

The Mechanical Properties of Metal Oxide Coated Polyester Films.

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Abstract

This communication reports on a study of the microstructure, mechanical and gas barrier properties of PECVD metal oxide coatings on heat stabilised (HS) PET [poly(ethylene terephthalate)], primer-coated HS PET, filled PET and PEN [poly(ethylene naphthalate)] substrates. The coatings are highly conformal and exhibit very few large scale defects. Internal stresses in the coatings are found to be compressive for all substrates. The substrate is found to influence some of the mechanical properties with the cohesive strength of the coating greatest for primer-coated HS PET and lowest on filled PET. Secondly, a primer layer also increases the adhesive strength between coating and substrate compared to plain PET and PEN.

Substrate surface roughness is found to influence the morphology of the SiO_x films but does not seem to adversely affect the barrier performance of the composites. We found that heat stabilised PET, with or without an additional acrylate primer layer and PEN produce superior composites than untreated PET film in terms of water vapour barrier. Using a mass spectrometry detection technique we measured a WVTR value as low as $2 \times 10^{-4} \text{ g m}^{-2} \text{ day}^{-1}$ for 1 μm thick coatings on PEN.

Introduction

The mechanical and barrier properties of oxide layers deposited on flexible plastic substrates are of interest to many areas of development, including flexible batteries, solar cells, displays and smart cards. This paper reports our observations of the microstructural, mechanical and barrier properties of plasma enhanced chemical vapour deposited metal oxide coatings on polyester substrates. The mechanical properties, such as the adhesion and cohesion strength of the deposited layers have been investigated and the coating microstructurally characterized using a combination of scanning electron and atomic force microscopy. The gas barrier properties of the films have also been studied.

Experimental Procedure

Fabrication of the films was performed by Applied Process Technologies Inc. (Tucson, USA), who used a pilot roll-to-roll coater to deposit PECVD SiO_x layers using their high density PDP source technology [1]. 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. The primer layer is a thermally cross linked terpolymer of 3 acrylate monomer species, and is designed to improve adhesion of layers to the film. Also investigated was a 75 μm thick PET film with 0.21 weight % of china clay filler particles (F-PET). All the materials were supplied by Dupont Teijin Films.

The films were plasma pretreated using nitrogen gas and precursor gases hexamethyldisiloxane (HMDSO) and oxygen to deposit a SiO_x layer of 1 μm thickness. Microstructural studies were conducted using confocal, atomic force and scanning electron microscopes. The fragmentation test [2- 4] was used to establish the cohesive and adhesive properties of the coatings. In-plane deposition-induced internal stresses were calculated using the radius of curvature of the films before and after deposition. The water vapour transmission rate (WVTR) was measured using a MOCON Permatran instrument (MOCON Co., W 3/31). Measurements were taken at atmospheric pressure and 100% relative humidity, at temperatures of between 30 and 50°C.

Results and Discussion

Physical Properties of Coatings

X-ray diffraction analysis showed the silicon oxide coatings to be amorphous, with no crystallinity apparent. X-ray photoelectron spectroscopy (XPS) analysis indicated that the silica is sub-stoichiometric at $\text{SiO}_{1.8}$ and the coatings were estimated to contain 18-25% carbon by atomic composition.

The high levels of carbon present in these films are most likely a consequence of using a relatively high flow rate of HMDSO in the deposition process so that some (totally/partially) unreacted monomer is incorporated into the film, as well as methyl (CH_3) radicals that are present in the plasma, and results in a slight colouring of the samples, though not to the same extent as others reported by this group. A small absorption in the UV-visible region between 320 and 450 nm is observed.

Surface Morphology Studies

The plain PET has the smoothest surface with an rms roughness of 0.8 nm. The heat stabilised PET surface is rougher with 1.5 nm. Significantly, if we look at the morphology of this surface it appears much more consistent with that of a crystalline surface than the plain PET counterpart.

The subsequent deposition of an acrylate primer on the HS PET increases the roughness significantly to 6.4 nm. This surface is also found to be more hydrophilic than PET (a contact angle for water of 67° opposed to 78° for PET) due to a greater density of functional carbonyl groups. Finally, the PEN surface is similar in morphology to that of the PET but is found to be rougher with an R_q of 1.5 nm over a 1 x 1 μm area. The contact angle of water on this surface is 83° due to the lower proportion of oxygen in its chemical structure.

The F-PET film contains 0.21 % china clay particles by weight. These particles protrude from the surface and increase the roughness. On a 20 x 20 μm scan it is clear to see filler particles which protrude from the surface by up to 400 nm and surrounding the particles appear to be trenches up to 100 nanometres deep. The number of particles detected in a series of AFM scans were counted and measured and found to show a particle density of approximately 4000 mm^{-2} .

Regarding 1 x 1 μm images taken in between the particles, the PET surface is very similar to that of unfilled PET surfaces.

The deposited SiO_x is found to coat the substrate conformally, and fully covers protruding filler particles. By examining a series of SEM images we find a minimum of pinhole and other

large-scale defects ($>0.5 \mu\text{m}$ in diameter), the defect density being less than 100 mm^{-2} . For the filled PET film this is a much lower density than for the china clay particles (4000 mm^{-2}) indicating that they do not create defects in the deposited film. The coatings on the plain PET film display more pinholes, approximately 300 mm^{-2} , which is most likely due to the relatively poor surface quality of this film. The roughest substrate, the HS PET_P, produces the roughest coating.

The quantity of nanometre-scale defects in the SiO_x was estimated by counting dark areas of contrast between the silica grains in the AFM images. Such areas are thought to be possible starting points for tortuous permeation pathways through the coating material, responsible for the transport of water vapour through the film. For the $1 \mu\text{m}$ thick SiO_x on each substrate the coverage of defects detected in the films is less than 1% and the average number of defects less than $10 \mu\text{m}^{-1}$.

Mechanical Properties of Films

Internal Stress Measurements

The internal stresses for SiO_x on the polyester substrates were measured and the results are shown in Table I. Internal stresses in the coatings are found to be compressive for all substrates.

Table I Internal stress values for PECVD SiO_x coatings on different substrates.

Substrate	Internal Stress (MPa) 1000 nm SiO_x
F-PET	-78 ± 14
HS PET	-483 ± 20
HS PET_P	-517 ± 16
PEN	-195 ± 18

The stress values for the filled PET are negligible and much lower than for the other films. Initially it was thought that the filler particles may have been responsible for stress concentrations in the silica that resulted in cracking and therefore stress relaxation. However, no cracks were observed in these samples by AFM/SEM and no obvious degradation in barrier is noticed for these samples. It was noted however that the coated film has a much larger radius of curvature in the machine direction of the roll with a stress level of 400-600 MPa. This phenomenon is not observed to be significant for the other composites. The F-PET film is anisotropic in that it has poorer mechanical properties and is much more prone to shrinkage in the machine direction, whereas the other films are fairly isotropic, especially in terms of thermal shrinkage. Perhaps preferential curvature in the machine direction, due to the anisotropy of the substrate (as it shrinks preferentially in the MD), results in little curvature in the transverse direction and the resultant low stress. The curvature in the MD also makes it hard to measure that in the TD and it is possible that the curvature was underestimated in the TD.

For the remaining samples the stress is much higher in the SiO_x on PET films and this could be a result of substrate thermal shrinkage as the plain PET is much more susceptible to this

than the other films. The coating on PEN is under less stress than on HS PET. The suggestion is that the internal stresses for the silica on the PEN and heat stabilised substrates are completely due to the growth related stress or differences in LCTE values and there is some natural variation in the deposition conditions.

Cohesive Strength

Table II shows the cohesive strength for 1 μm -thick coatings on four substrates with the superior properties of the HS PET_P composite being noticeable. The coating on the F-PET substrate is the weakest coating.

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

Substrate	$\max(l_c)$ GPa
F-PET	1.00 ± 0.03
HS PET	1.39 ± 0.26
HS PET_P	1.66 ± 0.11
PEN	1.3 ± 0.1

A pertinent factor may be the heating effect caused by deposition, which increases the temperature at the polymer surface to or above the region of T_g . Such heating may cause relaxation of constrained amorphous chains and in addition could induce crystallisation at the surface. The molecular motion of polymer chains at the surface may be responsible for creating defects in the interfacial region. The coating deposition process will cause substrate heating, therefore the heat stabilised PET and PEN composites see less deterioration in quality than the filled PET as they are more resistant to heat. Coatings on the primer-coated HS substrate suggest that the primer surface is not adversely affected by the heating experienced during deposition. Maybe, because the temperature of deposition is greater than the T_g of the acrylate, the surface of this film will be soft and allow the oxide to stick easily and form a dense layer without the acrylate molecules contracting and moving the initial SiO_x deposits around. Because the acrylate chains are not so stretched they are not expected to relax during deposition.

Adhesive Strength of the SiO_x Coatings on Different Substrates.

For the films shown in Table III it is interesting to note that the intrinsic interfacial shear strength (IFSS), σ_y , is found to be equal to, or greater than, the substrate shear yield stress σ_y for each composite. The IFSS is much greater than the estimated shear yield stress of the substrate for the heat-stabilised PET film. This is most likely a result of the increased degree of surface crystallization (which has been observed using AFM). A high degree of crystallisation is known to increase the tensile yield stress (hence shear yield stress) of PET. So for HS PET it appears that the crystalline surface morphology caused by heat treatment strengthens the polymer in the interfacial region allowing a superior IFSS to be observed that matches that of PEN.

Table III Interfacial shear stress values for SiO_x films on polyester substrates.

Substrate	σ , MPa	σ_y polymer (MPa)
Filled PET	79 ± 4	~ 58
HS PET	89 ± 33	~ 52
HS PET_P	120 ± 17	~ 52
PEN	85 ± 9	~ 80

The addition of the primer layer to the HS PET causes the IFSS to increase to above 110 MPa for this composite. Such a high IFSS value could be due to the increased functionality of the primer surface (shown by XPS and water contact angle measurements) resulting in substantially increased covalent bonding at the interface but the acrylate itself must also have superior mechanical properties.

Gas Barrier Properties

WVTR values for 1000 nm thick SiO_x on PET was found to be 0.19 g m⁻² day, but, however for HS PET, HS PET_P and PEN the rates are all below the limit of 0.01 g m⁻² day that our system can reliably measure. This signifies a barrier improvement of at least 750 times.

Mass spectrometry was used to characterise the WVTR of 1000 nm SiO_x on PEN, with the experiment carried out by Technolox Ltd, U.K. The value of WVTR for the 1000 nm film on PEN was found to be 2×10^{-4} g m⁻² day⁻¹ at 20°C. This represents an improvement of ~ 5000 times over the bare substrate and is lower than WVTR's reported in the literature for single layer SiO_x. What makes the performance more impressive is that the silica is deposited using a roll-to-roll process that is traditionally hard to perform for PECVD.

With the knowledge that the coating is deposited in layers by passing it through the deposition zone multiple times, it is possible to suggest that the initial layer is most prone to defects as it is in contact with the substrate, where debris and substrate thermal effects can cause imperfections in the silica, and is a poor barrier. Subsequent layers "block off" existing defects in the layer immediately below so that no defects propagate through the whole film after a number of layers are deposited. It is possible that the layers deposited directly upon silica rather than the substrate nucleate more densely and are intrinsically better barriers. The principle of this structure is similar to the multilayer stacks of inorganic/organic material but it has the advantage of not needing to deposit polyacrylate layers in between the oxide. However, the multilayer stacks have lower reported values of WVTR than the best SiO_x film reported here.

Conclusions

The microstructural, mechanical and water vapour barrier 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 coatings have very few large scale defects.
- The internal stresses are all compressive for the deposited coatings.

- The coating on primer coated PET is cohesively the strongest. The strength of coatings on heat stabilised PET matches that on PEN.
- The adhesive strength between the coating and primer coated PET is greater than for the PEN. Heat stabilisation of the PET enables the coating adhesion to match that on PEN.
- A WVTR value of $2 \times 10^{-4} \text{ g m}^{-2} \text{ day}^{-1}$ at 20°C has been measured for 1 µm thick coatings on PEN.

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References

- 1) J. Madocks, J. Rehwinkle and L. Barton, Proceedings of the Society of Vacuum Web Coaters, (2004)
- 2) Y. Leterrier, L. Boogh, J. Andersons and J.-A.E. Månson, *J. Poly. Sci. B: Polym. Phys.* **35**, 1449, (1997)
- 3) Y. Leterrier, *Prog. Mater. Sci.* **48**, 1, (2003)
- 4) Y. Leterrier, L. Medico, F. Demarco, J.-A.E. Månson, U. Betz, M.F. Escola, M. Kharrazi Olsson and F. Atamny, *Thin Solid Films* **460**, 156, (2004)