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Effect of a plasma treatment on water diffusivity and permeability of an unsaturated polyester resin

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Abstract

Unsaturated polyester resin films have been modified by a tetrafluoromethane microwave plasma. The treated surface morphologies investigated by contact angle, atomic force microscopy and permeation measurements show that the CF_4 plasma treatment decreases drastically the surface energy by increasing the hydrophobic character. The surface modification due to plasma fluorination decreases the water content diffusing through the UPR film and the time-lag diffusion coefficient and thus, the sorption kinetic. From these results, it is clearly shown that the CF_4 plasma treated layer improves drastically the barrier effects.

Keywords: Polyester; Plasma treatment; Fluorination; Barrier effect

1. Introduction

Dense polymers such as unsaturated polyester resins (UPR), are used in many applications and in many industrial fields (the building trade, electronics, military, space and naval industries). However, these resins are sensitive to water sorption. Water diffusion can be at the origin of reversible phenomena, such as plasticization and local strain, but also, irreversible phenomena such as chain ruptures and chemical degradations [1]. All these phenomena contribute to the ageing of the material.

To improve the hydrophobic or hydrophilic properties of the resins, various techniques can be used. In this field, surface treatment by the cold plasma technique appears suitable because it does not affect the properties in the bulk of the material. For example, it has been shown that plasma-deposited silicon-based dielectric layers (e.g. SiO, SiON or SiN) limit the moisture sorption [2]. By changing the plasma-deposited material, it is also possible to change the barrier properties. For instance, fluorinating cold plasma treatment [3–7] leads to a hydrophobic surface, while oxygenating or nitrogen cold plasma [8,9] leads to an increase of the hydrophilic character.

In this work, a UPR film has been modified by using the tetrafluoromethane low-pressure plasma. The modifications of the water diffusivity and permeability values resulting from this treatment were analyzed. The permeation measurements were performed with an apparatus developed in our laboratory [10]. To characterize the effects of the plasma treatment on the UPR surface morphology, contact angles were measured and surfaces were observed by means of optical and atomic force microscopy (AFM).

2. Experimental

2.1. Materials

The selected UPR was provided by Technibat Co [11]. It consisted of maleic anhydride (25% mol), isophthalic acid (25% mol) and propylene glycol (50% mol) mixed in a styrene monomer solution (38% w/w). First, the polyester was prepared by polycondensation of the propylene glycol with the maleic anhydride and the isophthalic acid. Both resin and styrene monomer were used as received without removing the inhibitor. Thus, the resin could be crosslinked by a radical process by using an initiator, methylethylketone peroxide (MEKP, Akzo) and an activator, a cobalt octoate (Akzo). To initiate the reaction, 0.2% (w/w) of the promoter solution (which contained 6% of cobalt octoate) was first mixed with the resin. Then 1.5% (w/w) of the initiator

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solution was added to the mixture (resin + styrene+ promoter).

Then, to get the desired constant thickness, the resin was cast between two polypropylene (PP) plates for 24 h at room temperature, then post-cured at 80°C for 6 h and at 120°C for 2 h. These PP plates are usually used to avoid sticking with the resin. This post-curing treatment allows the maximum degree of transformation to be reached and the final product was found to be chemically stable [1]. Fig. 1 shows the chemical structure of the unsaturated polyester resin obtained from the initial products. A UPR film with a thickness, $L = 0.0142$ cm and an area exposed to water sorption, $S = 30\ \mathrm{cm}^2$ was prepared for tetrafluoromethane plasma treatment.

2.2. Methods

The water-specific permeameter device has been already described [12].

The plasma equipment used in this work is a microwave plasma and the process is described in [5]. The sample was treated on both sides of the polymer film with a treatment duration of 2 min.

To characterize the surface chemical modifications, contact angle measurement was performed as described in [5]. From the contact angle measurements, the values of the surface energy according to the Young-Dupre [13] and Fowkes [14] relationships can be determined with γ the surface energy, θ the contact angle, the indexes s and l denoting the solid and liquid respectively, and the exponents d and p denoting respectively, dispersive and polar components of the surface energy. The surface energies of the different liquids, necessary to calculate γ, are listed in Table 1.

Atomic force microscopy experiments were performed with a Nanoscope II model from Digital Instruments (Santa Barbara, CA), in the contact mode, with a 150 and a 15 μm scanner for molecular resolution studies.

Table 1
Surface energies of the different liquids used for contact angle measurements

Liquid	γ_l mJ m^{-2}	γ_l^d mJ m^{-2}	γ_l^p mJ m^{-2}
Water	72.8	21.8	51.0
Glycerol	63.4	37.0	26.4
Diiodomethane	50.8	49.5	1.3

3. Results

Before the plasma treatment, the mean value of the contact angle is found to be $\theta = 41.5°$ and after plasma treatment the angle value obtained with water, increases drastically to reach $\theta = 83.3°$. More than five measurements were run to check the θ reproducibility, and the values are given with an uncertainty of $\theta = \pm 2°$.

Images from atomic force microscopy (Fig. 2a and b) at a scale of 50 μm × 50 μm show the aspect of the sample surface before and after the plasma treatment, respectively. It can be observed that, before the plasma treatment, the surface morphology of the unsaturated resin appears as a flat surface exhibiting a small-size granular structure. Drastic changes appear on the surface after the plasma treatment. Indeed a rough surface morphology formed by wide bumps is clearly highlighted. At this observation scale, the bump area distribution was estimated to be ≈30% of the UPR surface sample.

At the scale of 20 μm × 20 μm, the inhomogeneous coating morphology of the modified surface is conspicuous by the existence of irregularities. The unmodified surface, at this scale, remains almost flat, although this sample does not exhibit a perfectly smooth surface. Observations at a scale of 10 or 5 μm allow a better view of holes or pinholes and a nodular structure. Finally, at the 2 μm scale, the three-dimensional images displayed in Fig. 3 confirm firstly, that the plasma treatment transforms drastically the rough

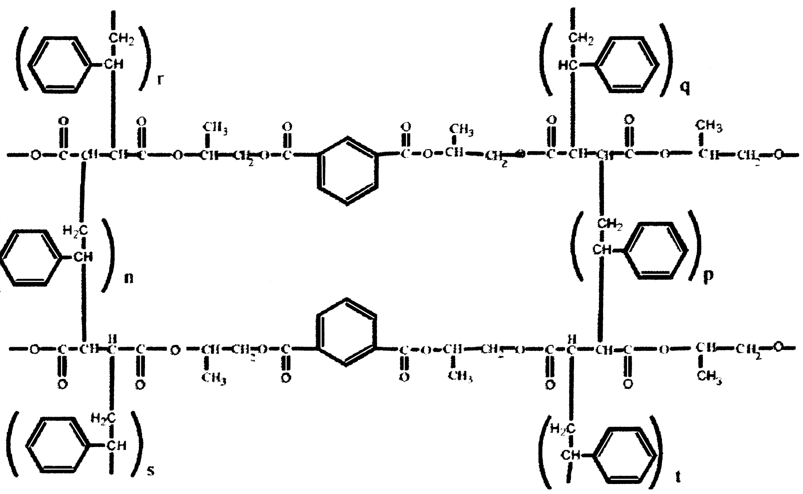

Fig. 1. Chemical structure of the crosslinked UPR used in this study.

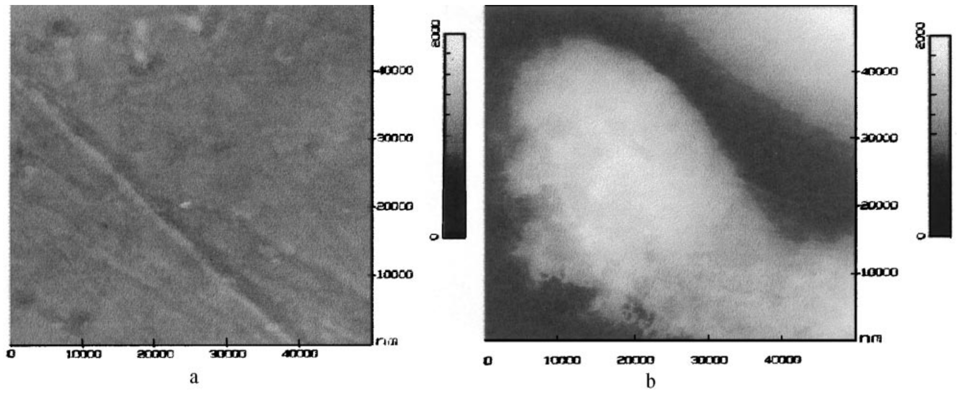

Fig. 2. AFM images of the same UPR surface at 50 μm (a) untreated (b) treated by CF_4 plasma.

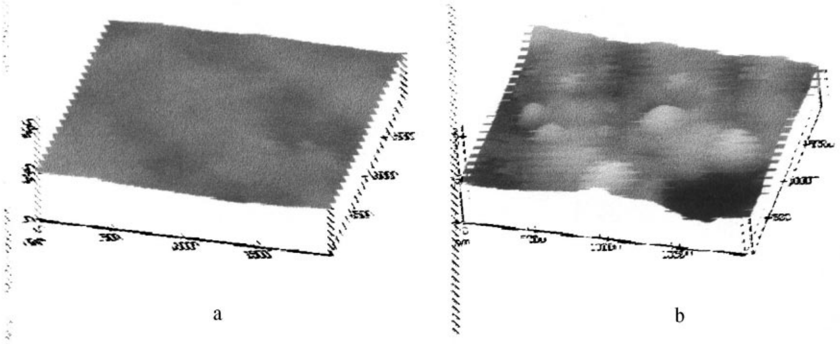

Fig. 3. Three-dimensional AFM images of the same UPR surface at 2 μm (a) untreated (b) treated.

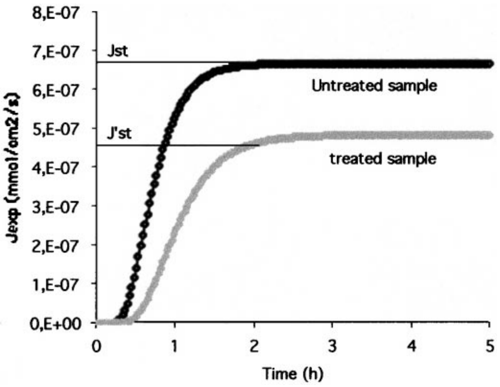

Fig. 4. Experimental curves $J = f(t)$ obtained from untreated sample then treated by CF_4 plasma.

surface, and secondly that a nodular structure appears at the sample surface (Fig. 3b).

Fig. 4 now shows the typical flux curves obtained with the same procedure from our sample before and after plasma treatment. In this steady state, the differences observed are significant (taking into account the very good accuracy of the chilled mirror hygrometer) and show that a lower value of J_{st} is obtained for the treated sample. On the other hand, it is possible to determine the water content versus time (see Fig. 5). From this representation, the value of the time-lag is obtained and we observe that the plasma treatment leads to an increase of this value ($t_L = 2732$ s for the untreated sample and 3908 s after its treatment).

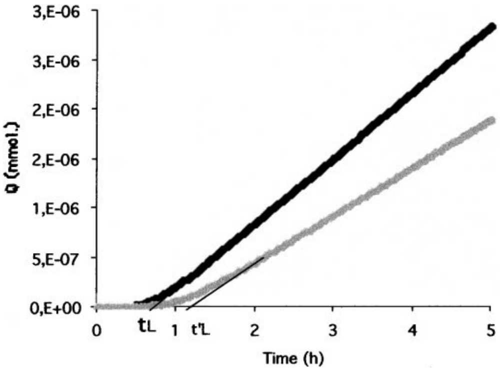

Fig. 5. Experimental curves $Q = f(t)$ obtained from untreated sample then treated by CF_4 plasma.

4. Discussion

It is now established that low-pressure glow discharge plasma modification of organic material surfaces results in functionalization, fluorination and degradation of the surface [15,16]. The fluorination creates fluorinated groups and should lead to a modification of surface energy, while the

Table 2
Contact angles and surface energy of UPR film first untreated and then treated by CF_4 plasma

	θ_{water}	θ_{glycerol}	$\theta_{\text{diiodomethane}}$	γ_s^d mJ m^{-2}	γ_s^p mJ m^{-2}	γ_s mJ m^{-2}
Before CF_4	41.5	66	49	23.7	21.7	45.4
After CF_4	83.3	74.3	45.2	33.5	2.4	35.9

degradation mainly changes the morphology of the surface. Fluorination of polymers [15–17] arises from the existence of fluorinated macroradicals that grow in the gas phase, F^*, CF^*, CF_2^*, leading to different mechanisms of grafting, substitution of the UPR chain hydrogen, addition or deposition of different fluorinated radicals.

The values of γ_s^d and γ_s^p obtained for our samples are reported in Table 2. Before the plasma treatment, no drastic differences between γ_s^d and γ_s^p are observed and the value of γ_s is 45.4 mJ m^{-2}. After the plasma treatment, the value of γ_s is reduced to 35.9 mJ m^{-2}.

At this stage of the discussion, it must be also taken into account the fact that the surface treatment leads to variations of the surface roughness. The value of the contact angle is also correlated to the roughness. Thus, the values of γ_s, γ_s^p and γ_s^d given in this work for plasma treated samples are not quite accurate. Nevertheless, the observed variations for these quantities are significant enough to validate the decrease of γ_s which is mainly due to the low value of γ_s^p. This low value of γ_s^p varies from 2.4 to 21.7 mJ m^{-2} and shows that the polar character of the solid surface decreases drastically. This is consistent with the study of Wang et al. [5], who suggest that the surface energy of hexatriacontane decreases mainly with the content of radical species CF_x. In the gas phase these are the key species which form the fluorinated layer.

In addition to contact angle results, AFM and optical microscopy investigations have shown the existence of a degradation process (holes or pinholes) and the existence of a fluorination process (bumps) which, according to Wang et al. [5], appear simultaneously. Consequently, both techniques, contact angle and microscopy, used to characterize the effect of plasma treatment on UPR surfaces, have highlighted the chemical modifications due to fluorinated groups.

Because of its hydrophobic character, the fluorinated layer should act as a barrier to the diffusion of hydrophilic liquids such as water.

Pervaporation measurements were carried out to characterize the role played by the CF_4 surface treatment on the values of the water flux J (stationary flux J_{st}), the permeability coefficient ($P = J_{st}L$), the time-lag t_L, and the time-lag diffusion coefficient D_L. For these measurements, it is necessary to know how much of the sample surface is actually exposed to water. From microscopic analysis, the CF_4 plasma treatment covers approximately 30% of the whole sample surface. Keeping in mind this consideration for the following, it will be assumed that sample, before and after treatment, exhibit the same surface exposed to water. Under this assumption, the apparent values of J, J_{st}, P, t_L and D_L can be determined as reported in Table 3.

Thus, taking into account the very good reproducibility of the material, the differences observed after plasma treatment are significant indicators of an increase in the barrier effect. This is expressed by a decrease in P (28%), D_L (30%) and an increase in the time-lag t_L (43%). These results are absolutely compatible with contact angles (decrease in surface energy) and microscopic analysis (existence of fluorinated groups). However, from experimental curves $Q = f(t)$, the times t_c corresponding to the first water molecules crossing the film, before and after treatment, seem to be almost the same. This last result is the evidence that a classical multilayer model, as drawn in Fig. 6a, cannot be used. Indeed, a uniform CF_4 layer must, because of its hydrophobic nature, increase drastically the value of t_c. Thus, we have to consider a model which supposes the existence of a water-exposed surface made of hydrophobic parts and untreated UPR parts as displayed in Fig. 6b. This model allows our experimental results to be interpreted easily: 30% decrease in P which results from approximately 30% of the surface being treated, and an increase in time-lag value caused by increasing the average distance between the two faces that were treated.

It could be interesting to establish a relationship between time-lag and a "three-layer model" of the treated film (two treated surfaces), assuming that the water sorption in the polymer is obtained instantaneously and knowing that, for such a system, the time-lag is linked to each layer characterized by a diffusion coefficient D_i, a solubility coefficient S_i and a permeability coefficient P_i as indicated in Fig. 6a. It is more reasonable in this work, as pointed out by

Table 3
Experimental results of the UPR sample ($L = 0.0142$ cm) tested in pervaporation, before and after the tetrafluoromethane plasma treatment

	Water flux J_{st} (mmol cm^{-2} s^{-1})	Permeability coefficient $P \times 10^9$ (mmol cm^{-1} s^{-1})	Time-lag t_L (s)	Diffusion coefficient $D_L \times 10^8$ (cm^2 s^{-1})	Resistance diffusion $L/P \times 10^{-6}$ (s mmol^{-1})
Untreated sample	6.70 ± 0.20	9.51	2732	1.23	1.5
Treated sample	4.84 ± 0.15	6.87	3908	0.86	2.1

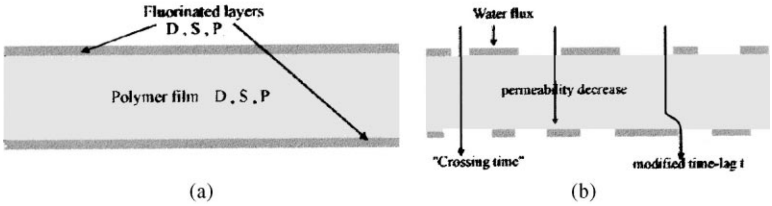

Fig. 6. Multi-layer model (a) classical (b) experimental.

Vogt [2], to consider only the permeability and additional resistances *L*/*P* towards water diffusion. In this case, we observe an increase in *L*/*P* (40%) (Table 3).

5. Conclusion

Owing to their favorable performances as high barrier materials, crosslinked polymer resins have found efficient applications as coatings or with fibre-reinforced composite systems. Thus, the barrier properties of UPR are used against moisture and water penetration. The CF_4 plasma treatment of UPR appears to be an efficient way to improve these barrier properties. Indeed, three methods of characterization were used to investigate our UPR film before and after plasma treatment: contact angle, atomic force microscopy and pervaporation measurements. These methods have shown that the effect of CF_4 plasma treatment on UPR films is mainly a surface modification with an increase in the hydrophobic character (decrease in the surface energy) due to formation of fluorinated groups, which leads to a decrease in the diffusion coefficient or the sorption kinetic and a decrease in the number of water molecules which pass through the film.

From these first results, and taking into account that degradation and fluorination rates depend on treatment time, our next goal will be to characterize the UPR surface modification for various quantities of reactive species. It will be necessary to improve the conditions of plasma treatment, by using CF_4 with argon for example, in order to obtain a homogeneous fluorinated layer and thus try to quantify the barrier effect on the multi-layer model.

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