Transparent SiO_2 barrier coatings: conversion and production status

Eric Finson and John Felts

ABSTRACT: Silicon oxide-based thin film coatings were deposited onto polyethylene terephthalate and oriented polypropylene with a plasma-based process in roll-to-roll equipment ranging from 0.3 to 1.5 meters wide. The current status of silicon oxide-coated polymer barrier performance, along with the conversion status, including specific inks, adhesives, and primers used to make laminated structures, is presented. Barrier performance of generic packaging structures is also discussed.

KEYWORDS: Bonding strength, coatings, deposition, flexible packaging, oxides, plasma, plastic films, polyethylene terephthalate, polypropylene, silicon compounds, vapor barriers.

Thin-film gas barrier depositions were introduced to the packaging industry through aluminum metallization of polymer substrates in the 1970s. Aluminized films have proven to be very useful in the packaging area, and their use has grown over the years. Transparent thin-film barrier materials based on oxides of silicon and aluminum, which give performance similar to an aluminization process without the opaque nature of a metal layer, were introduced to the packaging industry and continue to be developed for commercialization. The transparent webs are microwaveable and allow direct measurement with metal detectors during and after the fabrication of finished packages. There is also the perception that these transparent barriers are more environmentally friendly than conventional polyvinylidene chloride (PvDC) or polyvinyl chloride (PVC) clear barrier materials (1–3). Two methods of depositing the silicon and aluminum oxides are currently being commercialized: evaporation (for both aluminum and silicon oxides) and chemical plasma deposition (for silicon oxide only). This paper focuses on silicon dioxide depositions made using the plasma process only.

Finson is a senior research scientist and Felts was business manager at Airco Coating Technology, 420 Pike Lane, Concord, CA 94524.

Discussion

Transparent SiO_2 barrier films were deposited from plasma decomposition of 1,1,3,3-tetromethyldisiloxane (TMDSO) or hexamethyldisiloxane (HMDSO), oxygen, and helium in a 40-kHz plasma discharge onto polymeric webs. The films were deposited at 50 mTorr process pressure (**Fig. 1**). Common polymer packaging films polyethylene terephthalate (PET) and biaxially-oriented polypropylene (OPP) were used as substrates. Three plasma systems were used to deposit the films: a 0.3-m web width research machine, a 0.66-m web width pilot production machine, and a 1.5-m web width production-scale commercial coater. All of the machines feature roll-to-roll systems, although there are some configuration differences among them (**Fig. 2**).

Oxygen and water vapor transmission rates were measured using equipment based on Modern Controls (Mocon) technology and standard ASTM methods: oxygen transmission rate (OTR), ASTM D-3985, and water vapor transmission rate (WVTR), ASTM F-1249. The equipment was retrofitted specifically to maximize sample throughput and improve test accuracy/reproducibility. A dedicated sensor was installed on each of the ten test cells of the Mocon oxygen transmission station, facilitating a throughput of over 200 samples/week. A special manifold and water bath circulation system on the Mocon water

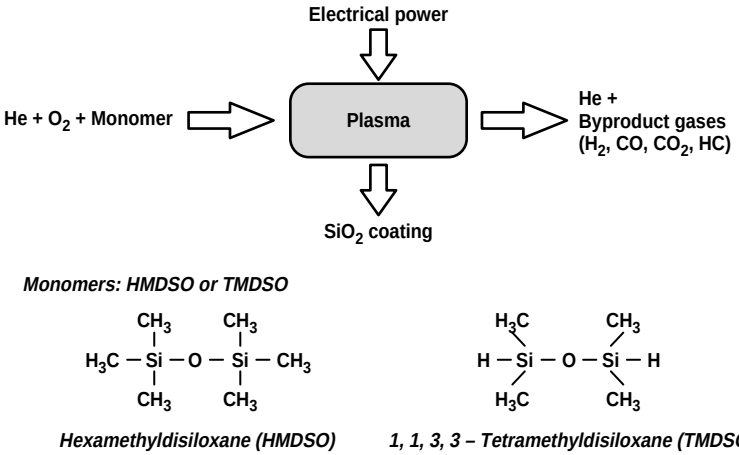
vapor equipment reduced temperature variation of the test cells to ± 0.5°C, allowing quicker equilibration.

Statistically significant interlaboratory correlation studies were routinely performed with outside testing laboratories to assure measurement accuracy and relevance as well as to reduce the need for incoming quality control testing. Thicknesses of deposited coatings were determined directly on the PET and OPP material using an X-ray fluorescence technique (Asoma model 200/400 benchtop unit). This measurement, quantifying the SiO_2 barrier coating thickness to ± 5 nm, helped establish an internal qualitative measurement of process stability.

The barrier properties achieved to date on PET and OPP are listed in **Figs. 3 and 4.** The 1.5-m-wide production machine is being statistically characterized to determine process capability and maximum production speeds. **Figure 5** indicates that the OTR barrier of the plasma-deposited SiO_2 coating is insensitive to humidity change. This is an advantage over conventional clear barrier technologies, such as ethylene vinyl alcohol (EVOH) resins, which are moisture sensitive.

The large-scale acceptability of transparent barrier materials is dependent on the ease of convertibility as well as their cost and performance in unlaminated form. To date, much work has focused on the deposition processes used to create transparent barrier coatings, principally on PET, and little effort was spent on commercializing transparent thin-film gas barriers through standard flexible packaging conversion and testing. The conversion process offers many obstacles to the success of transparent barriers and can drastically affect market acceptance. The balance of this paper focuses on establishing that plasma-deposited, silicon dioxide-coated PET is suitable through packaging conversion.

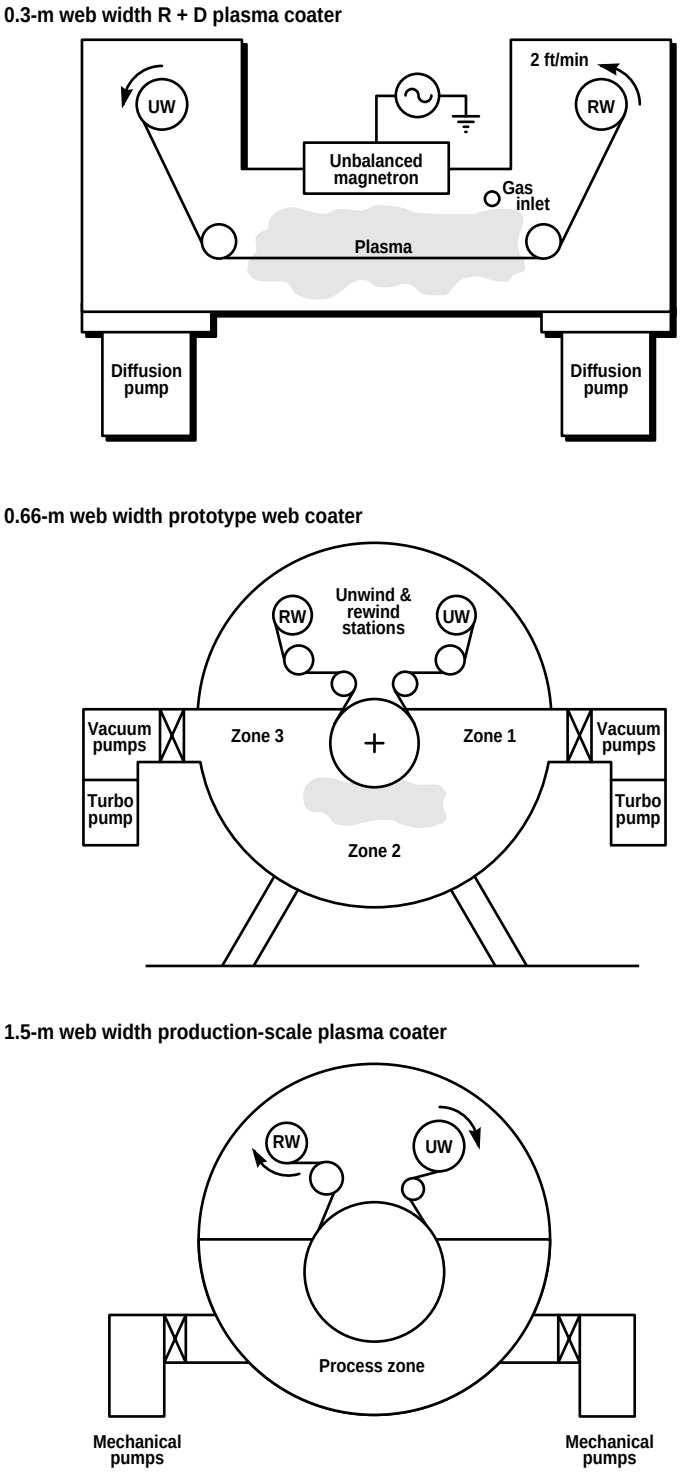
1. Low-pressure SiO_2 plasma deposition process



I. Dry-bonding adhesive lamination results (laboratory screening tests)

Adhesive	*Structure*	*Coating weight, lb/RM dry*	*Bond strength, g/in.*	*Heat seal strength, g/in.*
Takeda A-520/A-50 (Aged 4 days @ 40°C)	PET (SiO_2) adhesive/1mil CPP	2.3	850	7500
Liofol/Henkel (Europe) Tycel 7909/7283 (Aged 24 hours)	PET (SiO_2) adhesive/1mil LDPE	2	Film tear	Film tear
Century C-1045 + 5% catalyst (Aged 7 days)	PET (SiO_2) adhesive/1 mil CPP	1.8–2.0	460	Not tested

2. Plasma roll coaters



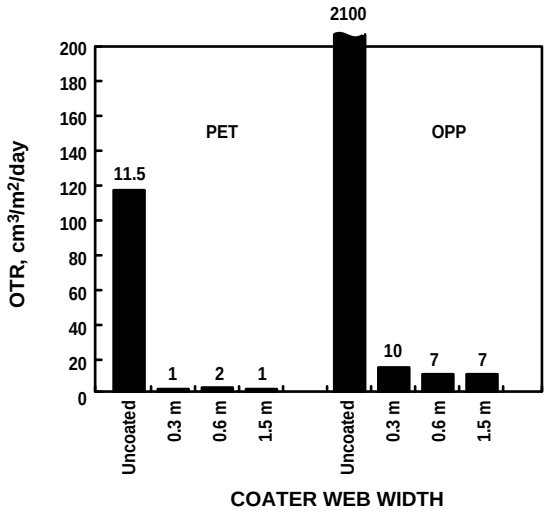
SiO_2-coated PET

Table I contains bond strength results generated from laboratory screening tests performed by adhesive suppliers. This was done to determine which adhesive products would provide the best bond strength results with the plasma-deposited SiO_2 coatings in typical flexible packaging constructions. Note that all of the adhesive suppliers indicated that even better bond strength results could be achieved under production conditions. Additionally, several packaging converters have successfully adhesive-laminated the SiO_2 surface, maintaining barrier properties with excellent bond results. **Table II** lists some typical examples of these properties after adhesive lamination in various constructions. Once laminated in a suitable construction, the SiO_2 barrier coating was successfully converted into filled finished packages on vertical form fill seal and horizontal form fill seal equipment.

Very good extrusion lamination bond results were simulated in the laboratory using a water-based preprimer with low-density polyethylene; this work was performed by MICA Corp. The G-782 primer, when diluted 1:1 with water, provided very good bond results, especially when the SiO_2 barrier surface was lightly corona treated (to 40 dynes/cm) to improve the water-based primer wettability (**Table III**). **Table IV** shows some examples of the barriers before and after extrusion coating/laminating. These data show that the SiO_2 barrier coating can maintain its properties through extrusion lamination processing conditions if handled properly.

Suitable printing systems for use with the plasma SiO_2 barrier coatings were also determined. Recommendations for solvent-based and aqueous systems are available (**Table V**). Some of the work resulting from the laboratory testing performed by Croda Inks is contained in **Table VI.** Good ink adhesion, while maintain-

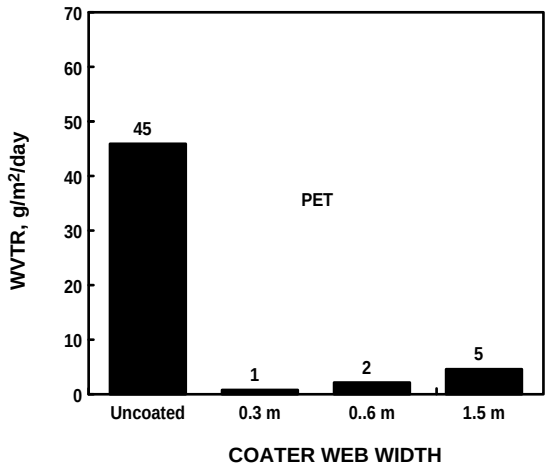
3. OTR of PET and OPP with SiO_2 coating in different machines



Test conditions: 23°C at 50% RH

Web width	*Machine process speed*
0.3 m	0.3 m/min
0.6 m	PET - 30 m/min, OPP - 15 m/min
1.5 m	PET - 100 m/min, OPP - 30 m/min

4. WVTR achieved on PET with SiO_2 coating in different machines



Test conditions: WVTR 37.7°C at 100% RH

Web width	*Machine process speed*
0.3 m	0.3 m/min
0.6 m	PET - 30 m/min
1.5 m	PET - 100 m/min

II. Barrier summary for adhesive laminations. The SiO_2 barrier-coated 48 ga. PET was produced on the 0.66-m web width prototype machine at 50 ft/min.

	Unlaminated barrier		*Laminated/coated barrier*		
Laminated construction	*OTR, cm³/m²/day*	*WVTR, g/m²/day*	*OTR, cm³/m²/day*	*WVTR, g/m²/day*	*Bond strength*
PET (SiO_2)/Adhesive/CPP sealant	1.1	1.3	0.8	1.4	Initial - 250 g/in. Destruct after 5 days
PET (SiO_2)/Adhesive/SiO_2 PET/ Adhesive/CPP sealant	1.1	1.3	0.5	0.6	Initial - 250 g/in. Destruct after 5 days
PET (SiO_2)/Adhesive/LDPE film	1.2	1.4	1.2–1.3	1.1	1344 g/in.
PET (SiO_2)/Adhesive/CPP film	1.2	1.4	1.7	1.3	930 g/in.

III. Pre-primer study with MICA Corp. (laboratory screening tests)

Primer applied to plasma SiO_2-coated surface of 12-µm PET	*Corona treatment*	*Wetting*	*Bond strength*
No primer	No	-	25 g/in.
G-782 diluted 1:1 with water	No	Poor	Partial film tear
No primer	Yes	-	25 g/in.
G-782 diluted 1:1 with water	Yes	Good	Complete film tear

IV. Barrier summary for extrusion lamination

	Unlaminated barrier		*Laminated/coated barrier*	
Laminated construction	*OTR, cm³/m²/day*	*WVTR, g/m²/day*	*OTR, cm³/m²/day*	*WVTR, g/m²/day*
PET (SiO_2)/LDPE/LDPE film	1.8	3.2	2.4	2.3
PET (SiO_2)/LDPE	2.1	1.8	1.6	1.5
PET (SiO_2)/LDPE/Coex. OPP film	2.1	2.0	Not tested	1.2

V. Recommended printing systems

Croda Inks

Extrusion and adhesion laminations:
Solvent: Rich Tuff 2000 special system
Aqueous: Polyester laminating inks

CZ Inks

Adhesive laminations:
Solvent: Versalam VEB and VHB
Aqueous: Aqualam G (AGB)

(Note: All material recommendations must be tested for suitability under the user's specific converting practices and applications.)

VI. Ink performance results on plasma SiO_2 barrier-coated surface

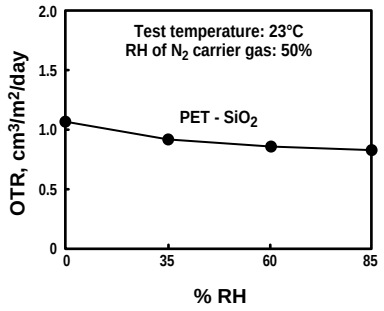
Ink system	*Type of ink*	*Ink adhesion (Tape test)*	*Crinkle resistance (10 cycles)*	*Adhesion lamination: Simulated bond, g/in.*		*Extrusion lamination: Simulated bond, g/in.*	
Rich Tuff Red/White	Solvent-based	100%	Excellent - no ink removal	Initial 420	Aged[a] 500	Initial 1450 FT[b]	Aged 2020 FT
Polyester laminating red	Aqueous	85%	Excellent - no ink removal	Initial 520	Aged 500	Initial 629	Aged 407 FT

[a]Aged 1 week at room temperature
[b]FT = Film tear

VII. Gelbo flex test results

Laminated structure	*Number of Gelbo cycles*	*Initial laminated barrier*		*Laminated barrier after Gelbo flexing*	
		OTR, cm^3/m^2/day	*WVTR, g/m^2/day*	*OTR, cm^3/m^2/day*	*WVTR, g/m^2/day*
PET (SiO_2)/Adhesive/CPP sealant film	50	3.5	2.0	4.5	2.7
PET (SiO_2)/LDPE/OPP Coex. film	20	-	1.2	-	1.7
Typical metallized control structure (OPP/LDPE/Metallized OPP)	20	-	0.8	-	1.9

5. OTR as a function of % relative humidity



ing printability, was achieved directly on the SiO_2 barrier surface.

We also evaluated how well the barrier properties are maintained after Gelbo flexing. This test is commonly used to simulate the stresses encountered in finished package shelf life in the marketplace. **Table VII** shows that the plasma-deposited SiO_2 coatings survived the testing when properly laminated in a finished packaging structure.

Summary

The following points summarize our findings:

- Progress continues to be made in developing and commercializing high-barrier, plasma-deposited SiO_2 coatings for use in the flexible packaging industry.
- Making these coatings fully commercially acceptable requires more than depositing transparent thin-film barriers onto polymer webs. Plasma SiO_2 coatings have been successfully printed; they have also been adhesive and extrusion laminated and made into finished packages. All of these steps play an integral role in the successful commercialization of new barrier technologies in the flexible packaging market. TJ

Literature cited

1. Felts, J. T. and Grubb, A. D., *J. Vac. Sci. Technol. A* 10(4): 1675 (1992).
2. Nelson, R. J., *35th Annual Technical Conference Proceedings,* Society of Vacuum Coaters, Baltimore, MD., 1992, p. 75.
3. Felts, J. T., *36th Annual Technical Conference Proceedings,* Society of Vacuum Coaters, Dallas, Texas, 1993, p. 25.

Received for review June 7, 1994.

Accepted July 19, 1994.

Presented at the TAPPI 1994 Polymers, Laminations and Coatings Conference.