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Controlled roughening of poly(ethylene terephthalate) by photoablation : study of wetting and contact angle hysteresis

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Résumé. — La surface lisse de films cristallins de polyéthylène téréphthalate est facilement rendue rugueuse par photodécomposition ablative obtenue par l'absorption du rayonnement UV lointain pulsé du laser à excimère. L'amplitude de cette rugosité (qui est de l'ordre du micron) est contrôlée par l'intensité du rayonnement pulsé et par le nombre de pulses reçus par la surface. La structure et l'orientation de la rugosité sont déterminées par la cristallinité du polymère qui est très bien contrôlée dans les échantillons commerciaux. L'hystérèse d'angle de contact induite par la rugosité est étudiée en fonction de l'amplitude et de l'orientation de la rugosité pour différents films de polyéthylène téréphthalate. Il est aussi montré que la ligne triple d'une goutte liquide étalée sur la surface ablatée est aussi affectée par l'orientation de la rugosité.

Abstract. — The smooth surface of crystalline poly(ethylene terephthalate) films is readily roughened by ablative photodecomposition obtained by absorption of the pulsed far-UV radiation of the excimer laser. The amplitude of this roughness (of the order of 1 μm) is controlled by the intensity of the pulsed radiation and by the number of pulses delivered to the surface. Structure and orientation of the roughness are determined by the crystallinity of the polymer, which is very well controlled in commercial samples. The hysteresis of the contact angle generated by the roughness, is studied as a function of roughness amplitude and orientation for different poly(ethylene terephthalate) films. It is also shown that the three phases contact line of a liquid drop resting on the ablated surface is also affected by the roughness orientation.

Introduction.

In 1982, Srinivasan [1] discovered that the irradiation of organic polymers with the high intensity far UV radiation of the excimer laser gives rise to a spontaneous etching called ablative photodecomposition (APD). One of the characteristics of this new dry etching process is that there is no heat damage on the etched surface, which makes it very suitable for etching or cutting heat sensitive substrates like polymers [2], living tissues [3] or microelectronic devices [4]. The mechanism of APD is still subject to many speculations [5].

It was very early seen [1] that the surface of poly(ethylene terephthalate) (PET) which is very smooth to begin with, gets quickly rough upon ablation with a few pulses. Only recently, we were more concerned with the origin of this phenomenon since we observed that amorphous polymers do not develop superficial roughness upon ablation. We speculated [6] that this ablation induced roughness

was due to the presence of microscopic crystallites at the surface of the PET film, which makes it heterogeneous despite its extreme surface smoothness. This theory is confirmed by the examination of a large number of samples of different crystallinity, since absence of crystallinity does not lead to a rough surface and an oriented crystallinity produces a roughness of the same orientation. We [6] showed also that the amplitude of the roughness can be controlled by the number of pulses delivered to the surface. In this work we studied the hysteresis of wetting as a function of roughness amplitude for samples differing only by their crystallinity level, and the macroscopic shape of the three phases contact line of a drop of liquid resting on these surfaces. It is shown that it is strongly affected by the orientation of the superficial roughness. We conclude that wetting measurements performed after ablative roughening of PET films can be developed as analytical tool to control the fabrication stage of the film.

Experimental section.

LASER IRRADIATION. — The laser irradiations were done with a Lambda-Physik EMG 500 excimer laser filled with the appropriate mixture of argon, helium and fluorine (193 nm) or krypton, helium and fluorine (248 nm). Each pulse (12 ns FWHM at 193 nm and 23 ns FWHM at 248 nm) delivered a maximum energy of 40 mJ at 193 nm and 100 mJ at 248 nm which did not allow us to achieve irradiations at fluence (energy per pulse) exceeding 200 mJ/cm². The energy per pulse was measured with a Gentec joulemeter. The fluence was varied by using a cylindrical lens (focal length 7.3 cm). All the laser experiments were performed in air.

POLYMER FILMS. — The PET samples were Mylar films provided by Du Pont. They were taken at different stages of the fabrication [7].

First, the amorphous film (sample A) is obtained by quenching the molten and freshly made polymer on the quench drum. The monoaxially oriented (sample MDS) film is obtained after stretching the amorphous film in the machine direction. A further stretching is done in the transverse direction yielding the biaxially stretched films, which have crystallinity oriented along two perpendicular directions. These low crystallinity samples may be annealed at different temperatures to yield different crystallinities: low crystallinity samples (sample LC) are obtained at lower annealing temperature. As will be seen below, higher annealing temperature leads to highly crystallized polymer films, (sample HC) but with a somewhat lost orientation. The biaxially stretched and annealed samples are commercially available under the name of MylarTM.

CONTACT ANGLE MEASUREMENTS. — Contact angles were measured by the sessile drop method, using a Rame-Hart Model A-100 goniometer. The measurements were done with water in a dust free atmosphere (air) at room temperature with a relative humidity of 70 %. Unlike acetone [6], water does not dissolve the irradiated PET surface.

The liquid drops were 5 μ L but the size of the drop had no influence on the contact angle. Each value reported is the average of at least two independent measurements. Reproducibility was within $\pm 2^\circ$.

Advancing contact angles were obtained by growing the liquid drop with the aid of the microsyringe whereas receding contact angles were measured by pumping some liquid out of the drop, so that the contact line started moving. The roughness is not affected by the contact with water and repeated measurements on the same spot give consistent results. This is important to be pointed out, since other authors have seen washing effect on nodules

produced by corona discharge on polyethylene surface [8].

Rough surfaces have an equilibrium contact angle θ_w (Wenzel angle) defined by

$$\cos \theta_w = r(\gamma_{sv} - \gamma_{sl}) / \gamma_{lv} = r \cos \theta_0$$

with

$$r = a/A$$

where θ_w is the Wenzel angle, θ_0 is the thermodynamic value for the smooth surface, a is the actual area of the interface and A is the *apparent* area of the *geometrical* interface.

Unfortunately θ_w , which would be a measure of a , is not easily observable. Therefore rough surfaces were characterized by both advancing θ_a and receding θ_r contact angles. The only relationship between those angles is $\theta_r < \theta_w < \theta_a$ in general, or $\theta_r < \theta_w < 90^\circ$ in the particular case of PET, since according to Wenzel's equation $\cos \theta_w$ cannot change sign.

CONTACT LINE VISUALIZATION. — The contours of the liquid drop resting on the different surfaces were extracted with an image processing system (I2S 512). The liquid drops were 5 μ L and they were observed with a microscope (Wild M 7 A). The camera, I2S Model IVC 500, was fixed on the top of the microscope. This camera, which has a two dimensional matrix of 512 $\times$ 512 pixels, was interfaced with an IBM-XT microcomputer through a Matrox single board controller. The Matrox card is essentially a memory buffer containing a digital representation of an image. Each pixel represents the intensity of light at that point to one of 256 discrete grey intensity levels.

SCANNING ELECTRON MICROSCOPY. — The SEM pictures were taken on a Cambridge Stereoscan 250 microscope. The samples were coated with $a \approx 350$ Å thick gold film prior to analysis.

Results and discussion.

LASER ABLATION CHARACTERISTICS. — APD was first described by a two step mechanism [9]: (1) Absorption of the light; (2) Ablation. Srinivasan [10] developed a new model, called the dynamic model. Ablation is a process occurring in the picosecond timescale and can be regarded as continuous within the excitation pulse. An instantaneous picture is given schematically in figure 1 and it should be emphasized that ablation occurs only when the intensity is above a well defined threshold whose value depends on the wavelength. The rate of ablation or etch depth per pulse against intensity has been measured by various authors [11] for a wide range of intensity. We recently [12] published a new method in order to measure precisely the slow etch

PHOTOABLATION

Fig. 1. — Instantaneous picture of Ablative Photodecomposition and time profile of the Intensity of the excimer laser pulse. The horizontal dotted lines labeled 193 nm and 248 nm are meant for visualization of the ablation threshold intensities.

rate in the neighbourhood of the ablation threshold. The etch curves of PET, measured by this method are displayed in figure 2 for the two wavelengths of the excimer laser used in this work. The interesting features of these curves are discussed elsewhere [13] but it is worth noting that ablation is faster at 248 nm than at 193 nm, wavelength for which the polymer is more absorbing. On the contrary, higher absorption provides a lower ablation threshold.

Fig. 2. — Ablation depth per pulse as a function of fluence measured as described in reference [12] for two different wavelengths of the excimer laser, 193 nm and 248 nm.

Below the surface left behind after ablation the polymer undergoes some modifications [6] such as expulsion of molecules like CO and CO_2 in the case of poly(ethylene terephthalate) [14]. The modified layer is composed of low molecular weight material which is soluble in acetone [6], but insoluble in water (see experimental part).

ORIGIN OF THE ABLATION DEVELOPED ROUGHNESS.

As said in the introduction the roughness appearance upon ablation at the surface of irradiated PET is due to the presence of crystallites at the surface, which makes its thermal properties inhomogeneous. It is particularly critical since the surface is transiently heated to very high temperature during laser irradiation. It is observed that the roughness amplitude increases linearly with the number of delivered pulses up to ten pulses and reaches a plateau above ten pulses. The precise mechanism of this roughness formation is still unclear, but it seems that the surface crystallinity would be responsible for temperature and surface tension inhomogeneities. An epitaxial recrystallization of the melted layer on this heterogeneous subsurface is very likely responsible for this roughness occurrence.

WETTING WITH WATER. — As we pointed out earlier [6] the surface of Mylar is very smooth. It is actually comparable to the surface of glass. It has a low enough surface tension to make a finite contact angle with water. In other words, water does not wet its surface. Hysteresis, defined as the difference between advancing contact angle θ_a and receding contact angle θ_r , is low on the surface of Mylar ($\approx 10^\circ$). Despite its smoothness, hysteresis is non zero because of a slight chemical heterogeneity due to the coexistence of crystalline and amorphous zones at the surface. The two other samples, A and MDS display a slightly higher hysteresis ($\approx 15^\circ$) probably because they present a low level of roughness. Upon laser ablation the newly uncovered surface is chemically different as we pointed out previously [6] by examination of the XPS emission spectrum. The surface ($500 \text{ \AA}$) loses some oxygen, the O1s/C1s XPS emission ratio is reduced by 35%. This causes a decrease in surface tension, more likely the polar component γ_p is reduced, and induces an increase of the contact angle with water. The important fact to note here is that this new chemical state of the surface does not vary with further laser irradiation. As we will show below, the only change occurring after the first pulse is a modification of the surface roughness, which is the parameter that we want to study.

We will therefore consider as negligible the chemical change, and its consequence on wetting, induced by irradiation with more than one pulse.

Hysteresis of contact angle is therefore induced on the surface of the four samples, as displayed in figures 3 and 4, by ablation with an increasing number of pulses. A striking fact is that the four samples of the same polymer give different results. These results can easily be related to the superficial roughness [15] developed by the treatment. In figure 5, SEM pictures of the surface roughened by ablation, are showed. The amorphous film (sample

Fig. 3. — Advancing θ_a and Receding θ_r contact angle of laser ablated PET surfaces, or contact angle hysteresis as a function of the number of delivered ablating pulses (193 nm and 100 mJ/cm²; total ablation depth 0.5 μ m). HC: Mylar of high crystallinity. LC: Mylar of low crystallinity. A: Amorphous PET Film. MDS: Machine Direction Stretched PET Film or monoaxially stretched PET. For LC, open circles and cross correspond to two perpendicular directions one of them (O) being the direction of maximum roughness amplitude. The same is true for MDS sample except that cross (+) are now the contact angle in the direction of maximum roughness amplitude.

A) exhibits a roughness of amplitude largely submicronic. In other words, unlike the other samples the amorphous film stays smooth during laser ablation, because it has no crystallinity. Therefore sample A develops only a moderate hysteresis (Figs. 3A and 4A). No significant difference is observed between the two different ablation depths 0.5 and 4 μ m respectively in figures 3A and 4A.

The three other samples are crystalline. They develop a roughness characteristic of the presence of crystallites in the polymer. The characteristic dimensions of this roughness are slightly greater than 1 μ m in periodicity and amplitude. The three pictures of figures 5B, C and D show different types of roughness. The HC sample (high crystallinity Mylar Fig. 5D) displays nodules randomly distributed on the surface which provides an isotropic roughness. This results in isotropic wetting characteristics.

When a drop of water is deposited on this surface the three phase contact line is circular (or almost circular), as shown in figure 6A. Therefore the contact angle hysteresis does not depend on the

Fig. 4. — The same as in figure 3 for a laser treatment at 248 nm and 200 mJ/cm²; total ablation depth 4 μ m.

direction of observation and the contact angle is constant along the contour. Moreover when the water droplet volume is increased, the speed of the contact line is the same in any direction. The contact angle hysteresis is clearly function of the roughness amplitude as we pointed out earlier [6].

The PET sample stretched in only one direction has a quite different laser roughened surface, as displayed in figure 5B. The roughness is constituted of parallel lines, whose direction corresponds to the direction of stretching. It is therefore a highly oriented surface. On the contrary to sample HC, the contour of water droplet resting on this surface is no longer circular but very substantially oval with a wide axis parallel to the stretching direction. It is easily comprehensible that the liquid spreads preferentially in the direction of the grooves. This is what actually happens and the contact angle hysteresis is maximum in the direction perpendicular to the grooves as displayed in figures 3MDS and 4MDS. No notable difference is seen by varying the etch depth (Figs. 3 and 4). The important result for this sample is that the picture of a single water droplet indicates the orientation of roughness which is not visible without this means by a macroscopic observation.

Sample LC has a roughness which can be considered as a mixture of that of sample HC and sample MDS. It is composed of nodules resting in a parallel alignment. Its characteristic dimensions are also of the order of 1 μ m. The orientation of the roughness is less pronounced than for the previous

A $\rightarrow 1\mu\text{m}$ B $\rightarrow 1\mu\text{m}$ C $\rightarrow 1\mu\text{m}$ D $\rightarrow 1\mu\text{m}$

Fig. 5. — SEM pictures of the different PET samples surfaces irradiated with 10 pulses of the 193 nm radiation of the excimer laser at an intensity of 100 mJ/cm^2 , total depth of ablation : $0.5 \mu\text{m}$. A : sample A or amorphous PET Film ; B : sample MDS or monoaxially stretched sample ; C : sample LC or Mylar of low crystallinity ; D : sample HC or Mylar of high crystallinity.

Fig. 6. — Contour of a water drop resting on the laser ablation roughened PET surface (248 nm and 200 mJ/cm^2). A : on high crystallinity Mylar, note that the contour is roughly circular. B : on MDS PET which has a highly oriented roughness, note that the contour is now oval and its wide axis is oriented perpendicular to the direction of highest roughness amplitude. The arrow indicates the direction of stretching.

sample, therefore the non-circularity of the contour of the water droplet is less evident. Nevertheless, a significant difference is observed when the contact angle is observed from the perpendicular directions of roughness orientation. These directions do not necessarily coincide with the stretching direction, in this particular type of sample and have to be determined by another way [16].

Ablation depth does not seem to affect significantly the wetting properties on this sample.

Conclusion.

The surface of poly(ethylene terephthalate) films, which are very smooth to begin with, reveals a roughness upon UV laser ablation, which is charac-

teristic of the crystallinity of the starting film. Wetting measurements (i.e. contact angle hysteresis, and three phases contact line observation) can reveal some microscopic features of this roughness, which are amplitude and orientation or randomness. We have observed that contact angle hysteresis may be used to determine the direction of maximum roughness amplitude in a sample with an oriented surface. This is also the direction in which the liquid spreading has the maximum resistance. In the opposite, the direction of minimum roughness offers less resistance to an advancing contact line. This results in an oval contact line. The surface of the three crystalline PET films taken at different fabrication stages can well be characterized by simple wetting measurements after UV laser ablation.

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