Toughened polyester for barrier films

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Chemically toughened polyester resins have excellent heat sealability and can be used in blown and cast coextrusions.

Polyesters were synthetically produced in Europe in the middle of the 1800s, but no major developments were made until researchers in England and the United States began producing fibers and film from polyethylene terphthalate (PET) polyester using orientation to make usable products. Wallace Carothers of Du Pont was among these researchers. He worked on PETs until he moved on to find higher melting polymers for fibers, which led to the invention of nylon. The PET market has grown rapidly and is estimated to be a 5.19-billion-lb/year industry today.

The estimated breakdown of PET into its various markets is shown in **Fig. 1**. The fiber industry, by far the largest user, uses PET to manufacture products ranging from textiles to carpets. Packaging and film represent the next two largest market segments. PET's use in carbonated soft-drink bottles is a real success story. A process that was developed by Du Pont in 1973 and then commercialized by Coca-Cola in 1977 has enabled PET to secure almost 100% of the 2-liter soda container market. This process is now used to manufacture PET containers for liquor, peanut butter, salad dressings, and other foods. Trays of crystalline PET are used to package frozen entrees. The film segment of the PET market uses PET in the manufacture of the films that are used as base sheets for magnetic and video tapes, floppy disks, and capacitors. This segment also includes packaging films, such as the oriented PET available from Du Pont, ICI, Hoechst, and others.

The packaging market has shifted from traditional metal and glass packages to plastics. This trend has generated intense interest within the industry for polymers with barrier properties. New polymers are being developed and existing polymers are being modified to meet these new applications. Ethylene vinyl alcohol (EVOH), polvinylidene chloride (PVDC), nylon, and PET all provide some degree of barrier.

Table I shows the oxygen and moisture barrier typical for these types of resin. EVOH and PVDC resins provide the highest barrier, especially for oxygen. EVOH is moisture sensitive and, thus, is used as an interior layer in coextrusions, whose outer layers protect the inner EVOH layer from moisture. PVDC can be used in coextruded structures or as coatings. Nylons offer good oxygen barrier and relatively good moisture barrier. There are many nylons available; various grades, oriented films, and the new amorphous nylons. PETs are next in the barrier list. They offer moderate barrier to oxygen and water. EVOH, PVDC, nylon and PET are good barriers to flavors, odors, and solvents.

The choice among these resins is determined by the level of barrier needed and the processing technique. The higher-barrier resins generally are more expensive, so it is not cost-efficient to use these if the barrier requirements do not demand them. The PETs offer adequate barrier for many applications.

Selar® PT: a toughened polyester

PET must be oriented or crystallized to obtain tough, usable articles. Amorphous, nonoriented PET parts are usually too brittle for use. The 2-liter carbonated-beverage bottles are produced by injection stretch blow molding, which orients the side walls. This process, developed by Du Pont, is now licensed to bottle manufacturers. PET films are biaxially oriented, and PET trays are crystallized to make them tough.

A newly developed and patented process of chemically toughening PET resins has eliminated the need for secondary processes. Chemically toughened PET films do not have to be mechanically stretched to gain toughness. This material is sold by Du Pont under the trademark Selar® PT.

There are two film resin grades to date. One complies with the FDA regulations for food contact (21CFR 177.1630); the other is designed for industrial uses and does not meet these regulations. Both are translucent and have optical properties similar to those of a high-density polyethylene (HDPE) film.

Barrier properties

The oxygen and moisture barrier properties of Selar® PT remains close to those of oriented PET, as seen in Table I. The oxygen barrier is moderate, offering about 100 times better barrier than HDPE, but less than the high-barrier EVOH and PVDC resins. When intermediate oxygen barrier is required, PET is a cost-effective alternative.

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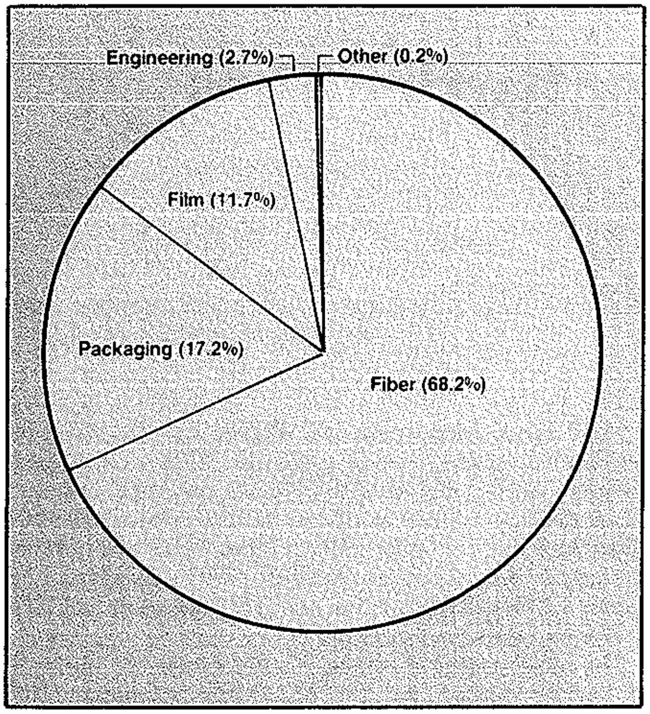
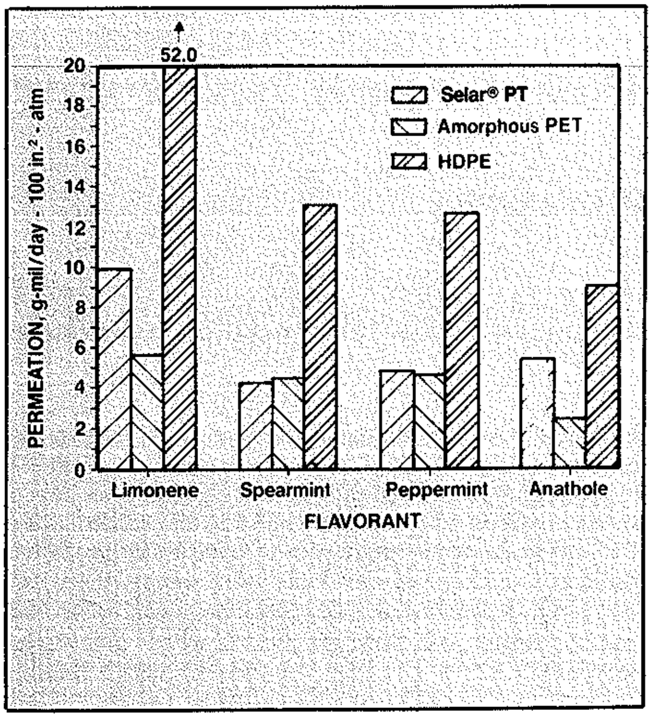
1. Estimated polyester markets, 1986.



2. Flavorant permeation for Selar® PT, amorphous PET, and HDPE. Results were determined using a modified test procedure (ASTM E96-80) at 55°C.



I. Oxygen and moisture barrier properties of various resins[a]

	Oxygen transmission rate,[b] cm³-mil/day-100 in.²-atm	Water vapor transmission rate,[c] g-mil/day-100 in.²-atm
EVOH	0.05	3.1
PVDC	0.1	0.1
B.O. nylon	6.0	10.0
Nylon 6	7.0	22.0
Selar® PA	1.5	3.0
Oriented PET	5.0	1.3
Selar® PT		
Food	16.3	2.5
Nonfood	17.1	4.9
LDPE	350	1.0
HDPE	150	0.3

[a]Data from MPE and/or product data sheets.[1,2]
[b]Determined by ASTM D3985 at 72° F, 50% RH.
[c]Determined by ASTM E96 at 100° F, 90% RH.
[1]Martino, R. J., ed., Modern Plastics Encyclopedia, Vol. 63, No. 10A, Oct. 1986.
[2]Du Pont product data sheets.

II. Solvent barrier properties of Selar® PT

Solvent	Permeation value, g-mil/day-100 in.²-atm
PET	
Xylene	1.0
Methylethyl ketone	0.4
1, 1, 1 trichloroethane	1.1
Methanol	0.9
Toluene	0.7
Isopropanol	0.7
Ethyl acetate	2.3
10% methanol/90% xylene	0.6
15% acetone/85% xylene	1.9
HDPE	
Xylene	150

*Test performed at 104° F (40°C) on 4-oz injection blow molded bottles.

However, PET's real advantage is found in its excellent barrier to solvents, flavors, and odors. **Table II** shows the solvent barrier properties of Selar® PT. The permeation values are in the 1-2 g-mil/day-100 in.²-atm range for aliphatic and aromatic hydrocarbons, as well as mixtures of solvents. In comparison, HDPE has a permeation value of 150 g-mil/day-100 in.²-atm for xylene.

Food packaging must provide an effective barrier to prevent loss of flavorants or migration of odors. Flavorants are expensive, and loss can cause the product to be less attractive to consumers. Odors can either be lost or picked up by a packaged food. PET can provide an effective level of barrier protection, as shown in **Fig. 2**. This chart shows that the toughened PET for food use is about equal to amorphous PET in barrier to some common flavorants (limonene, mints, anathole). This test was conducted following ASTM E96-80 for water vapor transmission, using pure flavorants in place of water. HDPE, which is shown for comparison, is not a good barrier to these flavorants. LDPE has even less barrier, with values

III. Weight gain for three polymer films immersed in limonene for 2 weeks, room temp.

	Weight gain, %
Selar® PT (food)	0.14
Amorphous PET	0.09
LDPE	14.1

IV. Physical properties of Selar® PT

Selar® PT	Film gauge, mils	Tensile strength, 10^3 psi		Yield strength, 10^3 psi		Elongation, %	
		MD	TD	MD	TD	MD	TD
Food	0.6	6.6	7.0	4.6	3.5	440	380
	1.15	7.0	7.7	3.9	3.7	400	400
	2.25	6.6	7.0	4.1	3.6	400	410
Nonfood	0.55	5.5	5.7	3.1	3.2	340	330
	1.1	6.4	6.1	3.6	3.4	350	360
	1.95	6.3	5.6	3.8	3.4	370	390

*Determined by ASTM D882.

V. Tear and impact properties of Selar® PT

Selar® PT	Film gauge, mils	Elmendorf tear (ASTM D1922), g/mil		Spencer impact (ASTM D3420), (in.·lb/mil)
		MD	TD	
Food	0.6	26	27	4.4
	1.15	38	58	4.8
	2.25	62	75	3.8
Nonfood	0.55	20	15	1.5
	1.1	35	26	3.6
	1.95	39	40	4.0

VI. Graves tear for 1.0-mil toughened and oriented PET films

	Avg. Graves tear (ASTM D1004), g
Selar® PT (nonfood)	780
Oriented PET	500

ranging from 20-100 g-mil/day-100 in.^{2}-atm for these flavorants.

Flavor scalping is another facet of the interaction between a food and its package. If the packaging material absorbs enough of a flavorant, the taste of the product can be affected, even without significant permeation through the package. The toughened PET is again comparable with amorphous PET and much better than the polyolefins. **Table III** shows the weight gain by films immersed in a pure flavorant at room temperature for two weeks.

Physical properties

Table IV shows tensile strength, yield strength, and elongation for food and nonfood films of Selar® PT at nominal gauges of 0.5, 1.0, and 2.0 mil. Elongation for the chemically toughened PET is notably higher than for oriented PET. Selar® PT had an average elongation of 380% in the machine direction (MD) and 375% in the transverse direction (TD), while oriented PET averages 140% in the MD and 120% in the TD. This facilitates forming and reduces brittleness.

Tables V and VI show the tear and impact properties of Selar® PT. Elmendorf tear is the test that simulates a propagating tear, while Graves tear is the test for tear initiation. The Graves tear for the toughened PET is higher than for oriented PET.

Table VII shows film modulus and the coefficient of friction (COF) for the toughened PETs. The film is stiff and slides easily over itself and over metal. Both of these properties are advantageous in packaging machinery.

A major feature of this new resin is its heat sealability. Unlike uncoated PET films, which do not heat-seal well, these have excellent seal strengths. **Figure 3** shows heat-seal curves for 0.5-, 1.0-, and 2.0-mil films of food-grade Selar® PT. The food grade, at 1.0 mil, begins sealing between 200°F and 225°F and reaches a maximum of around 1200 g/in. strength. The temperature limit is about 375°F, where film distortion begins to occur.

Figure 4 shows heat-seal curves for 0.5-, 1.0-, and 2.0-mil films of nonfood-grade Selar® PT. The grade designed for other-than-food packages is toughened using different chemistry, and it seals at even higher strengths. The maximum is about 1600 g/in. for a 1.0-mil film. The temperature range is approximately 225-375°F.

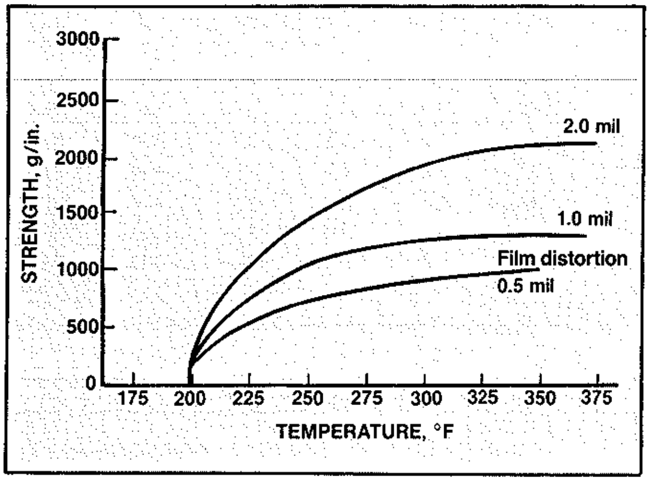
The ability of a film to retain a crease is an important property in packaging, especially from the consumer's viewpoint. Films for packages that should reclose, like cereals or snacks, should retain a crease well. **Table VIII** shows the results of a crease-retention test. This test is a modified ASTM D920-49 dead-fold procedure. A crease is formed under a known force. Then the amount the film unfolds in a given time is measured. The scale is set such that aluminum foil, which stays folded, is 100%, and a polyolefin that unfolds completely is 0%. Glassine, a standard film for dead fold, is 84%, and the Selar® PT monofilms are 72% and 87%, comparable with glassine. Of course, coextrusions must be evaluated individually to determine the crease retention of the total structure vs. that of the toughened-PET layer alone.

Processing

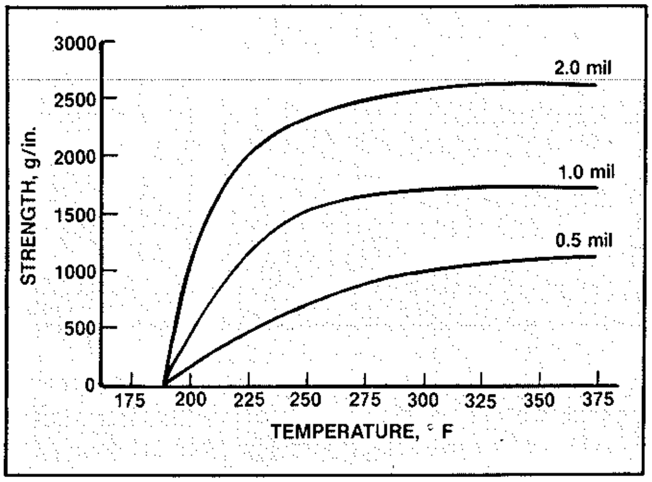
Selar® PT is versatile in processing because it does not require orientation. The resins can be cast or blown as single layers or in coextrusions.

All polyesters are moisture sensitive. Excess moisture present during melt processing will cause chain scission

3. Heat-seal strength for films of Selar® PT (food grade) at three different film thicknesses. (Seals at 30 psig, 0.5 s, 1-in. bar, no slip sheet.)



4. Heat-seal strength for films of Selar® PT (nonfood grade) at three different film thicknesses. (Seals at 30 psig, 0.5 s, 1-in. bar, no slip sheet.)



VII. Stiffness and coefficient of friction of Selar® PT

Selar® PT	Film gauge, mils	Secant modulus (ASTM D882), 10^3 psi MD	TD	CoF (ASTM D1894) film/film	film/metal
Food	0.6	190	190		
	1.15	190	180	0.31	0.25
	2.25	170	160		
Nonfood	0.55	150	110		
	1.1	160	140	0.31	0.26
	1.95	170	150		

VIII. Crease retention of Selar® PT in comparison with other films*

Film	Film gauge, mil	Crease retnetion, %
Aluminum foil	1.0	100
Glassine	1.3	84
Selar® PT		
Food	2.0	72
Nonfood	2.0	87
Polyolefin	1.65	0

*Determined by modified ASTM D920-49, 250-g weight.

and degrade the PET's properties and its melt strength. Thus all water must be removed by drying prior to processing. A desiccant hot-air hopper dryer is recommended. The toughened PETs should be dried to 0.01% H_2O or lower for film extrusion. Several hours of drying at 250°F is usually sufficient to reach this level of dryness. PET is also hygroscopic. After about 15 min of exposure to air, the moisture rises above the acceptable level. It is imperative that dry resin be maintained up to the extruder.

"General purpose" screws have been used successfully for processing. A typical screw is 24:1 L:D, 3:1 compression ratio, with 1/3 feed, 1/3 transition, and 1/3 metering sections. Screws designed for PET also work, but they are not mandatory. To optimize film extrusion, the dies and adaptors should be streamlined to minimize hold-up areas, where degradation can occur. Also they should be uniformly and consistently heated to prevent hot or cold spots.

The melt temperature of these resins is 510°F (265°C), and they begin to lose viscosity and discolor from degradation above 570°F (300°C). The recommended processing temperature range is between 515-530°F to maintain maximum melt strength. The power usage is expected to be higher than a polyolefin resin because the resin is tougher and harder to turn before melting. The pressures will be lower, though, because, once melted, the PET is quite fluid.

For blown film, a stepped profile from 475°F to 515°F is recommended. The film is stiff, so collapsing and windup should be designed to minimize wrinkles. This usually means a low angle of collapsing, a low tower, and appropriate spreader rolls. A profile for cast film should be about 10°F hotter than the blown profile. The chill roll should be around 100°F to optimize toughness.

Selar® PT can be used in blown and cast coextrusions. PET is a significantly different polymer from polyolefins, so there is little natural adhesion between the two. Therefore a coextrudable adhesive (CXA) is required. The adhesive must be capable of being processed at the toughened-PET temperatures without degradation. Adhesives developed by Du Pont for this purpose provide 560 g/in. of adhesion in the following blown structure: 1.3 mil Selar® PT 4368; 0.3 mil BYNEL® E-315 CXA; 1.2 mil HDPE.

This PET can be surface printed using PET-type inks after electrical-discharge treating. The film has also been successfully metalized in the laboratory. Master-batch colorants in the resin base have been developed for films.

Applications

Considering all the features of Selar® PT resins (barrier properties, heat-seal strength, and versatile processing), there are many potential applications for monolayers and coextrusions. A single layer of the food-grade film could be used as a food-contact layer to prevent flavor scalping in flexible or rigid containers. Monofilm of the nonfood grade could be laminated to paper for pet food packages or for bags containing products with solvents, such as easy-lighting charcoal briquettes.

Coextrusions of the Selar® PT with a polyolefin layer to provide the necessary moisture barrier could be used for cereal liners, snack-food packages, and cake-mix pouches. The toughened-PET barrier prevents flavors and odors from either escaping or entering, and thus altering the food's quality. For industrial packaging, a similar coextrusion could be used for a bag-in-box for solvents or for waste-pond linings.

Future developments

Work on this new family of toughened PETs is continuing. Plans include development of extrusion-coating grades and tailor-making grades to fit certain applications. Two necessary differentiations that are already apparent are a food grade with a lower seal-initiation temperature and a nonfood grade with an improved appearance. As markets develop, there will be more grades available.

Summary

A new, patented technique to chemically toughen polyester (PET) has led to a new resin family that is close to amorphous PET in barrier properties. Selar® PT can be heat sealed, and it provides enhanced elongation and better melt strength. The orientation step that is used to produce most PET film can thus be avoided. Given this unique combination of properties, Selar® PT should find many applications in the packaging field as a cost-effective barrier film.

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