

A TWENTY-YEAR RETROSPECTIVE ON PLASTICS: OXYGEN BARRIER PACKAGING MATERIALS

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ABSTRACT

An enumeration and critical analysis of the many worldwide developments and proposals of the past twenty years of oxygen barrier plastic package materials for food products. Introduced with great publicity, numerous oxygen barrier technologies have either disappeared or have evolved elsewhere. The rationales for their initiation and apparent reasons for their current positions are reviewed.

INTRODUCTION

Oxygen barrier packaging, often erroneously called barrier packaging, has been required for food, health care, and other product protection for centuries. Ceramic, glass and metal were or have been the most effective means to exclude oxygen-containing air from the package interior and thus protect the contents against oxidation and aerobic microbiological growth.

Since the advent of plastics for packaging, one objective of polymer chemistry and technology has been to develop materials with oxygen barrier properties approaching those of metal or glass. Without having achieved this objective, food, beverage, etc., packagers have compromised their oxygen barrier requirements by changing formulations, processing, and/or by reducing distribution times. Thus, a convergence of plastic barrier package materials and packagers' requirements has been occurring. It is difficult to predict when the two will precisely match, but it is not at all difficult to assert that this convergence is inevitable.

One of the more intriguing conclusions of a twenty-year review of the progress of oxygen barrier is that the more dramatic changes have taken place among the packagers than in oxygen barrier polymers and their derivatives. Virtually every oxygen barrier plastic in significant commercial use today was in commercial use in 1978. With only two developmental exceptions, every oxygen barrier plastic in either commercial use or in development today were well known in 1978. This time line does not, however, signify a lack of progress in oxygen barrier plastics- which are certainly more widely used today than at any time during the past two decades.

Oxygen barrier plastics may be achieved by:

- Monolayer oxygen barrier polymers
- Multilayer structures
 - Sandwich
 - Barrier inside
- Surface treatment (plasma, glass, etc.)
- Surface coatings
 - P V D C
- Blends

- O₂ scavengers
- Processing/Morphology
 - Crystallinity
 - Orientation

The following oxygen barrier materials/packages have existed or emerged during the past twenty years:

- PVOH
- EVOH
- PVDC
- Nylons
 - Types 6 and 66
 - Aromatic/Amorphous
 - * MXD6 nylon
- Acrylonitrile (PAN)
- PET
- PEN
- Polytrimethyl Terephthalate (PTT)
- Resorcinol
- Ormocers
- Liquid crystal polymers (LCPs)
- Aliphatic polyketones
- Oxygen scavengers
 - Sachets
 - In package walls
 - * Oxbar
- Coatings
 - Plasma glass coatings
 - Thermoset epoxy coatings
- Blends
- Nanocomposites

Table No. 1. Oxygen Barrier Polymers

Polymer	O ₂ Permeability at 73°F (cc-mil)/100 in ² -day-atmosphere)
Silica-coated PET	0.002 to 0.07
EVOH, dry	0.01
EVOH, typical coextrusion	0.04 to 0.07
Liquid crystal polymer	0.025
PVDC, extruded or coated	0.07
MXD6 nylon, dry	0.15
MXD6 nylon, coex	0.25
Polyacrylonitrile	1.0
PEN polyester	1.2
Amorphous nylon, wet	1.5
Amorphous nylon, dry	2.4
Nylon 6 or 66, dry	1.5
Nylon 6 or 66, wet	7.0
PET, 45% crystallinity (CPET)	3.0
PET, 25% crystallinity (bottle)	5.0
PET, amorphous	1.0

Polyvinyl Alcohol (PVOH)

Polyvinyl alcohol films can either be water soluble (when cast or extruded) or very high barrier packaging films if biaxially oriented (and even higher in barrier protection if PVDC coated).

In the United States, the Mono-Sol division of Chris Craft Industrial Products, Inc., is the leading producer of water-soluble PVOH films for such applications as hospital laundry bags and seed tapes.

In Japan, Kuraray Co., Ltd., is the leading producer both there and worldwide with their POVAL FILM. (They also produce POVAL resin and VINYLON fiber from PVOH resin.) They produce about 20 million pounds per year. By far their major market is textile packaging (clothing, bedding). Other outlets include mold release (plastic plywood or plastic board) and optical (polar film). Key properties are transparency, gloss, durability and being non-static.

As PVOH does not have a melting point, it cannot be extruded by conventional methods. This be done by completely dissolving the pellets at a high concentration. It is then extrusion melted at high water content onto a drier can.

Typical properties for POVAL grades Film-A, Film-K and Film-N are shown in Table No. 2. The A-type is for textile and general packaging. Grades K and N are for soft and hard type mold release agents, respectively.

Table No. 2. Kuraray POVAL Film Specifications*

		Film-A	Film-K	Film-N
Thickness (mm.)	0.02 ~ 0.03 Thin Film	Nominal Thickness ±7.5%	Nominal Thickness ±7.5%	Nominal Thickness ±7.5%
	0.04 ~ 0.075 Thick Film	Nominal Thickness ±5%	Nominal Thickness ±5%	Nominal Thickness ±5%
Equilibrium Moisture Content (W.B.%)		8 ± 1	8.5 ± 1	8 ± 1
Tensile Strength (kg./mm. ²)	Machine direction	4.5 ~ 6.5	4.0 ~ 5.5	4.5 ~ 6.5
	Transverse direction	4.5 ~ 6.5	4.0 ~ 6.0	4.5 ~ 6.5
Elongation (%)	Machine direction	150 ~ 400	300 ~ 500	270 ~ 400
	Transverse direction	300 ~ 550	300 ~ 550	400 ~ 550
Young's Modulus (kg./mm. ²)	Machine direction	20 ~ 30	9 ~ 10	20 ~ 30
	Transverse direction			
Tear Strength** (kg./mm.)	Machine direction	15 ~ 65	20 ~ 90	30 ~ 65
	Transverse direction	25 ~ 85	50 ~ 90	40 ~ 85
Impact Strength (kg.cm.)		20 ~ 75	30 ~ 80	25 ~ 75
Water-Resistant*** Temperature (°C)		70 ~ 80	60 ~ 70	70 ~ 80
Clarity ****		35 ~ 50	35 ~ 50	35 ~ 50

Notes:

- * The values in this table were determined at 20°C and 65% RH
- ** Tear strength represents values determined with Elmendorf tester.
- *** Determined with the temperature, at which the film tensioned under the load of 10g/mm.² is dissolved to be cut in water. The temperature of water is raised at a rate of 3°C per minute.
- **** Clarity is determined by the maximum layers of film through which the letters of 9 point type remain readable.

Table No. 3 shows POVAL's MVTR versus other films.

Table No. 3. Moisture Vapor Transmission of POVAL Film versus Other Packaging Films

	Method of Measurement	POVAL Film	Cellophane	PVC	Polyethylene
MVTR (g./m ² /24 hrs 30μ thickness)	JIS-Z0208	788	1,340	148	21
	JIS-Z1503	1,500~2,000	1,300~2,000	120~180	35~180

Note: Relative humidities of faces of the film, 0% and 90% ±2%; temperature 40 ±1°C

For high barrier packaging applications, Japan offers two biaxially oriented versions of PVOH film. These are BOVLON from Nippon Gohsei Film Co., Ltd. and EMBLAR-OV from Unitika Ltd., The latter is two-side PVDC-coated and offers the best barrier properties.

BOVLON, through the orientation process, not only has improved resistance against humidity but also greater mechanical strength, reduced elongation, more dimensional stability, and increased flex strength. It is used in food packaging as well as industrial, electronics and pharmaceutical applications. Certain bacteria can degrade it to CO₂ and H₂O.

EMBLAR-OV was the world's first biaxially oriented PVOH film. With its PVDC coatings, it is the best gas barrier among films. There are two basic types, both 60 gauge, called #1500 and 1500H. The latter inhibits heat sticking of the surface PVDC. Table No. 4 shows their typical properties including an O₂TR of <0.03 cc/100 in.²/24 hrs/atm.

Table No. 4. Biaxially Oriented PVA Film EMBLAR-OV Properties

Properties	Test Method	EMBLAR-OV #1500 (15μ) PVDC Coated	EMBLAR-OV #1500H (15μ) Anti-Heat Stick Type
Tensile Strength (psi) (kg./cm ²)	ASTM D882 68°F (20°C), 65% RH	3.7 x 10 ⁴ (2.6 x 10 ³)	3.7 x 10 ⁴ (2.6 x 10 ³)
Elongation (%)	ASTM D882 68°F (20°C), 65% RH	50 ~ 80	50 ~ 80
Tensile Modulus (psi) (Kg/cm ²)	ASTM D882 68°F (20°C), 65% RH	6.8 x 10 ⁵ (4.8 x 10 ⁴)	6.8 x 10 ⁵ (4.8 x 10 ⁴)
Tear Propagation Resistance (g)	ASTM D1938 68°F (20°C), 65% RH	2.6	2.6
Shrinkage (%)	For 5 min. in air circulating oven at 320°F (160°C)	<4.0	<4.0
Water Vapor Permeability (g/100 sq.in./24 hrs) [g/m ² /24 hrs.]	ASTM E96 104°F (40°C), 90% RH	0.4 [6]	0.4 [6]
O ₂ Gas Permeability (cc/100 sq.in./24 hrs./atm) [cc/m ² /24 hrs./atm]	ASTM D1434 68°F (20°C), dry	<0.03 [<0.5]	<0.03 [<0.5]
Transparency (%)	ASTM D1003 68°F (20°C), 65% RH	85 ~ 86	84 ~ 87

PVOH is also finding its way onto OPP and PET films for improved barrier performance. Mobil's Bicolor AOH is an OPP film with a PVOH layer. Rhone-Poulenc and more recently DuPont have developed polyester-based films with a PVOH layer.

EVOH Films

Kuraray and Okura offer EVOH-based films. The former has cast, biaxially oriented and vacuum metallized, under the EVAL FILM tradename. The latter, using Nippon Gohsei's Soarnol resin, produces EXCEED biaxially oriented EVOH film. (See Table No. 5.)

Table No. 5. EVAL Film

	Film Type	Ethylene Content (mole %)
EF-E	Cast	44
EF-F	Cast	32
EF-XL	Biaxially oriented	32
VM-XL	Biaxially oriented and vacuum metallized	32

The cast films are available in gauges of 50, 60, 80, and 100. The biax film comes in 50 and 60 gauge. Table Nos. 6-12 show their properties.

Table No. 6. Oxygen Transmission Rate of EVOH Composite Films @ 68°F

Outside (mils)	Film Structure		Inside 100% RH						Inside 10% RH					
	Middle (mils)	Inside (mils)	65% RH		80% RH		65% RH		80% RH		65% RH		80% RH	
			Middle % RH	O ₂ TR	Middle % RH	O ₂ TR	Middle % RH	O ₂ TR	Middle % RH	O ₂ TR	Middle % RH	O ₂ TR	Middle % RH	O ₂ TR
OPP (0.8)	EF-F (0.6)	LDPE (2.0)	84	0.11	91	0.24	34	0.01	40	0.02	34	0.01	40	0.02
OPP (0.08)	EF-F (0.6)	Ct'd PP (2.0)	80	0.08	89	0.19	41	0.02	49	0.02	41	0.02	49	0.02
PET (0.5)	EF-F (0.06)	LDPE (2.0)	70	0.04	83	0.10	57	0.02	69	0.04	57	0.02	69	0.04
ON (0.6)	EF-F (0.6)	LDPE (2.0)	66	0.04	81	0.08	63	0.03	77	0.06	63	0.03	77	0.06
Ct'd Nylon (0.8)	EF-E (0.8)	LDPE (2.0)	65	0.10	80	0.16	64	0.10	78	0.15	64	0.10	78	0.15
EF-XL (0.6)	-	LDPE (2.0)	-	0.02	-	0.04	-	0.02	-	0.04	-	0.02	-	0.04

Table No. 7. EVOH Transmission Rate (g. mil/100 in²/24 hrs.)

Film Type	Chloroform	Xylene	Kerosene
EF-F	0.10	0.054	>0.001
EF-E	0.16	0.074	0.0025
EF-XL	0.006	0.016	0.001
BOPP	190	17.8	2.69
LDPE	351	41.9	9.65

Table No. 8. EVOH Mechanical Properties

Property	Unit	Test Method	EF-XL	EF-F	EF-E	ON	PET	PVDC Ct'd BOPP	Saran HB-100
Thickness	mils	-	0.6	0.6	0.8	0.6	0.5	0.9	1.0
Tensile Strength @ Break	MD	ASTM D638	29,700	11,600	10,150	23,450	22,760	24,100	12,000
	TD	10%/min.	28,300	7,550	6,400	31,290	27,025	31,200	20,000
Elongation @ Break	MD	ASTM D638	100	180	260	90	140	140	100
	TD		100	140	190	90	60	60	50
Young's Modulus (Stiffness)	MD	ASTM D638	510,000	284,000	284,000	242,000	498,000	284,000	-
	TD	10%/min.	510,000	270,000	270,000	213,000	570,000	370,000	-
Tear Strength	MD	ASTM D638	260	380	460	500	200	300	180
	TD		330	300	440	450	200	200	280
Bursting Strength	psi	JIS P8112	56.8	18.5	18.5	56.8	42.7	56.8	-
Dimensional Stability @ 14°C, 1 hr.	MD	-	-4.0	-2.7	-1.6	-1.5	-1.6	-10.4	-
	TD		-0.5	-0.9	-1.2	-0.9	+0.3	-12.5	-
Melting Point	°C	DSC	181	181	164	220	260	165	-
Water Vapor Trans. Rate	*	40°C, 90% RH	2.6	6.5	2.3	16.8	3.2	0.3	0.05

* g/100 in²/24 hrs.

Table No. 9. EVOH Optical Properties

Film	Thickness	Haze	Gloss
EF-XL	0.6	0.5	95
EF-F	0.6	1.5	90
EF-E	0.8	1.7	90
ON	0.6	2.0	85
PET	0.5	2.5	95
PVDC Cr'd BOPP	0.9	3.5	90
Saran HB-100	1.0	2.5	90

Table No.10. EVOH Films Specifications

Grade	Gauge	Microns	Yield (in ² /lb.)	Width (inches)
EF-F	50	12	46,920	16-49
	60	15	39,106	16-51
	80	20	29,325	16-51
EF-E	60	15	40,830	16-49
	80	20	30,623	16-51
	100	25	23,440	16-51
EF-XL	50	12	46,920	14-52
	60	15	39,100	14-52

Table No. 11. EVOH Dimensions

Grade	Type	Thickness (μ)	Width (mm)	Length (m)	Application
EF-XL	Biaxially oriented	12 15	500-1,200	4,000	Two- or three- layer structure high barrier package
EF-F	Non-oriented	12 15 20	500-1,200	4,000	Three-layer structure high barrier package
EF-E	Non-oriented	15 20 25	500-1,000	2,000	High barrier thermoformed package
VM-XL	Vacuum metallized	12 15	500-1,200	4,000-8,000	More high barrier package

Table No. 12. EVOH Physical Properties

Item	Unit	Measuring Method	Measuring Condition	EF-XL	EF-F	EF-E
Thickness	μ	JIS B7509		15	15	20
Tensile strength (Breaking)	MD	ASTM D882	20°C, 65% RH	21	9	4
	TD			20	4	260
Elongation (Breaking)	MD	ASTM D882	20°C, 65% RH	100	140	190
	TD			100	220	180
Young's modulus	MD	ASTM D882	20°C, 65% RH	360	220	180
	TD			340	220	180
Elmendorf tear strength	MD	JIS P 8116	20°C, 65% RH	9	4	5
	TD			10	8	7
Quadrature tear strength	MD	JIS K 6732	20°C, 65% RH	260	380	460
	TD			330	300	440
Impact strength	kg•cm		20°C, 65% RH	8	0.6	4.7
Burst strength	kg/dm ²	JIS P 8112	20°C, 65% RH	4	1.3	1.3
Pinhole strength	g	JAS	20°C, 65% RH	800	290	310
Water vapor transmission rate	g/m ² •24 hrs	JIS Z 0208	40°C, 90% RH	40	100	35
Water absorption	%		30°C, 24 hrs	5.9	8.6	6.7
Equilibrium moisture absorption	%		20°C, 65% RH	2.8	3.9	2.8
Dimensional stability under heat	MD		140°C, 1 hr.	-4.0	-2.7	-1.6
	TD			-0.5	-0.9	-1.2
Oxygen transmission rate	cc/m ² •24 hrs•atm	JIS Z1707	35°C, 0% RH	0.4	0.5	3.2
		ASTM D 3985	20°C, 65% RH	0.3	0.5	1.5
			20°C, 85% RH	1	2	3.3
			20°C, 100% RH	6	25	10
Electric Resistance ps (surface)	Ω		22°C, 38% RH	2.7x10 ¹⁵	1.9x10 ¹⁵	2.1x10 ¹⁵
Oil resistance	hrs.	JIS Z 1515	20°C, 65% RH	∞	∞	∞
Melting point	°C			181	181	164
Haze	%		20°C, 65% RH	0.5	1.5	1.7
Slip factor	degree		20°C, 65% RH	35	30	30

EVOH/Nylon Oriented Coextrusions

This is an early 1990s development out of Japan. Pioneered by Gunze (Heptax) and Sumitomo Bakelite (Sumilite CLO), these high barrier films can come in 3, 5, 7 or more layers and may also incorporate a heat sealant such as Surlyn. They compete with other high barrier clear films such as BOVLON, EMBLAR-OV, EVAL FILM and EXCEED, and also aluminum foil. Typically markets are in institutional liquid pouch packaging as an alternative to the #10 can. They can also be used in promotional balloons.

EVOH (Ethylene Vinyl Alcohol copolymers)

EVOH resins are copolymers of ethylene and vinyl alcohol made by the hydrolysis of ethylene vinyl acetate copolymers. The leading manufacturers are Kuraray (EVALCA) and Nippon Gohsei. To be a high oxygen barrier plastic, the copolymer must contain at least 50 mole % vinyl alcohol. The most common materials are 56% and 62% vinyl alcohol, but higher vinyl alcohol content grades have been developed. These materials possess very high gas barrier properties, but lack a H₂O barrier. In addition, they are very sensitive to water, and unfortunately lose barrier rapidly upon exposure to moisture. Therefore, the majority of applications have been in sandwich-type coextrusions with protective water vapor barrier layers on each side. (See Table No. 13.)

The materials can be made less moisture-sensitive by means of biaxial orientation. A typical rigid container using EVOH would be coextrusion or co-injection stretch blow molded. It would contain at least three layers: inner and outer would be the structural material, with the EVOH in the middle—between 0.001 to 0.004 inches thick. The water vapor barrier properties of the structural layers are key to the ultimate gas barrier of the multilayer, with the polyolefins (PP) offering the best protection for the EVOH.

In coextrusion blow molding, because EVOH does not adhere to PP, adhesive layers must be used. In the case of PET and co-injection stretch blow molding, tie layers often are not used, relying instead on mechanical forces to keep the layers together. Once the interlayer bond is broken, the layers can usually be stripped apart. This has been cited as an advantage in recycling. An original American use, however, of EVOH in 1983 was for the PP/x/EVOH/x/PP ketchup bottle (ketchup needs a high O₂ barrier) and which later on converted to PET/EVOH/PET (no adhesives) to gain both clarity and ease of recycling.

A second large EVOH rigid packaging use also originated during the mid-1980s and was for retorted shelf-stable “lunch-bucket” cans and similar shelf-stable lunch and dinner trays. These needed the high oxygen barrier of the EVOH as well as the retortability and H₂O barrier of PP. One of the problems with this package, however, was the high level of H₂O permeating the PP during retorting and entering the EVOH, thus lowering its oxygen barrier properties. In order to solve this problem, desiccants were added to the adhesive layers to trap the moisture. Since their introduction, the retail retort tray has almost disappeared in the United States, and the bucket cans have declined dramatically from their original heights. For product content and marketing reasons, a variation, a small tray for pet food, is also available in the marketplace.

The flavor barrier of EVOH is excellent, and is not lost as easily as its O₂ barrier property when it is exposed to moisture. EVOH has been used primarily as an organic flavor barrier on the inside of PE-coated paperboard gable-top containers. A typical application is for orange juice, where the loss of limonene from the juice into the PE layer is blocked by the EVOH. Even though it gets completely “wet” by being in contact with the juice, it still maintains an excellent barrier to the limonene.

Table No. 13. O₂ Permeability (cc-mil) / (100 in²-day-atmosphere) of EVOH under Various Conditions

Ultra-barrier, bone-dry	0.01
Ultra-barrier, coex with PP (100°F, 50% RH)	0.05
Normal EVOH (38%*), bone dry	0.02
Normal EVOH (38%*), coex with PP	0.08
Normal EVOH (38%*), coex with PET	0.18
Lower barrier EVOH (44%*), coex with PP	0.30

* Mole % ethylene

Polyvinylidene Chloride Copolymers (PVDC) (Saran)

PVDC was probably the original high oxygen barrier plastic, having been developed by World War II by Dow Chemical under the tradename Saran. Until the 1970s development of EVOH, and despite its processing limitations, PVDC was almost the only commercial high oxygen barrier polymer.

On a per-gauge basis, PVDCs are second only to EVOH in gas and flavor barrier. Although they are not as good as dry EVOH, they do not experience the loss of barrier experienced by EVOH upon exposure to H₂O and as a result in typical applications they can come out nearly on a barrier par with EVOH and often at a lower cost. In addition, they possess high water vapor barrier properties which is unusual among gas barrier plastics. On the downside, PVDC's gas barrier is adversely affected by rising temperature.

Although PVDC does have the moisture-insensitivity advantage over EVOH, it is not in as wide use due to its difficulty in handling and processing (yellowing and degrading, giving off HCl) and in using re-grind for the same processing reasons. PVDC is primarily used in flexible packaging applications, plus some sheet/thermoforming. It is essentially not used in blow molding except as a coating resin where it finds limited applicability.

Essentially, three different PVDC resin types are offered:

- High barrier extrusion grades for coextrusion
- Plasticized grades for "Saran film" extrusion (free-film)
- Coating grades, applied from either solvent- or water-based emulsions

The first and third types are very high barrier, while typically Saran films have lower O₂ barrier properties due to the plasticizer.

The high barrier materials compete with EVOH in the same type of film/sheet coextrusions. They have the advantage of no loss in barrier with H₂O exposure. Like EVOH, they require adhesive layers.

Saran film has been available for many years and is used extensively as a home food wrap. In its coextruded Saranex form, it is used industrially as a barrier packaging film. Saran film's O₂ permeability is about ten times higher than either the extrusion or coating grades. Its big advantages among films are its high O₂ barrier, high fat barrier, and very high water barrier all in a monolayer film and at a reasonable price.

In addition, high barrier Saran films for laminations as an alternative to foil or other gas barrier plastics is also marketed.

A major application for "coextruded" PVDC film is sub-primal meat packaging. Cryovac is the market leader with their EVA/PVDC/EVA "Barrier Bags."

Although coating grades are either solvent-based (MEK, acetone, esters) or water-based emulsions, the latter have been of most interest. Emulsion coatings for bottles are used for the PET beer bottle, primarily in the United Kingdom where the beer is not pasteurized. It has a very high barrier and can be applied at 0.7 mils with one pass. It lowers the O₂ permeability of a PET bottle by nearly 60%. Several companies produce PVDC emulsions for coating films such as nylon, PE, OPP, and PET to improve their oxygen (and moisture) barriers. Emulsion-coated films such as flexible lidding for trays, and nylons for thermoformed meat packaging have been standard for more than 20 years.

Nylon Resins

Nylon 6. Nylon 6 has been employed as a modest oxygen barrier for more than twenty years. Like most nylons, nylon 6 loses its gas barrier when exposed to moisture, and thus most nylon 6 film is either coated with PVDC, or coextruded with or laminated to a good water barrier such as PE or ethylene copolymers. Nylon 6 is a poor water vapor barrier, another reason why for food packaging it is almost always combined with other materials along with its heat seal properties.

The majority of applications for nylon 6 in food packaging is with film. There is some blow molding—coextrusion and blending of nylon 6 with PE—into bottles, but these are mainly for the industrial and household chemical markets.

Nylon is relatively expensive, but, considering its high degree of gas and flavor barrier, this is not out of line. Most uses include almost any food product that needs a high-barrier film or thermoformed package, such as processed meat and cheese, provided the nylon is coated or laminated.

MXD6. Nylon MXD6 is a high-barrier, high melting crystalline nylon developed during the 1970s by the Japanese (Mitsubishi Gas Chemical for resin and Toyobo for film). It can be used as a higher barrier nylon film and blow molding resin. It can also be blended with PET (as was the situation during the late 1980s in the development of the Oxbar oxygen scavenger technology) and nylon 6. It contains the monomer metaxylylene diamine, hence the MXD name.

Because MXD6 so closely matches the melting and crystallization points of PET, it is excellent for co-injection into a three-layer preform (PET/MXD6/PET) and then stretch blow molded into an oriented bottle.

The barrier properties of MXD6 are not adversely affected by moisture until the humidity climbs above about 70%.

In a multilayer PET bottle, MXD6 can lower the O₂ permeability by about 70% at only a 0.003” to 0.004” gauge.

Because of its expense and the lack of a domestic source, MXD6 has found limited use in the United States but has a much wider market in Japan. In other parts of the world, there have been non-pasteurized beer bottles and carbonated soft drink bottles with an MXD6 layer on the market. There are some juice bottles in the U.S. that have MXD6 in their structure.

Isophthalic/Terephthalic Acid Hexamethylenediamine Nylon (6I/6T) Amorphous Nylon. Like the high barrier polyesters, Selar PA amorphous nylon was developed by DuPont as a monolayer answer to the multi-layer bottle. It has a good O₂ barrier and, unlike commercial nylons such as nylon 6, the gas barrier is not decreased by water. As a matter of fact, the gas barrier is improved by about 20% when the polymer is wet.

In appearance, the material looks like PET (with a very slight tint that is easily masked). It has high heat resistance (190°F when dry) but cannot be retorted.

It has limited FDA approval, and has found only minor uses in rigid packaging due to its high cost. It is a tough material and does not need to be oriented. It is amorphous and thus remains clear under all conditions. It has found some applicability in flexible packaging as in blends with nylon 6. EMS of Switzerland (U.S. plant in South Carolina) has a similar material called Grivory G21 which is also used in blends with nylon 6 for film.

Polyacrylonitrile Copolymers

The copolymer with styrene was developed during the 1960s by Monsanto Co. as a high barrier monolayer bottle for foods and beverages. It has a very low permeation rate which makes it suitable for single-layer use. It was removed from the market in 1977 by the FDA after being used in the first plastic Coca-Cola bottles. It was re-approved for beverages during the mid-1980s, and for beer in the late 1980s. It is only approved for beverages (it has no listing with the FDA for non-beverage foods). It can be hot filled (190°F) and pasteurized but not retorted. The shadow of the FDA concern coupled with the position of PET in the bottle arena has largely precluded its commercial use as an oxygen barrier plastic bottle resin.

PAN is a rigid, yellowish, brittle plastic which needs biaxial orientation for adequate toughness. It processes on equipment similar to PET bottles. It can be colored (it is amorphous and has good clarity) but cannot be made glass-clear like PET or PVC. Typical containers were green or amber in color. As a bottle, it has a five times better gas barrier than PET, but is not as good as the EVOH multilayer bottle. It has only a fair water vapor barrier.

The only known use was in Japan by Yoshino which uses resin made by a joint venture of Monsanto and Mitsubishi to produce a returnable beer bottle for Sapporo beer. The bottle was expected to have a life of more than ten trips. Because of its high O₂ barrier, the beer “sees” only 1 ppm of O₂ over its expected three-month shelf life.

In addition to its high gas barrier, PAN has one of the best flavor retention profiles of any plastic, being indistinguishable from glass in taste tests.

Barex was developed by SOHIO (now BP) shortly after Monsanto's development. It differs in that it has methyl acrylate as the comonomer, and it is inherently tougher due to the addition of rubber (it does not need orientation for toughness) but it has about the same barrier properties due to the fact that the acrylonitrile level is about the same (70%). It also differs in heat resistance (limited to 160°F) and has less color due to the fact that it can be extruded at a lower temperature than Monsanto's resin. Barex's chief disadvantages are in the area of flavor retention (due to its rubber content) and in the fact that it does not have FDA approval for beverage use. On the other hand, it is used for processed meat packages, multilayer film and sheet for O₂-sensitive foods, and for many non-food uses. It has excellent solvent resistance and thus is used for garden chemicals, "white-out" liquids, and other organic-based liquids.

Polyethylene Terephthalate Polyester (PET)

Although PET as a polymer and film has been around for decades, the real breakthrough for food/beverage packaging came during the late 1970s with the development of the two-step process to convert it to a rigid bottle and the abrupt FDA ban on PAN for carbonated beverage bottles, a move that thrust the inferior barrier PET into the leadership position. Originally developed for carbonated beverages, PET has become the "workhorse" plastic jar/bottle for food/beverage packaging as an alternative to glass. It is clear, unbreakable, inexpensive, and has fair gas/flavor barrier properties. There are, however, many foods and beverages which do not need "super" barriers, or which do not need extended shelf life. There is much pressure on the food packers to consider PET for the above reasons, as well its recycleability (monolayer). Many carbonated and non-carbonated soft drinks, juices, salad dressings, some instant coffee, vegetable oil, and peanut butter have converted from glass into PET. Larger sizes which require handles, and smaller single-serve sizes (<16 oz.) which may have more severe barrier needs due to their unfavorable surface volume/area ratio, present greater difficulties for monolayer PET bottle..

One of the early drawbacks of PET containers was their low heat distortion temperature (70°F) which prevented hot-filling of fruit juice and tomato-based products. Recently developed processes, however, allow containers with higher crystallinity to be made and heat set which are capable of >80°F filling temperatures.

When highly crystallized (at which point the material is opaque), the O₂ barrier increases by about 40%, a factor that thrust CPET into a position as a retortable monolayer material briefly during the early 1990s.

Polyethylene Naphthalate (PEN)

PEN is a homopolymer of dimethyl-2,6-naphthalene dicarboxylate (NDC) and ethylene glycol, differing chemically from PET in that, instead of terephthalic acid, the ester of naphthalene dicarboxylic acid is used.

PEN has five times better oxygen barrier properties and superior temperature resistance when compared to PET.

The current main disadvantages of PEN are:

- Its high cost,
- Limited regulatory approval, and
- Unsettled sources of monomer technology/supply.

Japan has been a leader in commercializing PEN film along with the UK's ICI. Teijin produces both resin and film, the latter under the Teonex name. Teijin has been making film since 1990. Since 1990, DuPont and Teijin have had a worldwide joint venture (except for Japan) in polyester films, including PEN. DuPont has also recently acquired ICI's polyester business including its Melinex PET film and Kaladex PEN film operations.

One of the main drivers behind PEN is Amoco Chemical which started construction of a 110-million-pound-per-year NDC plant in 1993 in Decatur, Alabama, where they also produce PTA and p-xylene. Their technology will use ortho-xylene to produce NDC, rather than naphthalene as the feedstock which could reduce the manufacturing cost of

PEN resin to the \$1.20/pound range. New NDC technology from Japan's Kobe Steel along with Mobil Chemical may be able to reduce costs even further.

Blends of PET and PEN are possible for improved economics at a compromise in barrier and other properties. Such blends have been proposed for beer bottles. Blends with nylon, polycarbonates, LCs, polyolefins, PEI and other resins have also been looked at.

Other ways to reduce costs, at the expense of barriers and heat resistance, are through either copolymers or multilayer structures.

In addition to film, PEN is also a candidate for rigid containers, particularly with its hot fill, i.e., high temperature resistance, potential. In appearance, PEN looks like PET. Like PET, containers are typically biaxially oriented (standard injection molded preform followed by reheat/blow molding). Unlike PET, they can be hot-filled at higher temperatures and have better O₂ barrier properties.

PEN is available in limited quantities in the United States. FDA acceptance to date is only for the homopolymer.

If the basic problem of the high cost of the monomer is not resolved, its future as a major barrier packaging resin is in doubt.

Poly(Trimethylene Terephthalate)—PTT or 3GT

This is not a new polyester resin but it is only now being commercialized due to new technology which has lowered its manufacturing cost.

The two major players are Shell Chemical and DuPont, utilizing different routes. The monomers are purified terephthalic acid (used to produce PET and PBT) and trimethylene glycol, also known as 1,3-propanediol (PDO) or 3G. Chemically, the three carbon glycol monomer places it between PET and PBT and makes it an "odd" number polyester.

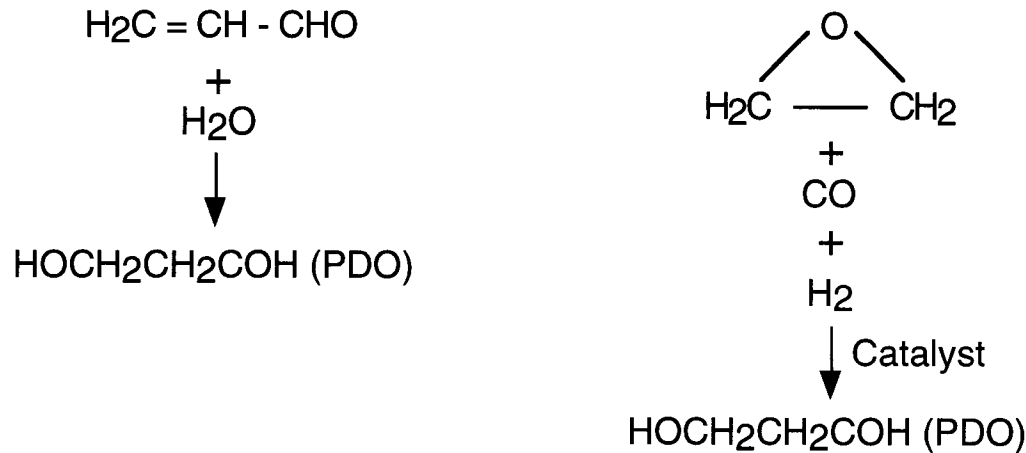
Shell Chemical first produced PDO in the early 1960s through acrolein hydration. They abandoned this route in favor of continuous hydroformylation of ethylene oxide. It wasn't however, until the early 1990s when a catalyst breakthrough occurred that this process offered commercial feasibility.

DuPont has two potential routes, one from sugar and the other from acrolein. Working with Genencor International, the world's second-largest producer of industrial enzymes, a fermentation process was developed for converting sugar directly to 3G. This replaces using naturally occurring yeasts to first transfer the sugar into glycerol, and then using bacteria to complete the reaction of glycerol to 3G. DuPont claims that this technology could approach the economics for manufacturing ethylene glycol.

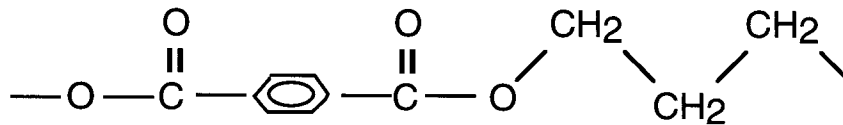
The other approach available to DuPont is through the acquisition of the PDO business of Degussa AG. This was announced in the summer of 1997 and involves swapping Degussa's PDO for DuPont's hydrogen peroxide business. In February 1998, regulatory red flags were raised regarding the H₂O₂ portion of the deal and DuPont has stated that the PDO sale will go through regardless. Degussa has a 4.4 million pound per year capacity plant in Antwerp, Belgium.

Degussa manufactures PDO from acrolein as shown below, along with Shell's ethylene oxide process:

Acrolein Route: Ethylene Oxide Route:



The polymer produced, PTT or 3GT (PET can also be called 2GT) is shown below:



Initial targeted market for PTT is fibers due to its resiliency and chemical resistance. It will compete here with nylon.

PTT is also an engineering resin and will be used in injection molding applications, both neat and glass filled.

Shell is also looking at PTT as a film resin where it could compete with nylon. Relative oxygen barrier properties of PTT, PET and nylon at 0% RH are:

Table No. 14. Relative Oxygen Barrier Properties

Nylon	1
PTT	1.6
PET	1.9

PTT's O₂TR is about 6 cc-mil/100 in²/day-atm.

Longer term, Shell is also looking at PTT as a blow molding resin. It is considering ways to tailor the polymer to enhance its barrier to moisture, oxygen and carbon dioxide.

PTT exhibits properties in some areas that are similar to PET (T_g), and in other areas the properties are closer to those of PBT (T_m, density, crystallization rate, impact strength). Its neat tensile strength, stiffness and HDT are higher than are PBT's. Typical properties are density of 1.33, melting point of 228°C (442°F), and T_g of 45° to 65°C (113°-149°F). Its moisture absorption is 0.03% after 24 hours and 0.15% after 14 days.

Properties vs. PET, PBT, nylon and polycarbonate are shown in Table No. 15.

Table No. 15. Physical and Electrical Properties of Unreinforced EPT Polymers

Physical Property	PET	PTT	PBT	Nylon 6/6 Dry	PC	Nylon 6 Dry
Tensile Strength, MPa	72.5	67.6	56.5	82.8	65.0	65
Flexural Modulus, GPa	3.11	2.76	2.34	2.83	2.35	2.2-2.7
HDT @ 1.8 MPa, °C	65	59	54	90	129	60
Notched Izod Impact, J/m	37	48	53	53	640	58.6
Specific Gravity	1.40	1.35	1.34	1.14	1.20	1.14
Mold Shrinkage, m/m	0.030	0.020	0.020	0.015	0.007	0.015
Melt Temperature, °C	265	225	228	265		230
Glass Trans. Temp., T _g , °C	80	45-75	25	50-90	150	50
Dielectric Strength, V/mil	550	530	400	600	380	380
Dielectric Constant, 1 MHz	3.0	3.0	3.1	3.6	3.0	3.3
Dissipation Factor, 1 MHz	0.02	0.015	0.02	0.02	0.01	0.024
Volume Resistivity, Ohm-cm	1.00 E+15	1.00 E+16	1.00 E+16	1.00 E+15	8.2 E+16	1.00 E+15

Shell started up a 5 million pounds per year PDO plant in Geismar, Louisiana, and followed this with bringing on-stream a 12 million pound PTT plant in Point Pleasant, West Virginia, at the end of 1996. They are constructing a 100 million pound PDO and 400 million pound PTT plant. The latter will be in two trains and the first is scheduled to be brought on-stream by the end of 1998.

Resorcinol Copolymers

Synthesis of PET with various resorcinol comonomers appears to yield a resin capable of reducing oxygen and carbon dioxide permeation. Data substantiating the contribution of resorcinol di(betahydroethyl)ether and other resorcinol derivatives indicate a similarity of the resorcinol structure with that of isophthalic acid—another monomer known to enhance barrier properties. It is this similarity, notably the 1-3 meta linkages, that appears to be a key factor contributing to improved gas barrier performance. (The use of isophthalic acid was pioneered in the early 1980s by Owens-Illinois and is now being pursued by Mitsui Petrochemical under the name of B-010.)

Liquid Crystal Polymers (Superex Polymer)

LCs can be very expensive, well above the per-pound price of competitive materials. It is expected that, with time and volume, these prices will decline, but it remains to be seen whether they will be competitive. They are also difficult to process but have very high heat resistance as well as being very gas impermeable. Liquid crystals outperform both EVOH and PVDC from a gas barrier perspective. Work led by Superex Polymer has been underway since the early 1990s to develop processing technologies for these thermotropic plastics to produce high barrier packages. Superex's initial efforts were in producing oriented films and has since expanded to tubes and bottles, the latter primarily for beer. Most of their work has been aimed at multi-layer structures with PET as the major component.

Aliphatic Polyketones

While aliphatic polyketones (PK) have been known for many years, it was not until Shell Chemical in 1992 developed new palladium catalyst technology that their commercial reality could be foreseen.

These polymers are made from simple monomers, ethylene and carbon monoxide, and their chains are in an alternating 1:1 mole ratio of these two raw materials. Small quantities of propylene and butylene can also be added.

Today, the two sources for aliphatic PK are Shell Chemical and BP Chemicals. The latter has a joint research and market development agreement with GE Plastics. The two tradenames being used are Carilon for Shell and Ketonex for BP. Shell has a plant in Carrington, England, which came on-stream in October 1996 with 22 million pounds of

capacity. BP has a pilot plant in Grangemouth, Scotland. Shell has announced plans to build a 60 million pound plant in Geismar, Louisiana, to be ready in early 1999. They have been supplying resin in the U.S. since late 1996 following their introduction in Europe in 1995. A semi-works facility in Moerdijk, The Netherlands, started producing resin in 1994.

Both Shell and BP have high expectations that aliphatic PK will be a major new engineering plastic. They have been focusing on injection molding applications but have released enough information to indicate that there is potential for them in film and blow molding applications in both industrial and packaging uses.

These are high-temperature crystalline polymers with a melting point of 428°F (220°C) and a specific gravity of 1.24. They are strong and tough with good friction (wear resistance and superior resiliency). They maintain their stiffness close to their melting point. A heat distortion temperature of 221°F at 264 psi is typical for one of the twelve Carilon grades.

Initial markets targeted by Shell are automotive, electrical, industrial and consumer appliances. Other potential markets include fibers, film, industrial packaging and coatings.

As a barrier plastic, in addition to its high heat resistance, it resists permeation by volatile organic compounds such as hydrocarbons, has good chemical and solvent resistance, and is hydrolytically stable with low moisture absorption.

BP is looking at Ketonex in coextruded cast films with LDPE and coextruded bottles with PP. Its hydrocarbon resistance makes it a candidate for automotive gas tanks where it can be used in place of EVOH. In this application, only 3 or 4 layers would be needed versus usually 6 with EVOH tanks, as the polyketone can be the inside gasoline contact layer. A typical structure would be:

HDPE / regrind / tie layer / PK

This 4-layer structure might be reducible to 3 if the HDPE and regrind layers are combined.

Shell is working with tie layer suppliers and hopes to have something by 1999 that can be used to bond PK to HDPE.

Automotive fuel lines, as an alternative to nylon, is another potential outlet for PK resins.

In blow molding, the pesticide and hazardous chemical market, versus Selar RB, PAN, and PVC, is also a possibility.

BP is also looking at blends with Carilon to improve barriers. Blend resins include HIPS and PVC. The latter development is in conjunction with Geon Co.

Shell's two extrusion grades are D26FX100 and D26CX100. The latter has the highest molecular weight of any the Carilon resins.

Oxygen Scavengers

The highly publicized Aquanautics scavengers of the early 1990s were a series of organo-metallic compounds (called "ligands") that mimic the activity of hemoglobin, i.e., they actually grab and hold O₂ rather than reacting directly with it. This is O₂ scavenging.

The first use of these materials was in the addition of small amounts as a blend to the plastic liner of beer bottle caps and crowns. The cap is activated only after it is applied to the bottle, at which point it rapidly absorbs any remaining O₂ in the headspace of the package. The cap was given the name "SmartCap" and is being manufactured and sold by Zapata (a leading manufacturer of beer bottle crowns and liners). It is believed that removing O₂ in the headspace of beer bottles will not only give a fresher-tasting product, but will also enhance its shelf life.

More recently, since 1995, Japanese companies such as Mitsubishi Gas Chemical and Toyo Seikan have incorporated ferrous iron salts into plastics which are then converted into sheet for thermoforming into trays. These

materials, when wetted by moisture evaporated from the contained product, have ferrous ions that can be oxidized into the ferric state, thus “scavenging” the oxygen from the package’s interior. Obviously, a good oxygen barrier must face the air side. Problems include the ability of the interior sealant to pass sufficient moisture to activate the iron. The concept, however, is quite effective theoretically and has attracted considerable commercial attention.

Even more recently in the United States, Amoco Chemical has introduced an oxygen scavenger tradenamed Amosorb™, being incorporated into film by Cadillac Products. These scavenger films have been applied to the interiors of flexible laminations for military rations for very-long-term shelf life.

With all the activity, we might expect many more developments for scavenger incorporation in the future. One question is: Can these current scavenging systems have sufficient capacity to function as effective long-term oxygen barriers?

Oxbar

This was a 1980s oxygen scavenger plastic bottle development by CarnaudMetalbox (CMB) in the United Kingdom. Essentially, it was a PET blend containing 5% MXD6 nylon plus 100-200 ppm of a cobalt catalyst. The catalyst is specific for the oxidation of the nylon. Thus, as O₂ permeated the wall of the bottle, it would react with and oxidize the nylon, thus preventing the O₂ from reaching the inside of the container. The packages were thereby nearly impermeable to O₂ until all of the MXD6 was oxidized, a reaction that could require a year or more. None of the other properties of the PET were changed except for a slight haze due to the addition of the nylon. (In somewhat similar fashion, the interaction between MXD6 and CO₂ helps to prevent delamination at the MXD6 and PET interface in PET/MXD6/PET carbonated soft drink bottles.)

This was a unique method of producing a very high plastic barrier package. Currently, the system does not have FDA approval. The packages have EC approval for oil-based foods only.

Another advantage was that with the oxygen scavenger as part of the container’s wall, no separate sachet or special closure is required.

The potential cost of this system would not be much greater than PET alone, and thus it could have one of the lowest cost/benefit of any O₂ barrier plastic package.

CMB is now part of Crown Cork & Seal, and their oxygen scavenger technology is being pursued by other organizations.

Coatings

Silica-Coated Polymer Films. The shelf life of foods, in part, depends on the gas barrier protection provided by its container. All plastic materials have some permeability to oxygen, carbon dioxide, and water. Thus there have been continuous developments to improve the barrier properties of plastic films and thin-walled containers.

Outstanding barrier protection can be obtained from laminations of aluminum foil and plastic films. Vacuum-deposited aluminum coatings on plastic films can also provide very good gas barrier protection. These films are widely used and provide good performance. However, they may not be transparent—a desirable feature in many packaging applications. Moreover, aluminum-coated or foil-laminated films have limited use in microwave ovens.

While a number of glass or ceramic-like materials have been used to coat plastic films, silicon dioxide (silica) has been the dominant material used since 1989. Because the sublimation temperature of silica in a vacuum is 2,000°C, a high energy electron beam source has been the conventional method of vaporizing silica. This requires that the coating system be radiation shielded.

The vaporized silica precipitates on the plastic film, forming a continuous coating as the film passes through the vacuum chamber. The resulting coating can be as thin as 0.04 microns. Such thin layers are required if the coating is to have the necessary degree of flexibility. Such thin coatings are possible because SiO_x coalesces on the substrate as a continuous coating, rather than in columns, as is the case with vapor-deposited aluminum.

The vaporized silica molecules do not coalesce on the surface as SiO_2 , but as SiO_x , where x can vary between 1 and 2. This is a major problem associated with the process. While SiO_2 is transparent, SiO is yellow. Since SiO has a lower vapor pressure than SiO_2 , it is easier to form. Silica coatings are usually a mixture of silicon oxides and have a characteristic yellow color. Oxygen is usually added to the chamber to increase the level of x above 1.5, which will reduce the color in the coating.

A biaxially oriented PET film coated with SiO_x has an oxygen permeability of only 1.5 $\text{cc/m}^2\text{-day-atm}$. When the glass coating is overcoated with OPP it produces a film that has an oxygen permeability of 0.5 $\text{cc/m}^2\text{-day-atm}$. The oxygen barrier properties of this film remain intact for over a year and during microwave heating.

In addition to PET, film substrates coated by this technology include OPP and BON.

Until the mid-1990s, most of the work involved in developing this technology utilized an electron beam energy source. Many companies considered this approach too expensive for commercial use. Thus, a number of alternative approaches to producing silica coatings have been investigated. Chemical plasma deposition has been used to apply a 0.1 micron thick SiO_x coating to plastics. In this process, an organic silane is activated by a radio frequency source in a soft vacuum to produce a charged gas that deposits on the target substrate. The process can be used to coat either films or three-dimensional objects. Chemical vapor deposition has been used to deposit SiO_x coatings on plastic films.

The barrier protection provided by very thin silica coatings can be superior to that provided by PVDC, EVOH, and vacuum-metallized films. The barrier protection of the silica-coated films is not affected by moisture or temperature. The coating thickness cannot be increased much above 0.1 micron or the coating will become brittle and crack when flexed. Even at a thickness of only 0.05 μm , the coating is still too brittle to permit creasing and repeated flexing.

Some vacuum deposited glass coated film packages are used today in the United States primarily for medical device packaging, and in Europe for a variety of applications, mostly where high oxygen barrier plus transparency are required. In Europe, companies are made sensitive to the environmental issues surrounding chlorinated compounds such as PVDC.

Proposed to complement silica coatings are Ormocers, a mid-1990s development from Germany. Ormocers, or organically modified ceramics, may be applied in conjunction with or independently of silica to enhance oxygen barrier. To date these have been applied only in laboratory settings.

In addition to silica, aluminum oxide (Al_2O_3) coatings have been commercially developed on polyester films. These have particularly good moisture barriers.

Thermoset Epoxy-Amine Coatings. For the past few years, a different approach to imparting oxygen barrier to plastic sheet and film has been the application of thermoset epoxy-amine coating by PPG Industries. Under the tradename BAIROCADE™, these coatings are two-component epoxy-amines sprayed onto the bottle's surfaces. The glossy thermosets reportedly increase the oxygen barrier of polyester bottles by 2 to 12 times. The supplier reports an extension of shelf life of polyester carbonated beverage bottles by more than three times. They also claim plastic closure gas barrier enhancements by four or more times. Coating performance is not affected by pasteurization or retort temperatures.

Blending

Blending is used for a number of reasons. It can improve processability and reduce costs. The latter is very important with high-cost polymers such as PEN and LCP as they are incorporated into PET in an attempt to achieve a balance of oxygen barrier plus cost. This technology will also impact resin properties. Sometimes a synergistic effect will occur and the blend will have properties better than that of the individual components. Reactive blending can take place as, for example, with the mixing of different polyester polymers (transesterification), or polyester and nylon (polyesteramide formation). More frequently, blends result in a compromise of properties by falling between those of the individual resins. A common objective of blending is to improve the deficient properties while maintaining as much as possible of the desirable properties of the major component.

Blends can also sometimes lead to unexpected regulatory problems. The approval of the individual components of a blend does not ensure that the blend itself will receive regulatory acceptance.

Packaging blends that have been used commercially include PVC/Paraloid HT 510 and DuPont's Selar RB, neither of which enhances oxygen barrier, and nylon 6/amorphous nylon. Selar RB was introduced by DuPont in the mid-1980s as a hydrocarbon barrier for household and agricultural chemical bottles and automotive gas tanks. It is based on the tortuous path concept by blending about 10% nylon 6 into an HDPE matrix. The technology forms the nylon into very thin, parallel platelets around which oxygen molecules need to pass in order to diffuse through the continuous HDPE phase. During the late 1980s, DuPont incorporated mica platelets into plastics to enhance oxygen barrier properties—successful technically but not commercially. More recently, a version has been developed with EVOH instead of nylon.

Probably the packaging resins most involved in blend developments are polyesters (PET and other types), nylons, EVOH, and liquid crystal polymers. LCPs, which are primarily thermotropic polyesters, may be the most extensively evaluated resins today for blends and alloys, some of which are of potential interest to packagers, particularly the work of Superex Polymer with LCP/polyester and other resin combinations for biaxially oriented blown film. Work continues with LCPs and polyimides, nylon 6, nylon 12, polyamide-imide, HDPE, PP, epoxies, fluoropolymers, and a host of other engineering resins.

Kuraray has reported on their work with PET/EVOH blends for the beverage industry—soft drinks, beer and wine. The technology was designed to compete with PVDC-coated PET bottles and multilayer PET/EVOH/PET bottles. The barriers were superior to the PVDC-coated but not as good as multilayer bottles. One feature of the blends was that they enhanced orienting and heat setting of the PET bottles which, in turn, reduced the moisture sensitivity of the EVOH thereby improving the container's overall barrier properties.

Another promising PET blend reported during the mid-1980s and also targeted at the one-half-liter soft drink container market was developed by Owens-Illinois and used a copolyester resin. Owens-Illinois licensed this copolyester resin to Mitsui Petrochemical Industries, Ltd., which marketed it in Japan under the Gas Barrier Resin B-010 name. While nearly twice the price of PET (\$1.20/pound versus \$0.64/pound), Owens-Illinois showed reduced raw material costs for an 87% PET/13% copolyester blend with comparable shelf life. The copolyester had four times lower CO₂ transmission rates than did the PET (25 versus 6 at 0°C) allowing for down-gauging from 27 to 21 grams while still maintaining a 12-week shelf life and acceptable rigidity.

Blends of polyester with nylon have also been of interest to the packaging world. During the mid-1980s, Nissei suggested these as outer layer(s) of beverage bottles with nylon as the core. Nissei also did work using Mitsubishi's high barrier MXD6 nylon as the core layer surrounded by PET in injection stretch blow molded bottles. It is also possible to blend PET with MXD6. As early as 1986, blends of 70% PET and 30% MXD6 had a US FDA regulatory letter of no objection.

Another polyester resin candidate for blends is polyethylene naphthalate or PEN. The most promising candidate is a blend of PEN with PET, but work has also been done with polyolefins, nylons, polycarbonate, LCP, PEI and other polyesters. Eastman recently reported on their work which was done in a single screw extruder. The melt blending resulted in transesterification which could be controlled primarily by time and temperature.

As shown above, nylons have also been prime candidates for blending, e.g., nylon 6 with HDPE (Selar RB), MXD6 with PET (Oxbar), nylon 6 with amorphous nylon, and nylon with LCPs. Nylon and EVOH adhere to each other in coextrusions without the need for a tie layer and are compatible in blends.

Nanocomposite

Somewhat similar to blends and tortuous path technology is the development of nanocomposites. It started in the 1980s in Japan by Toyota in their Central Research Labs and was then licensed to Ube Industries. Initial focus was with nylon resins for automotive applications and then to packaging films. The technology is based on using very fine smectite clay particles as fillers. The clay particles contain multiple layers that are slightly less than one nanometer thick but have surface dimensions of about 1,000 nanometers or one micron. This results in a surface area-to-weight ratio of about 750 m²/gram. These clays swell by absorbing water or other polar ions. The montmorillonite form of smectite can absorb 20 to 30 times its own volume in water. Their surface can also be modified to absorb organic chemicals instead of water.

Ube developed its first nylon composite in 1989 for an automotive timing belt cover. They have since developed film packaging grades in nylon 6, nylon 66, nylon 6/66 copolymers, and nylon 12. These are called nylon clay hybrids, or NCH. The addition of about 2% clay in nylon 6 can reduce its gas permeability by about one-half.

In the U.S., Nanocor (part of amcol International) has been in the forefront of developing these composites. Nylon resin suppliers such as AlliedSignal and Solutia have also done work in this area.

Other resins besides nylon that are potential candidates for nanocomposites include PP, polyester, polystyrene, fluoropolymers and epoxies. DuPont has been active with fluoropolymers, and ICI uses this technology for a new higher barrier version of its Melinex polyester film. (Their Melinex business has since been acquired by DuPont.)

In addition to films, injection molding and thermoforming fabrication processes also have potential uses for this technology.

CONCLUSION

The history of oxygen barrier plastic packaging has been virtually written during the past twenty years. Strangely, most of the innovation dates from the 1970s and 1980s with only what might be regarded as slow development since that period. Meanwhile, food packagers have been steadily reducing their oxygen barrier requirement, leading to two possibilities:

- Metal cans and glass bottles may inevitably be obsolete
- The need for the elusive perfect oxygen barrier plastic may be obviated

Meanwhile, additives such as oxygen scavengers, and coatings, and blends appear to be as potentially promising as the development of new resins, although aromatic polyketones and PTT are exciting new developments.

Twenty years is a short time in the history of modern industrialized society, but a long time in the brief history of plastics. In retrospect, the accomplishments of the past twenty years, although not dramatic, are remarkable in that they have nearly met the market's needs.