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The angle dependence of structure formation on excimer laser ablated ramps in stretched poly(ethylene terephthalate)

F. Wagner, P. Hoffmann*

Institute of Applied Optics, BM, Swiss Federal Institute of Technology Lausanne, CH-1015 Lausanne EPFL, Switzerland

Abstract

Excimer laser ablation of a scanned substrate shows some particularities of interest in micro fluidics compared to standard static excimer laser ablation. In particular, the surface topography of a structure, which was ablated in scanning mode, originates from the structure on the irradiated ramp. We already investigated in detail the influence of the irradiation conditions on the surface structure of the ramps and the channel floor [Appl. Surf. Sci. 154/155 (2000) 627] and found the structure to be dependent on the ramp angle. Here, we explain the reason of the observed structure changes on ablated ramps in stretched poly(ethylene terephthalate) films. The three different structures, observed on the ramps, are different stages of a suppression of the static structure formation. The latter occurs due to the frozen stresses in the material [Appl. Phys. A 53 (1991) 330]. All features of the observed structures on ramps can be explained by a component of the frozen stresses becoming inactive for structure formation, due to its geometrical orientation with respect to the ramp. Experimental evidence is given, that the suppression of the structure formation is initiated by a component of the frozen stresses perpendicular to the irradiated surface. The necessary perpendicular stress with respect to the tangential stress is different for the stress component in the ramp direction and for the component perpendicular to the ramp direction.

Keywords: Laser ablation; Structure formation; Stretched polymers; Poly(ethylene terephthalate)

1. Introduction

Since the very beginning of research in excimer laser ablation there has been interest in non-coherent structure formation occurring in polymers upon laser ablation with fluences well above the ablation threshold [3,4]. Stretched poly(ethylene terephthalate) (PET) being a frequently used polymer where a structure develops in a wide fluence range was investigated in detail by many authors. Arenholz et al. evidenced in 1991 that a structure develops only when stretched substrates are used. In uniaxially stretched PET, a ''wall-type structure'' was found to develop with its orientation perpendicular to the stretching direction. In biaxially stretched samples, a ''nap-type structure'' was found [2]. Lately, we found that upon ramp ablation in stretched PET the above-summarized characteristics are apparently no longer valid. Two structure changes occur on ablated ramps at certain ramp angles α_1 (Fig. 1b): Below the first limiting angle $\alpha^* = 10°$, the structure on the ablated ramp is equivalent to the structure of a statically ablated sample and we name it *static structure*. Between the first and the second limiting angle the *scanning structure* forms, i.e. the structure aligns with the direction of the ablated ramp (as defined by the gradient). It also

* Corresponding author: Tel.: +41-21-693-60-18; fax: +41-21-693-37-01.
E-mail address: patrik.hoffmann@epfl.ch (P. Hoffmann).

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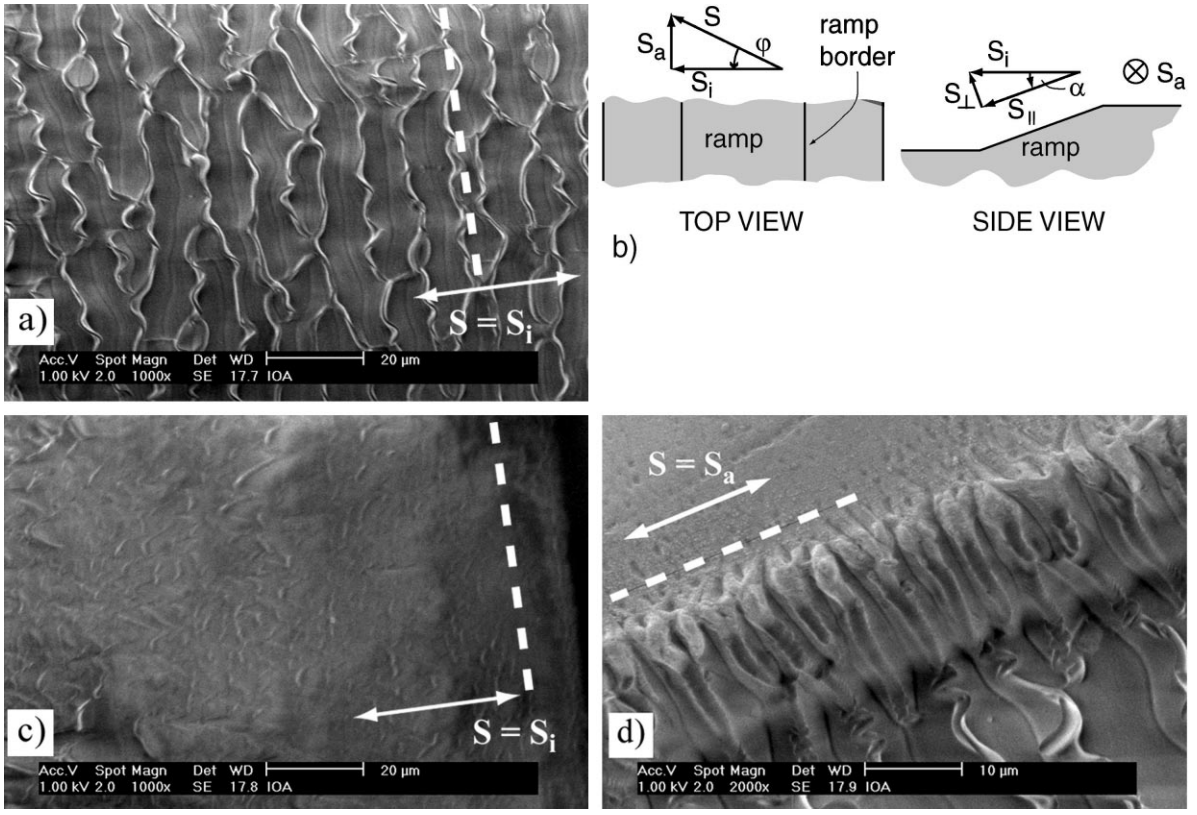

Fig. 1. SEM micrographs of structures on ablated ramps in uniaxially stretched PET. The dashed lines give the direction of the ramp border, the ramp direction is perpendicular to this. The double arrows indicate the direction of the frozen stress ***S***. In (a), (c) the stresses are oriented in the direction of the ramp. In (d) the stresses are oriented parallel to the ramp border. The ramp angles α are: (a) 2.2°; (c) 11°; (d) >70° (Fluence = 1000 mJ/cm^2, 200 shots, 10 Hz pulse repetition rate). Whereas (b) shows a schematic of the stress orientation in the sample and defines the symbols used for the different components of the stress vector ***S***, which originates from sample stretching.

shows no longer naps, even in biaxially stretched polymers. Above the second limiting angle ($\alpha^{**} = 25°$) finally, a smooth surface was observed. Up to now, the nature and reason for these structure changes were not known. However, it was already clear, that the angle of incidence for the laser light has no influence, and that the α_1 are independent of the laser fluence (75–1200 mJ/cm^2) [1].

2. Experimental

As a starting point for the sample fabrication, we used an amorphous 500 μm thick PET film (Goodfellow). We then used two methods in order to produce uniaxially oriented samples: (i) we stretched pieces of 3 cm × 2 cm at room temperature in a traction test machine (809 Axial/Torsial Test System, MTS) with a constant bracket speed of 5 mm/min. The deformation occurred with necking and resulted in highly oriented slightly hazy samples [5]; and (ii) samples with different degrees of chain orientation were prepared by stretching pieces of 1 cm × 3 cm at 80°C, i.e. above the glass transition temperature and below the melting temperature of PET, to draw ratios (DR) between 1.5 and 4.0. For this purpose, a testing system MTS 810 equipped with an interface MTS 458 and a temperature chamber regulated at 80 ± 0.5°C by means of a temperature controller (Barber Coleman) was used, and the deformation rate was 0.003 l/s. The samples

were quenched after fabrication in order to avoid crystallization, which was not initiated by the chain alignment itself. The procedure resulted in transparent samples with slightly enhanced crystallinity at draw ratios >2 [6].

Ramps were ablated in the samples by opening a freestanding molybdenum mask during the irradiation with an ArF excimer laser at 50 Hz pulse repetition rate. We used 200 pulses at a fluence of 1000 mJ/cm^2 and varied the ramp angle α between 2.2 and 70° by changing the velocity and distance of the mask movement [1].

3. Results and discussion

Fig. 1a, c and d show SEM micrographs of the structure on ramps that were ablated in PET samples, which were stretched uniaxially at room temperature. In Fig. 1a, c the stretching direction (indicated by the double arrow), i.e. the direction of the frozen stress $\boldsymbol{S}$ in the material, is in the direction of the ramp. In this case the ramp becomes smooth at $\alpha \geq \alpha^* = 11°$ without any intermediate structure. In Fig. 1d the stretching direction was perpendicular to the direction of the ramp, i.e. parallel to the ramp border. No structure change could be observed in this configuration, even at $\alpha = 70°$. In fact, the formation of the static structure could even be observed on the walls of the ablated region (Fig. 1d). In a third experiment (not shown) we oriented the stretching direction at 45° with respect to the ramp border. In this case the orientation of the structure, which was perpendicular to stretching direction for $\alpha \leq \alpha^*$, was in the direction of the ramp for $\alpha \geq \alpha^*$, and the structure formation was completely suppressed for $\alpha \geq \alpha^{**}$. Thus, when considering a sample with frozen stress vector $\boldsymbol{S}$, its component $\boldsymbol{S}_i$ (Fig. 1b) becomes inefficient for the formation of the static structure on the ramp for $\alpha \geq \alpha^*$. On the contrary, the component $\boldsymbol{S}_a$ (Fig. 1b) is active for the structure formation process on the ramp at all ramp angles $\alpha \leq \alpha^{**}$, and even at $\alpha > \alpha^{**}$ if no stress component perpendicular to the irradiated surface exists. Otherwise said, the stress field, which is responsible for the structure formation on the ramp at $\alpha^* \leq \alpha \leq \alpha^{**}$, is always of the uniaxial type with the stress vector oriented parallel to the ramp border. Here "always" means for biaxially stretched and uniaxially stretched substrates with arbitrary orientation between sample and ramp. This explains all features of the scanning structure: (i) the vanishing of the naps in biaxially stretched substrates (the active stress field is of uniaxial type), and (ii) the alignment of the structure orientation with the ramp direction (the active stress field is oriented perpendicular to the ramp direction).

We performed another experiment in order to obtain more information about an eventual stress dependency of the limiting angle from where on $\boldsymbol{S}_i$ becomes inactive for structure formation. That is, we determined the limiting angles α^* in the sensitive configuration ($\boldsymbol{S} = \boldsymbol{S}_i$) for samples with different chain alignments and slightly different crystallinities. The samples were prepared, following the description given by Chang et al. [6]. We found for all samples of DR ≥ 2 the same limiting angle $\alpha^* = 13 \pm 1°$. For the samples with DR ≤ 1.5 no structure formation could be observed, even with static ablation ($\alpha = 0°$). The stretching process aligns the polymer chains more and more (as seen for example by birefringence) but it also enhances the crystallinity of the samples with DR ≥ 2.5. Due to the creation of new crystallites, representing knots in the rubber network, it is probable that the frozen stresses are constant in these samples.

Independently of a probable saturation of the frozen stresses all observations can be explained by the following theory: The formation of the static structure requires a certain minimal frozen stress in the sample [2], which was not reached for DR ≤ 1.5. The component $\boldsymbol{S}_i$, or better $\boldsymbol{S}_\parallel$, of the frozen stresses becomes inactive for structure formation, if $\boldsymbol{S}_\perp / \boldsymbol{S}_\parallel \geq \tan(\alpha^*) \approx 0.23$. The component $\boldsymbol{S}_a$ of the frozen stresses becomes inactive for structure formation, if $\boldsymbol{S}_\perp / \boldsymbol{S}_a \geq \sin(\alpha^{**})/\tan(\varphi) \approx 0.5$ (for $\varphi = 45°$).

4. Conclusion

The structure changes on ablated ramps in stretched polymers are caused by the fact that above a certain ramp angle the component of the frozen stresses, being in the direction of the ramp, becomes inactive with respect to the formation of the static structure. Thus, above this limiting angle the active stress field on an ablated ramp, in an arbitrarily stretched substrate, is similar to one in an uniaxially stretched

substrate with the stretching direction parallel to the ramp border. The origin of the successive suppression of the static structure formation is the component of the stresses, which is perpendicular to the irradiated surface.

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