Characterization of wettability properties of polyester films and nuclear membranes

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(Received 28 January 1992; revised 2 September 1992)

The wettability of microfiltration membranes has been examined. The analytical method used is an application of the Wilhelmy plate procedure. The use of a new sample holder especially designed for this purpose enables the surface analysis of polymer films even if they present two physically different faces. The evolution of wettability properties during the membrane production process has been determined for nuclear microfiltration membranes obtained from poly(ethylene terephthalate) (PET) and polycarbonate (PC). A grafting procedure in solution, which can be applied to PET- and PC-based materials, enhances the wetting properties of membranes and make them similar to those reached by poly(vinylpyrrolidinone) adsorption.

(Keywords: nuclear membranes; wettability; grafting; polycarbonate; poly(ethylene terephthalate))

INTRODUCTION

It is important for the production of microfiltration membranes to have a knowledge of the wetting properties of the polymeric materials used in their construction. Two different analytical procedures are widely used for studies of wettability properties of polymers. In the first one[1,2], a drop of liquid is placed on the solid to be analysed and the contact angle between the two surfaces is measured. In the second one[3,4], called the Wilhelmy plate technique, a glass coverslip coated with a film of polymer is immersed and the force that is created on its surface by the liquid meniscus is measured. This method presents the advantage of being a dynamic one and seems to be particularly well suited to the study of the wettability of microfiltration membranes: the facility to make water pass through such membranes depends on the hydrophilicity or hydrophobicity of the materials used. Nevertheless, the preparation of polymer-coated coverslips does not allow direct analysis of polymer films, as the coating procedure implies dissolution of the polymer in a solvent, which is evaporated before the measurements. In order to investigate the wettability properties of microfiltration membranes from poly(ethylene terephthalate) (PET) and polycarbonate (PC), we have developed a new sample holder, which allows the use of polymer films without prior preparation and thus the characterization of the raw material itself. The effect of each step of the production process on the wettability properties is then readily observed. The relation between the molecular structure of the materials and their wetting behaviour could therefore be investigated.

Then, in order to improve the wetting properties of membranes, a grafting experiment was carried out. Though grafting on polyester is usually initiated by γ-ray irradiation[5,6] or by glow discharge[7], the method used in this work is a chemically initiated grafting of acrylic acid. With this new way of hydrophilization, the wetting characteristics of membranes could be made the same as those of membranes that have been immersed in a poly(vinylpyrrolidinone) (PVP) bath. However, the wettability reached by grafting is irreversible, which is not the case by an adsorption procedure.

EXPERIMENTAL

Membranes

Membranes are manufactured after irradiation of polycarbonate (amorphous, thickness 30 μm) or poly(ethylene terephthalate) (crystalline, thickness 23 μm) films by heavy ions (Kr^{6+}) in Ganil, the cyclotron at Caen. These energetic particles damage the structure of the polymer along their trajectories: these highly destroyed zones are called 'latent tracks'. After exposure to u.v. light, the films are etched in an alkaline bath and the tracks dissolve away, leaving cylindrical holes in the film, the size of which depends on the chemical treatment parameters (reaction time, temperature, [NaOH]).

Device and method used for wettability measurements

The procedure used is a modified Wilhelmy plate method. An electrobalance, onto which the sample to be analysed is hung, is connected to an amplifier and a plotter (*Figure 1*). A motor drives the stage to raise or lower the water container at a controlled speed (2 mm min^{-1}) and the measurements are conducted at 20°C.

As soon as a solid comes into contact with an aqueous medium, it supports a force created on the surface by the

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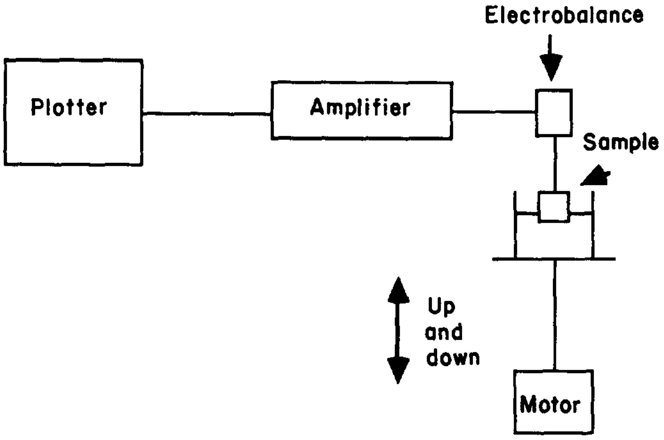

Figure 1 Schematic representation of the apparatus set-up for the wettability measurements

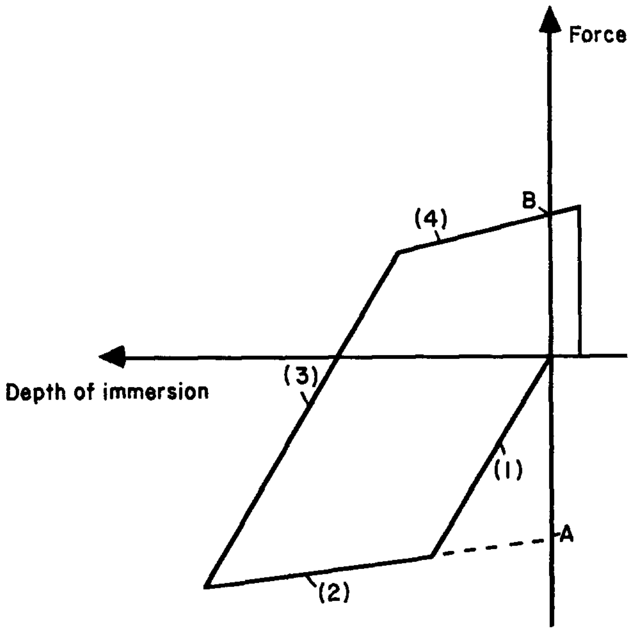

Figure 2 Wetting curve: (1) the buoyancy and the advancing angle vary simultaneously during the immersion of the sample; (2) the equilibrium advancing angle is reached; (3) the buoyancy and the receding angle vary simultaneously during the emersion of the sample; (4) the equilibrium receding angle is reached (the depth of immersion is the distance between the bottom of the sample and the liquid surface)

liquid meniscus. This force (F) is related to the contact angle (θ), the wetted perimeter (L) of the material and the surface tension (γ) of the liquid according to:

$$F=\gamma L\cos(\theta) \qquad (1)$$

By moving the sample up and down in the liquid, wetting curves are obtained from which θ_a and θ_r, respectively the values of advancing and receding angles, can be deduced (*Figure 2*). After extrapolation of the plots to zero immersion depth (points A and B), the contact angles are calculated (the more hydrophilic the material, the lower are these angles), from:

$$F_a/\gamma L=\cos(\theta_a) \qquad (2)$$

$$F_r/\gamma L=\cos(\theta_r) \qquad (3)$$

For each studied membrane or polymer film five different samples have been prepared and their wetting curves have been measured.

Sample holder

This sample holder is a Teflon® or glass ring (external diameter 2.6 mm, height 10 mm, thickness 1 mm) on which a piece of the polymer film to be studied is stuck (*Figure 3*). The ring shape gives rigidity to the film, which allows its immersion into a liquid. If the sample to be analysed presents two faces with different physical properties, the use of a piece of double-faced adhesive (*Figure 4*) enables the analysis of the two surfaces separately (a former study has shown that the double-faced adhesive does not change the surface tension of water, which means that no surfactant compound is lost during the measurement time).

Grafting

The procedure developed in our laboratory[8] has been applied to samples of membranes (PC, PET), all having the same size (2400 mm^2), during different reaction times.

At the end of the reaction, the acrylic acid homopolymer was eliminated by repeated washings: first in alkaline, then in acidic media, and at least several times in distilled water for a total time of 192 h. Finally, they were dried and their wetting properties were measured as indicated above.

Proof of grafting

In order to prove the grafting of poly(acrylic acid) onto polycarbonate, an experiment has been carried out after

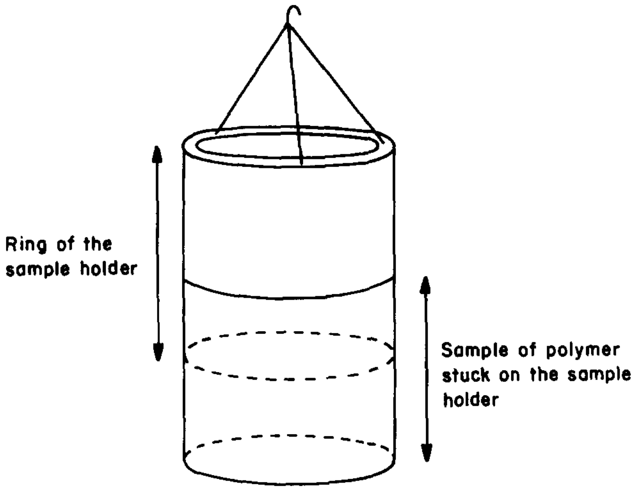

Figure 3 Sample holder

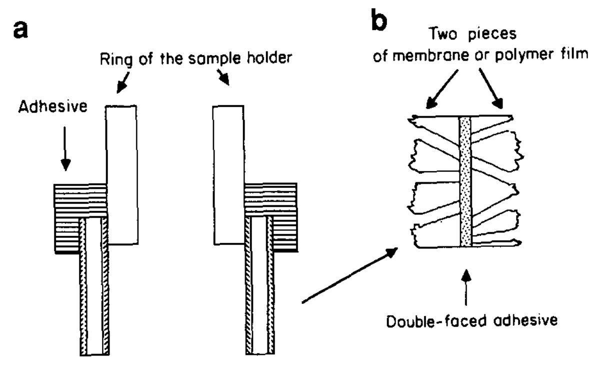

Figure 4 (a) Design of the sample holder and (b) preparation of the sample

a longer reaction time (18 h). The final product has been immersed in a methanol bath in order to eliminate the remaining poly(acrylic acid), and then in methylene chloride in order to dissolve the polycarbonate. The insoluble residue was analysed through infra-red spectroscopy.

Determination of poly(acrylic acid) graft ratio[7]

Rhodamine 6G was dissolved in a pH 11 buffered solution and extracted with toluene. The grafted membrane was dissolved in dimethylformamide (DMF) and a known amount of the toluene solution of the rhodamine 6G was added to the DMF solution: an increase of the absorption at 534 nm was observed. Standard DMF solutions of acetic acid were used to obtain a calibration curve to which the polymer solution was compared.

Materials

Acrylic acid (Aldrich, Janssen) was distilled immediately before use. Distilled water, the surface tension of which was controlled by tensiometric method with a platinum stirrup (72.6 mN m^{-1} at 20°C), was used for the wettability measurements. Films and membranes (PET, PC) were supplied by Biopore. Hydrophilic membranes (with PVP) were purchased from Nuclepore.

RESULTS AND DISCUSSION

Wettability of polycarbonate membranes

The polycarbonate film used for manufacturing membranes presents two different faces ('bright' face and 'matt' face). This is also the case for the derived products. The different behaviours of the two faces towards the wetting process (*Table 1*) could be correlated to a difference of rugosity between the surfaces (*Figure 5*).

The contribution of each step of the manufacturing process to membrane wettability was studied. Interest was focused on the effect of film hydrolysis during the NaOH treatment. The results show that the etching process used to reveal the latent tracks (NaOH hydrolysis) leads to a decrease of the θ_r value: during the hydrolysis of polycarbonate, phenolic groups are probably created at the surface. Such an increase of its surface polarity influences the hydrophilic behaviour. On the other hand, the NaOH treatment changes only the θ_a value of the 'matt' face when there are no pores: this evolution could be related to an erosion of the rugosity during etching (it has been confirmed by scanning electron micrographs of membrane and film surfaces). Nevertheless, the presence of porosity for membranes implies an increase of θ_a with respect to a film of polycarbonate that had not been irradiated with heavy ions but etched by NaOH. This observation could be explained by the presence of air bubbles in the membrane pores, which resist immersion of the sample. At least, it should be noticed that the pore diameter and the pore density have no influence on the membranes' wetting properties.

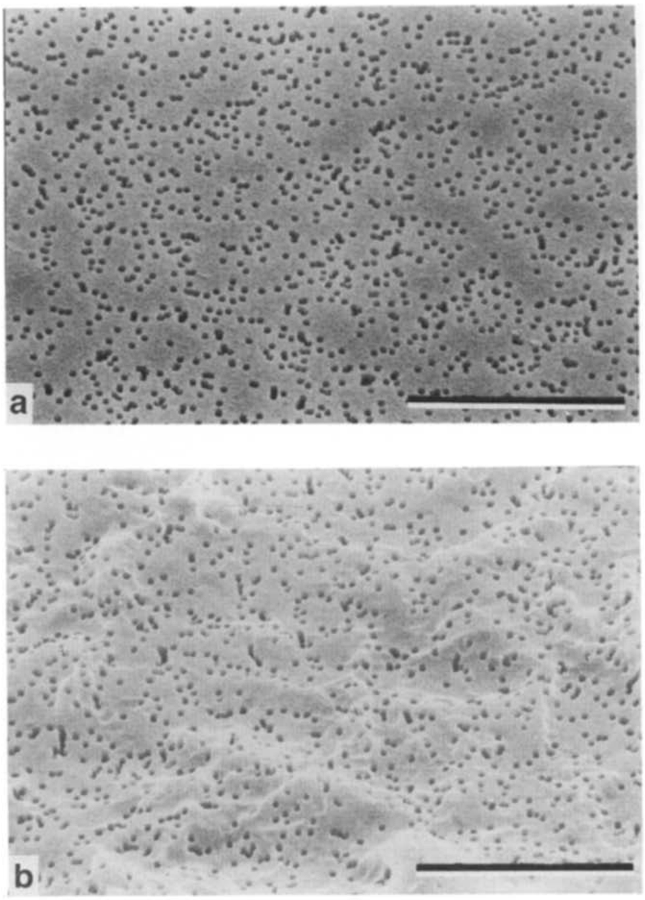

Figure 5 Scanning electron micrographs of polycarbonate membranes: (a) 'bright' face, (b) 'matt' face (scale bar = 10 μm)

Table 2 Comparison of the wettability properties of smooth surfaces of two PC membranes (pore diameter 0.4 μm, porosity 10%): (1) PC membrane, (2) hydrophilic (commercially available with PVP) PC membranes; θ_a, θ_r, advancing and receding angles (deg); $\bar{\sigma}$, standard deviation for five measurements

	1	2
θ_a	102	80
$\bar{\sigma}$	1	1
θ_r	52	8
$\bar{\sigma}$	1	2

Table 1 Evolution of the wettability properties of (a) the 'bright' face and (b) the 'matt' face of PC film during the production process of PC membranes: (1) raw material, (2) film etched by NaOH without any heavy-ion irradiation, (3) PC membrane (pore diameter 0.2 μm, porosity 10%); θ_a, θ_r, advancing and receding angles (deg); $\bar{\sigma}$, standard deviation for five measurements

(a)	1	2	3
θ_a	92	90	103
$\bar{\sigma}$	1	1	2
θ_r	73	56	53
$\bar{\sigma}$	1	1	1

(b)	1	2	3
θ_a	110	96	108
$\bar{\sigma}$	1	1	1
θ_r	45	37	28
$\bar{\sigma}$	1	1	1

It is interesting to compare these results with a wettability study of the same kind of membranes that had been hydrophilized by PVP adsorption (*Table 2*). These have better wettability properties for both advancing and receding angles. These conclusions are very well illustrated by the shape of the wetting curves (*Figure 6*): in the case of PVP-impregnated membranes, the hydrophobic part of the curve has disappeared.

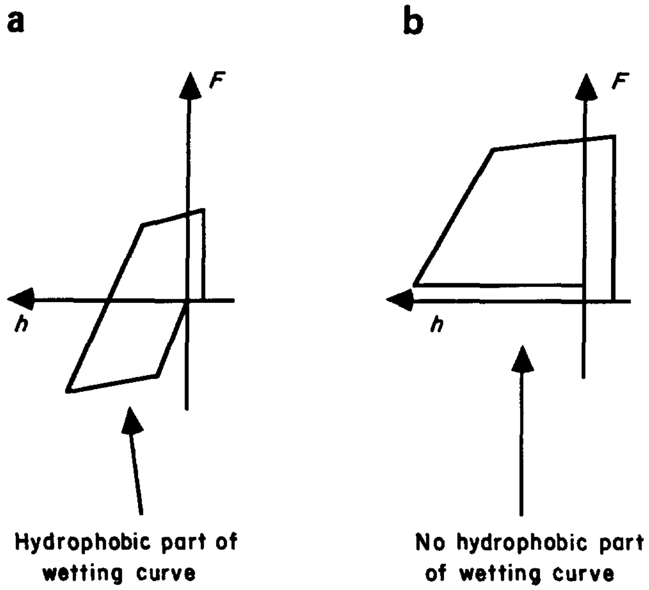

Figure 6 Comparison of wetting curves: (a) polycarbonate membrane, (b) hydrophilized polycarbonate membrane with PVP

Table 3 Evolution of the wettability properties of a PET film during the production process of membranes: (1) raw material, (2) film etched by NaOH without any heavy-ion irradiation, (3) PET membrane; θ_a, θ_r, advancing and receding angles (deg); $\bar{\sigma}$, standard deviation for five measurements

	1	2	3
θ_a	83	83	83
$\bar{\sigma}$	1	1	1
θ_r	53	24	20
$\bar{\sigma}$	1	2	2

Wettability of poly(ethylene terephthalate) membranes

A similar study has been conducted on PET membranes. However, contrary to polycarbonate, PET film does not exhibit two faces with different physical properties. The evolution of the wetting behaviour of the material with the chemical treatment is the same as observed for polycarbonate (*Table 3*): the θ_r value decreases and θ_a remains constant when the film is etched by NaOH. Furthermore, the PET membranes are more hydrophilic than the PC ones. This could be explained by the mechanism of PET hydrolysis during the production process: when PET films are etched by NaOH, acidic and alcoholic groups are created at the surface, which increase the surface polarity more than the phenolic groups do in the case of PC.

Acrylic acid grafting contribution to wetting properties

The grafting procedure developed in our laboratory[8] has been applied to polycarbonate membranes. The infra-red analysis of the grafted polymer (*Figure 7*) isolated after extraction of the polycarbonate and poly(acrylic acid) homopolymers shows the characteristic signals both of polycarbonate (1775 and 1500 cm^{-1}) and of poly(acrylic acid) (1700, 1410 and 1450 cm^{-1}).

A study of the evolution of wettability properties *versus* reaction time demonstrates that after 5 min of reaction, the membrane surfaces become as hydrophilic as those impregnated with PVP (with a grafting rate lower than 1% in weight). A titration was carried out to determine the concentration of the acidic groups on the membrane surface: the analysis gives a value of 3×10^{-8} mol cm^{-2} after 30 min of reaction.

In *Figure 8* are shown the results obtained under three identical experimental conditions. The lack of reproduci-

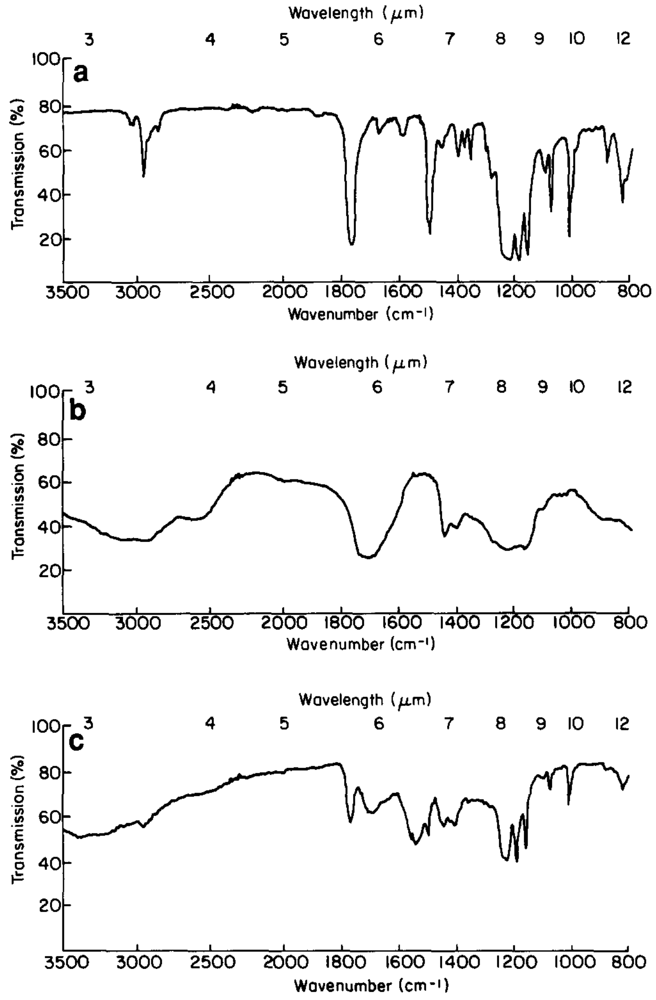

Figure 7 I.r. spectra: (a) poly(acrylic acid), (b) polycarbonate, (c) acrylic acid-grafted polycarbonate (residue after extraction using methanol and then methylene chloride)

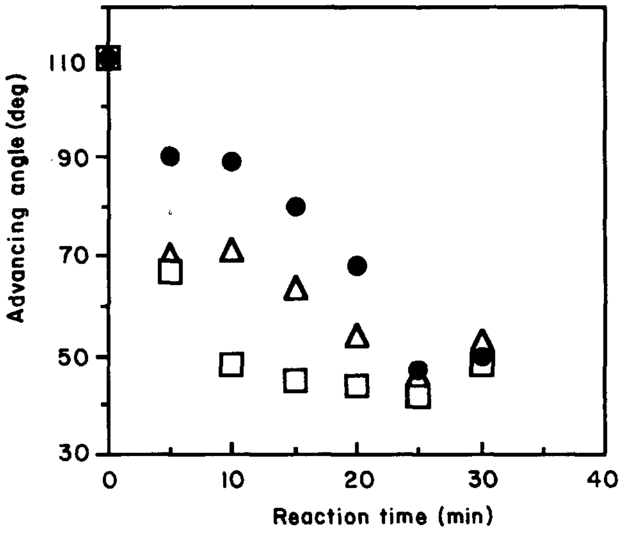

Figure 8 Advancing angle as a function of grafting reaction time for three identical experiments

bility of these data may be caused by unknown concentrations of impurities in the reaction mixture (particularly O_2). However, it should be noted that the three experiments exhibit the same minimum value after 25 min of reaction.

The grafting procedure has also been applied to poly(ethylene terephthalate) membranes. In this case, the reaction seems to proceed more slowly: 1 h is needed to reach wetting properties characterized by $\theta_a = 60°$.

CONCLUSION

Direct analysis of the behaviour towards wettability of polymer films and membranes was made possible by the use of a new sample holder. The difference of surface properties between polycarbonate and poly(ethylene terephthalate) was discussed in terms of surface polarity caused by polar chemical groups. A new acrylic acid grafting procedure, which can be used for both PET and PC, leads to irreversible modifications of surface properties for both materials: they became as hydrophilic as can be obtained (reversibly) by PVP adsorption.

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