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Comparison of the wetting behaviour of polyamides presented as particles and films—Influence of a plasma microwave treatment

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The wettability of two types of polyamide powder (ORGASOL® and RILSAN), differing by their shape and chain ends, has been studied by three methods: inverse gas chromatography, capillary ascension and contact angle measurement on films obtained by the compression at room temperature of the powders. The results are compared with the contact angles measured on the films realized with the melted powders. All the techniques give the same classification of the wettability of the two kinds of polyamides but not the same absolute values of contact angles. In particular, the influence of the shape of the particles has been shown on ORGASOL® by capillary ascension and by contact angle performed on films obtained by compression at room temperature of the powder. A N_2/O_2 plasma treatment applied to the particles leads to an increase of the water wettability of the powders but the treatment was found less efficient than on the melt powder based films. © *2000 Kluwer Academic Publishers*

1. Introduction

To improve the toughness of glassy thermoset resins, especially epoxy networks, two different methods can be used:

- The incorporation of initially miscible elastomers or thermoplastics. In this case it is very important to control the competition between the cure kinetics and the phase separation phenomenon because it conditions the morphology and the fracture behaviour [1–3] of the final network.
- The incorporation of particles with a well defined size. Core-shell particles [4, 5] are often used because they have a small diameter ($D < 0.5\,\mu$m) and changing the nature of the core and the shell can lead to varied properties of the reinforcing particles. In a previous study [6], polyamide particles have also been introduced into an epoxy network. These powders, ORGASOL® manufactured by Elf Atochem, are very fine microporous polyamide powders with a narrow particle size distribution. The nature of the polyamide (PA6, PA12, copolymer 6–12) and the average particle

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size (from 5–60 μm) may be chosen. Introducing these particles into an epoxy/anhydride network leads to an increase of the critical stress intensity factor but poor adhesion was observed between the particles and the matrix. It seemed then interesting to modify the surface of the powder in order to increase its surface energy and to learn if a relation exists between this property, the adhesion properties and the reinforcement.

For this purpose, a preliminary study [7] was performed on films made with melt ORGASOL® powders. The adhesion between the film of ORGASOL® and the epoxy network was evaluated. Different plasma treatments were applied increasing the polar component of the PA film surface energy and the adhesion between the epoxy network and the treated films was shown to increase greatly. Before relating the observations made on the epoxy-PA film assemblies and the observations made on the particle reinforced networks, it was necessary to characterize the surface of the powder, the modifications induced by the plasma treatments and to compare these results with those obtained with the films.

Few techniques are reported in the literature concerning the study of the wettability of powders: the floatation technique [8, 9], the contact angle measurement of a liquid deposited on a film obtained by the compression at room temperature of the powder [10–14], inverse gas chromotogaphy [15, 16] and capillary ascension [14, 17–20] Each of these methods has its specific difficulties either in carrying out the experiments or in interpreting the results.

In this study, the results obtained by three techniques (contact angle measurement on a film obtained by compression at room temperature of the powders, inverse gas chromatography and capillary ascension) will be analysed and discussed. Two types of PA powders have been studied: RILSAN particles that differ from ORGASOL® particles notably by their size and shape factor but also by their chain ends. Finally all the results obtained with the powders will be compared with those obtained by the contact angle measurement on the films realized with the melt powders.

2. Materials

The ORGASOL® particles chosen are polyamide 12 type (ORGASOL® 2002D). They are round (Fig. 1) and their mean diameter is $20 \pm 2\,\mu$m. They are obtained directly by an anionic polymerization process of ε-caprolactam and ω-laurolactam. In order to limit the polymerization degree, a chain regulator is used and it composes the chain ends of the polymer.

RILSAN PA11 particles, obtained by grinding, have an angular shape (Fig. 2). Their mean diameter is 30 μm and the size distribution is larger than that in the case of ORGASOL®. The RILSAN chain ends are NH_2 or COOH type.

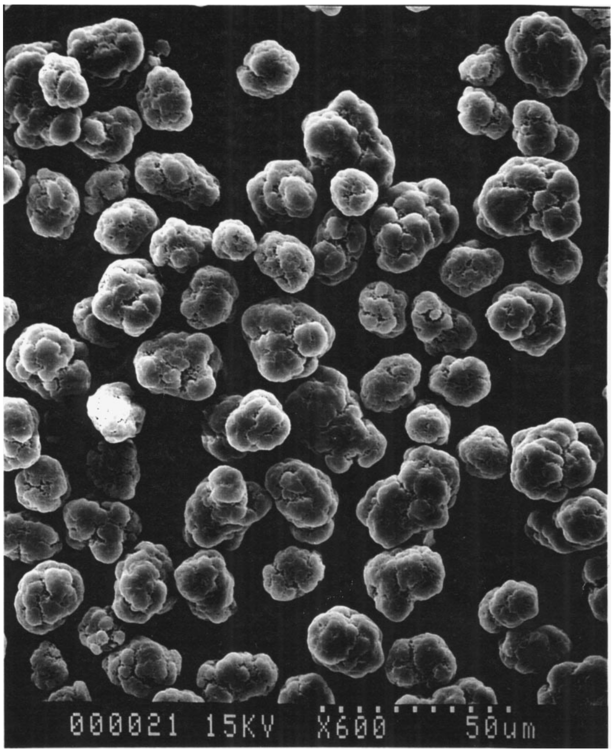


Figure 1 ORGASOL® particles observed by S.E.M.

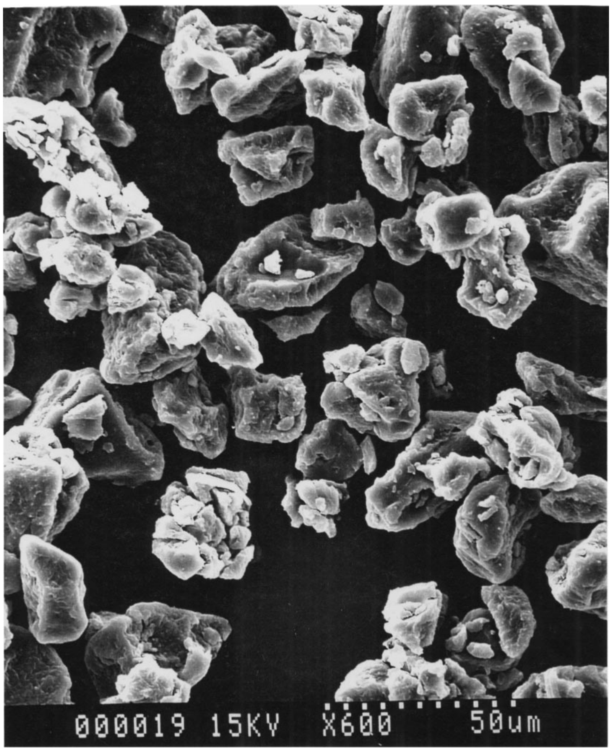


Figure 2 RILSAN particles observed by S.E.M.

3. Experimental methods

3.1. X-ray photoelectron spectroscopy (X.P.S.)

The X.P.S. experiments were carried out with an Escascope apparatus from Vacuum Generators using an unmonochromatized Al X-ray source ($h\nu = 1486.6$ eV). The X-ray source power was set to 300 W in order to prevent degradation of the sample during measuring. The vacuum was in the 10^{-9} mbar range. Charge compensation was partially realized with a flood gun (electron energy 3 eV). The binding energies were calibrated against a value of the CC, CH C1s component centered at 285.0 eV. The atomic ratios were determined from the peak areas corrected for photoionization cross-sections, mean free path and transmission [21].

3.2. Contact angle measurement

The contact angle was evaluated at 24 °C from the height and the base diameter of a sessile drop, assuming the contour to have a circular shape. The experimental procedure is described in detail in a previous study [22].

These measurements were made on films obtained by melt powders and on films obtained by room compression temperature of the powders.

3.3. Inverse gas chromatography (I.G.C.)

The determination of the dispersive component of the surface energy of the PA powders was carried out at 35 °C using a Delsi apparatus DI 700 equipped with a flame ionization detector and coupled with an Enica 21 integrator. The columns (diameter = 4.7 mm and length = 10 cm) were filled with the powder. The retention time of various alcanes (C_6H_{14} to $C_{11}H_{24}$) were measured at infinite dilution (e.g. for each probe, we injected 0.15 ml of vapor, a mixture of the probe and methane). The dispersive component of the surface energy of the powders was determined by the plot of $RT \ln V_n$ as a function of $a(\gamma_L^D)^{0.5}$ according to the following equation:

$$RT \ln V_n + c = 2N_A a\left(\gamma_S^D \gamma_L^D\right)^{0.5} \tag{1}$$

with R, the gas constant; T, the temperature; V_n, the retention volume; N_A, the Avogadro number; a, the surface occupied by an adsorbed molecule [15]; and γ_S^D and γ_L^D, respectively the dispersive component of the surface energy of the solid and the alcane.

3.4. Capillary ascension

A 5 mm inside diameter glass tube was filled with the PA powder and the lower extremity of the tube was closed with a paper filter having a low resistance to the flow. The tube was brought into contact with the liquid. From the measurement of the weight of the liquid going up in the tube, the height of liquid in the column as a function of time was deduced.

Washburn [17] has related the length of liquid in an horizontal tube to time by the following equation:

$$l^2 = \frac{\left(P_A + dgh + 2\frac{\gamma}{r}\cos\theta\right)(r^2 + 4\varepsilon r)}{4\eta} t \tag{2}$$

with ε, the sliding factor of the liquid; g, the gravitational acceleration; η, γ, and d respectively the viscosity, the superficial tension and the density of the liquid; P_A, the atmospheric pressure; r, the capillary radius; and θ, the contact angle.

In the case we are concerned with, the case of vertical capillary, the equation is more complex (Equation 3) and it must take into account the fact that the ascension is finite. It stops when the equilibrium of the pressures is attained.

$$\frac{(r^2 + 4\varepsilon r)dg}{8\eta} t + l = -\frac{\left(P_A + dgh + 2\frac{\gamma}{r}\cos\theta\right)}{dg} \times \ln\left(1 - \frac{P_A + dgl}{dgh + 2\frac{\gamma}{r}\cos\theta}\right) \tag{3}$$

In most of the studies [18, 19] reported in the literature, a simplified relation is used. This equation is obtained if the liquid is assumed to progress only under its own capillary pressure, if the air resistance is neglected and if the logarithmic term is simplified. In that case the Equations 2 and 3 lead to the same expression:

$$l^2 = \frac{\gamma \cos\theta}{2\eta} r t \tag{4}$$

This simplification can be used in the case of vertical capillaries if they are thin and if we consider a low liquid ascension.

For a porous medium the capillary can be considered as n parallel capillaries with a mean radius noted $\bar{r}$. The Equation 4 can then be written as follow:

$$l^2 = \frac{\gamma \bar{r} \cos\theta}{2\eta} t \tag{5}$$

The $\bar{r}$ term related to the nature and the distribution of the powder in the capillary can be calculated using a liquid that perfectly wets the powder (in that case, $\cos\theta = 1$). In our case octane ($\gamma_L = 21.7$ mN/m) was chosen as the perfect wetting liquid. Afterwards the contact angles of different liquids can be determined using Equation 5.

3.5. Microwave plasma treatment apparatus

The plasma apparatus was described in a previous study [22]. Briefly, it consists of a 2.45 GHz microwave generator from Rayteck (RK L1200 LRT) which can deliver a power from 0 to 1200 W. The plasma is created by means of a surface guide in a quartz tube (diameter 16 mm). The gas flow is measured with mass flow controllers (Tylan FC 280) in the 0–200 sccm (standard $cm^3\ min^{-1}$) range. This apparatus initially conceived to treat bulk samples was adapted for the powder treatment. In particular, a reactor with two upper openings and containing the powder was connected by one outlet to the quartz tube. It was equipped with a stirring system in order to favor an homogeneous treatment of all the particles. Furthermore, in order to allow the free travel of the plasma species through the reactor and to prevent the powder going out of the reactor to the vacuum pump, a system associating different filters was placed at the outlet of the reactor. With this adaptation the powder was treated downstrean and a stirring of 170 r.p.m. was sufficient to obtain an homogeneous treatment of 25 g of powder. The gas used to treat the powder was a mixture of oxygen and nitrogen with the following composition 20 : 80. The power was set to 200 W and the treatment time was equal to 360 s.

4. Results and discussion

4.1. Comparison between untreated powders and the corresponding plates

4.1.1. Characterisation of the films made with melt powders

The films made with melt polyamides are obtained in both cases by the fluidized bed method. A steel plate is heated up to a temperature higher than the melting

TABLE I Characteristics of the films realised with melt powders of ORGASOL® and RILSAN

	θ_{water} (°)	$\theta_{\text{diiodomethane}}$ (°)	$\theta_{\text{bromonaphtalene}}$ (°)	γ_S^D(mN/m)	γ_S^P(mN/m)	γ_S(mN/m)
ORGASOL®	78.5 ± 1.6	48.5 ± 1.9	34.7 ± 2.0	37	4.6	41.6
RILSAN	75.5 ± 2.0	42.5 ± 1.6	27 ± 2.1	40	5.0	45

temperature of the polyamide. It is then introduced in the PA fluidized bed allowing the formation of a PA film with a thickness of around 450 μm. The film is then unstuck from the steel plate and the characterization is carried out on the face exposed to air during the film formation.

Table I presents the water, methylene iodide and bromonaphtalene contact angles measured on ORGASOL® and RILSAN films; The dispersive and polar component of the surface energy of the two polyamides are calculated using Fowkes equation [23]. Only a slight difference in the dispersive component of the surface energy is noticed between the two polyamides and the surface energy of the two films studied are in the range of the common values given for polyamide.

4.1.2. Characterisation of the powders

i) Determination of γ_S^D by IGC. The Fig. 3 shows the results obtained with different alcane probes for the RILSAN powder. The plot of $RT \ln V_n$ as a function of a$(\gamma_L^D)^{0.5}$ is linear and the slope of the straight line leads to a γ_S^D value equal to 37 mN/m.

ii) Determination of contact angles by capillary ascension. The capillary ascension has been studied only on ORGASOL® powder due to its spherical shape and low size dispersity. At first, the determination of the mean capillary radius was made using octane. A good reproducibility of the square ascension height as a function of time was noticed (Fig. 4) and the mean value of $\bar{r}$ was calculated from the slope of the experimental straight line using Equation 5 ($\bar{r} = 0.61\ \mu$m). The ascension of bromonaphtalene and water was then studied. For the first liquid, a linear variation of the square of the ascension height as a function of time was observed and a mean value of the contact angle was deduced from 4 experiments: $\theta = 76.6 \pm 0.6°$. Concerning water, no ascension was observed in the ORGASOL® filled tube indicating that the contact angle of this liquid on the powder is higher than 90° preventing the liquid from entering the tube.

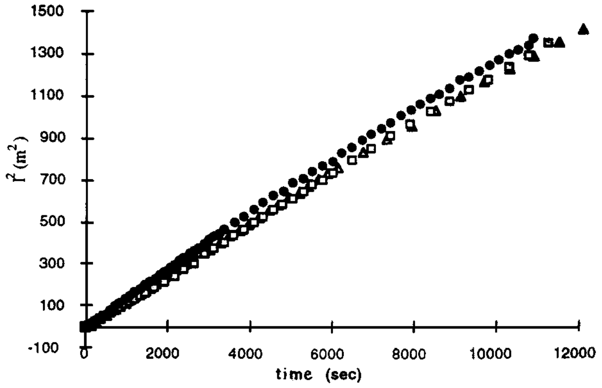


Figure 4 Square of the octane ascension height as a function of time for three tubes filled with untreated ORGASOL®.

iii) Determination of water contact angle on films obtained by the compression at room temperature of the powders. The evolution of the water contact angle measured on ORGASOL® as a function of the compression stress is shown in Fig. 5 and it agrees with other results obtained in the literature [11]. Varying the compression stress from 0 to 4.10^8 Pa leads to a decrease of the water contact angle from 127.5° to about 98°. For stress values between 4.10^8 and 1.25.10^9 Pa, the water contact angle remains constant.

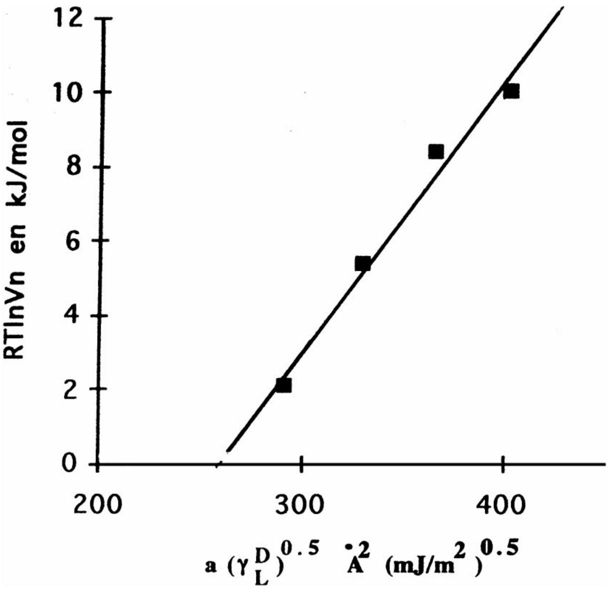


Figure 3 Representation of I.G.C. data for RILSAN powders at 35 °C allowing the determination of the dispersive component of the surface energy of the powders.

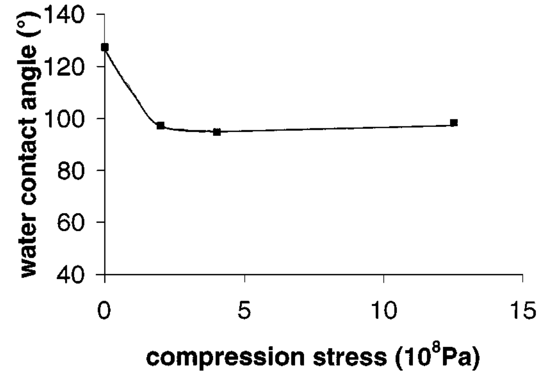


Figure 5 Evolution of the water contact angle measured on films obtained by compression at room temperature of the ORGASOL® powder as a function of the compression stress.

For RILSAN, the water contact angle decreases from 125.6° for a compression stress equal to zero to a constant value equal to about 68°.

5. Discussion

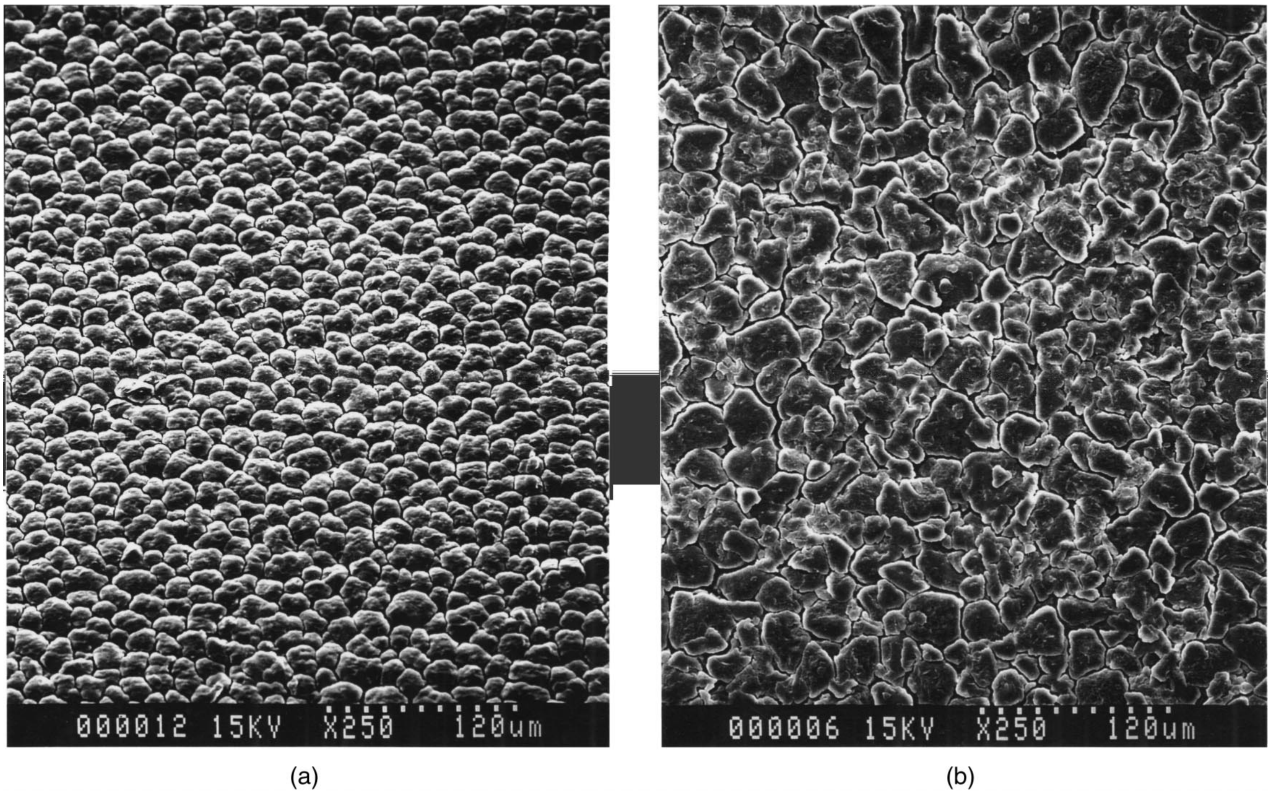
The different results obtained on films and powders are gathered in Table II. A good correlation is obtained between γ_S^D values determined on RILSAN by wettability on melt powder based film and by IGC on powders. The results obtained on ORGASOL® by capillary ascension and wettability on compact lead to the same conclusion. The water contact angle on ORGASOL® powder is higher than 90°. The nature of the polyamide does not induce variation in the wettability on film realized with melt powder on one hand ($\theta_{H_2O} \approx 76°$) and on uncompressed powders on the other hand ($\theta_{H_2O} \approx 126°$). This underlines that the chain ends have no influence in this case on the wettability of the two kinds of polyamides. On the contrary, the water contact angle is largely higher on the film obtained by compression of ORGASOL® at room temperature than on the film obtained by the same method with RILSAN. The value measured for ORGASOL® is near to that measured on uncompressed powder whereas the value measured for RILSAN is of the same order of magnitude as that measured on the melt powder based film. The difference observed between ORGASOL® and RILSAN can only be explained by a difference in the roughness of the samples.

Fig. 6 shows the surface of the RILSAN powder compressed under 1.25 GPa and that of the ORGASOL® powder compressed under the same stress. We can note that the specific shape of ORGASOL® particles are not destroyed.

As a conclusion the results obtained by all the techniques used in this study show that the classification of the wettability of the polyamides does not depend on the technique used contrarily to the absolute value of the contact angle. For capillary ascension and contact angle measurement on films obtained by compression

TABLE II Comparison between the wettability of the polyamides presented as films or powders

				Powder				
							Wettability on compact powders	
Film realised with melt powder								
Used technic	Wettability			I.G.C	Capillary ascension		Compression stress = 0	Compression stress = 1.25 GPa
Polyamide nature	θ_{H_2O} (°)	$\theta_{bromonaphtalene}$ (°)	γ_S^D(mN/m)	γ_S^D(mN/m)	$\theta_{bromonaphtalene}$ (°)	θ_{H_2O} (°)	θ_{H_2O} (°)	θ_{H_2O} (°)
ORGASOL®	78.5 ± 1.6	34.7 ± 2.0	37	Not measured	76.6 ± 0.6	>90°	127.5 ± 2.6	98.1 ± 2.4
RILSAN	75.5 ± 2.0	27 ± 2.1	40	37	Not measured	Not measured	125.6 ± 3.8	67.9 ± 3.6



(a) (b)

Figure 6 S.E.M. image of the surface of the films obtained by the compression under 1.25 GPa of: a) ORGASOL® and b) RILSAN.

TABLE III Influence of a O_2/N_2 microwave plasma treatment on the O/C and N/C ratios measured by X.P.S. on the powders and on the films and on the water contact angle measured on the compact powders[a] (compression stress: 1.25 GPa) and on the films obtained with the melt powders[b]. The composition of the plasma is $O_2:20/N_2:80$, the power is 200 W and the exposure time is 360 s

	O/C	N/C	θ_{water} (°)
Untreated ORGASOL® powder	0.12	0.10	98[a]
Plasma treated ORGASOL® powder	0.29	0.13	80[a]
Untreated ORGASOL® film	0.22	0.09	78[b]
Plasma treated ORGASOL® film			24[b]
Untreated RILSAN powder	0.11	0.13	68[a]
Plasma treated RILSAN powder	0.22	0.10	40[a]
Untreated RILSAN film	0.18	0.07	75[b]
Plasma treated RILSAN film	0.63	0.08	27[b]

at room temperature of the powders, the influence of roughness on the value of the contact angle has been underlined.

5.1. Influence of the microwave plasma treatment

The powders treated have been studied by the preceeding techniques except inverse gas chromatography. In fact, with this method, we only determined the dispersive component of the surface energy of the powders and it is well known that the oxidative plasma treatments do not affect this component of the surface energy [24, 25]. Furthermore it was verified that on the treated melt powder based film no evolution of γ_S^D was noticed [7].

As shown in Table III, the plasma treatment leads principally to an increase of the O/C ratio of the powders and no significative difference has been observed between ORGASOL® and RILSAN powders. On the other hand the effect of the treatment is lower on the powders than on the respective melt powder based films. In fact, after plasma treatment, the O/C value is higher by a factor less than 2 for the powders whereas the multiplicative factor is about 3.5 for the films. This trend was also confirmed by the water contact angles measured on the compact powders. These results were obtained by applying onto the untreated and treated powders a compression stress of 1.25 GPa. Comparing the powders and the respective films (Table III), we can notice that the decrease of water contact angle induced by the treatment is lower for the film obtained by compression of the powder at room temperature than for the films obtained with melt powders and the difference is enhanced in the case of ORGASOL®, due to an additional effect of the rugosity of the films obtained by compression of the powder, as previously discussed.

At least the ascension of 1-bromonaphtalene and water was made easier in a glass tube filled with plasma treated ORGASOL® powder. The contact angle of 1-bromonaphtalene decreases from 77–55°, leading to a significative difference in the slopes of the linear curves representative of the square ascension height of 1-bromonaphtalene as a function of time (Fig. 7). As the ascension of water in the tube filled with untreated powder was impossible, the plasma treatment applied to the powders allow this phenomenon to occur. However the ascension was very slow (5 mm during 30 min) and we preferred not to give any value for the water contact angle. Thus all of the results significatively show that an oxidative plasma treatment increases the wettability of polyamide powders.

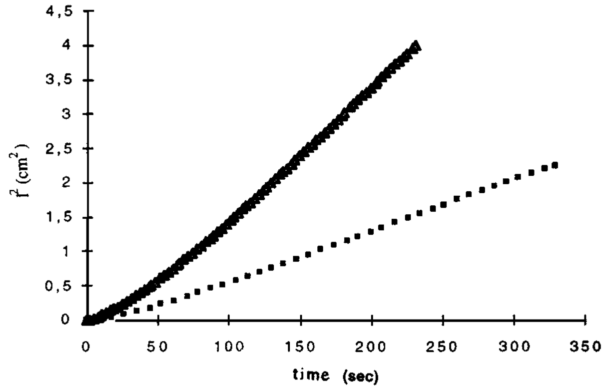


Figure 7 Influence of the O_2/N_2 plasma treatment on the ascension of 1-bromonaphtalene in tubes filled with ORGASOL®. Ascension (■) before treatment, (▲) after treatment.

6. Conclusion

The surface of two kinds of polyamide powders (PA11 : RILSAN and PA12 : ORGASOL®) was studied by different techniques: X-ray photoelectron spectroscopy, inverse gas chromatography, capillary ascension and contact angle measurement on room temperature compact powders. The results were compared to those obtained on the films made with the respective melt powders.

The values of the dispersive component of the surface energy obtained on RILSAN powders and films are quite similar and identical values of the water contact angle have been measured on films obtained by room temperature compression of the powders and by the melt powder. On the other hand, the contact angles measured on ORGASOL® powder are always higher than on the corresponding film. This difference has been attributed essentially to the specific shape of ORGASOL® powders.

An oxidative plasma treatment was carried out on the powders. It leads to an increase of the water wettability of the powder related to an increase of the O/C ratio measured by X.P.S. on the powder surface. Nevertheless, for the same experimental conditions, the treatment has been found less efficient on the powders than on the respective films obtained with melt powders.

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References

1. R. MULHAUPT, *Chimica* **44** (1990) 43–52.
2. A. R. PEARSON, in "Rubber Toughened Plastics," edited by C. K. Riew and A. J. Kinloch, Advances in Chemistry, Series no. 233, Washington DC, (1993) chap. 17, p. 405.
3. J. HEDRICK, I. YILGOR, G. WILKES and J. MCGRATH, *Polymer Bulletin* **13** (1985) 201.
4. G. LEVITA, A. MARCHETTI and A. LAZZERI, *Makromol. Chem., Macromol. Symp.* **41** (1991) 179.
5. L. BECU, A. MAAZOUZ, H. SAUTEREAU and J. F.GERARD, *J. Appl. Poly. Sci*. **65** (1997) 2419.
6. C. GIRODET, E. ESPUCHE, H. SAUTEREAU, B. CHABERT, R. GANGA and E. VALOT, *J. Mater. Sci.* **31** (1996) 2997.
7. P. LENNON, E. ESPUCHE, D. SAGE and H. SAUTEREAU, *International Journal of Adhesion and Adhesives* **19** (1999), 273–279.
8. E. I. VARGHA-BUTLER, T. K. ZUBOVITS, H. A. HAMZA and A. W. NEUMANN, *J. Dispersion Sci. and Tech.* **3**(6) (1985) 357.
9. A. M. Al TAWEEL, B. DELORY and J. WOZNICZEK, *Colloids and Surfaces* **18** (1986) 9.
10. G. BUCKTON, *J. Adhesion Sci. Tech*. **3**(7) (1993) 205.
11. G. BUCKTON and J. M. NEWTON, *Powder Tech.* **46** (1986) 201.
12. J. KIESVARRA and J. YLIRUUS, *Acta. Pharm. Nord.* **3** (1991) 171.
13. G. PARSONS, G. BUCKTON and S. CHATHAM, *J. Adhesion Sci. Tech.* **7**(2) (1993) 95.
14. W. DUNCAN-HEWITT and R. NISMAN, *ibid.* **7**(3) (1993) 263.
15. J. SCHULTZ and L. LAVIELLE, Inverse Chromatography, *Characterisation of Polymers and Other Materials*, edited by D. R. Lloyd, T. C. Ward and H. P. Schreiber, Amer. Chem. Soc. Symp., Series no. 391, Amer. Chem. Soc. (Washington DC, 1989) pp. 12–58.
16. L. LAVIELLE, J. SCHULTZ and N. NAKAJIMA, *J. Appl. Polym. Sci.* **42** (1991) 2825.
17. E. WASHBURN, *Phys. Rev.* **XVII 3** (1921) 273.
18. H. G. BRUIL and J. J. VAN AARTSEN, *Coll. and Poly. Sci.* **252** (1974) 32
19. M. L. STUDEBAKER and C. W. SNOW, *J. Phys. Chem.* **59** (1995) 973.
20. G. BUCKTON and J. M. NEWTON, *J. Pharm.* **38** (1986) 329.
21. J. H. SCOFIELD, *Electron Spectrosc.* **8** (1976) 129.
22. J. P. BADEY, E. ESPUCHE, D. SAGE, B. CHABERT, Y. JUGNET, C. BATIER and TRAN MINH DUC, *Polymer* **37**(8) (1996) 1377.
23. F. M. FOWKES, *Ind. Eng. Chem.* **12** (1964) 40.
24. R. CUEFF, G. BAUD, J. P. BESSE, M. JACQUET and M. BENMALEK, *J. Adhesion* **42** (1993) 249.
25. K. GRUNDKE, H. J. JACOBASCH, F. SIMON and S. T. SCHWEIDER, *J. Adhesion Sci. Tech.* **9**(3) (1995) 327.
26. R. E. JOHNSON and R. H. DETTRE, *Adv. Chem. Ser., Ed. Amer. Chem. Soc.* **43** (1964) 112.
27. *Idem., ibid.* **43** (1964) 136.
28. R. J. GOOD, *J. Amer. Chem. Soc.* **74** (1952) 5041.

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