

Microstructural and Mechanical Properties of PECVD Films on Polyester Films

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Abstract

This short communication reports on an on-going study of the mechanical properties of PECVD SiO_x coatings on PET, primer coated PET and PEN substrates. Preliminary results have found that the internal stress and strain of the coatings are all compressive and relatively low. There was no significant difference in either the stress or strain between the films. The cohesion of the deposited coating on PEN is the strongest and on PET is the weakest. It was also found that the adhesive strength between the coating and primer coated PET is greater than for either plain PET or PEN substrates.

Introduction

The properties of transparent metal oxide layers deposited on flexible plastic substrates are of interest to the display industry for the future development of flexible displays. In the past, work reported by the Oxford research group has mainly focused on the performance of PVD coatings. PVD films tend to be rigid and are susceptible to fracture during the converting process causing the loss of barrier performance. It has been reported elsewhere that in comparison PECVD films exhibit improved adhesion, stretch-ability, flexibility as well as good gas barriers properties[1]. This short communication presents early results of an on-going study into the mechanical properties of PECVD coatings on polyester substrates.

Theory

Internal stress/strain measurements

In-plane deposition-induced internal stresses, σ_i , were calculated using the radius of curvature of the films before, R_1 , and after, R_2 , deposition [2] using equation (1):

$$\sigma_i = -\frac{E_s h_s^2}{6(1-\nu_s)h_c} \left(1 + \frac{h_c}{h_s} \left(4 \frac{E_c}{E_s} - 1 \right) \right) \cdot \left(\frac{1}{R_2} - \frac{1}{R_1} \right) \quad (1)$$

E_s and E_c are the Young's moduli of substrate and coating respectively, ν_s is the substrate Poisson's ratio and h_s and h_c are the respective thicknesses. Compressive stresses are denoted as being negative. The radii R_1 and R_2 of the samples supported freely on two vertical aluminium plates were measured with an Olympus SZH binocular lens. The Young's modulus of SiO_x is assumed to be 80 GPa, following

literature reports [3]. The Young's modulus of the substrates (PET and PEN) were found to be 4.8 GPa and 5.8 GPa respectively after tensile testing, and the Poisson's ratio assumed to be 0.3 (manufacturer's data).

Cohesive strength

The cohesive strength of the coating, σ_{max} , can be estimated from the early stages of tensile failure of the thin coating during loading of the substrate, assuming a two parameter Weibull distribution [3]. In this model the average fragment length at small strains is equal to $l_0(\sigma/\beta)^{-\alpha}$ where l_0 is a normalizing factor of 1 μm , σ is the axial stress in the coating and α and β are the strength distribution parameters, derived from a linear extrapolation of the initial part of the crack density (CD) v strain plot in logarithmic coordinates.

With these parameters the coating strength at critical length $l_c = \frac{3}{2}\bar{l}$, \bar{l} being the inverse of the CD in the saturation regime of the fragmentation process [4], is:

$$\sigma_{max}(l_c) = \beta(l_c/l_0)^{-1/\alpha} \cdot \Gamma(1 + 1/\alpha) \quad (2)$$

Where Γ is the gamma function.

Adhesive Strength of Coatings on Polymer Substrate.

The adhesion between the coating and polymer, defined as the interfacial shear stress, τ , is derived from the CD at saturation following an adapted version of the Kelly-Tyson model [4,5,6].

$$\tau = 1.337 h_c \sigma_{max}(l_c) CD \quad (3)$$

where h_c is the coating thickness.

Experimental Procedure

Fabrication of the films was performed by Applied Process Technologies Inc. (Tucson, USA), who used a pilot roll-to-roll coater with a web width of 150 mm to deposit PECVD SiO_x layers using their high density PDP source technology. The substrates were 125 μm thick poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN) films, and 175 μm thick primer coated PET supplied by Dupont Teijin Films. The films were plasma pretreated using nitrogen gas and a web speed of 0.6m/min. Precursor gases hexamethyldisiloxane (HMDSO) and oxygen were used at a flow rate of 50 sccm and 30 sccm respectively to deposit a SiO_x layer of 1 μm thickness. The base pressure during deposition was 20 mTorr. Microstructural studies were conducted using a confocal, atomic force and scanning electron microscopes.

In the fragmentation test [4], the onset and development of cracking of the brittle coating is monitored as a function of the applied uniaxial tensile load in-situ under an optical microscope. Rectangular film specimens (approx 40x10 mm) undergo tensile loading in a computer-controlled Minimat unit (Rheometric systems) by means of a stepper motor (load 200 N). This unit provides measurement of displacement with an accuracy of 1 μm . Accurate measurement of specimen strain was achieved by a non-

contact video extensometry technique described by Leterrier *et al* [5]. The tensile unit was placed under an optical microscope (Olympus BX60) for analysis. Cracking of the coating was analyzed at increasing strain levels in terms of crack density, defined as the inverse of the average fragment length (l) and calculated from the average number of cracks, N_i , counted on k micrographs of width W at strain ε , as

$$CD = (1 + \varepsilon) \sum_{i=1}^k N_i / kW \quad (4)$$

The factor $(1 + \varepsilon)$ corrects for crack opening to the first approximation.

Results and Discussion

Microstructural Studies

Surface morphology studies of 1 μm -thick PECVD coatings deposited on the three substrates established that the roughness of the coated surface depended on that of the uncoated substrate surface. It was found that the primer and PET samples had the roughest and smoothest surface respectively, as shown in Figure 1 and Table I. Fine-scale defect analysis of features less than a micron showed that there was no significant difference in the defect size and density between the samples.

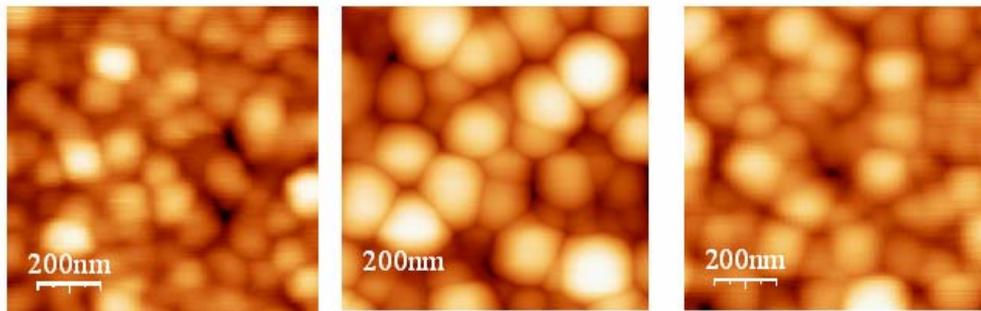


Figure 1 AFM images of SiO_x coatings on PET (left), Primer PET (middle) and PEN (right)

Table I Surface roughness, average grain size and defect analysis of PECVD SiO_x coatings on 3 different substrates.

Substrate	Substrate RMS* (nm)	Coating RMS* (nm)	SiO_x average particle size (nm)	Defect density (μm^{-2})	Defect Surface Coverage (%)
PET	0.8	1.5	143±25	16±13	1.95±1.52
Primer PET	2.4	6.2	230±68	6±3	0.76±0.28
PEN	0.9	3.0	172±46	9±4	1.01±0.57

* Scan area 1 μm x 1 μm

Internal Stress/Strain Measurements

Considering the coating thickness, the calculated internal stresses and strains are compressive and relatively low (see Table II) compared to previously reported values for SiO_x /polymer films [4]. This observation may be related in part to the presence of organic matter in the deposited coatings, a common feature when fabricating layers by PECVD. Table II also shows that there is no significant difference in either the stress or strain levels observed between the samples.

Table II The internal stress and strain values of PECVD SiO_x Coatings on Different Polymer Substrates.

Substrate	Substrate thickness (μm)	Coating thickness (μm)	Internal stress (MPa)	Internal Strain (%)
PET	125	1	-142 ± 25	-0.12 ± 0.02
Primer PET	175	1	-160 ± 39	-0.14 ± 0.03
PEN	125	1	-182 ± 5	-0.16 ± 0.01

Cohesive Strength

The crack onset strains for the PECVD films listed in Table III (shown also in Figure 2) are significantly higher than those predicted for an equivalent 1 μm thick PVD coating, which would be about 0.4% [4]. The coating on PEN seems to be the strongest – it has the highest cohesive strength of the three and the highest crack onset strain (see Table III). The next strongest is the coating on the primer surface which shows superior properties to the coating on the plain PET. α is the Weibull shape parameter controlling the defect size distribution, and β is a scale parameter. The value of α is generally higher for all our coatings than equivalent silica coatings reported in the literature [4-6], showing that there is a relatively narrow Weibull defect distribution in these coatings. The strength, however, is much lower than for values found in the literature – the reason for this is the much greater thickness of the coatings used in this study (1 μm compared to 10-100nm).

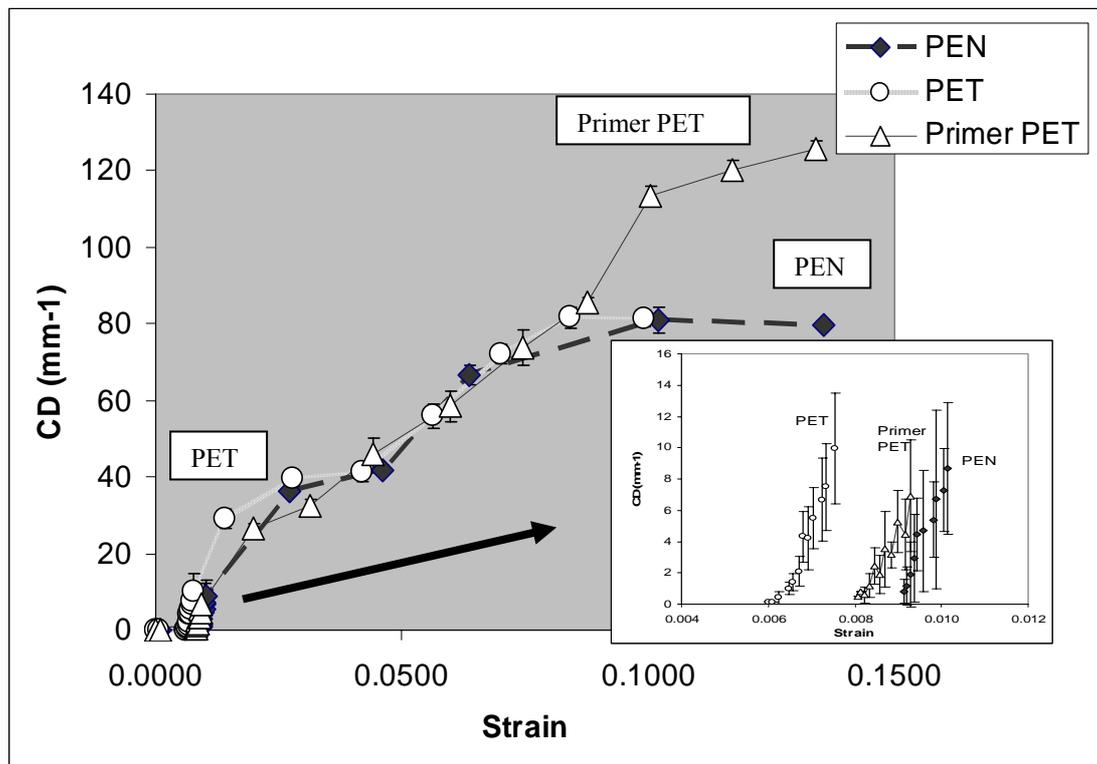


Figure 2. Crack Density v Strain for the three coated substrates. Insert shows a close-up of the crack onset and early fragmentation region.

Table III The Cohesive Strength of PECVD SiO_x Coatings on Different Polymer Substrates.

Sample	Crack Onset Strain %	α	β (MPa)	$\sigma_{\max}(I_c)$ (MPa)
PET	0.68 ± 0.07	23 ± 10	390 ± 40	650 ± 120
Primer PET	0.82 ± 0.02	20 ± 4	460 ± 35	780 ± 25
PEN	0.92 ± 0.06	27 ± 8	570 ± 95	850 ± 40

Adhesive Strength of the SiO_x Coatings on Different Substrates.

It is immediately evident when looking at Table IV that adding the primer to PET almost doubles the interfacial shear stress (IFSS). The primer is a thin coating of various acrylate species, and has a higher density of functional groups compared to PET which increases the extent of interfacial bonding. The primer surface is also significantly rougher so there is an increase in surface area between the two components which will enhance the adhesion properties.

The interfacial shear stress between the coating and PEN also appears greater than for the PET sample. This may be due to the mechanical properties of the substrates rather than interfacial bonding. The shear yield stress of PET is found to be lower than that of PEN using the Von Mises relationship [4] ($\tau_y = \sigma_y/\sqrt{3}$ where τ_y is the shear yield stress and σ_y is the tensile yield stress of the polyester film). The values of shear yield stress for the substrates are the same as their corresponding IFSS in the case of PET and PEN, showing that the shear behaviour of the interface and the bulk polymer are comparable in each composite. It therefore appears that the greater IFSS value for coated PEN is due to the superior shear properties of the substrate.

Table IV The Adhesive Strength of PECVD Coatings on Polyester Films

Sample	Crack onset strain %	Strain at saturation %	CD _{sat} mm ⁻¹	τ MPa	τ_y substrate MPa
PET	0.68 ± 0.07	10	84 ± 6	66 ± 16	~ 55
PEN	0.92 ± 0.06	12	77 ± 6	87 ± 8	~ 80
Primer PET	0.82 ± 0.02	12	116 ± 3	121 ± 7	~ 55

Conclusions

An outline of an on-going study of the mechanical properties of PECVD SiO_x coatings deposited on PET, primer coated PET and PEN substrates has been presented. The main findings are listed below:

- The internal stress and strain are all compressive and relatively low for the deposited coatings. No significant difference in either the stress or strain values is observed between the samples.
- The coating on PEN seems to be cohesively the strongest. The next strongest is the coating on the primer surface which shows superior properties to the coating on the plain PET.
- The adhesion strength between the coating and PEN is greater than for the PET. The presence however of a primer on PET almost doubles the interfacial shear stress.

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