

## Mechanical properties of SiO<sub>x</sub> coated PET films characterized by AFM equipped with micro tensile stage

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### Abstract

Direct observation of early stage fragmentation of nanosized SiO<sub>x</sub> coating deposited by PECVD on poly(ethylene terephthalate) (PET) film substrates is investigated by means of micro tensile device coupled with atomic force microscope (AFM). This arrangement allows fast measurement of fragmentation patterns of SiO<sub>x</sub> coatings with thickness below 30 nm. Nanometer thick SiO<sub>x</sub> coatings are deposited on three grades of PET films containing pre-determined anti-blocking particle density ranging from 0 to 1800 mm<sup>-2</sup>. Crack onset strain and fragment densities of SiO<sub>x</sub> coatings are compared with previously obtained data from SEM observations. The results confirm the negative influence of anti-blocking particles on mechanical properties of coatings. The cohesion strength and the interfacial adhesion are modeled using a constant interfacial strength approach with a Weibull-type probability of fracture.

### 1. Introduction

Its outstanding mechanical and optical properties give bioriented PET (BOPET) films widespread uses in the packaging industry for conditioning numerous varieties of food products. The processability of such films is improved in particular by anti-blocking particles embedded in the polymer melt before the film forming stage. These particles induce micron size protuberances surrounded by a thin polymer skin, forming protrusions of few hundreds of nanometers height above PET surface.

As showed by Sobrinho et al. [1] these particles have negative effect on the barrier properties of thin oxide coatings, such as those deposited by plasma enhanced chemical vapor deposition (PECVD) on PET films in order to improve the film's barrier properties [2]. Effectively, they induce sites of barrier defects [3] and internal stress of the oxide layer [4]. The mechanical performance of the coated film, such as cohesive strength of the thin oxide layer and its adhesion to the polymer substrate, might be strongly modified because these two factors are controlled by the defect structure and internal stress state of the oxide, as well as by process induced modifications of the interfacial region and of the polymer substrate [5]. This might results in a loss of barrier against diffusion of oxygen, water vapor and aromas.

In order to characterize the mechanical performance of such polymer substrates coated with ultrathin oxide coatings (of thickness less than 30 nm), uniaxial fragmentation has shown to be one of the most relevant technique [6]. This method, in which the progressive development of a crack pattern in the coating is analyzed as a function of substrate elongation, has proven to be very efficient as a means of determining the coating cohesion and adhesion to the substrate in cases where the substrate is more compliant than the coating. A method to characterize the mechanical properties of the coated film using scanning electron microscopy (SEM) has been developed by Rochat et al. [6]. This is time-consuming, and requires depositing an additional conductive layer on the coating in order to dissipate the charges accumulated at the film's surface, thus being able to observe the very first cracks in the coating. A precise control of the effects induced by this conductive layer is required in order to avoid creating measurement artifacts, which is definitely a limitation of the technique.

In order to circumvent to those limiting factors, the authors propose a new technique in order to determine the mechanical properties of thin oxide coatings plasma-deposited on polymer substrates. The cohesive and adhesive properties were derived from the analysis of uniaxial fragmentation tests carried out on a micro tensile device coupled with atomic force microscope (AFM). The cohesive strength of the coating was thereafter determined assuming a Weibull probability of failure of the oxide, and the coating/substrate interfacial shear strength (IFSS) was calculated by means of a stress transfer analysis with a perfectly plastic interface.

To validate the analysis method, 10 and 20 nm thick silicon oxide coatings were deposited on 3 grades of PET substrates presenting different additives population at the surface. These additives were shown in a previous study to impact the defect population within the coating, therefore affecting both the barrier and mechanical performance of the system [3, 6]. The measurements are reproduced with the AFM tensile stage, and the obtained results are confirmed.

## 2. Experimental

### 2.1 Materials

Thin silica coatings ( $\text{SiO}_x$ ) were deposited by plasma enhanced chemical vapor deposition from oxygen-diluted hexamethyldisiloxane (HMDSO) vapor on 12  $\mu\text{m}$  BOPET films. Oxide coating thicknesses were determined by XRF centered on the fluorescence signal of silicon atoms (Philips, PW4025 MiniPal Spectrometer). For aim of demonstration, 10 and 20 nm thick silica coatings were studied. Three types of co-extruded, biaxially oriented films made of polyethylene terephthalate (PET), provided by Mitsubishi Polyester Films, Wiesbaden, were investigated. RNK12 (Hostaphan<sup>®</sup> RNK, 12  $\mu\text{m}$ ), RDO12 (not commercialized RDO, 12  $\mu\text{m}$ ) and RHB12 (Hostaphan<sup>®</sup> RHB, 12  $\mu\text{m}$ ) were chosen because of their different surface topography. While the surface structure of one surface of RDO12 and RHB12 was the same as standard RNK12, the functional surface side (on which the coating was applied) displayed an extremely regular structure at the polymer surface with very low roughness due to stepped down quantity of anti-blocking particles for RDO12, and due to the presence of a thin additive-free PEN layer for RHB12. The films were characterized by reflection optical microscopy to specify the number density of anti-blocking particles at the polymer surface, as discussed in a previous communication [3]. The particles density was found to be of 1710 and 290  $\text{mm}^{-2}$  for the RNK12 and RDO12 substrates respectively, whereas RHB12 presented a defect-free surface.

### 2.2 Fragmentation

For determining  $\text{SiO}_x$  cohesive strength and  $\text{SiO}_x$ -PET interfacial shear strength (adhesion strength), uniaxial fragmentation tests were carried out on a micro tensile device coupled with an atomic force microscope (VEECO Dimension 3100, Digital Instruments). The samples were mounted in the elongation cell placed in the microscope and were stepwise loaded up to predefined nominal strain levels  $\epsilon$ . Coating cracks in  $\text{SiO}_x$  layer initiated when the coating cohesive strength was reached, resulting from the transfer of tensile stress of the PET substrate through interfacial shear. The cracks propagate almost instantaneously across the sample width, perpendicular to the tensile direction. At each selected strain, the crack density, defined as the inverse of the average fragment length, was determined by dividing the number of counted cracks on a micrograph by the micrograph length. The result was multiplied by  $(1+\epsilon)$  for taking into account the substrate crack opening between fragments.

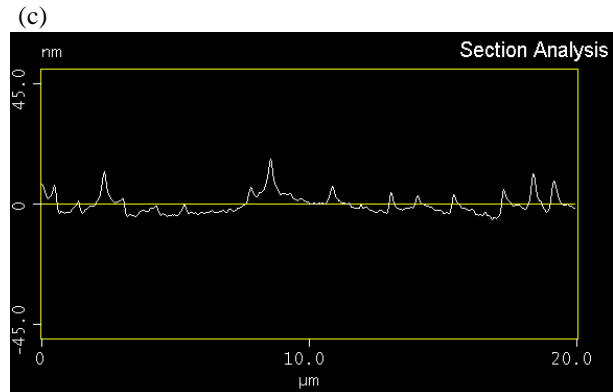
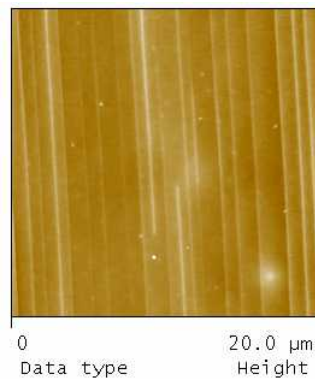
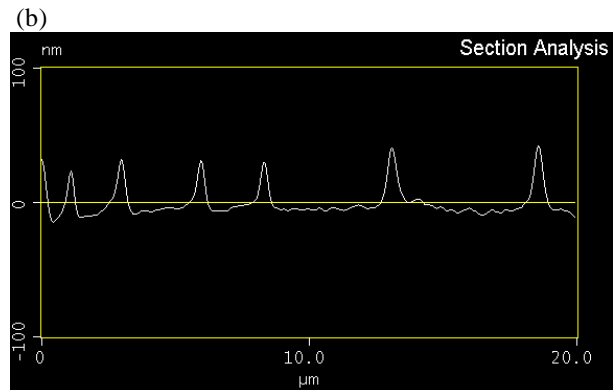
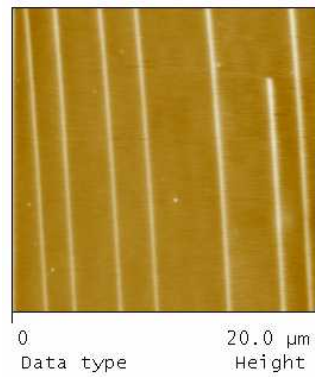
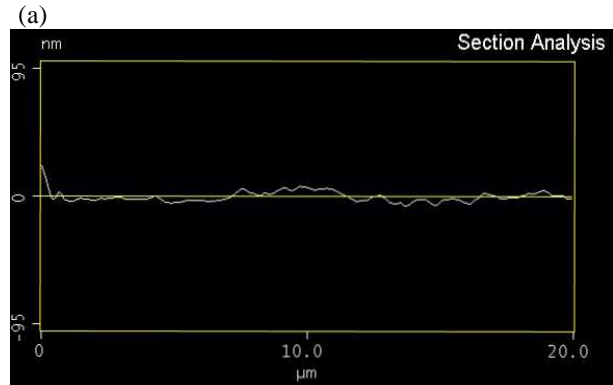
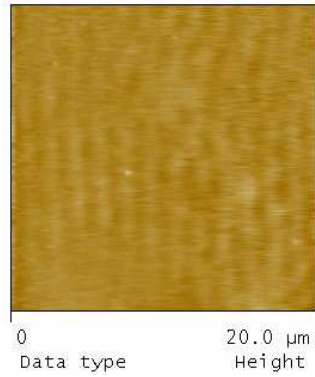
## 3. Results and discussion

### 3.1 Fragmentation process

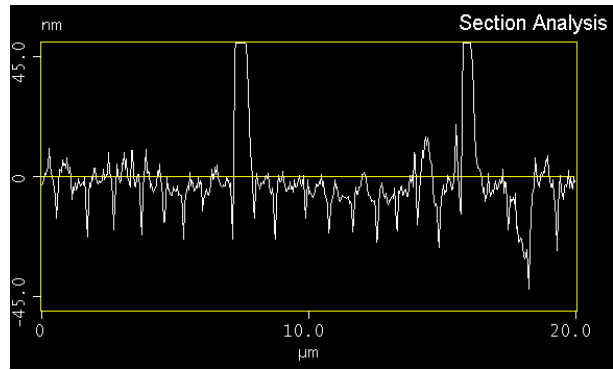
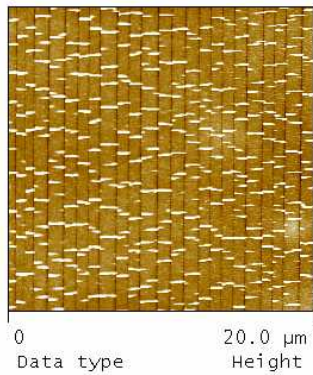
During its progressing straining on the tensile stage, the stress applied to the PET substrate is transferred to the coating by shear through the interface. The behavior of the coating/substrate system can be described in 3 definite steps, and the stepwise deterioration of the coating with increasing strain is shown in Figure 1:

- I. Before the stress in the coating reaches its cohesive strength, thus leading to the appearance of cracks, unexpected wrinkles are observed perpendicularly to the tensile direction. As these wrinkles do not cause fracture of the coating, they do not affect the barrier properties (at least in a first approximation). Some further analyses are requested in order to determine the cause for these wrinkles, which could be due to local relaxation of the bioriented polymer;
- II. As the stress in the coating reaches its cohesive strength, the first cracks are observed which propagate perpendicularly to the tensile direction. This crack onset behavior is characteristic of the coating resistance. In addition, we observe an increase of the density of wrinkles;
- III. As the nominal strain is further increased, the crack density increases, and finally reaches a saturation level, which is determined by the capacity of the interface to transfer the stress from the substrate to the coating and thus of the interfacial adhesion. The density of wrinkles finally decreases, and cancels before the crack density at saturation is reached (see Fig. 3).

**Figure 1:** Evolution of coating surface pattern investigated by AFM with increasing applied strain for a RDO12 substrate coated with a 10 nm thick SiO<sub>x</sub> coating (left column) with a corresponding height scan throughout the width (right column). a) 0 % strain: Initial non-damaged coating surface. b) 3% strain: Appearance of first wrinkles on the coating surface, without cracking the coating. c) 5% strain: Appearance of first cracks in addition to surface wrinkles. d) 15% strain: Appearance of transverse buckling failures in the coating when cracking process comes close to saturation.

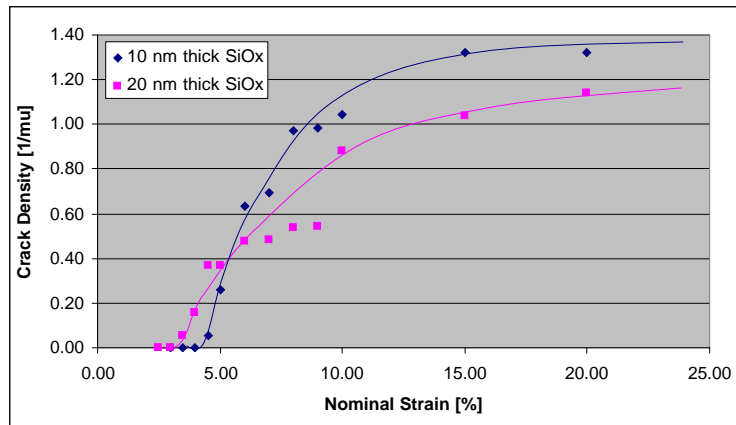


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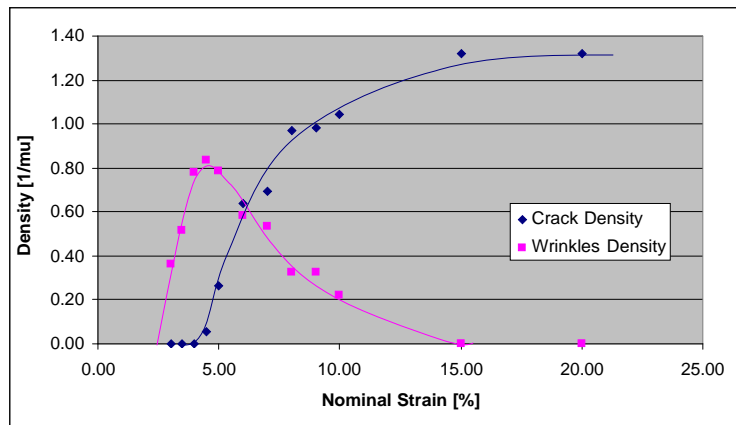


The evolution of the crack density in the coating layer as a function of the applied nominal strain is given in Figure 2 for 10 and 20 nm thick coating onto RDO12 substrate. In parallel, Figure 3 compares the evolution of the density of cracks and wrinkles as a function of nominal strain for a 10 nm thick SiO<sub>x</sub> coating on RDO12 substrate.

**Figure 2:** Evolution of the coating crack density as a function of the applied strain for 10 and 20 nm thick SiO<sub>x</sub> coatings onto RDO12 substrate.



**Figure 3:** Evolution of the density of cracks and wrinkles as a function of the applied strain for a 10 nm thick SiO<sub>x</sub> coating onto RDO12 substrate.



### 3.1.1 Crack onset strain

The crack onset strains obtained for the different materials tested are listed in Table 1.

*Table 1: Crack onset strain for the systems tested*

PET substrate	SiO <sub>x</sub> Coating thickness [nm]	Crack Onset Strain [%]

RNK12	20	3.0%
	10	3.5%
RDO12	20	3.5%
	10	4.5%
RHB12	20	3.6%
	10	4.5%

As experienced in previous works [5], the crack onset strain increases with decreasing thickness for all substrates studied. In addition, the presence of processing additives in the superficial layers of the RNK12 polymer substrate is shown to lead to a decrease of the coating crack onset strain by up to 25% compared with the additive-free substrates (RHB12 and RDO12). This is mainly caused by additional microdefects created by plasma arching around additive particles, due to dielectric variations in the plasma environment [3].

### 3.1.2 Crack density saturation

The crack density at saturation obtained for the different materials tested are listed in Table 2.

Table 2: Crack density at saturation for the systems tested

PET substrate	SiOx Coating thickness [nm]	Crack density at saturation [ $\mu\text{m}^{-1}$ ]
RNK12	20	1.44
	10	1.63
RDO12	20	1.14
	10	1.32
RHB12	20	1.08
	10	1.80

The crack density at saturation is shown to be strongly dependent of the tested system, as it is a combination of both the coating cohesive strength, and the interfacial resistance. The decrease of the coating thickness leads to an increase of the crack density at saturation in all cases, which is due to the fact that less energy is needed to fracture of thinner coating (assuming equivalent interfacial adhesion).

### 3.2 Coating cohesive strength

In order to determine the mechanical properties of the coated system, the early stages of the fragmentation process were analyzed assuming a Weibull-type size-dependent probability of failure for the coating fragments. The size-dependent coating cohesive strength of a fragment of length  $l$  was thereafter deduced:

$$\sigma_{\max}(l) = \beta \cdot (l/l_0)^{-1/\alpha} \cdot \Gamma(1+1/\alpha) \quad (\text{Eq. 1})$$

Where  $\alpha$  is the Weibull shape factor,  $\beta$  is the Weibull scale factor and  $l_0$  is a normalizing length taken equal to 1  $\mu\text{m}$ . The parameters  $\alpha$  and  $\beta$  were determined according to the method described by Leterrier et al. [7]. It has to be noticed that in this analysis the internal stresses in the coating were neglected, which is relevant in a first approximation for such system.

A useful characterization of the resistance of the coating layer is given by evaluating (Eq. 1) for coating fragments of length equal to the critical stress transfer length,  $l_c$ , defined as the smallest fragment that can undergo failure. The latter is related to the crack density at saturation,  $CD_{\text{sat}}$ , by  $l_c=2/(1.337 CD_{\text{sat}})$  [8].

### 3.3 Interfacial shear strength

The adhesion strength between the coating and the substrate was assessed according the perfectly plastic approach from the Kelly-Tyson model, assuming a constant interfacial shear stress equal to the interfacial shear strength,  $\tau$ :

$$\tau = \frac{2 \cdot h_c \cdot \sigma_{\max}(l_c)}{l_c} \quad (\text{Eq. 2})$$

Table 3 gathers the values of the critical fragment length, the Weibull parameters, and the cohesive and adhesive strengths for the 3 systems studied.

Table 3: Mechanical properties for the tested systems

PET substrate	Coating thickness [nm]	$l_c$ [ $\mu\text{m}$ ]	$\alpha$	$\beta$ [GPa]	$\sigma_{\max}(l_c)$ [GPa]	$\tau$ [MPa]
RNK12	20	1.04	6.3	3.4	3.2	120.0
	10	0.92	3.9	4.5	4.2	95.5
RDO12	20	1.45	7.8	4.1	3.6	90.2
	10	1.13	9.2	4.9	4.5	119.2
RHB12	20	1.39	11.4	3.2	2.9	84.6
	10	0.83	20.7	3,9	3.8	91.5

The interfacial shear strength shows no direct relation with neither the coating thickness, nor the presence of additives in the superficial layers of the substrate, and can in a first approximation be considered as constant with a value around 100 MPa. This value which is similar to the cohesive strength of the substrate demonstrates the covalence of the interfacial bonds created by the plasma deposition process.

On the contrary, the Weibull parameters and, as a consequence, the coating cohesive strength, are strongly dependent on the coating thickness and on the substrate surface morphology.

First of all, the Weibull scale parameter  $\beta$  is shown to decrease with increasing coating thickness, which confirms that the population of critical defects in the coating increases with increasing thickness. This is one reason for the decrease of crack onset strain with increasing thickness mentioned in [5].  $\beta$  does not seem to be significantly affected by the presence of superficial additives; effectively, whereas its values are higher with the RDO12 substrate compared to the RNK12 one, they are lower with the RHB12.

Secondly, the variation of the Weibull shape parameter  $\alpha$  shows no clear correlation with the coating thickness, whereas it is significantly higher in the case of the RHB12 substrate. This higher value reflects a narrower distribution of the population of critical defects, and therefore leads to a more homogeneous probability of fracture throughout the coating when increasing the applied strain. This contributes to an increase in the crack onset strain.

From these evaluations, it can be determined that the reason for the increased of the crack onset strain in the cases of substrates with smoother superficial layers has to be linked with different properties of the coating/substrate system. Whereas in the case of the RDO12 substrate, the absence of surface additives clearly leads to a decrease of the population of critical defects, thus increasing the coating's intrinsic strength, in the case of the RHB12 substrate, the PEN surface layer appears to modify the deposition process, and despite creating a coating with lower intrinsic strength, leads to a narrower distribution of defects with decreases the probability of failure at low strain.

Those results demonstrate that the presence of additives in the superficial layer of a polymeric substrate might lead to a significant decrease of the mechanical properties of inorganic barrier coating deposited onto it. The additives have been shown to decrease the crack onset strain of  $\text{SiO}_x$  coatings by up to 25%, and it has been demonstrated that this was due to a decrease of the density of critical defects and/or to a broadening of the critical defect distribution, thus increasing the probability of failure at low strains.

This correlates perfectly with what has been observed using in-situ in a scanning electron microscope fragmentation, thus proving that investigations of fragmentation process using AFM provides a reliable and fast method to determine the mechanical properties of ultra-thin coatings on polymers, as no specific preparation of the samples is required. In addition, high resolution of AFM has made possible the observation of initial wrinkles, which have also been shown to develop before initial coating cracking; this need nevertheless to be confirmed by further investigations, and its cause has to be determined.

#### 4. Conclusions

Fragmentation monitored in-situ by an AFM module has shown to be a versatile technique in order to characterize barrier films made of ultra-thin coating deposited on a polymer substrate, being more efficient and precise than the existing evaluation methods.

This experimental technique coupled with a basic analysis of the stress distribution allows determining the mechanical properties of the coating as well as of the interfacial region. This has permitted to analyze the mechanical properties of silicon oxide coatings plasma-deposited on 3 different PET substrates presenting different surface patterns, including the presence or not of processing additives. Results of previous analyses carried out using electron microscopy have been confirmed by demonstrating the detrimental impact of the process additives on the mechanical properties of barrier coatings.

Finally, this method has revealed the appearance of wrinkles at the film's surface before the development of cracks damaging the barrier properties. This phenomenon, which might have been hidden when using electron microscopy, requires more investigations.

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