High-performance AlOx thin films for next-generation sustainable flexible packaging: Part 2

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AlO_x has long been touted as a suitable transparent layer for packaging applications and indeed has found use in a range of retort applications based on high-performance PET substrates. However, the drive toward sustainable-packaging solutions using a polyolefin "mono-material" architecture has resulted in an increased desire to use softer, reduced-stiffness substrate materials. Standard reactive evaporation of these AlO_x thin films no longer can be used to deposit high-quality, mechanically resilient coatings capable of surviving downstream converting at high yield. Alternative substrate-engineering techniques and/or AlO_x-deposition technologies therefore are required to compensate for these effects. This paper describes the use of an engineered-BOPP substrate in combination with a high-density, plasma-assisted, AlO_x-deposition technique and focuses on the fundamental differences in mechanical & resultant barrier performance achievable with both the standard reactive deposition and plasma-assisted deposition approaches. Conclusions also are provided indicating the inherent suitability of the plasma-assisted approach for high-yield, high-performance, transparent-barrier solutions required for the next generation of sustainable flexible packaging.

Editor's Note: *This technical paper is based on the authors' presentation at the 2022 AIMCAL R2R Europe Conference held June 7-9, 2022, in Valencia, Spain. Part 1 of this paper covered AlOx deposition technologies and their intrinsic layer properties, and mechanical characteristics and crack behavior under tensile loading.*

The complex interplay between the mechanical properties of the substrate & the AlO_x layer itself ultimately control the tensile behavior of the coated substrate. The crack onset strain (COS) is related to the AlO_x layer thickness, h_c, the layer fracture energy-release rate, G_c, the AlO_x layer elastic modulus, E_c, & Poisson's ratio, v_c and finally the elastic contrast parameter of the Dundurs parameters, $g(\alpha;\beta)$. This relationship can be described by Equation 1 [3].

EQUATION 1.
$$COS = \left(\frac{2G_c(1 - v_c^2)}{\pi h_c E_c g(\alpha;\beta)}\right)^{1/2}$$

The crack onset strain can be maximized by reducing the AlO_x layer thickness and the elastic contrast function value while maximizing the fracture energy-release rate. The elastic contrast function value is itself dependent upon the plain strain elastic mismatch between the substrate skin layer and the deposited AlO_x layer described by the so-called Dundurs α parameter shown in Equation 2 [12-13].

EQUATION 2.
$$\alpha = \frac{\overline{E_c} - \overline{E_s}}{\overline{E_c} + \overline{E_s}}$$

$\overline{E_c}$ and $\overline{E_s}$ represent the plain strain elastic moduli of the AlO_x layer and the substrate skin layer, respectively. The plain strain moduli are related to the specific material elastic modulus and Poisson's ratio, as defined by Equation 3.

EQUATION 3.
$$\overline{E_i} = \frac{E_i}{(1 - v_i^2)}$$

Here, $\overline{E_i}$ represents the plain strain modulus, $\overline{E_i}$ represents the substrate or AlO_x layer's elastic modulus, and v_i
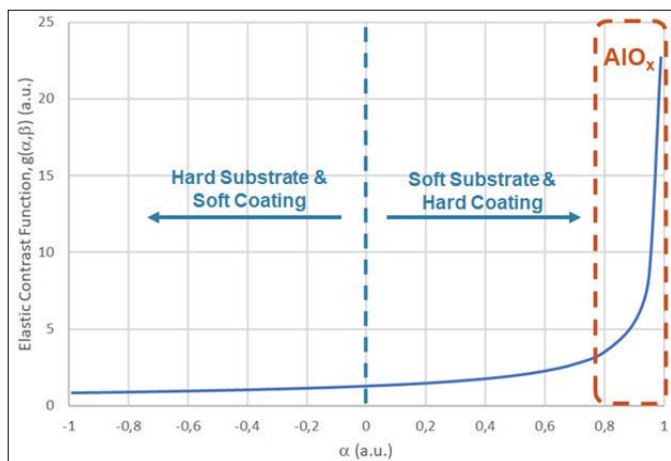
FIGURE 5. *Elastic contrast function variation as a function of Dundurs α parameter [12].*

represents the substrate or AlO$_x$ layer's Poisson's ratio, respectively. When a "soft" & flexible substrate is combined with a "hard" & stiff AlO$_x$ coating, the net result is a high elastic-contrast function value, as shown in Figure 5. The larger this elastic mismatch, the lower the resultant crack onset strain observed for the specific substrate / AlO$_x$ material couple. As such, successful AlO$_x$ layer deposition on softer polymeric substrate materials, such as the polyolefin-based substrates BOPP, CPP and PE, requires significant additional improvements in elastic mismatch to ensure continued coating integrity under tensile loading conditions.

Benefits of "buffer layers"

This elastic mismatch can be minimized through use of a mechanical "buffer layer." This buffer layer serves to reduce the mismatch between the primary substrate material and the AlO$_x$ layer. Engineered polyolefin substrates typically used in mono-material packaging often employ EVOH or PVOH outer skins to both reduce the mechanical property mismatch to the vacuum-deposited oxide layer and to significantly improve the substrate's barrier performance. EVOH and PVOH skin layers also exhibit more hydrophilic

surface-group terminations that more readily support AlO$_x$ layer nucleation and growth than typical polyolefin surfaces. As such, the use of these materials, as an integral part of the engineered substrate skin, provides a path toward reducing the elastic contrast function value while maximizing the fracture energy-release rate, thereby enabling improvements in crack-onset strain.

The impact of elastic contrast function engineering on barrier performance can be seen in Figure 6. As the Dundurs α parameter value increases (see Table 2), a decrease in barrier improvement factor (BIF) can be observed. The analysis shown here uses the barrier improvement factor to effectively normalize the substrate-dependent impact and is defined by the ratio of the barrier performance of the uncoated substrate relative to that of the AlO$_x$ coated substrate. A significant difference in BIF also is observed between the two AlO$_x$ material types. Functional barriers can be deposited only on stiff substrates or substrates that employ interface engineering to reduce the elastic mismatch (e.g., PET and EVOH-skinned BOPP). However, the more robust plasma-assisted AlO$_x$ material could be used to create a functional barrier on the full range of substrates tested both with and without skin-layer engineering. This is despite a near two-fold increase in elastic modulus relative to standard reactive AlO$_x$ and predominantly is attributed to the high fracture energy-release rate and fracture toughness of the high-power plasma-assisted coating.

The final coated substrate performance levels referred to in Figure 6 are provided in traditional form in Table 3.

Impact of layer performance on secondary converting

Typical converting processes for AlO$_x$ coated substrate materials involve the gravure application of a topcoat prior to lamination and graphics printing. Each of these steps possesses the ability to damage the brittle AlO$_x$ coating following tension application during web handling. The more robust high-density, plasma-assisted AlO$_x$ material shows increased propensity for use in high-yield, high-volume, transparent-barrier manufacturing.

As shown in Figure 7, the barrier level can be successively improved following the application of both a protective topcoat and the subsequent lamination / printing steps. This improvement can be at levels of up to 10x relative to the as-deposited material, depending upon the specific topcoat and lamination chemistries used. The performance of standard AlO$_x$, in contrast, only improves after topcoat application and

TABLE 2. *Impact of packaging substrate & AlOx layer type on Dundurs α parameter.*

Substrate	AlO$_x$ Type	α (a.u.)
Commodity PET	Reactive	0.84
Commodity PET	Plasma Assisted	0.91
BOPP With EVOH Skin	Reactive	0.87
BOPP With EVOH Skin	Plasma Assisted	0.93
Commodity BOPP	Reactive	0.90
Commodity BOPP	Plasma Assisted	0.94
Commodity CPP	Plasma Assisted	0.95
Commodity LDPE	Plasma Assisted	0.99

FIGURE 6. *Water vapor barrier improvement factor vs. Dundurs α parameter.*

The provision of an intermediate-stiffness buffer layer reduces the risk of the ceramic layer cracking under tensile loading. Improvements in deposition technology also have enabled the preparation of ultra-robust transparent AlO_x materials, exhibiting higher crack onset strain levels than are achievable using conventional reactive evaporation techniques. The use of a high-plasma-density, hollow-cathode array system to activate & ionize the deposition precursors results in the deposition of a higher performing, mechanically robust, transparent AlO_x layer. The combination of an EVOH-skin-enhanced BOPP substrate together with this plasma-assisted approach ultimately enables the preparation of barrier solutions compatible with secondary conversion under high-volume manufacturing conditions. ■

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any further expected barrier performance improvement following lamination. This is, in fact, offset by crack generation during handling. Consequently, barrier-performance improvement levels of around 3x relative to the as-deposited levels are more typically observed.

As stated earlier, the high-density, plasma-assisted AlO_x can be converted successfully without an additional topcoat due to its inherent mechanical robustness. EVOH-skinned PEs, including MDOPE, have been used to create fully converted packages with WVTR and OTR levels better than 1 gsm/day & 0.1 cm^3/m^2/day, respectively, without significant yield loss during conversion. Similar performance levels have been observed with SiO_x using buffer-layer-supported polyolefin substrates, demonstrating the value of combining skin-layer engineering and use of mechanically robust, ceramic-layer processing.

Summary

The drive toward mono-material-based recyclable packaging has resulted in a renaissance in polyolefin substrate engineering. Modified skin layers now are available to interface with vacuum-deposited ceramic layers typically used in transparent-barrier applications.

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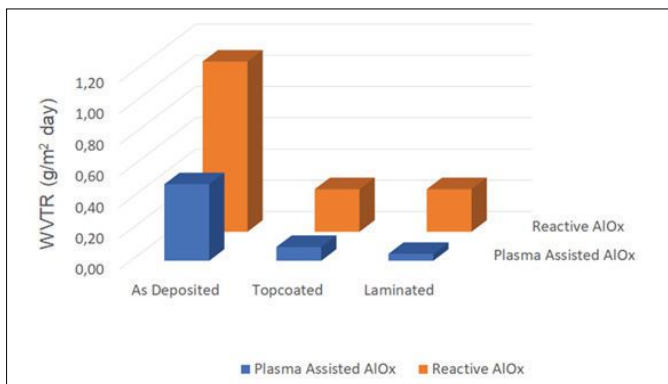
TABLE 3. *Impact of packaging substrate and AlOx layer type on optical transmission and barrier performance*

Substrate	AlO_x Type	Transmission (%)	WVTR @ 38°C/90% RH (g/m² day)	OTR @ 23°C/50% RH (cm³/m² day)
Commodity PET	Reactive	~ 88-90	< 1.0	< 1.5
Commodity PET	Plasma Assisted	> 99	< 0.5	< 0.5
BOPP With EVOH Skin	Reactive	~ 88-90	< 0.5	< 0.2
BOPP With EVOH Skin	Plasma Assisted	> 99	< 0.3	< 0.2
Commodity BOPP	Reactive	~ 88-90	< 7.0	< 50
Commodity BOPP	Plasma Assisted	> 99	< 0.3	< 35
Commodity CPP	Plasma Assisted	> 99	< 0.4	< 40
Commodity LDPE	Plasma Assisted	> 99	< 1.5	< 150

FIGURE 7. *Impact of conversion on barrier performance for reactive and plasma-assisted AlOx deposited on PET*

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