EXTRUSION POLYMERS

Single-site catalyst produced polyolefin plastomers for extrusion coating and laminating

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ABSTRACT

The use of ethylene polymers and copolymers made from single-site catalysts is expanding into the extrusion coating and laminating markets. These polymer products are available with physical properties that provide extrusion coating and lamination converters with new tools to meet the increasing demands of these technologies. Single-site catalysts can produce ethylene α-olefin copolymers that are markedly different in structure and performance compared with conventional Ziegler-Natta-catalyzed polyolefins such as HDPE, LLDPE, ultra low density polyethylene, and high pressure free radical polymerized LDPE. This paper discusses the products and technology derived from conventional Ziegler-Natta catalysts and single-site catalysts with special emphasis on products derived from constrained-geometry catalysts and the unique physical properties that derive with appropriate use of such catalysts.

Application:

Single-site catalyzed polymers and copolymers offer excellent properties for coextrusion or monolayer coating and laminating applications.

Conventional Ziegler-Natta catalyzed semi-crystalline linear polymers have been available since the middle 1960s *(1)*. Single-site catalyzed polymers date from the early 1970s *(2)*. They range from semi-crystalline to elastomeric. Since then, industry research activity in single-site catalysts has been tremendous. One industry consultant stated in 1993, "There are more than 60 companies and institutions working in the area that have made patentable discoveries, and there are many more that have not yet reached the patenting stage *(3)*." This paper discusses the structure of Ziegler-Natta catalysts and single-site catalysts and describes how the structure of the catalyst can influence polymer properties. The discussion also covers specific polymers and their performance properties with emphasis on polymers produced using constrained-geometry catalysts. Constrained-geometry catalysts differ from other single-site catalysts and can produce polymers with unique physical properties.

CATALYST STRUCTURE

Ziegler-Natta catalysts

Conventional Ziegler-Natta catalyst systems typically have several catalytic sites attached to each support particle as **Fig. 1** shows. The activity of each transition metal site for polymerization is different. This causes the formation of polymer molecules with a plurality of molecular weights and copolymer molecules with a variety of compositions. These attributes strongly influence other polymer properties.

Single-site catalysts

Single-site catalysts have a singular polymerization site. One type of single-site catalyst that has had extensive study uses a sandwich structure containing two cyclopentadiene rings. Using the term originally applied to these sandwich structures in the 1950s, the catalysts have the name metallocene catalysts. **Figure 2** is a diagram of such a structure. Polyethylene products produced with these metallocene catalyst systems were available commercially at least as early as 1991.

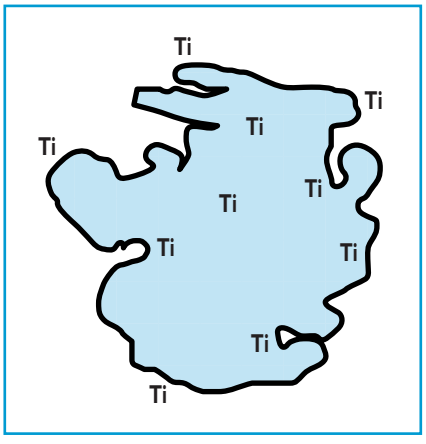
A new class of single-site catalysts has recently come into use. These catalysts use constrained-geometry complexes that have only one cyclopentadiene ring structure attached to the metal. Constrained-geometry catalysts are highly effective for olefin copolymerization because of their unique structural attributes. Under appropriate conditions, these allow the production of polymer products with unique physical properties that have commercial significance.

A new family of polyolefin plastomers (POP) uses constrained-geometry catalyst technology (CGCT). The patented CGCT *(4)* differs from other catalyst technologies. The catalytic activity of CGCT uses group IV transition metals covalently bonded to a monocyclopentadienyl group and bridged with a heteroatom. The three components connect to form a constrained cycle structure with a metal center. **Figure 3** shows this geometric feature. The constrained angle at the ligand site results in an enlarged exposure of the single catalytic site that is unique to this class of molecules. Constrained-geometry catalysts produce polymers that have unique structural and performance properties *(5)*.

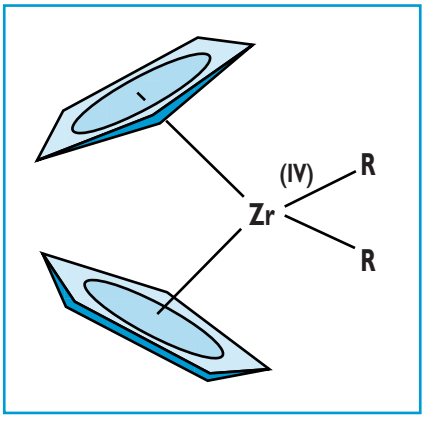
POLYMER PROPERTIES

Ziegler-Natta catalysts

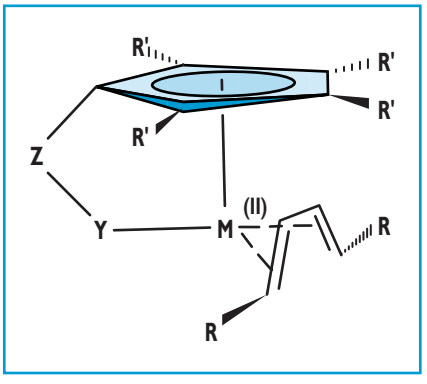
Conventional Ziegler-Natta catalyst systems typically have several catalytic sites attached to each support particle. The activity toward



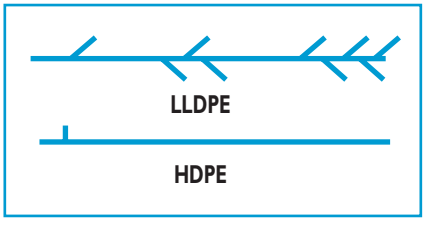
1. Conventional Ziegler-Natta catalyst structure



2. Typical metallocene catalyst structure



3. Typical structure of a constrained-geometry catalyst



4. Traditional Ziegler-Natta-catalyzed polymers

monomer insertion at each site therefore differs. Molecules produced by Ziegler-Natta catalysts have an uneven distribution of the co-monomer side chains along the backbone of the main polymer chain as **Fig. 4** shows and contain a high density fraction.

Some catalytic sites are deep within the pores of the support media. This allows polymerization of only the small ethylene molecule. Some are more open and can polymerize larger α-olefins such as 1-octene. This explains the broad comonomer and molecular weight distribution associated with traditional linear low density polyethylene (LLDPE) produced by Ziegler-Natta catalysts. LLDPE also contains significant amounts of high density polyethylene (HDPE). This fraction is a direct result of excluding larger α-olefins from the sterically confined transition metal site buried in the support media. Analyzing the short chain branching distribution using analytical temperature rising elution fractionation (ATREF) can detect this high density fraction. **Figure 5** shows the crystallinity distribution produced by typical Ziegler-Natta catalyst systems. Note that the confined catalytic sites that only polymerize ethylene generate some of the highest molecular weight polymer chains due to the faster polymerization of ethylene compared with other large monomers such as hexene or octene.

Single-site catalysts

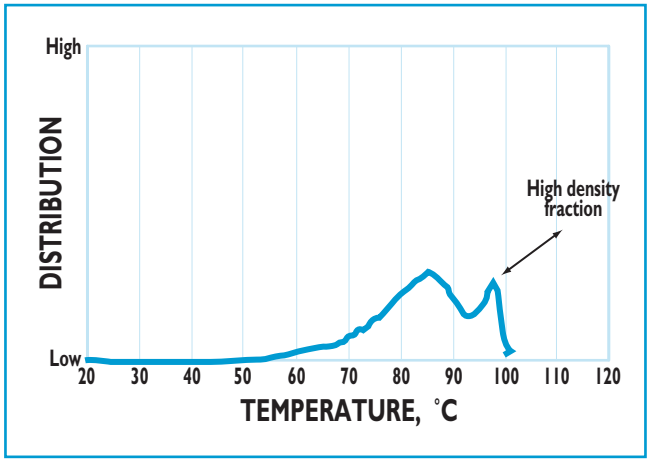
Single-site catalysts differ from conventional Ziegler-Natta catalysts in one significant way. They have only a single active metal site for each catalyst molecule. The activity of polymerization at the transition metal is therefore identical for each catalyst molecule. Polymers produced by single-site catalyst systems exhibit narrow composition distribution. They usually do not contain a high density fraction because each catalyst site produces polymers of similar composition.

Single-site catalyst systems also provide a means for more comonomer incorporation *(2)*. Low polymer densities are therefore possible for butene, hexene, and octene copolymers. This leads to new terminology that typically describes these polymers using density. The term polyolefin elastomers (POE) refers to single-site products with densities less than 0.880 g/cm^3. POP refers to single-site products with densities of 0.880 g/cm^3 and higher.

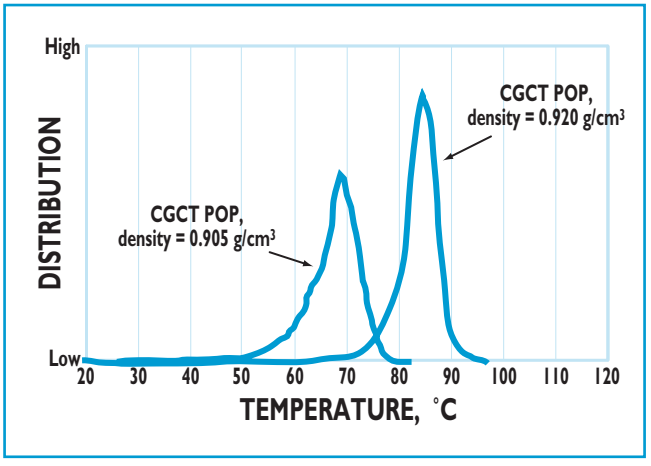
For the constrained-geometry catalyst, the open arrangement in the single-site catalyst molecule also opens the metal center for monomer and comonomer insertion. One can therefore design a single-site catalyst that will copolymerize ethylene, butene, hexene, octene, or styrene equally well because of the openness and availability at the transition metal. This technology allows the manufacturer to control the polymerization of olefins selectively with concomitant control of molecular weight (MW), molecular weight distribution (MWD), short-chain branching distribution (SCBD), and comonomer distribution (CD). This then provides increased impact strength and improved toughness, clarity, and organoleptic properties. Linear, single-site catalyzed polymers typically have randomly distributed side-chain branching of **Fig. 6** and narrow molecular weight and comonomer distribution.

Under appropriate conditions, CGCT systems can produce polymers not only lacking the high-density polymer fraction of **Fig. 7** but also most importantly having a level of long chain branching that imparts unique physical properties to the polymers.

CGCT opens the catalyst geometry to the extent that it allows vinyl-terminated polymer chains to attach or polymerize to a growing chain to form the long chain branches of **Fig. 8** *(5)*. Polymers produced with



5. Crystallinity distribution produced by typical Ziegler-Natta catalyst for a typical LLDPE using ATREF

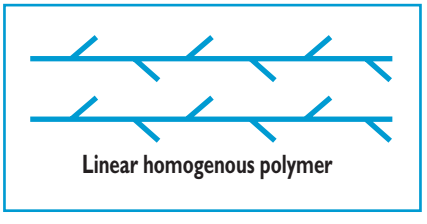


7. Crystallinity distribution produced by single-site constrained geometry catalyst using ATREF

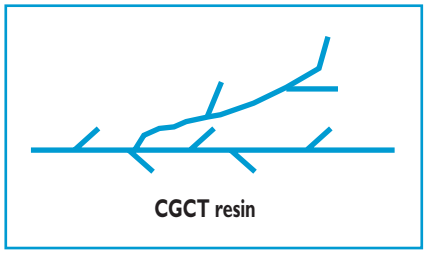
CGCT have narrow molecular weight distributions. Narrow molecular weight distribution typically results in harder processing. The long chain branching in CGCT polymers minimizes this effect. These long chain branches also give higher melt strength that reduces the necking-in of the molten polymer curtain for extrusion coating applications and provides additional bubble stability for blown film applications.

A molecular weight distribution—also called polydispersity or M_w/M_n—of approximately 2 is standard for single-site polymers such as a CGCT POP with 0.920 g/cm³ density shown in **Fig. 9**. Two major benefits result from this narrow molecular weight and comonomer distribution:

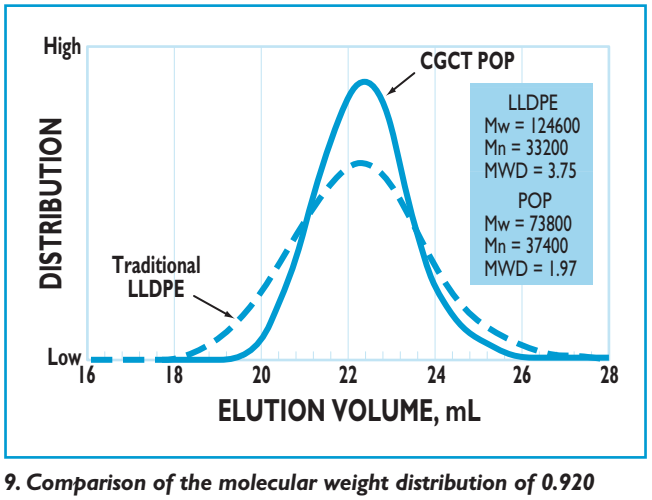
- The absence of the high density and high molecular weight component that yields undesirable high melting points and poor optics in existing conventional multi site linear catalyzed products
- The elimination of the low molecular weight, low density component that imparts high extractables and unwanted blocking tendency in linear polymers.



6. Single-site catalyzed polymer with randomly distributed side chains



8. Polymer produced with CGCT containing randomly distributed side chains and long chain branching



9. Comparison of the molecular weight distribution of 0.920 g/cm³ density resins

EXPERIMENTAL

The coating performance of a 7.5 melt index and 0.902 g/cm³ density POP produced by CGCT was compared with LDPE, LLDPE, ethylene acrylic acid copolymer (EAA), ethylene vinyl acetate (EVA), and an ionomer *(6)*. All resins were evaluated on a pilot extrusion coating line having a 3.5-in. diameter primary extruder with a 30:1 L/D single-flight screw, a 2.5-in. and a 2-in. extruder, and a feed block for coextrusion. A 30-in. coat hanger die deckled to 24 in. with a 20-mil die gap and a 6-in. air gap was used for all evaluations. A microprocessor system that included weigh cell feed hoppers for rate calculations and control of coextrusion controlled the extrusion line. A mirror pocket glycol-cooled chill roll was controlled at 14°C. **Table I** describes the polymers evaluated for this study.

Designation	Density, g/cm³	Melt Index, g/10 min.
POP	0.902	7.5
LDPE	0.916	8.0
LLDPE	0.923	5.5
EVA	0.940	8.0
EAA	0.938	10.0
Ionomer	0.940	5.0

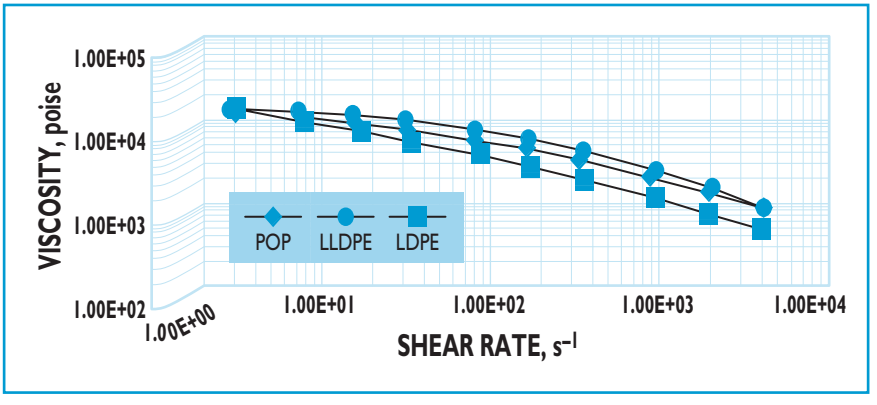
I. Resins evaluated

Physical property	POP	LLDPE	LDPE
Octene comoner, %	13.5	7	N.A.
Melt index, dg/min.	7.5	5.5	8
Density, g/cm³	0.902	0.923	0.916
DSC meltiing point, °C	98	119	103
Vicat softening point, °C	77	99	85
Tensile yield, psi	850	1870	1400
Ultimate tensile, psi	2180	1970	1500
Elongation, %	950	705	580

II. Bulk physical property data

Property	1 mil	2 mil
Tensile yield, psi, MD	1080	840
CD	840	770
Ultimate tensile, psi, MD	7270	5435
CD	4720	4300
Elongation, %	620	750
20° Gloss	46	50
Dart, g	248	452
Puncture, ft•lb/in.³	178	166
Tear, g, MD	88	348
CD	316	580

III. POP cast film properties



10. Rheology data

Resin	Melt Temp., °C	Amps	Neck-in, in.	Min. Thickness mil
POP	288	142	4.9	<0.25
POP	316	138	5.3	<0.25
LDPE	288	101	1.6	0.70
LDPE	316	94	1.6	0.50
LLDPE	316	150	4.5	<0.25
EAA	288	110	3.0	0.42
Ionomer	288	126	1.8	0.63
EVA	232	121	4.6	0.35

IV. Coating performance

Monolayer coating evaluations using the primary extruder used 50-lb kraft paper. The polymers were extrusion coated at a 3.5-in. screw speed of 90 rpm (approximately 250 lb/h) at their recommended melt temperature. Neck-in values were determined at 440 ft/min. (1 mil coating thickness). The substrate speed was then increased until the molten web completely pulled from the die. Any edge tear or draw resonance was noted.

Samples for heat seal, hot tack, and sensory testing were prepared by coextruding a 1.5-mil coating using an EAA (8 melt index and 6.5% acrylic acid concentration by weight) copolymer as the tie layer (20% layer thickness) onto 48-gauge primed polyethylene terephthlate (PET) film and a paper/polyethylene/foil (0.00035 A wettable) substrate. Cast film samples were produced on a pilot cast film line with a 30-in. die. Film samples were tested for physical and optical properties.

Heat seal and hot tack

Lab heat seals were formed on 1-in. wide strips of the substrate and sealed at 40 psi bar pressure with a 0.5-s dwell using heated bars at temperatures of 80°C–150°C on a commercially available hot tack tester. After aging the sealed samples for 24 h at ambient temperature, the force in pounds required to pull the seal apart was determined with the use of a tensiometer at 10 in. per min. crosshead speed and a 90° "T" peel.

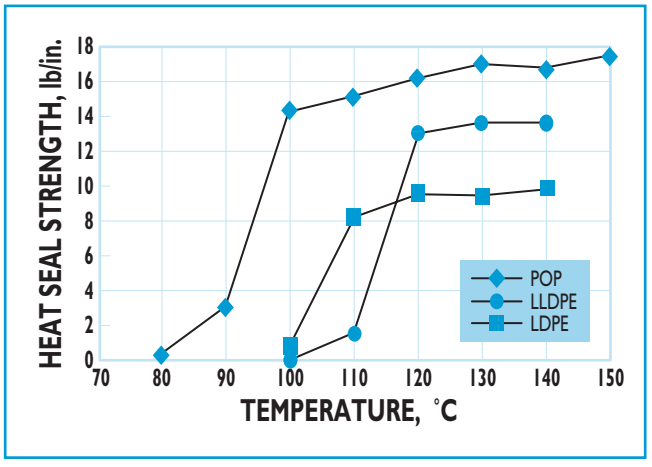
Hot tack strength testing used the same hot tack tester. A 1-in. wide sample was clamped at both ends. The top stationary clamp was attached to a load cell, and the bottom clamp was attached to a piston that moved downward at a constant peel speed of 150 mm/s. The folded sample was placed between the seal bars that were then closed for 0.5 s with a 0.2-s delay and 40-psi bar pressure. When the seal bars were released, the piston moved to exert an instant downward force on the seal. The peak force in Newtons/25 mm to break the seal was recorded.

Tear testing

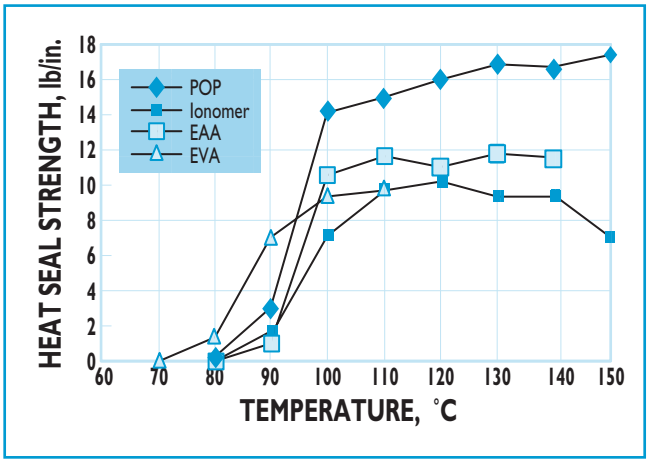
Tear data were generated on 1-mil monolayer coatings on 50-lb kraft paper. A conventional tensile tear tester was used.

Sensory testing

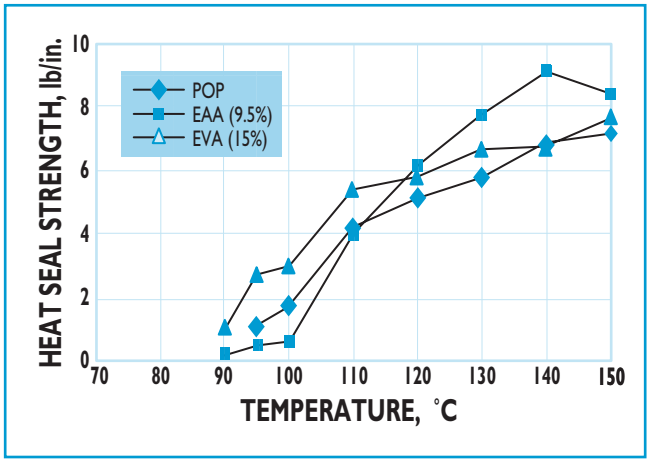
Sensory data were generated using 24 trained panelists to evaluate the film samples in a ranking and paired comparison format. The samples were coded with random three-digit numbers and presented according to a balanced block design to minimize bias. Evaluations were conducted in an air medium and commercial drinking water. The data were ana-



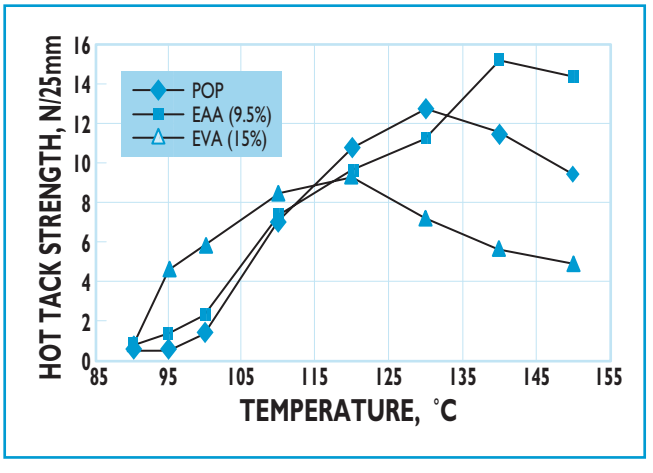
11. Heat seal data using 48 gauge PET/1.5 mil coextruded EAA (20%)/sealant (80%)



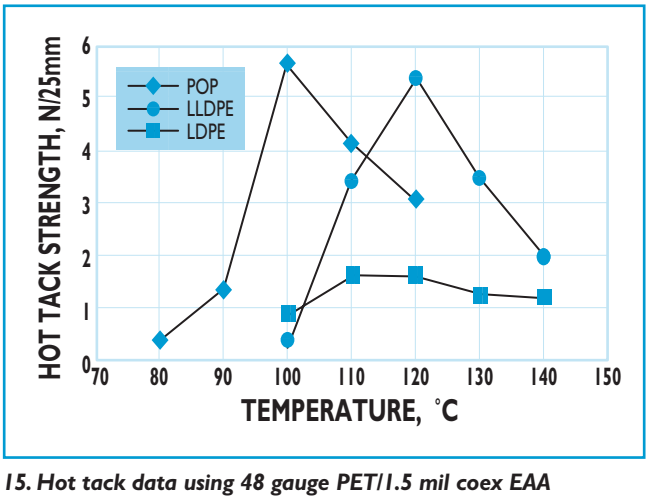
12. Heat seal data using 48 gauge PET/1.5 mil coextruded EAA (20%)/sealant (80%)



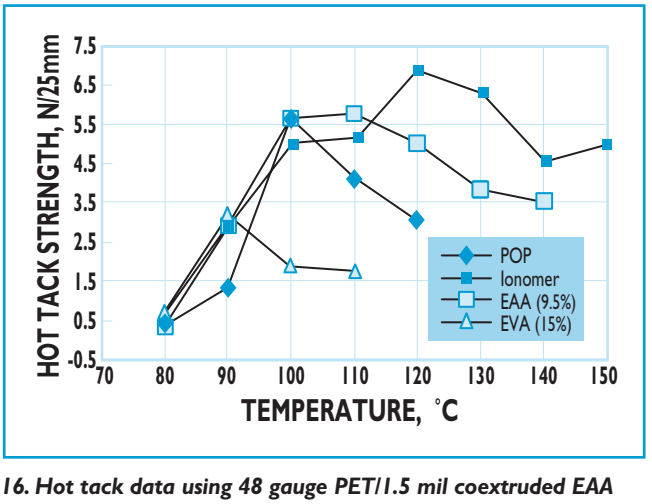
13. Heat seal data using [paper/polyethylene/foil (0.00035)]/1.5 mil coextruded EAA (20%)/sealant (80%)



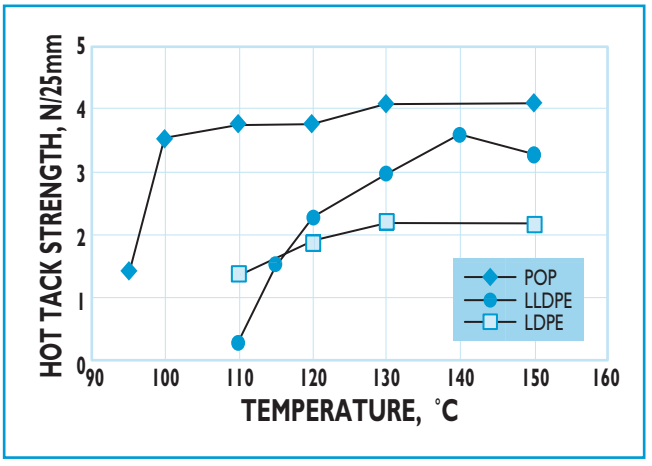
14. Hot tack data using [paper/polyethylene/foil (0.00035)]/1.5 mil coextruded EAA (20%)/sealant (80%)



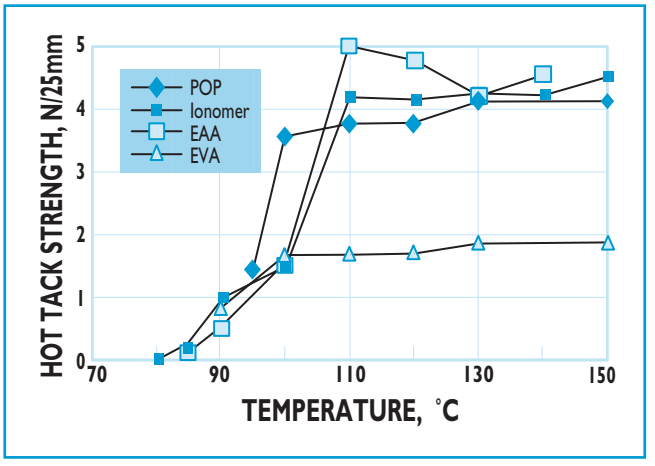
15. Hot tack data using 48 gauge PET/1.5 mil coex EAA (20%)/sealant (80%)



16. Hot tack data using 48 gauge PET/1.5 mil coextruded EAA (20%)/sealant (80%)



17. Heat seal data for 1-mil coating on 50 lb kraft paper at 316°C



18. Heat seal data for 1-mil coating on 50 lb kraft paper

Resin	Elmendorf Tear, g MD	CD
Pop	373	366
LDPE	133	141
EVA	152	216
EAA	165	123
LLDPE	271	289
Ionomer	134	173

V. Elmendorf tear data using 1 mil on 50 lb kraft paper

lyzed using Friedman Analysis of Variance for ranked data followed by Duncan Multiple Range comparisons *(7)*. T-tests were used for the paired comparisons.

Adhesion data

Slip sheets of different substrates—oriented polypropylene (OPP), foil, and primed PET—were coated at 1-mil thickness to check adhesion. The adhesion values were obtained by pulling at 90° using a "T" peel configuration on a tensiometer at 10 in./min. crosshead speed.

RESULTS AND DISCUSSION

Properties

Table II shows bulk physical properties. **Table III** shows cast film properties of the POP resin for thicknesses of 1 and 2 mils.

Rheology

Figure 10 compares the shear rheology of POP to the LLDPE and LDPE having the bulk physical properties listed in Tables I and II. The enhanced shear thinning behavior of this POP is due to the presence of long chain branching that improves processability. The LDPE shear-thinned the most because it has more long chain branching and broader molecular weight distribution than the POP.

Extrusion coating performance

Monolayer coating results in **Table IV** show that the POP had a higher neck-in—4.9 vs. 1.6 in. at 288°C—and required more energy as seen by higher amps to process than the LDPE resin. The POP was easier to process than the LLDPE resin as shown by 8% lower amps when extruded at 316°C. The POP could be drawn down to less than 0.25 mils without any draw resonance problems. The rheology data also supports this.

Heat seal and hot tack

Figures 11 and 12 show laboratory heat seal data on the primed PET films. The POP had a lower heat seal initiation temperature than LDPE, LLDPE, EAA, and the ionomer. The plastomer also had the highest ultimate seal strength (>30%) of all the polymers evaluated on the PET film. The POP had a heat seal initiation temperature (2 lb/in.) 18°C lower than LDPE, 26°C lower than the LLDPE, and 5°C lower than the EAA and the ionomer. The seal initiation temperature of the POP was 5°C higher than the EVA (15% vinyl acetate). This suggested that the POP would have equal performance to an EVA containing approximately 12% vinyl acetate.

Heat seal performance in **Fig. 13** on the foil substrate showed the POP had lower seal initiation temperature and seal strength than the EAA resin. The seal initiation temperature of the POP was 10°C higher than the EVA on this thicker structure. Adhesion failure at the foil interface limited the seal strength of all the sealants.

The hot tack performance on the foil structure in **Fig. 14** showed the POP had a higher ultimate hot tack strength (13 vs. 9 N/25 mm) and a broader hot tack window (> 8 N/25 mm) than the EVA copolymer (35°C vs. 15°C). When compared with the EAA, the POP had similar ultimate hot tack strength but a narrower hot tack window. Because hot tack strength strongly depends on substrate adhesion, the same EAA tie layer was used for all sealants to ensure the same adhesion to the substrates.

All the resins exhibited much lower hot tack values on the PET film. This is due to the lack of a fast heat transfer medium (foil) to help in accelerated cooling of the sealant. The ultimate hot tack strength of the POP was much better than the LDPE (5.5 vs. 1.5 N/25 mm). The POP achieved approximately the same ultimate hot tack as the LLDPE resin but at approximately 20°C lower temperature as **Fig. 15** shows. The hot tack window of the POP was narrower than the EAA and the ionomer sealants as **Fig. 16** shows.

Resin	OPP adhesion, g	Foil adhesion, g	Primed PET adhesion, g
POP @ 288°C	472	41	36
POP @ 316°C	335	241	636
LDPE @ 288°C	72	41	41
LDPE @ 316°C	123	45	268
LLDPE @ 316°C	77	159	822
EVA @ 232°C	36	54	41
EVA @ 288°C	45	454	341
Ionomer @ 288°C	45	368	318

VI. Adhesion data

On 50-lb kraft paper in Figs. 17 and 18, the heat seal strength of the POP was twice that of the LDPE (4 vs. 2 lb/in.) and even greater than the LLDPE. The POP initiated a seal at a temperature 20°C lower than the LDPE and LLDPE. All the resins were coated at 316°C. The heat seal strength of the EAA and ionomer (coated at 550°F) was a little better than that of the POP. The EVA (coated at 288°C) had the lowest heat seal strength (2 lb/in.) and did not show an advantage in heat seal initiation. The POP had the lowest heat seal initiation temperature on the paper substrate.

Tear properties

POP extrusion coated onto paper showed excellent tear resistance as Table V shows. The Elmendorf tear values of the POP were more than 2.5 times that of LDPE (373 vs. 133 g) and even higher than the LLDPE (373 vs. 271 g). The tear properties of the POP were also more balanced in the machine and cross directions.

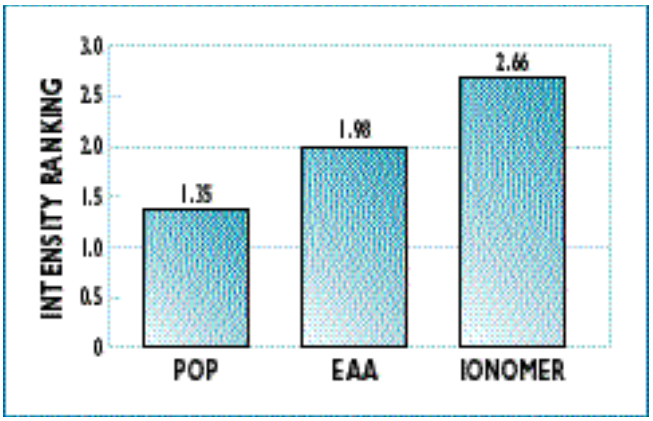
Adhesion

POP demonstrated excellent adhesion (> 400 g) to the treated high energy industrial grade oriented polypropylene (OPP) of 70 gauge and the primed PET films but only fair adhesion (< 200 g) to foil as Table VI shows. If higher foil adhesion is necessary, the POP can be coextruded with an EAA tie layer that will provide excellent foil adhesion. Previous work also confirmed excellent adhesion to LLDPE films *(8)*.

Sensory results

Taste and odor evaluations shown in Figs. 19 and 20 for the polymers coated on the primed PET showed that the POP contributed the least intense taste and odor compared with the EAA and ionomer.

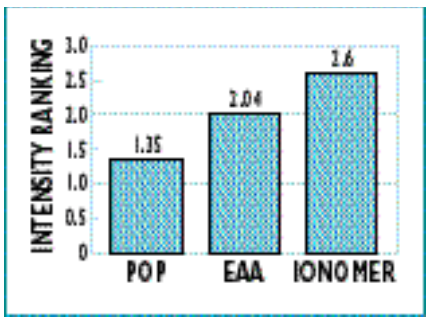
In a separate comparison with the EVA in Figs. 21 and 22, the POP showed the least odor intensity. The EVA contributed the least intense taste to water probably due to lower oxidation of the polymers at lower processing temperatures (232°C vs. 302°C).



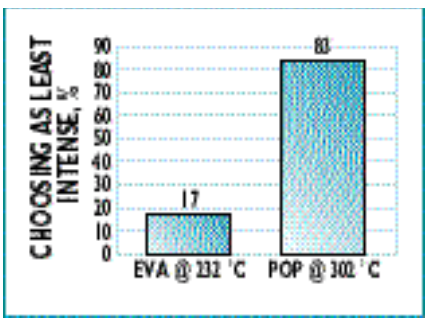
19. Taste intensity ranking with a 99% confidence level of difference between 1.35 and 2.66

CONCLUSIONS

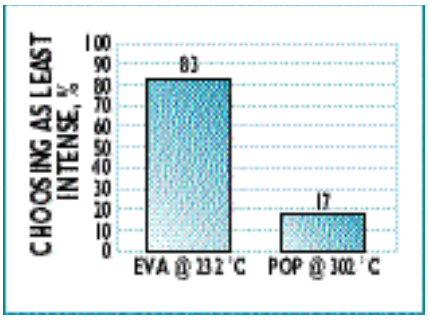
The performance properties of single-site catalyzed polymers and copolymers make them well suited for coextrusion or monolayer coating and laminating applications. Because tie layers are necessary to achieve the desired adhesion level to some substrates—foil, unprimed PET, nylon, machine glazed paper, coextrusions will be important to achieve the best combination



20. Odor intensity ranking with a 99% confidence level of difference between 1.35 and 2.6



21. Odor intensity in air using paired comparison



22. Taste intensity in water using paired comparison

of cost and performance. POP is also an excellent choice for overall economics compared with more expensive specialty copolymers.

POP can provide flexible coatings that offer good sealing properties and excellent toughness and tear resistance. Their optical properties allow their use in laminating applications that require good clarity. The low modulus of POP should allow their use as coatings for woven and nonwoven scrims for such applications as tarpaulins, tapes, medical applications, and consumer products such as tents and high strength tote bags requiring toughness and flexibility.

The POP products lower seal initiation temperatures, provide excellent seal strengths, and have good hot tack performance. They meet the requirements for form, fill, and seal applications. On foil-containing structures with outer layers that limit sealing jaw temperatures below 140°C, the performance of POP should compare very favorably to premium sealants especially when cost is a consideration. In nonfoil structures that do not require a broad hot tack window, POP can provide excellent seal strength. An excellent combination of cost and performance with good taste and odor properties makes single-site-based POP a good choice for extrusion coating and lamination applications. **TJ**

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