Transparent SiO_2 Barrier Coatings: Conversion and Production Status

E. Finson and J. Felts, Airco Coating Technology, Concord, CA

Keywords: Permeation barrier coatings; Reactive evaporation; SiO_2

ABSTRACT

Silicon oxide based thin film coatings were deposited onto poly (ethylene terepthlate) (PET) and oriented polypropylene (OPP) with a plasma-based process in roll-to-roll equipment ranging in width from 0.3-1.5 meters. 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 will be presented. Barrier performance of generic packaging structures will also be presented.

DISCUSSION

Thin film gas barrier depositions were introduced to the packaging industry through aluminum metallization of polymer substrates in the 1970's. Aluminized films have proved to be very useful in the packaging area and have grown in use over the years. Transparent thin film barrier materials based on oxides of silicon and aluminum, that give similar performance as 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 a perception in the marketplace that these transparent barriers are more environmentally friendly than conventional PvDC or PVC clear barrier materials. Two methods of depositing the oxides of silicon and aluminum are currently being commercialized: *evaporation* (for both aluminum oxide and silicon oxide) and *chemical plasma deposition*, CPD (for silicon oxide only). This paper focuses on silicon dioxide depositions made only using the plasma process.

Transparent SiO_2 barrier films were deposited from plasma decomposition of 1,1,3,3-tetramethyldisiloxane [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 (Figure 1). Common polymer packaging films poly (ethylene terepthalate) [PET], and biaxially oriented polypropylene [OPP] were used as substrates. Three different plasma systems were used to deposit

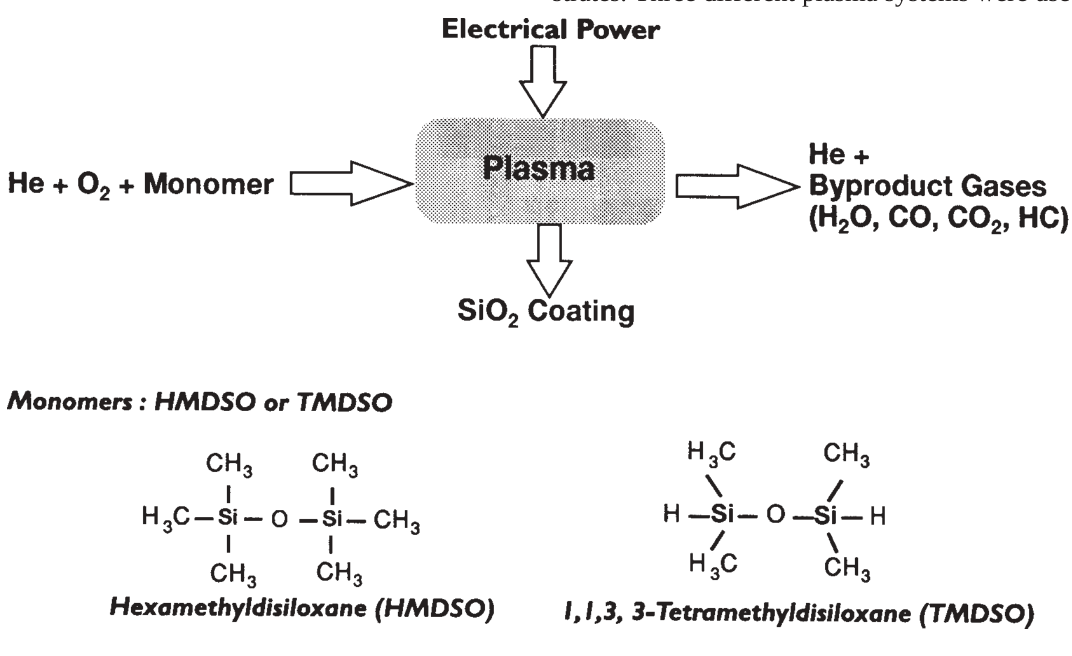


Figure 1 - Low Pressure SiO_2 Plasma Deposition Process

Society of Vacuum Coaters 505/856-7188
37th Annual Technical Conference Proceedings (1994) 1-878068-13-X

the films; a 0.3 meter web width R&D machine, a 0.66 meter web width pilot production machine, and a 1.5 meter web width production scale commercial coater. All of the machines utilize roll to roll systems, although there are some differences in configuration among them (Figure 2).

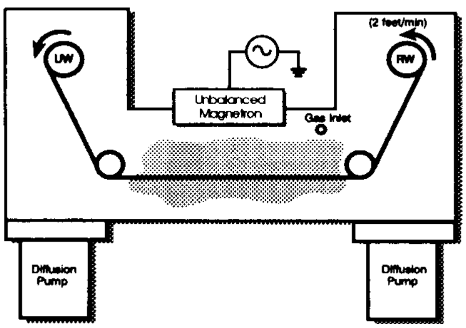
Oxygen and water vapor transmission rates were measured on equipment based on Modern Controls (Mocon) technology and standard ASTM methods (Oxygen transmission rate (OTR) ASTM D-3985, water vapor transmission rate (WVTR) ASTM F-1249). The equipment was retrofitted specifically to maximize sample throughput and improve test accuracy/reproducibility. Each of the 10 test cells on the Mocon oxygen transmission station was modified with its own dedicated sensor facilitating a throughput of over 200 samples per week. A special manifold and water bath circulation system on the Mocon water vapor equipment reduced temperature variation of the test cells to less than +/- 0.5C 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.

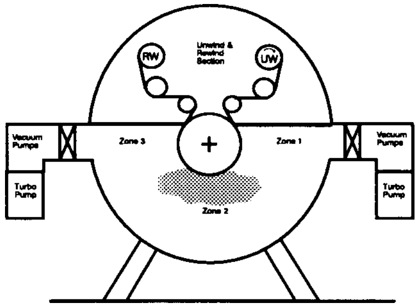
Thicknesses of deposited coatings were determined directly on the PET or OPP material using an x-ray fluorescence technique (Asoma model 200/400 benchtop unit). The measurement quantified the SiO_2 barrier coating thickness to +/- 5 nanometers. This measurement helped establish an internal qualitative measurement of process stability.

The barrier properties achieved to date on PET and OPP are listed in Figures 3 and 4. The 1.5 meter wide production machine is in the process of 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 EVOH resins, which are moisture sensitive.

(R-9) 0.3 meter web wide Plasma Coater



(FLEX-1) 0.66 meter Web Width Prototype Web Coater



(FLEX-3) 1.5 meter Web Width Production Scale Plasma Coater

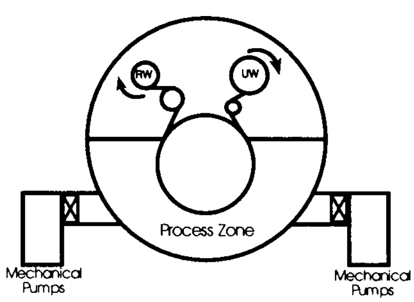
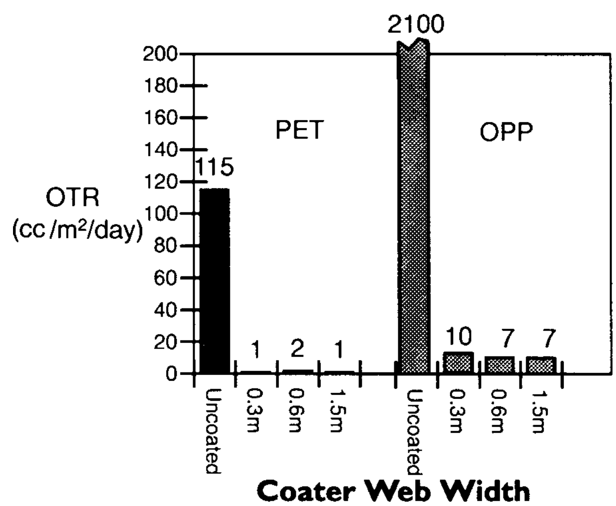


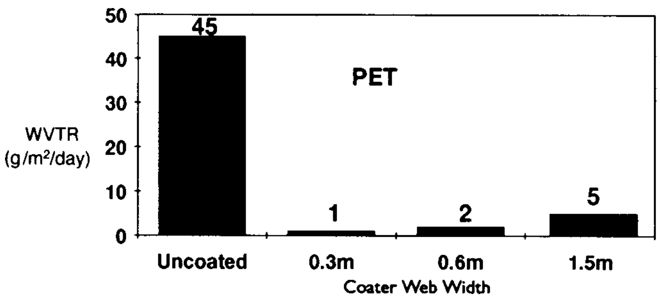
Figure 2 - Plasma Roll Coaters



TEST CONDITIONS: 23°C at 50% R.H.

Machine Process Speeds	
Web Width	Speeds
0.3m	0.3 m/min
0.6m	PET - 30m/min, OPP - 15m/min
1.5m	PET - 100m/min, OPP - 30m/min

Figure 3 - OTR of PET and OPP with SiO_2 Coating in Different Machines



TEST CONDITIONS: WVTR 37.7°C at 100% R.H.

Machine Process Speeds	
Web Width	Speeds
0.3m	0.3 m/min
0.6m	PET - 30m/min
1.5m	PET - 30m/min

Figure 4 - WVTR Achieved on PET with SiO_2 Coating in Different Machines

The large scale acceptance 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 to create transparent barrier coatings, principally on PET, and little effort was spent on the commercialization of 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.

Figure 6 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. It should be noted that all of the adhesive suppliers noted that

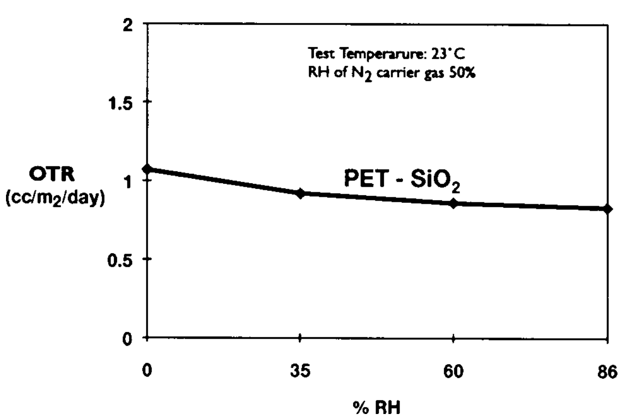


Figure 5 - OTR as a Function of %RH

Adhesive Description	Structure	Coating Weight (lbs./RM dry)	Bond Strength (g/in)	Heat Seal Strength (g/in)
1. Takeda A-520/A-50 (Aged 4 days @ 40C)	PET (SiO_2) adhesive/1mil CPP	2.3	850	7500
2. Liofol/Henkel (Europe) Tycel 7909/7283 (Aged 24 hours)	PET (SiO_2) adhesive/1mil LDPE	2	Film tear	Film tear
3. Century Adhesive C-1045 + 5% catalyst (Aged 7 days)	PET (SiO_2) adhesive/1mil CPP	1.8-2.0	460	NT

NT - Not tested

Figure 6 - Dry Bonding Adhesive Lamination Results (Laboratory Screening Tests)

even better bond strength results could be achieved under actual production conditions. Additionally, several packaging converters have successfully adhesive laminated the SiO_2 surface maintaining barrier properties with excellent bond results. Figure 7 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 (VFFS) and horizontal form fill seal (HFSS) equipment.

Very good extrusion lamination bond results were simulated in the laboratory using a water-based pre-primer with low density polyethylene. This work was performed by MICA Corporation and the G-782 primer when diluted 1:1 with water gave 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 (Figure 8). Figure 9 shows some examples of the barriers before and after extrusion coating/laminating. This data shows 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 (Figure 10). Some of the work resulting from the laboratory testing performed by Croda Inks is contained in Figure 11. Good ink adhesion while maintaining printability was achieved directly on the SiO_2 barrier surface.

Another area which has been evaluated for laminations is how well the barrier properties are maintained after Gelbo flexing. This test is commonly used to simulate the stresses which can be encountered in a finished package's shelf-life in the marketplace.

Laminated Construction	Unlaminated Barrier		Laminated/Coated Barrier		Bond Strength
	OTR ($cc/m^2/day$)	WVTR ($g/m^2/day$)	OTR ($cc/m^2/day$)	WVTR ($g/m^2/day$)	
1. PET (SiO_2)/Adhesive/CPP Sealant	1.1	1.3	0.8	1.4	Initial - 250 g/in Destruct after 5 days
2. PET (SiO_2)/Adhesive/SiO2 PET/ Adhesive/CPP Sealant	1.1	1.3	0.5	0.6	Initial - 250 g/in Destruct after 5 days
3. PET (SiO_2)/Adhesive/LDPE Film	1.2	1.4	1.21.3	1.1	1344 g/in
4. PET (SiO_2)/Adhesive/CPP Film	1.2	1.4	1.7	1.3	930 g/in

The SiO_2 barrier coated 48 ga. PET material was produced on the 0.66m web width prototype machine at 50 fpm.

Figure 7 - Barrier Summary for Adhesive Laminations

Primer applied to plasma SiO_2 coated surface of 12 micron PET	Corona Treatment	Wetting	Bond Strength
1. No primer	No		25 g/in
2. G-782; Diluted 1:1 with water	No	Poor	Partial film tear
3. No primer	Yes		25 g/in
4. G-782; Diluted 1:1 with water	Yes	Good	Complete film tear

Figure 8 - Pre-Primer Study with MICA Corporation (Laboratory Screening Test)

Laminated Construction	Unlaminated Barrier		Laminated/Coated Barrier	
	OTR ($cc/m^2/day$)	WVTR ($g/m^2/day$)	OTR ($cc/m^2/day$)	WVTR ($g/m^2/day$)
1. PET (SiO_2)/LDPE/LDPE Film	1.8	3.2	2.4	2.3
2. PET (SiO_2)/LDPE	2.1	1.8	1.6	1.5
3. PET (SiO_2)/LDPE/Coex. OPP Film	2.1	2.0	NT	1.2

NT - Not Tested

Figure 9 - Barrier Summary for Extrusion Lamination

Croda Inks

Extrusion and Adhesion Laminations:

Solvent: Rich Tuff 200 Special System

Aqueous: Polyester Laminating Inks

CZ Inks

Adhesive Laminations:

Solvent: Versalam UEB and VHB

Aqueous: Aqualam G (AGB)

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

Figure 10 - Recommended Printing Systems

Figure 12 shows that the plasma deposited SiO_2 coatings survived the testing when properly laminated in a finished packaging structure.

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 500	Initial 1450 FT	Aged 2020 FT
Polyester laminating red	Aqueous	85%	Excellent no ink removal	Initial 520	Aged 500	Initial 629	Aged 407 FT

FT - Film Tear Aged = 1 week at room temperature

Figure 11 - Ink Performance Results on Plasma SiO_2 Barrier Coated Surface

Laminated Structure	Number of Gelbo Cycles	Initial Laminated Barrier		Laminated Barrier after Gelbo Flexing	
1. PET (SiO_2)/Adhesive/CPP sealant film	50	OTR 3.5	WVTR 2.0	OTR 4.5	WVTR 2.7
2. PET (SiO_2)/LPDE/OPP Coex Film	20		WVTR 1.2		WVTR 1.7
3. Typical Metallized Control Structure (OPP/LDPE/Metallized OPP)	20		WVTR 0.8		WVTR 1.9

Figure 12 - Gelbo Flex Test Results

SUMMARY

1. Progress continues to be made in the development and commercialization of high barrier plasma deposited SiO_2 coatings for use in the flexible packaging industry.

2. For these coatings to be fully acceptable in the market it requires more than depositing transparent thin film barriers onto polymer webs. Plasma SiO_2 coatings have been successfully printed, adhesive and extrusion laminated, plus made into finished packages. All of these steps play an integral role in the successful commercialization of new barrier technologies into the flexible packaging market.

REFERENCES

1. Felts, J. T. and Grubb, A. D., "Commercial-scale application of plasma processing for polymer substrates: From laboratory to production", J. Vac. Sci. Technol., A 10(4), Jul/Aug 1992.

2. Nelson,R.J., "Scale-Up of Plasma Deposited SiOx gas diffusion Barrier Coatings", Society of Vacuum Coaters 35th Annual Technical Conference Proceedings, pp. 75-79, 22-27 March 1992.

3. Felts, J. T., "Transparent Barrier Coatings Updates: Flexible Substrates", Society of Vacuum Coaters 36th Annual Technical Conference Proceedings, 25-30 April 1993.