frequency and microwaves) [14]. The activation of polymer surfaces by any of these methods is sensitive to environmental and storage conditions. In many cases, the surface properties after-treatment can be ineffective even after a few hours, which is a direct consequence of the tendency of polymeric chains rearranged at the surface of the polymer, looking for a chemical stability with the environmental conditions [15]. In the past three decades, the modification of the polymer surfaces with plasma has been widely investigated and it is important for many important industrial areas [16]. According to Tran et al. [17], plasma treatment is a convenient technique for improving the hydrophilicity of polymeric surfaces. The particles formed by the cold plasma can penetrate into the top of several nanometers of the polymer surface to form a fairly uniform surface having distinct properties. The interactions between the ionized medium and the polymer surface lead to different reactions onto the surface, such as cross-linking, degradation, functionalization, and radical formation [18]. Depending on the type of polymer film, polar groups such as hydroxyl, carboxyl, and amine can be formed over the surface of the film, keeping the volume properties of the materials [14, 19]. Also, by changing the process parameters of the plasma treatment, such as type of gas, treatment pressure, and time length of treatment, the surface properties of the polymers can be controlled [16]. Changes in the surface energy of materials lead to changes in wetting properties. Wetting is a physical-chemistry phenomenon that has a great technological importance in various industrial processes, such as for painting, printing, or adherence to other films, and also for biological processes [20]. Wetting is usually evaluated by measuring the contact angle between a liquid drop formed over any solid surface. The contact angle (θ) is a parameter that evaluates the solid–liquid interaction, from the thermodynamic equilibrium among the interfacial energies involved. These interfacial energies are the solid–liquid surface tension (γ_{SL}), the solid–vapor surface tension (γ_{SV}) and the liquid–vapor surface tension (γ_{LV}), according to Eq. 1 proposed initially by Young [14, 21]:

$$\gamma_{\mathrm{SV}} = \gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}} \cos\theta \tag{1}$$

The objective of the present work was to evaluate microwave low temperature plasma treatment generated at low pressure, to modify the surfaces of the PAN films obtained by melt extrusion process. The surface energy and work of adhesion were evaluated according to models of Young–Dupré, Fowkes and Wu [22–24].

Experimental

Materials

A PAN polymer was obtained by suspension polymerization, whose composition was 94%/mass of the acrylonitrile monomer (AN) and 6%/mass of vinyl acetate (VA). The material will be designated as PAN AN/VA throughout the paper. The film was obtained by continuous dry extrusion with 25%/mass of glycerol and the final thickness was 10 μm. The extruded PAN film was washed in warm water at 40 °C for 80 min for complete removal of plasticizer. The films were then properly layered over a glass sheet forming a smooth surface for plasma treatment.

Plasma treatment equipment

The PAN AN/VA film surface studies were performed on rectangular samples of 7.5 × 1.5 cm. Plasma treatments were performed in a homemade aluminum

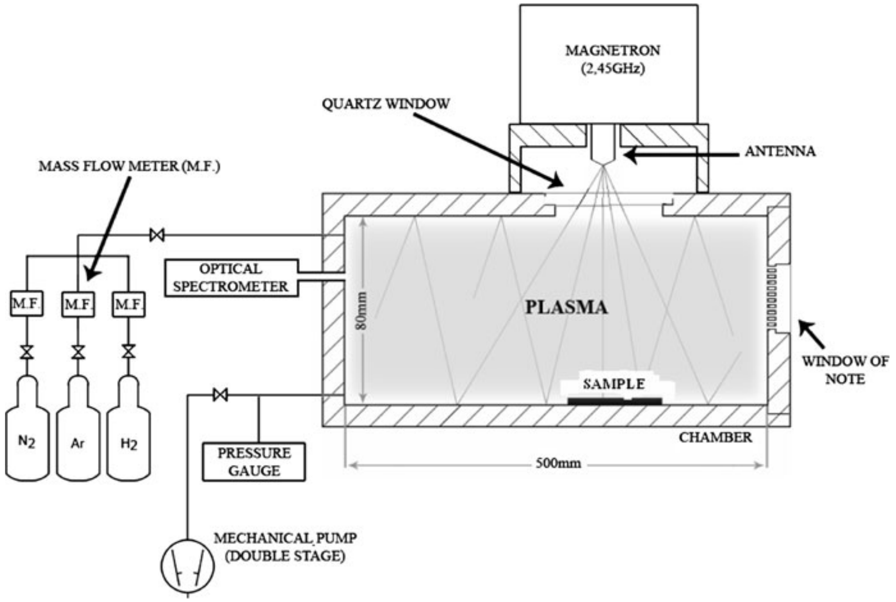

Fig. 1 Experimental apparatus for microwaves plasma generation

rectangular 2.45 GHz microwave excited plasma reactor, schematically shown in Fig. 1. A microwave oven magnetron with nominal power of 1 kW was used. The available microwave energy in the magnetron cathode region is launched in a short waveguide that reflect it into the plasma chamber through a fused silica window. The waveguide is similar to the one used in domestic microwave oven. For simplicity, the plasma system does not have any system to measure the incident and reflected microwave power, neither a coupling system to minimize the reflected power. The plasma chamber with internal dimensions of 23.1 × 7.8 × 49.3 cm was pumped by a mechanical vacuum pump, and the experiments were performed in the 26.7 Pa, gas flow rate of 25.0 sccm. The gases used in the PAN AN/VA film surface treatment were nitrogen, 99.999% purity, and argon, 99.999% purity. The treatment times were set as 5, 10, 30, 60, and 120 s.

X-ray diffraction

A PANalytical, X'Pert PRO MPD 3060 X-ray diffractometer with Ni-filtered CuKα ($\lambda = 0.1541837$ nm) radiation was used to determine the structures of PAN AN/VA films. Samples were tested with a voltage of 40 kV and an electric current of 45 mA. The scanning speed was 0.42°/s with the scanning step of 0.0167°. For the calculation of the lattice spacing the equation of Bragg was used.

$$2 \cdot d \cdot \sin\theta = n \cdot \lambda \tag{2}$$

where $n = 1$, $\lambda = 0.1541837$ nm, d is the lattice spacing for the group of planes hkl (index of Miller) of the crystalline structure, and θ is the half of the diffraction angle.

Contact angle measurement

Contact angle technique was used to characterize the surface properties of untreated and treated samples of the PAN AN/VA film. Contact angles were measured by dropping deionized water and diiodomethane over the PAN AN/VA film as soon as the treatment was completed. The properties of the deionized water and diiodomethane are shown in Table 1 and they were taken from the literature [21]. An appropriate syringe set a drop over the film surface.

An aging test of the PAN AN/VA film was performed on samples treated under nitrogen and argon plasma atmospheres. Temperature and humidity can alter the surface activity of the PAN film. The plasma treated PAN films were aged for 12 days at ambient air, for better representing the environmental exposure of the PAN film during shelf life, instead of exposing the samples in special controlled humidity and temperature environment. The air humidity and temperature data were recorded during the period of aging, as shown in Figs. 2 and 3, respectively [25].

Several mathematical methods have been proposed to evaluate the work of adhesion and the surface energy of solid, using values of contact angle of different

Table 1 Energy properties of deionized water and diiodomethane used in the contact angle measurements

	Polar component (mN/m)	Dispersive component (mN/m)	Surface energy (mN/m)
Deionized water	50.7	22.1	72.8
Diiodomethane	6.7	44.1	50.8

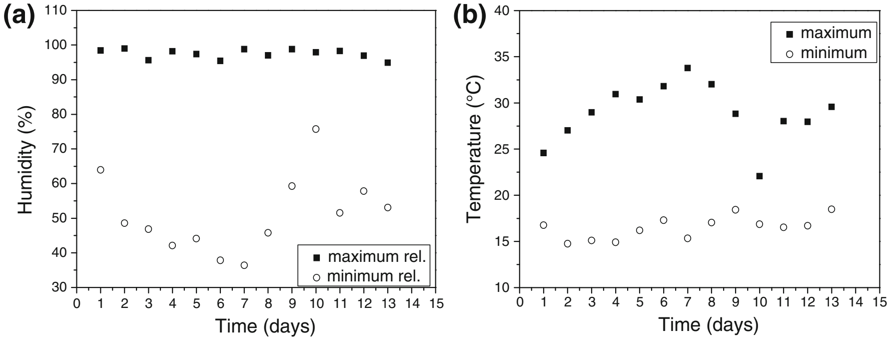

Fig. 2 Air relative humidity (**a**) and temperature (**b**) during the period of environmental aging for the nitrogen plasma treatment for the PAN AN/VA film. Data were collected from 03/12/08 until 15/12/08 [25]

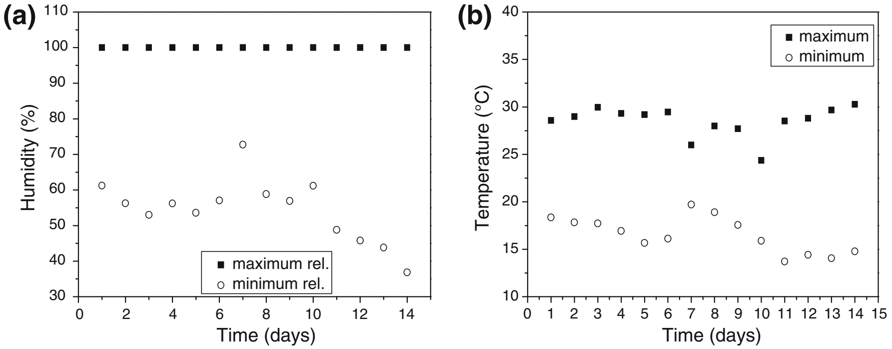

Fig. 3 Air relative humidity (**a**) and temperature (**b**) during the period of environmental aging for the argon plasma treatment for the PAN AN/VA film. Data were collected from 07/04/09 until 21/04/09 [25]

liquids with their respective known surface tensions. One of these methods used Eq. 1 from the work of adhesion proposed by Dupré and suggested a new relationship, named Young–Dupré equation [26]. In the Young–Dupré equation, the liquid surface tension and the contact angle of the liquid over the surface are considered in the calculations.

$$W_{\mathrm{AD}} = \gamma_{\mathrm{LV}} \cdot (\cos\theta + 1) \tag{3}$$

If the contact angles made by two liquids of known γ^{d} and γ^{p} are measured, it is possible to solve Eq. 4 (geometric mean) or 5 (harmonic mean) and calculate $\gamma_{\mathrm{S}}^{\mathrm{d}}$ and $\gamma_{\mathrm{S}}^{\mathrm{p}}$ for the solid. From the contact angle of deionized water and diiodomethane over the PAN AN/VA film, the surface energy was calculated using Eqs. 4 and 5 [21, 24]

$$\gamma_{\mathrm{LV}}(1+\cos\theta) = 2\left[\left(\gamma_{\mathrm{LV}}^{\mathrm{d}}\gamma_{\mathrm{S}}^{\mathrm{d}}\right)^{\frac{1}{2}} + \left(\gamma_{\mathrm{LV}}^{\mathrm{p}}\gamma_{\mathrm{S}}^{\mathrm{p}}\right)^{\frac{1}{2}}\right] \tag{4}$$

$$\gamma_{\mathrm{LV}}(1+\cos\theta) = 4\left[\left(\frac{\gamma_{\mathrm{LV}}^{\mathrm{d}}\gamma_{\mathrm{S}}^{\mathrm{d}}}{\gamma_{\mathrm{LV}}^{\mathrm{d}}+\gamma_{\mathrm{S}}^{\mathrm{d}}}\right) + \left(\frac{\gamma_{\mathrm{LV}}^{\mathrm{p}}\gamma_{\mathrm{S}}^{\mathrm{p}}}{\gamma_{\mathrm{LV}}^{\mathrm{p}}+\gamma_{\mathrm{S}}^{\mathrm{p}}}\right)\right]. \tag{5}$$

Results and discussion

X-ray diffraction analysis

The X-ray diffraction plot of the PAN AN/VA film is shown in Fig. 4. Two strong characteristic peaks can be observed at $2\theta = 17.3°$ and 29.9°, which correspond to the (100) and (110) planes, respectively, of the unit cell of PAN. Coexistence of crystalline and amorphous phases is characteristic of PAN materials. According to Bragg equation, d values of the two characteristic diffraction peaks of PAN films at $2\theta = 17.3°$ and 29.9° are $d_{17.3} = 0.5123$ nm and $d_{29.9} = 0.2987$ nm, respectively. These results were similar to the results obtained from He et al. [27], which were found for PAN fibers that have been synthesized using acrylonitrile/itaconic acid, and obtained by the wet-spinning method using dimethylsulfoxide as a solvent.

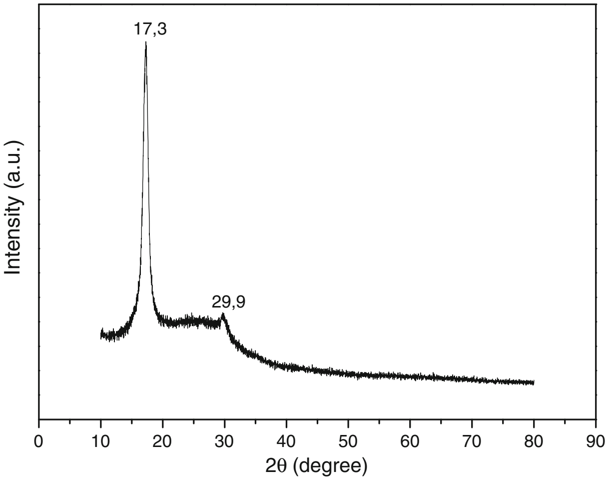

Fig. 4 X-ray diffraction of the PAN AN/VA film obtained by extrusion process

Contact angle and work of adhesion

The results regarding the contact angles of the PAN AN/VA film without and with treatment in nitrogen and argon plasma atmosphere are shown in Figs. 5 and 6. It is observed that diiodomethane gives rise to a lower contact angle in relation to the deionized water over the PAN AN/VA film, regardless the plasma treatment atmosphere. This is due to differences in liquid surface tensions, i.e., diiodomethane has a higher dispersive component (44.1 mN/m) of surface tension compared to deionized water (22.1 mN/m).

In Fig. 5a, it can be seen that only 30 s of plasma treatment under nitrogen is necessary to reduce the contact angle from 65° to 20°, when measured with water, and from 45° to 11°, when measured with diiodomethane. Similarly, Fig. 6a, only 30 s of plasma treatment under argon is necessary to induce a reduction of the contact angle from 65° to 28°, when measured with water, and from 45° to 17°,

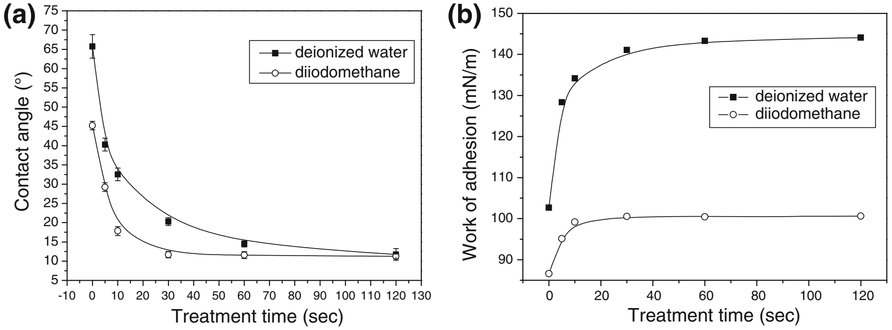

Fig. 5 **a** Contact angle and **b** work of adhesion of PAN AN/VA film treated by nitrogen gas plasma

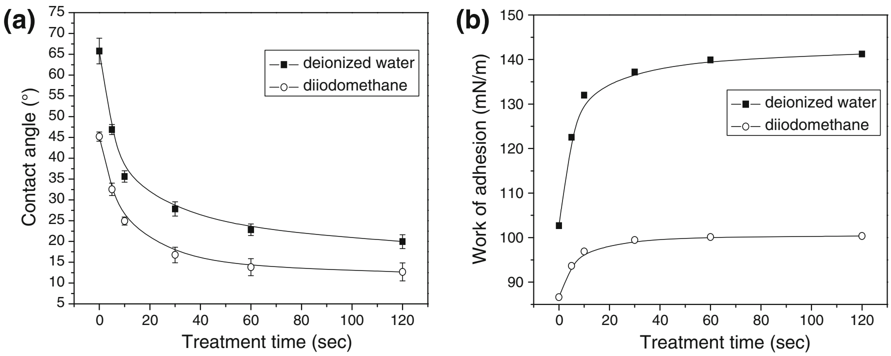

Fig. 6 **a** Contact angle and **b** work of adhesion of PAN AN/VA film treated by argon gas plasma

when measured with diiodomethane. This 45° and 37° reduction in water contact angle shows that surface wettability of PAN AN/VA film is increased significantly following plasma treatment under nitrogen and argon, respectively.

The plasma treatment introduces the formation of polar groups in the film surface. As dipole–dipole intermolecular forces (van der Waals) exists among polar molecules, then one of the reasons for the reduction of the deionized water contact angle is the interactions among the strong dipole of the molecule of water with the dipole of the nitrile group ($C\equiv N$) in the PAN polymer. Also, interactions with OH, COOH, and $CONH_2$ which are introduced in the composition of the surface of PAN film are also possible [14, 19]. This increase in interaction, the so called adhesive forces (intermolecular forces between dissimilar molecules), which emerges from electrostatic attraction between electron clouds and atomic nuclei from the new groups, overcome the cohesive forces (intermolecular forces between similar molecules) from the liquid. As a consequence, the surface of the liquid has an increase attraction to the surface of the film. The reduction in the contact angle of diiodomethane, which is apolar, onto the film, is due to induced dipole forces. The nitrile group induces an instantaneous dipole in the molecule of the diiodomethane leading to the wetting of the film surface.

In fact, contact angle is also influenced by the surface roughness. Plasma surface treatment was done on commercial PAN fibers having ~15 μm, under nitrogen atmosphere [19]. For surfaces having a contact angle lower than 90°, increasing roughness will decrease the contact angle. But, according to Liu and Lu [19] at an average surface roughness below ~100 nm there is no influence on the contact angle. In Liu's work, a surface for a commercial PAN fiber treated for 3 min, under a 300 W power plasma, resulted in a surface energy of 65.1 mN/m equivalent to 30.17 nm average roughness [19]. In our work, a maximum 2-min treatment, under 1 kW nitrogen plasma resulted in a surface energy of 70 mN/m. So, even using a high power plasma, similar results of surface energy were found, which is possible within the range of roughness that do not have influence on contact angle.

From the contact angle measurements, the work of adhesion was calculated using the Young–Dupré equation. The change in chemical surface activity of the PAN AN/VA film increased the surface energy due to the creation of active sites leading to a more polar character. The nitrogen plasma treatment can enhance the formation of nitrile group over the surface of the film. Probably, the carbonyl (C–O) groups can be formed because VA is part of the film formulation. Figure 5b also shows that the work of adhesion of deionized water over the PAN AN/VA film after 30 s of treatment increased by 35%. On the other hand, for diiodomethane the increase was approximately 14%.

The effect of plasma treatment on surface energy

Tables 2 and 3 show the results obtained by the harmonic average and for the geometric average for plasma treatments under nitrogen and argon. It is observed that before the plasma treatment, the dispersive component (γ^d) of the surface energy of the PAN AN/VA film is higher than the polar component (γ^p). The plasma treatment changes the dispersive component only slightly, while in the polar component a steady increase is observed as a function of treatment time. These results show that the main contribution to the increase in surface energy is due to the polar component and consequently a good wettability is obtained when the polar component of the surface energy is high.

The surface energies calculated by the harmonic average and for the geometric average in both gases of N_2 and Ar, the increment values that are obtained in the nitrogen plasma treatment (30 mN/m) are somewhat higher than the one in argon

Table 2 Surface energy of PAN AN/VA film treated by nitrogen plasma

Time of treatment (s)	Harmonic average			Geometry average		
	γ^d (mN/m)	γ^p (mN/m)	γ_S (mN/m)	γ^d (mN/m)	γ^p (mN/m)	γ_S (mN/m)
Untreated	26.96	18.45	45.41	24.94	15.31	40.26
5	31.22	30.77	61.99	24.15	33.28	57.43
10	34.03	33.43	67.46	26.09	36.60	62.69
30	34.76	38.12	72.88	24.84	43.68	68.63
60	34.65	39.90	74.55	24.16	46.47	70.63
120	34.66	40.53	75.19	23.93	47.44	71.37

Table 3 Surface energy of PAN AN/VA film treated by argon plasma

Time of treatment (s)	Harmonic average			Geometry average		
	γ^d (mN/m)	γ^p (mN/m)	γ_S (mN/m)	γ^d (mN/m)	γ^p (mN/m)	γ_S (mN/m)
Untreated	26.96	18.45	45.41	24.94	15.31	40.26
5	30.47	27.49	57.96	24.76	28.30	53.06
10	32.34	32.66	65.00	24.57	35.93	60.51
30	34.08	35.53	69.61	25.26	39.89	65.14
60	34.48	37.35	71.83	24.95	42.59	67.54
120	34.60	38.31	72.91	24.70	44.03	68.73

plasma treatment (27 mN/m). These values are related to the untreated film. The increase of surface energy is mainly due to the presence of hydrophilic groups on the film surface after plasma treatment.

According to Liu and Lu [19], the formation of amide (–$CONH_2$) and carboxyl (–COOH) groups occurs mainly through the elimination of the cyanogens and ester groups. These polar groups are prone to moisture absorption through hydrogen bonding, which can effectively enhance the surface energy and wettability of the PAN AN/VA film.

Environmental aging of the PAN AN/VA film

The tests of environmental aging were performed on PAN AN/VA films treated for 2 min, under nitrogen and argon plasma treatment, as shown in Fig. 7. After 2 min of treatment on the PAN AN/VA film surface, no significant change is found in the value of the contact angle and in the work of adhesion as the time of treatment increase, as can be seen in Figs. 5 and 6.

During aging, a sharp increase in the contact angle is observed in the first 24 h, reaching a value of 20–25° for the nitrogen and argon plasma treated samples. After this period the increase in contact angle was 40% for the nitrogen plasma treated PAN AN/VA film, and for the argon plasma treated PAN AV/VA the increase in contact angle was 50%. During the argon plasma treatment of PAN films, roughness and active sites are created mainly by chain scission, and then the water contact angle exhibits a significant increase. On the other hand, during the nitrogen plasma treatment of PAN AN/VA films, besides the creation of roughness and the active sites by chain scission, also introduces other polar groups in the PAN AN/VA film surface, which can interact with water, resulting in a smaller increment in the contact angle in relation to the argon plasma treated film [15, 18].

The increase in the contact angle leads to a decrease in the work of adhesion as a function of time of exposure to ambient. The work of adhesion measured by water over the PAN AN/VA film treated by nitrogen plasma and argon plasma reduced

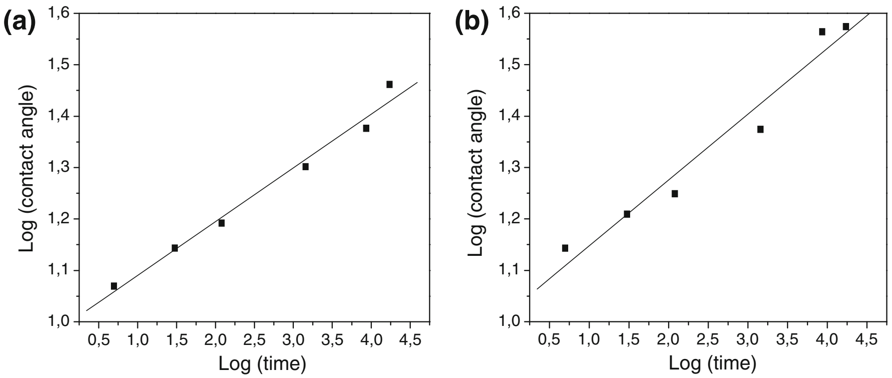

Fig. 7 Variation of the water contact angle according to time of exhibition to the atmosphere after plasma treatment of nitrogen (**a**) and argon (**b**), for a period of 12 days

from 144 mN/m to 136 mN/m, and from 143 mN/m to 130 mN/m, respectively. These results are still far above the work of adhesion from the AN/VA untreated film (103 mN/m).

Conclusions

Polymeric films of PAN/VA obtained by the extrusion process were submitted to microwave plasma treatment under nitrogen and argon atmospheres. These plasma treatments, up to 120 s, induce significant changes onto the surface energy of the PAN/VA extruded films, in relation to the untreated film. The treatment is more effective when it is done up to 40 s. The total surface energy increases from 40 mN/m to 70 mN/m, either for treatment under nitrogen or argon atmospheres.

Contact angles of the untreated and treated PAN/VA extruded films were measured by using goniometry. Polar and dispersive surface energy were calculated for untreated and treated films by using the harmonic and geometric averages.

The environmental aging of argon and nitrogen plasma treated PAN films, after 12 days, have values of contact angle that are still far the untreated PAN AN/VA film (65°), i.e., 37° for the aged nitrogen plasma treated sample, and 28° for the aged argon plasma sample treated sample.

The results indicate that the technology of microwaves plasma, for surface treatment of polymeric surfaces, are a potential alternative to improve the adherence of polymeric films.

Acknowledgments We thank the Quimlab Company for the supply of the PAN film samples, CNPq, CAPES and FAPESP for the financial support.

References

1. Masson JC (1995) Acrylic fiber technology and applications. Marcel Dekker, New York
2. Morgan PE (2005) Carbon fibers and their composites. Taylor & Francis Group, London
3. Chung DDL (1994) Carbon fiber composite. Butterworth-Heinemann, USA
4. Bortner MJ (2003) Melt processing of metastable acrylic copolymer carbon precursors. Doctorate Thesis, Virginia Polytechnic Institute
5. Hutchinson SR (2005) Thermoplastic polyacrylonitrile. Master Thesis, Faculty of North Carolina State University
6. Blickenstaff RA (1976) Acrylonitrile polymer filaments. US Patent 3,984,601, n. 294, 184
7. Yoon HS, Son TW, Lee CJ, Min BG, Cho JW (1995) U.S. Non-spun, short, acrylic polymer, fibers. US Patent 5,434,002, n. 148, 629
8. Yoon HS, Son TW, Kin BC, Lee CJ, Min BG, Cho JW (1996) Unspun acrylic staple fiber. US Patent 5,589,264, n. 446, 287
9. Smierciak RC, Eddie WJ, Ball LE (1997) Process for making an acrylonitrile, methacrylonitrile and olefinically unsaturated monomers. US Patent 5,602,222, n. 543, 230
10. Smierciak RC, Eddie WJ, Ball LE (1997) Process for making a high nitrile multipolymer prepared from acrylonitrile and olefinically unsaturated monomers. US Patent 5,618,901, n. 387, 303
11. Alves NP, Brito CA, Garcia E (2009) Um novo material de grande potencial tecnológico obtido com glicerina de biodiesel. Revista Plástico Moderno, n. 412
12. Alves NP (2007) Acrylic and modacrylic polymer fusion process, acrylic and modacrylic polymer, acrylic and modacrylic polymer composition and acrylic and modacrylic polymer usage. WO Patent 147 224

13. Brandrup J et al (1975) Polymer handbook. Wiley-Interscience, New York
14. Baldan A (2004) Adhesively-bonded joints and repairs in metallic alloys, polymers and composite materials: adhesives, adhesion theories and surface pretreatment. Review. J Mater Sci 39:1–49
15. Chan CM, Ko TM (1996) Polymer surface modification by plasmas and photons. Surf Sci Rep 24:1–54
16. Chen Z, Lu X, Chan CM, Mi Y (2006) Manipulating the surface properties of polyacrylamide with nitrogen plasma. Eur Polym J 42:2914–2920
17. Tran TD, Mori S, Suzuki M (2007) Plasma modification of polyacrylonitrile ultrafiltration membrane. Thin Solid Films 515:4148–4152
18. Bogaerts A, Neyts E, Gijbels R, Mullen JVD (2002) Gas discharge plasmas and their applications. Review. Spectrochim Acta B 57:609–658
19. Liu YC, Lu DN (2006) Surface energy and wettability of plasma-treated polyacrylonitrile fibers. Plasma Chem Plasma Process 26:119–126
20. Kumar G, Prabhur KN (2007) Review of non-reactive and reactive wetting of liquids on surfaces. Adv Colloid Interface Sci 133:61–89
21. Shimizu RN, Demarquette NR (2000) Evaluation of surface energy of solid polymers using different models. J Appl Polym Sci 76:1831–1845
22. Fowkes FM (1964) Dispersion force contributions to surface and interfacial tensions, contact angles, and heats of immersion. In: Fowkes FM, Gould RF (eds) Contact angle, wettability and adhesion. Advances in chemistry series 43, American Chemical Society, pp 99–111
23. Wu S (1971) Calculation of interfacial tension in polymer systems. J Polym Sci C 34:19–30
24. Hansen FK (2004) The measurement of surface energy of polymers by means of contact angles of liquids on solid surfaces. A short overview of frequently used methods. University of Oslo, Oslo
25. www.funcate.org.br, Fundação de Ciências, Aplicações e Tecnologia Espaciais, 2009
26. Chaudhury MK (1996) Interfacial interaction between low-energy surfaces. Review. Mater Sci Eng 16:97–159
27. He D, Wang C, Bai Y, Lun N, Zhu B, Wang Y (2007) Microstructural evolution during thermal stabilization of PAN fibers. J Mater Sci 42:7402–7407