ELSEVIER

European Polymer Journal 38 (2002) 235–242

EUROPEAN POLYMER JOURNAL

www.elsevier.com/locate/europolj

New breathable and waterproof coatings for textiles: effect of an aliphatic polyurethane on the formation of PEEK-WC porous membranes

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Received 13 February 2001; received in revised form 29 June 2001; accepted 4 July 2001

Abstract

PEEK-WC is an amorphous polyetheretherketone with high chemical stability, excellent thermal resistance and significant solubility in various solvents. It has been used to prepare flat membranes by the phase inversion technique. The water vapour permeability through a porous PEEK-WC film was 1350 g/m^2 day at 26 °C and its liquid entry pressure (LEP) of water equivalent to a column of 2.0 m. These values were remarkably improved by addition of an aliphatic ether polyurethane (PU) into the PEEK-WC/DMF dopes: the water vapour flux was increased up to 2000 g/m^2 day and the LEP was equivalent to 12.5 m. This improvement is correlated to the different structure of the membranes: a spongy, porous and almost symmetric structure for the PEEK-WC/PU membranes, and an asymmetric structure with fingers for PEEK-WC membrane. The presence of PU influences also the mechanical properties of the blend membranes. The role of the PU on the resulting membrane morphology is rationalised on the basis of the mechanism of phase separation.

Keywords: PEEK-WC; Polyurethane; Phase separation; Membrane morphology; Breathability; Impermeability

1. Introduction

Poly(oxa-1,4-phenylene-oxo-1,4-phenylene-oxa-1,4-phenylene-3,3-(isobenzofurane-1,3-dihydro-1-oxo)-diyl-1,4-phenylene) or PEEK-WC is a chemically stable polymer with excellent thermal and mechanical resistance and, differently from PEEK, with substantial solubility in various solvents (e.g. amides, chlorinated hydrocarbons) due to its lack of crystallinity [1–3]. These properties, and the latter in particular, suggest its use for membrane preparation by phase inversion method. In this method a thermodynamically stable polymeric solution is made unstable by diffusion in or out of it, or by temperature changes [4–6]. The phase separation, which takes place, leads to the formation of a polymer rich phase (the nascent membrane) and of a polymer poor phase (the voids).

In this study PEEK-WC has been considered for the coating of commercial fabrics as a suitable substitute of the porous membranes made of poly(tetrafluoroethylene). It will be shown that several characteristics of PEEK-WC porous membranes (water vapour transmission rate, impermeability, mechanical resistance) are enhanced by the presence of an aliphatic ether polyurethane (PU). The change is directly related to the almost homogeneous porous structure brought about by the PU. PU, in turn, speeds up the demixing of the dope in the coagulation bath. The structure of these films is

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0014-3057/01/$ - see front matter
PII: S0014-3057(01)00186-0

Nomenclature

J_i	volumetric flux through the membrane, $L^3\,t^{-1}$	L	length
L_i	pressure normalised volumetric flow rate, $L^4\,t\,M^{-1}$	t	time
l	pore length, L	–	adimensional
LEP	liquid entry pressure, $M\,L^{-1}\,t^{-2}$	*Greek symbols*	
N_i	number of pores with radius r_i, –	δ	water/gas surface tension, $M\,t^{-2}$
P	bubble point pressure, $M\,L^{-1}\,t^{-2}$	η	viscosity of air, $M\,L^{-1}\,t^{-1}$
r	porous radius, L	θ	contact angle, °
M	mass	τ	tortuousity coefficient, –

different from those of the commercial PU or polyester materials commonly used for textiles.

2. Materials

PEEK-WC is an amorphous glassy polymer (T_g = 228 °C) [1]. The PEEK-WC powder ($[\eta]_{sp/c}$ = 0.62 dl/g 0.5 wt.% in $CHCl_3$ at 25 °C) was used with no further purification. The PU elastomer containing aliphatic ether segments was supplied in DMF (35 wt.%). DMF (Ashland Italia S.p.A., Reagent grade, 98%, 0.03 wt.% in water) and tap water were used as solvent and non-solvent, respectively. All materials were used as received.

3. Membrane preparation

The membranes were prepared using the direct immersion–precipitation method. The compositions of polymeric dopes are listed in Table 1.

The polymeric solutions were prepared by adding PU solutions (35 wt.% in DMF) to PEEK-WC/DMF solutions. These solutions were stirred at room temperature until clear, viscous but homogeneous solutions were obtained. The dopes were cast uniformly on a glass plate, previously washed with water and dimethyl ketone and dried up, by means of a hand-casting knife (BRAIVE Instruments) with a knife gap set at 100–250 μm, and after 2 s were coagulated in a water bath at 15 °C. The membranes were washed with water overnight and dried at room temperature for at least one day. All samples were prepared many times to verify the reproducibility of their properties.

4. Analytical methods

The surfaces and cross-sections of the dried membranes were examined using SEM (Cambridge, Stereoscan 360). The functional groups of dry thin films of the blends were investigated by FT-IR analysis in the transmission mode from 4000 to 400 cm^{-1}, with a resolution of 4 cm^{-1} and ten of scans (Perkin–Elmer 1330). The thermogravimetric analysis (TGA) were performed in air flow (10 $cm^3\,min^{-1}$) with a heating rate of 10 °C min^{-1} in the temperature range 20–800 °C (Simultaneous Thermal Analyzer Mod STA 409 C, Netzsch-Gerätebau-GmbH). The bubble point values were interpreted by using the Cantor equation. The liquid entry pressure (LEP) of water was measured on a cell for flat membranes according to the 5122 UNI procedure, and also on an ultrafiltration cell (Berghof GmbH) for water columns in excess of 2.5 m. The water vapour transmission rate was measured by the cup method, according to the 4818 UNI part 26 procedure. The static

Table 1
PEEK-WC/PU/DMF dopes

Sample	Casting thickness (μm)	PEEK-WC (wt.%)	PU (wt.%)	DMF (wt.%)	PEEK-WC/PU (mass ratio)	Total concentration polymer (wt.%)
1	100	11.57	3.84	84.59	3.01	15.41
2	200	13.57	3.30	83.13	4.11	16.87
3	150	14.20	7.20	78.60	1.97	21.40
4a	150	14.86	3.80	81.34	3.91	18.66
4b	250	14.86	3.80	81.34	3.91	18.66
5	150	15.87	4.04	80.09	3.93	19.91
6	150	18.0	–	82.0	∞	18.0

contact angle of distilled and filtrated water was measured using a CAM 100 device produced by KSV Instruments, Ltd. The mechanical characteristics were measured using an INSTRON 1122 according to the UNI 7315 procedure. The sampling rate was 9.103 pts/s, the crosshead speed was 50 mm/min, the full scale load range was 10 kg. The mechanical tests were carried at 65% relative humidity and at 20 °C temperature.

5. Results and discussion

5.1. Morphology

The SEM images of the PEEK-WC/PU membranes **1**, **3**, **4a** and **5**, (see Table 1) prepared by phase inversion, show a spongy and a slightly asymmetric structure. The cross-section of samples **1**, **3**, **4a** and **5** (Figs. 1–4) show the presence of a skin on the upper surface, exposed to the air during the casting, and an open porous lacy structure. These structures suggest that the precipitation process of the casting PEEK-WC/PU/DMF dopes is dominated by a rapid liquid–liquid demixing. The mass exchange of solvent and non-solvent across the interface probably brings the polymeric solutions into the spinodal region where the liquid–liquid demixing process is immediate [6]. However, the phase separation is not rapid enough to prevent completely the asymmetry of the films, and the pore size reduces on the surface. From Figs. 5–7 it is possible to observe the presence of very small pores uniformly distributed on the membrane surfaces, whose size is some tens of nm. The membranes **6** from the PEEK-WC/DMF dopes coagulated in water bath have different morphology (Fig. 8). They, in fact, show a porous asymmetric structure characterised by different regions. On the surface it is possible to observe a skin under which some fingers, consisting of a cellular

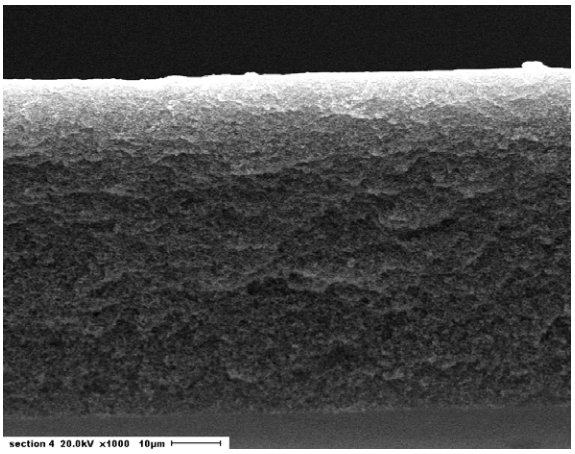

Fig. 2. Cross-section of the membrane **3**.

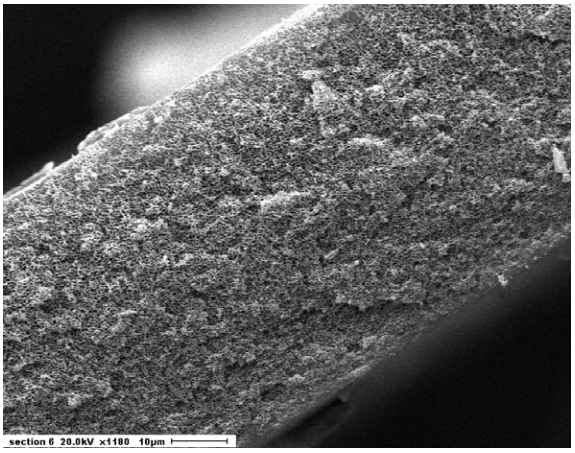

Fig. 3. Cross-section of the membrane **4a**.

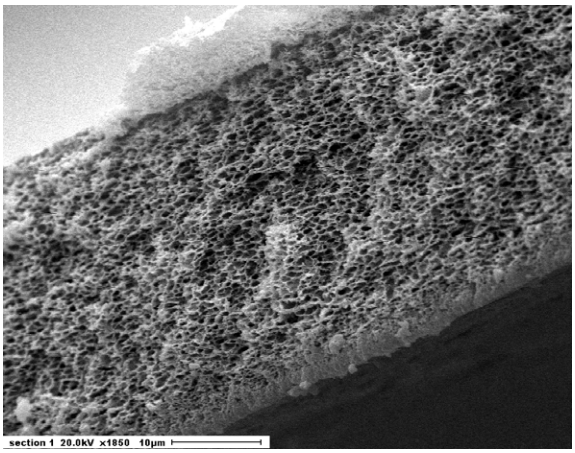

Fig. 1. Cross-section of the membrane **1**.

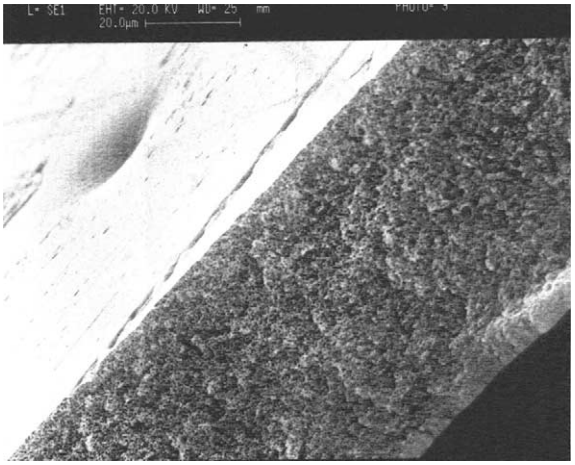

Fig. 4. Cross section of the membrane **5**.

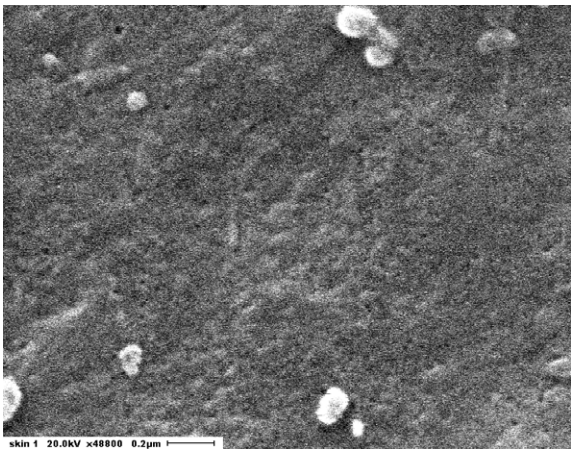

Fig. 5. Top view of the membrane **1**.

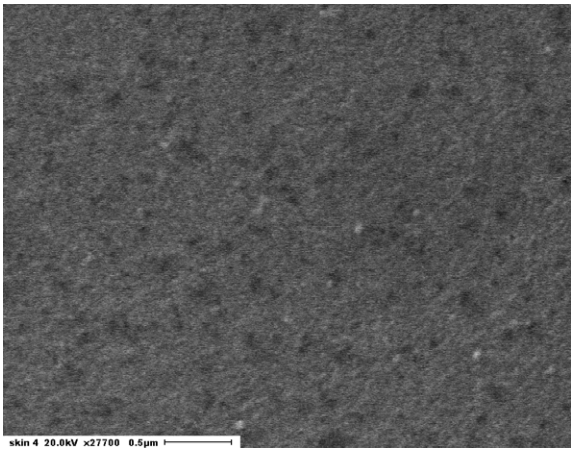

Fig. 6. Top view of the membrane **3**.

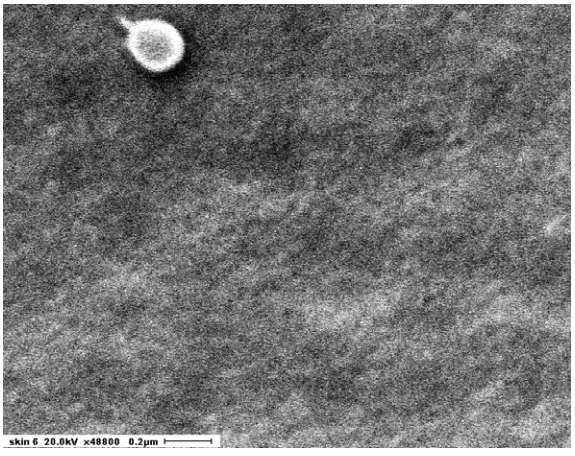

Fig. 7. Top view of the membrane **5**.

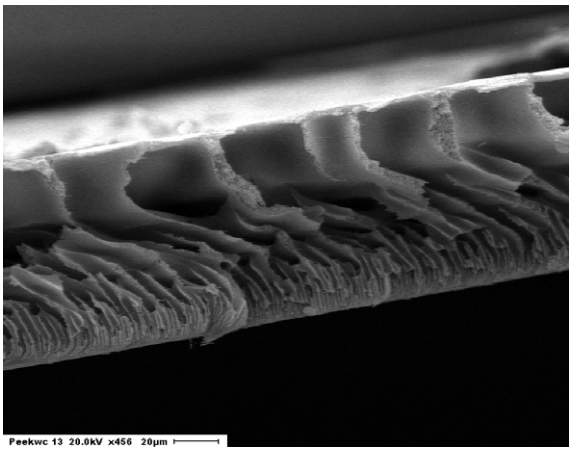

Fig. 8. Cross-section of the membrane **6**.

structure, open. The homogeneous polymer solution is far away from the region of instability, and for this reason the phase separation is not fast. The slowness of the process allows the fusion of the polymer poor phase to form the fingers. The presence of PU in the dope avoids the formation of the fingers and at the same time increases the openness of the skin, probably by bringing the polymeric solution close to the immiscibility gap.

5.2. FT-IR analysis

FT-IR spectroscopy was used to investigate the presence of chemical groups [7] of the PEEK-WC and PU in the PEEK-WC/PU membranes. In the blend spectrum the peaks at 3066–3032 cm^{-1} and at 757, 691 and 606 cm^{-1} are assigned to the stretching and the out-of-plane ring bending of the aromatic C–H bonds of PEEK-WC, respectively. The intense peaks at 2941, 2859 and 2797 cm^{-1}, assigned to the aliphatic C–H bonds, are due to the PU contribution. The peak at 3327 cm^{-1} is typical of the stretching of polyurethanic N–H bonds, and the broad absorption band at 1773 cm^{-1} can be attributed to ketonic and esteric C═O stretching of the PEEK-WC and to N(C═O)O of the PU.

5.3. Water vapour transmission

Water vapour transmission test is a useful method to evaluate the transport properties of the polymer membranes [8]. The spongy structure and the high porosity of the PEEK-WC/PU membranes **2**–**5** allow large water vapour flux (Fig. 9). At 27 °C the values of water vapour permeation rate measured through the PEEK-WC/PU films were about 2000 g/m^2 day, higher than that measured through the PEEK-WC membrane **6**. Fig. 9 shows a significant increase of the flux through the films in which the PU is contained. The increase of the PU

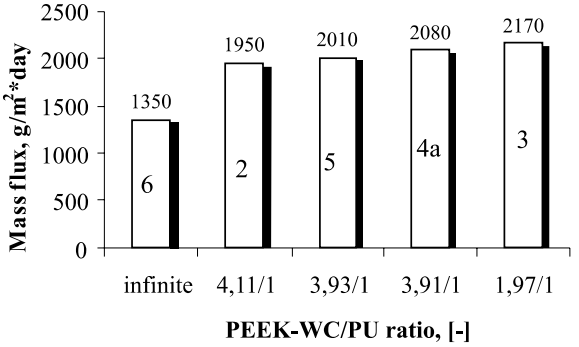

Fig. 9. Water vapour flux data at 27 °C for the samples **2**–**6**.

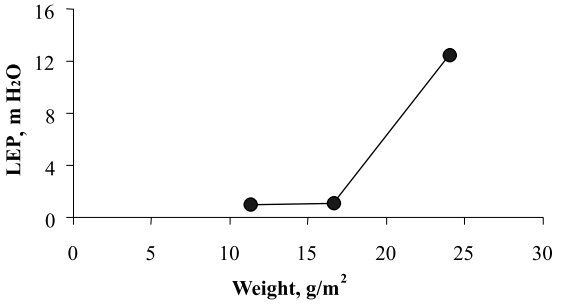

Fig. 11. Effect of polymer weight on liquid entry pressure for PEEK-WC/PU film **5**.

amount in the films increases the water vapour flux. These data are in agreement with the different morphology of the membranes. The presence of the PU, in fact, promotes the tendency to form a more opened skin.

5.4. Liquid entry pressure (LEP) of water

The structure and the hydrophobic nature of these films allow an easy transport of water vapour but prevent liquid water from entering into the membrane. It was observed that the PEEK-WC/PU membranes **4a** and **5** had a high LEP. Fig. 10 shows a LEP of water equivalent to a column of 2.0 m for the PEEK-WC membrane **6**. The presence, in a range of concentrations, of the PU excludes the formation of fingers, but does not assure a high LEP. A total polymer concentration too low and a PU concentration too high in the mixtures (Table 1) make the porous structure too open with low LEP. The ideal PEEK-WC/PU mass ratio is 3.9/1 when the total polymer concentration is greater than 18 wt.% A liquid water column equal to 12.5 m was measured for the PEEK-WC/PU membranes **4a** and **5**, characterised by 24 g/m^2 of polymer deposited (Fig. 11). PEEK-WC membrane **6** shows a denser skin than that of the blends, but probably the presence of fingers makes the film not much resistant to the water pressure.

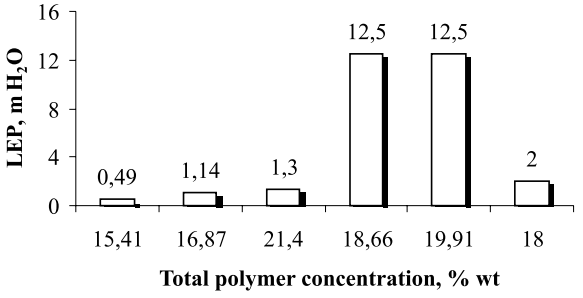

Fig. 10. Liquid water entry pressure data at 27 °C for the samples **1**–**6**.

5.5. Mechanical properties

The films **3**, **4a** and **4b** (PEEK-WC/PU) and **6** (PEEK-WC) were characterised in order to estimate the influence of the PU on the mechanical resistance of the PEEK-WC films. Table 2 shows that the resistance of the PEEK-WC/PU films is higher than the one of the PEEK-WC film. In this table are reported the data relative respectively to the casting direction (length direction) and to that orthogonal to it (width direction) on the plane. The results are in agreement with the different morphology of the films. The fingers, in fact, are points with low mechanical resistance where crazes are prove to develop and propagate. The casting direction influences the max load and elongation, too. At the same casting thickness, the PU amount into the blends influences more the max load than the elongation with respect to the PEEK-WC film. However, the decrease of PEEK-WC/PU ratio determines an improvement on the max load resistance keeping about constant the elongation value.

5.6. Bubble point test

The bubble point test was used to evaluate the pore size of the membranes. The samples were immersed inside liquid water to fill all the pores. The upper surface of the membrane was in contact with the liquid water and the bottom surface with the gas. Increasing the pressure, the formation of the bubbles into the liquid was observed. The bubble point of a membrane is defined by the minimum pressure at which a gas starts flowing through a wetted membrane. This pressure is called the bubble point pressure and is characteristic measure of the diameter of the largest pore in the membrane [9,10]. The pressure can be connected with the radius of the largest pore by the Cantor equation:

$$P = \frac{2\delta}{r}\cos\theta \quad (1)$$

Table 2
Mechanical properties of PEEK-WC/PU films

Sample	Orientation	Casting thickness (μm)	Max. load (kg)	Elongation at max. load (%)	Specific load (N/mm)[a]	Elongation at break (%)
PEEK-WC/PU **4b**	Length direction	250	0.84	15.4	0.37	16.1
	Width direction		1.01	7.9	0.44	8.4
PEEK-WC/PU **4a**	Length direction	150	0.37	7.9	0.12	8.8
	Width direction		0.59	7.3	0.20	8.4
PEEK-WC/PU **3**	Length direction	150	0.91	7.3	0.31	8.5
	Width direction		0.56	4.9	0.12	6.6
PEEK-WC **6**	Length direction	150	0.19	5.5	0.06	6.4
	Width direction		0.18	4.6	0.08	4.9

[a] Sample width: 20.00 mm.

where P is bubble point pressure, δ, water/air surface tension, θ, contact angle and r, pore radius.

The liquid displacement into the smaller pores needs an increase of pressure. Measuring the flux at increasing pressures, it is possible to plot the gas flux versus the applied pressure and the number of pores versus their radius, up to the burst pressure of each film [11]. In Figs. 12(a) and 13(a) is reported, as a reference term, the straight line representing the gas flow rate that should permeate through the dry membrane. If we ignore layer of the membrane made of large pores and approximate with cylinders the shape of the pores and we consider the films as homogeneous, hypotheses that are valid in the membrane skin, the Hagen–Poiseuille equation can be

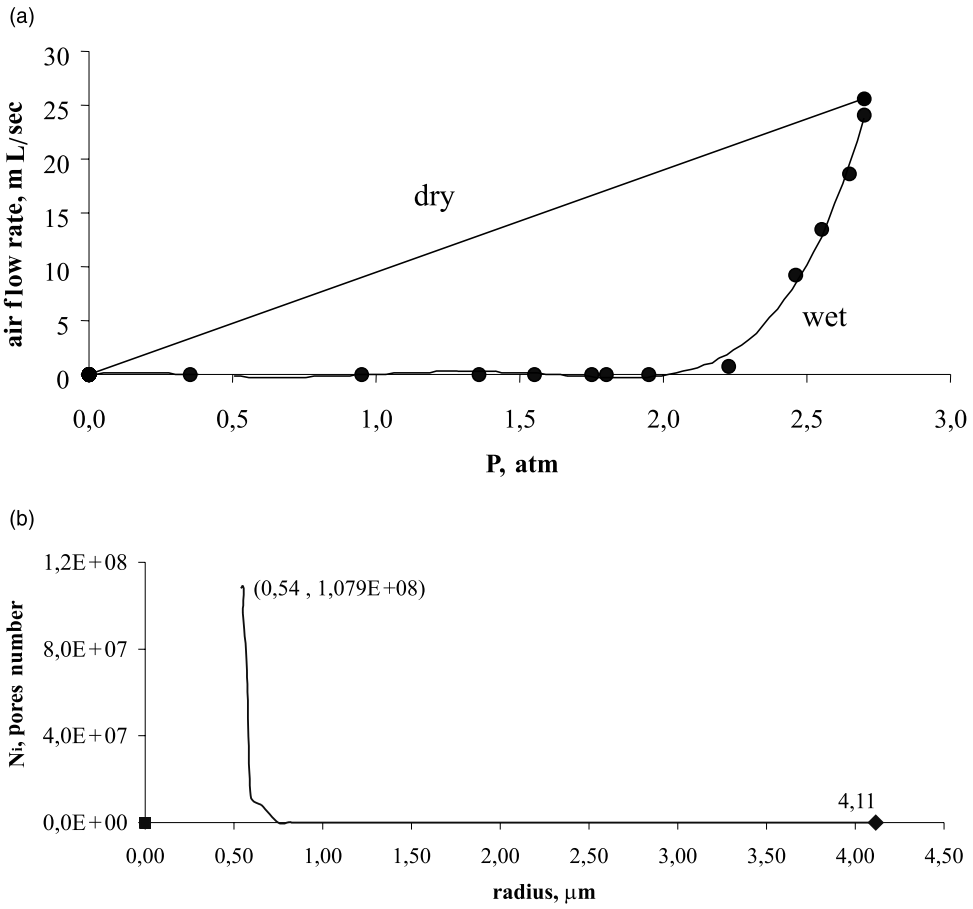

Fig. 12. (a) Air flow rate through the wet **4a** sample vs. applied pressure, (b) pores number of the **4a** sample.

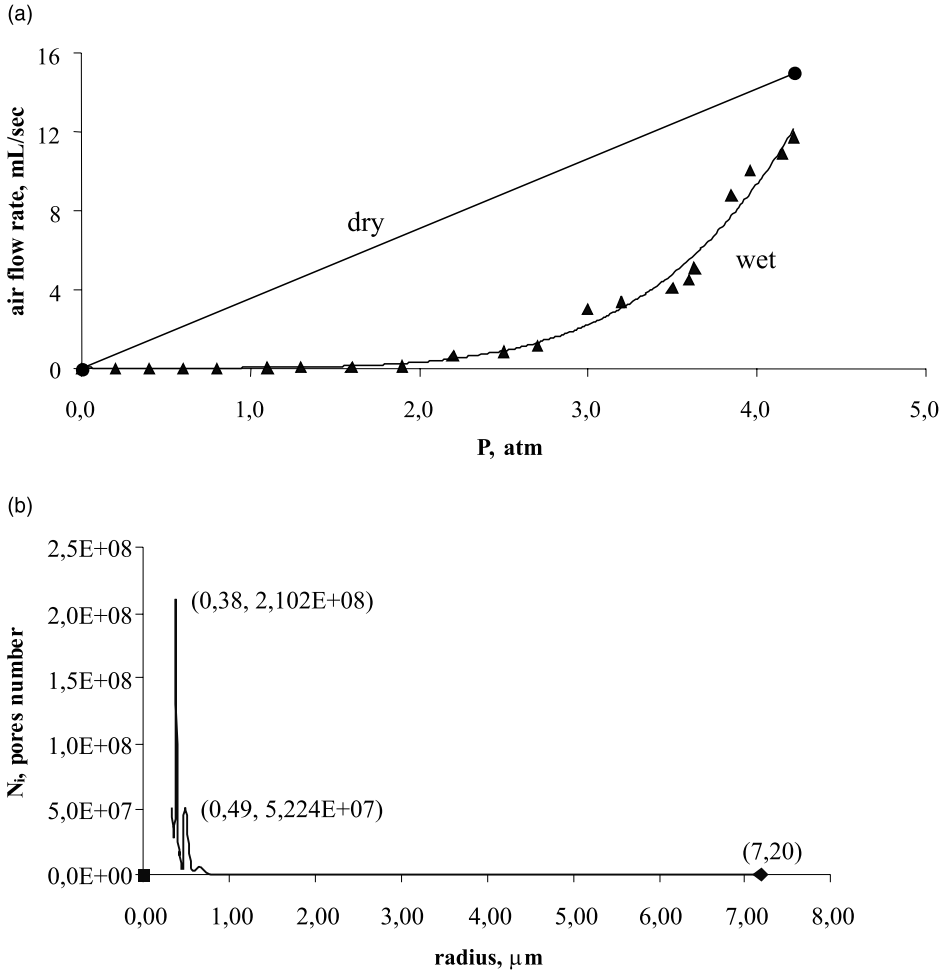

Fig. 13. (a) Air flow rate through the wet **5** sample vs. applied pressure, (b) pores number of the **5** sample.

used to express the transport of air through the membranes [12]:

$$L_i = \frac{\pi}{8\tau l \eta} N_i r_i^4 \tag{2}$$

where L_i is volumetric flow-rate normalised on driving force, τ, tortuousity coefficient, l, pore length, η, viscosity of air and N_i, number of pores with radius r_i.

From the Hagen–Poiseuille and Cantor equations it is possible to calculate the number of pores with radius r_i,

$$N_i = \frac{\mathrm{d}\eta}{2\pi\delta^4} P_i^3 J_i \tag{3}$$

where J_i is volumetric flow rate through the membrane, P_i, pressure and with J_i, $L_i P_i$.

Figs. 12(b) and 13(b) show a partial distribution of the pore numbers of the membranes **4a** and **5** respectively.

5.7. Thermogravimetric analysis

The TGA of PEEK-WC **6** indicates a 5 wt.% loss at 480 °C in air flow. For the PU, instead, weight losses of 5% and 20% can be observed at 250 and 360 °C, respectively. A significant degradation take places beyond 300 °C, with dramatic weight losses at 404 and 424 °C. At 380 °C the PU loses about 30% of its weight, while in correspondence of 500 °C the 80% of mass is lost. In the DTG curve of the membrane **4a** the weight loss of about 20% at 380 °C and of about 25% at 480 °C were observed. The blend sample was completely burned at 580 °C. A minimum is found at 330 °C, which can be due to PU, and a dramatic weight loss occurs at about 560 °C,

probably due to PEEK-WC. The percent of weight loss at 330 and 560 °C is roughly proportional to the masses of PU and PEEK-WC in the membrane.

5.8. Contact angle

The contact angle values for distilled and filtrated water were measured on the upper surface [4] of the films prepared from the single polymer and their blend solutions. The values measured on the PEEK-WC/PU membrane **4a** and **5** are equal to 72° and are not very different from that obtained on the PEEK-WC film **6**, 75°.

6. Conclusions

The aim of this study is the correlation of the membrane morphology with the phase separation behaviour of the membrane prepared from PEEK-WC/DMF and PEEK-WC/PU/DMF systems. From PEEK-WC/DMF dopes membranes with the presence of fingers were obtained. By addition of the PU into the PEEK-WC/DMF dopes is it possible to prepare flat membranes with spongy structure and without fingers. The mechanical and the transpiration properties of these films can be correlated to the morphology. The morphology, in turn, can be correlated to the rate of the demixing of the polymeric solutions in the coagulation bath. The coating of commercial fabrics with PEEK-WC/PU blends proves to be a very interesting alternative to fluorinated membranes for the manufacture of breathing and waterproof fabrics.

Acknowledgements

We thank Dr. F. Falco and Dr. M. Davoli, Dipartimento di Scienze della Terra, University of Calabria, for the SEM images and Dr. L. Pasqua, Dipartimento di Ingegneria Chimica e dei Materiali, University of Calabria, for the TG analyses. We thank also Dr. M. Canetti, Stazione Sperimentale per la Cellulosa, Carta e Fibre Tessili Vegetali ed Artificiali, Milano, for the mechanical tests. This work has been supported by the Italian Ministry of University and Scientific and Technological Research (Murst PNR 3 Textile).

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