A new family of linear ethylene polymers provides enhanced sealing performance

Dirk G. F. Van der Sanden and Richard W. Halle

A new family of linear ethylene polymers possess many interesting properties, such as low seal initiation temperatures, low hexane extractables, and low film haze.

Many different types of polyolefins are specified as seal layers in multilayer flexible packaging structures, depending upon the combination of converting, packing, and end-use performance required in a given application. Many factors, such as polymer selection, seal layer thickness, converting and packing conditions, polymer additives, etc., influence the seal layer's performance. Many of these factors were discussed in an earlier paper (*1*). Factors a polymer manufacturer has control over are the polymer's molecular structure and the additives used. This paper describes a new family of linear ethylene polymers having different molecular structures than what can be obtained using traditional linear polyolefin manufacturing technologies. These new ethylene polymers possess a unique set of heat-sealing characteristics.

Polymer structure overview

Better control of a polymer's molecular structure, thus better control of its melt-flow and solid-state properties, has been a long-time goal of all polyolefin manufacturers. For ethylene polymers, molecular structure is normally defined by five key structural parameters: average molecular weight, molecular weight distribution, and the type, amount, and distribution of branches contained in the polymer chains.

A polymer's average molecular weight (MW) and its molecular weight distribution (MWD) are equally important in establishing its melt and solid-state properties. For ethylene polymers, the MW is most often described by the polymer's melt index and the MWD by a melt index ratio.

Branching is the other important determinant of a polymer's properties, since branching establishes the polymer's functionality and crystallinity. In ethylene polymers, branches can be either long or short, can contain functional groups [such as vinyl acetate in ethylene vinyl acetates (EVAs)], can be distributed across the polymer chains differently, and can be distributed in an individual polymer chain in some sequence.

To a first approximation, the intrachain sequence distribution of branches in the ethylene polymers considered here is random. Long-chain and functional polymer branches are prominent features of high pressure, free radically produced ethylene polymers. The new ethylene polymers discussed here are linear backbone resins containing no functional or long-chain branches.

The short-chain branching in linear polymers is formed by the comonomer employed, such as butene, hexene, or octene. The amount of comonomer controls the concentration of branches, which regulates the polymer's crystallinity and those properties associated with crystallinity such as density, modulus, toughness/stiffness balance, and tensile strength. Density is normally used as a measure of branching. The other significant branching parameter, the composition distribution (CD), is the distribution of comonomer (number of branches) over polymer chains of different lengths. A narrow CD is one where the comonomer is uniformly distributed across all the polymer chains regardless of chain length, whereas a broad CD is one where the amount of comonomer is a strong function of chain length.

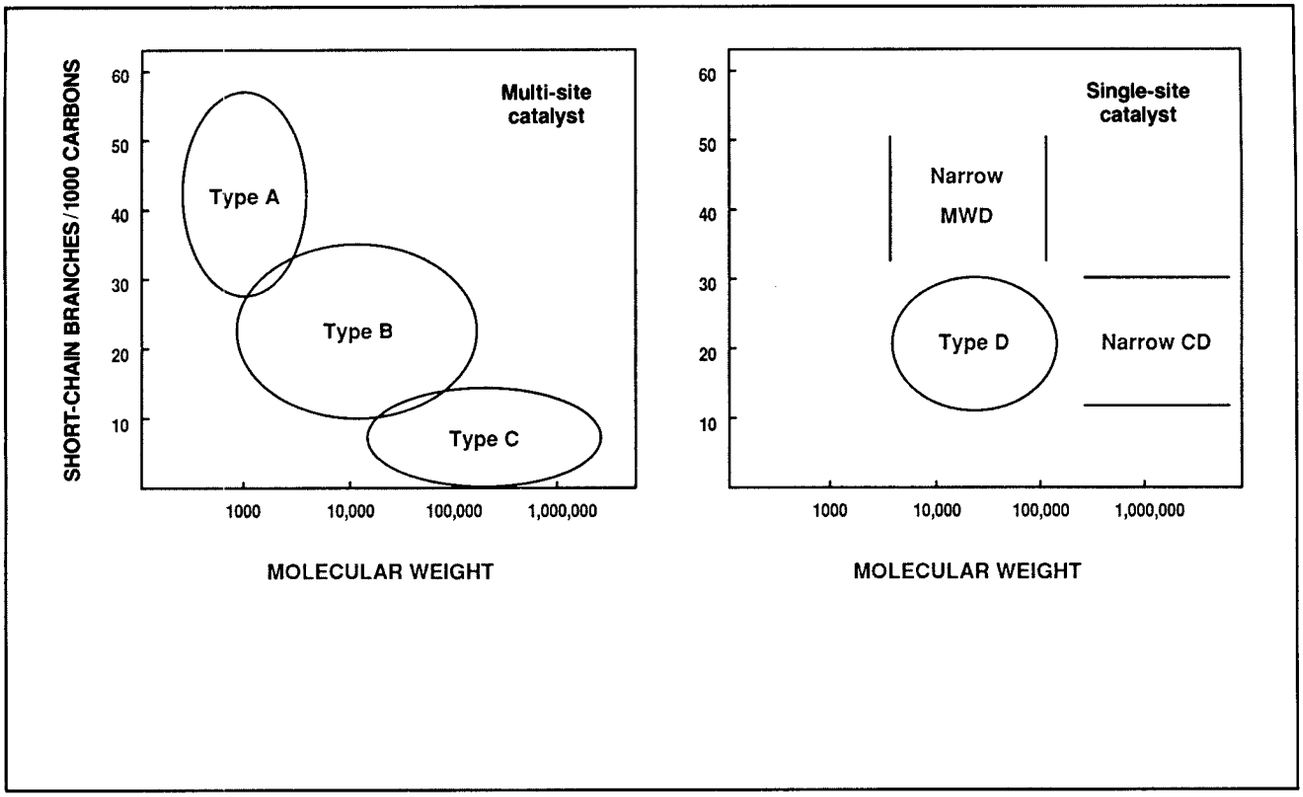
Structural control in linear ethylene polymers

In designing linear ethylene polymers, the polymer manufacturer is somewhat limited in how the polymer's structure (properties) can be varied as measured by its average MW, its MWD, its average branching, and its CD. The average MW and branching are primarily controlled via the amount of chain transfer agent and the comonomer used in the polymerization. The MWD and CD are for the most part fixed by the catalyst and process technology used and as such have been difficult to adjust independently.

Most linear ethylene polymers are made today using some type of Ziegler Natta, multisite catalyst. This

Van der Sanden is senior research engineer for Exxon Chemical Co., Polymers Group, Nieuwe Nijverheidslaan 2, Machelen, B 1831, Belgium. Halle is senior staff scientist for Exxon Chemical Co., Polymers Group, Baytown Polymers Center, 5200 Bayway Dr., Baytown, TX 77522.

1. Effect of catalyst type on molecular weight and composition distributions



multisite catalyst contains several different active sites, each producing polyethylene molecules with different average molecular weight and comonomer content. Most of the catalyst sites do produce polymer chains with the overall target MW and branching density (Type B in **Fig. 1**). But another type of active site (Type A in Fig. 1) inevitably present in the same catalyst produces relatively low-MW polymers with a high branch density. These low-MW polymers make up the extractable/low-MW wax fraction of the polymer. A third type of catalyst site (Type C in Fig. 1) generates high-MW polymer with very few branches (high-density polyethylene). This polymer fraction is associated with the higher haze and high peak melting point typical of linear polyethylene.

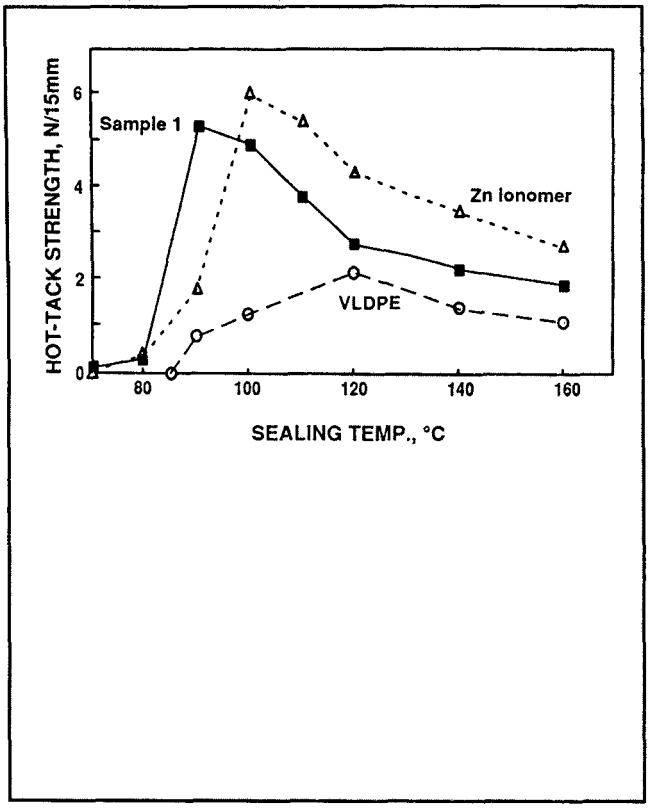
Single-site catalysts, such as those used in the new technology discussed here, contain only one active catalyst site, which produces just one type of ethylene polymer molecule, as shown in Fig. 1 as Type D. This yields a polymer with very narrow MWD and CD as opposed to the broad MWD and CD produced via multisite catalysts. These differences in MWD and CD are shown in Fig. 1.

The very uniform, narrow CD of these new ethylene polymers generates interesting property shifts when compared to conventional linear polyethylenes. The narrow CD means almost no highly branched, low-MW polymer is present. Thus these narrow CD polymers have very low hexane extractables. The absence of the high-MW homopolymer fraction means that the clarity of these new ethylene polymers is superior to conventional materials. The narrow CD leads to a narrow melting point range and a lower peak melting point than a "standard" linear polyethylene with a similar melt index and density. These key changes in the melting characteristics translate into a much lower seal initiation temperature than conventional linear polyolefins with higher toughness and strength than high-pressure, low-density polyethylene (LDPE) or EVAs. Some general property comparisons are presented in **Table I**. Further discussion of the structure-property relationships for these new polymers is presented elsewhere (*2*).

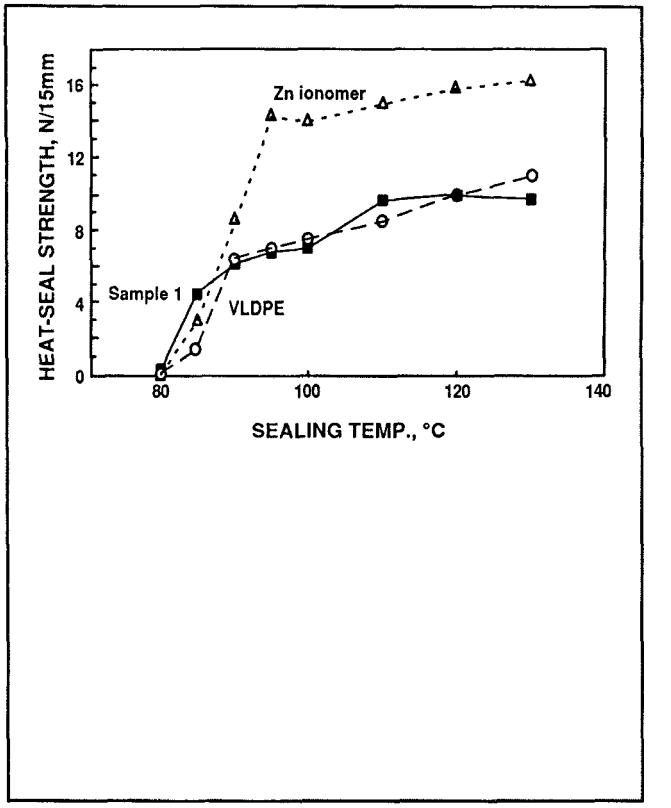
I. New ethylene polymer properties vs "standard" polyethylene

	New ethylene polymer	*"standard" polyethylene*
Melt index, dg/min	1.0	1.0
Density, g/cc	0.918	0.917
Haze, %	8	15
Hexane extractables, %	0.5	2.5
Seal initiation temp., °C	100	115
Melting point, °C	115	120
Tensile, MD/TD, 1000 psi	7/6	7/6
60-in. Dart impact, g/mil	250	175
	(1.25-mil cast film data)	

2. Hot-tack strength comparison of first generation ethylene polymer vs. ionomer/VLDPE (50-μm blown monolayer film backed with polyester tape. Seal time = 0.5 s, delay after seal = 0.4 s. Peel speed = 200 mm/s, press = 0.5 MPa)



3. Heat-seal strength comparison of first generation ethylene polymer vs. ionomer/VLDPE (50-μm blown monolayer film. Seal time = 0.5 s, press = 0.5 MPa. Peel speed = 500 mm/min)



II. Seal failure mode results (Sample 1)

Temperature, °C	*Sample 1*	*Ionomer*	*VLDPE*
80	Peel	No Seal	No Seal
85	Peel	Peel	Peel
90	Peel/Tear	Peel	Peel/Tear
95	Peel/Tear	Tear/Peel	Peel/Tear
100	Tear/Peel	Tear	Peel/Tear
110	Tear	Tear	Peel/Tear
120	Tear	Tear	Tear
130	Tear	Tear	Tear

Narrow MWD/narrow CD products are only a small facet of this new technology. It is well known that narrow-MWD polymers are somewhat more difficult to process due to their higher melt viscosities and lower melt strength. But since this new technology permits independent adjustment of MWD and CD, the MWD can be broadened to improve the ability to process while maintaining a narrow CD and its associated property advantages. Molecular tailoring has also been found to produce synergistic property effects such as improved toughness and improved ability to process. With conventional technology, one must normally sacrifice toughness to improve processing.

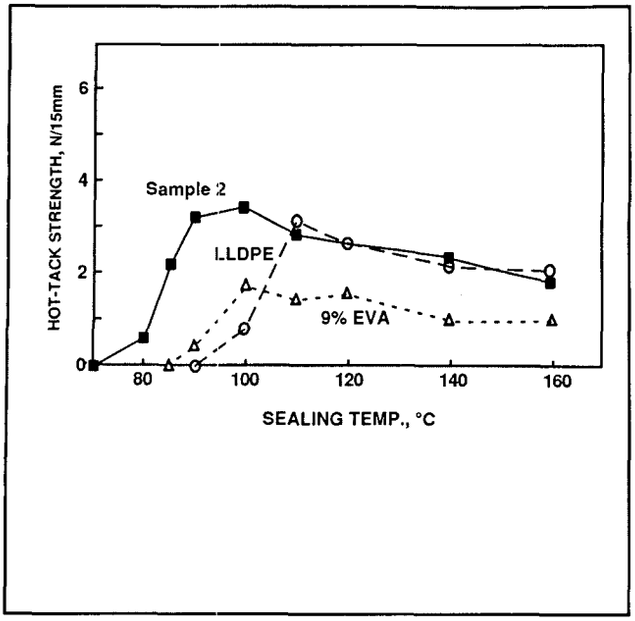
Seal performance of narrow-MWD, narrow-CD ethylene polymers

In any packing application, sealing materials must satisfy multiple requirements that can be grouped into three categories: converting requirements, packing requirements, and end-use requirements. Each converting method (coextruded film, extrusion coating, lamination, etc.) has its own processing requirements (melt strength, thermal stability, coefficient of friction, etc.), which must be satisfied for a converter to economically produce the packing film.

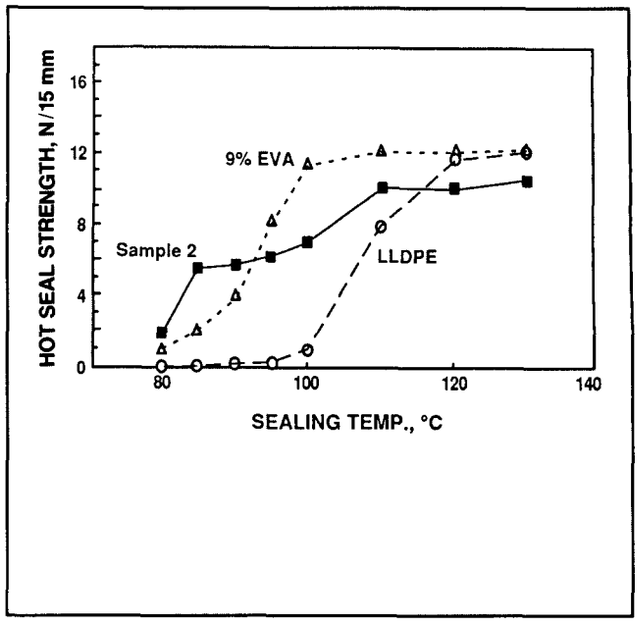
Likewise, each end use has its specific requirements which are related to the convenience of the package (appearance, ability to open, clarity, etc.), its integrity (shelf life, puncture resistance, seal tightness, etc.), and its interaction with the product packed (odor, off-taste, etc.). For the seal layer, this is translated into sealing attributes such as seal strength and seal failure mode (peel, tear) and seal-through contamination.

The packing operation is very cost-sensitive and the majority of its requirements are related to operational effectiveness and packing speed. For a sealing polymer, this means a low seal initiation temperature, high hot-tack strength, and, to account for fluctuations in the packing process, a broad seal range is desirable.

4. Hot-tack strength comparison of first generation ethylene polymer vs. EVA/LLDPE (50-μm blown monolayer film backed with polyester tape. Seal time = 0.5 s, delay after seal = 0.4 s. Peel speed = 200 mm/s, press = 0.5 MPa)



5. Heat-seal strength comparison of first generation ethylene polymer vs. EVA/LLDPE (50-μm blown monolayer film. Seal time = 0.5 s, press = 0.5 MPa. Peel speed = 500 mm/min)



As a first approximation of packing and end-use seal performance, much information can be derived from the hot-tack and seal-strength curves together with information on the seal failure mode (*3*). Several versions of the new linear ethylene polymers introduced here have exhibited unique sealing characteristics as measured by their hot-tack and heat-seal curves. The two sample polymers described below, which differ mainly in melt index and density, have been identified as first generation linear ethylene polymers and have narrow MWDs and narrow CDs. A detailed discussion of the structural differences between these two example polymers and between the different generations of this new polymer family is beyond the scope of this paper.

The narrow MWD and CD distributions produce a lower peak melting point and a more uniform crystal structure than a linear low-density polyethylene/very low-density polyethylene (LLDPE/VLDPE) with the same melt index and density. These differences generate advantageous changes in hot-tack and heat-seal performance. **Figure 2** compares the hot-tack strength of Sample 1 of this first generation polymer to a VLDPE with similar melt index and density and to a Zn ionomer. Sample 1 exhibits hot-tack strength which is more comparable to the ionomer than the VLDPE. Also, its peak hot-tack strength is attained at a very low temperature.

The seal strength curves for the same polymers are given in **Fig. 3**. Especially at the lower sealing temperatures, Sample 1 displays an excellent combination of high hot-tack and seal strength. Important seal strength information not always visible in the heat-seal curves is available by comparing the seal failure modes of the polymers, as shown in **Table II**. Sample 1 exhibits an early transition from a peel failure to a tearing failure.

Hot-tack and heat-seal testing was also conducted using polymers in the low-density range. **Figure 4** presents the hot-tack performance of Sample 2 versus a commercial LLDPE of comparable melt index and density and an EVA with 9% vinyl alcohol content. Here again the excellent low-temperature hot-tack strength of these narrow-MWD/CD ethylene polymers is evident. **Figure 5** gives the seal strength comparison for the same three polymers. The seal failure results shown in **Table III** are indicative of stronger low-temperature heat seals for Sample 2 as compared to the LLDPE or EVA.

III. Seal failure mode results (Sample 2)

Temperature, °C	*Sample 2*	*EVA*	*LLDPE*
80	Peel	Peel	Peel
85	Peel	Peel	Peel
90	Peel/Tear	Peel	Peel
95	Peel/Tear	Peel/Tear	Peel
100	Tear/Peel	Tear	Peel
110	Tear	Tear	Peel/Tear
120	Tear	Tear	Tear
130	Tear	Tear	Tear

This data shows that these new linear ethylene polymers, because of their unique molecular structure, can be utilized as high-performance seal layers in many high-value packing applications. Another key attribute of these first generation linear ethylene polymers is their low extractable content. In many ethylene polymers, low extractables give rise to reduced blocking, better coefficient of friction control, and lower slip/antiblock requirements, which can yield significant improvements

in converting and packing performance. The lower additive needs also can lead to better sealing and printing performance.

Sealing performance adjustment via polymer structure control

For many sealing applications, the ideal polymer would possess a low seal initiation temperature, high hot-tack and seal strength, and a very broad sealing range. With most polymers, modification of the polymer's sealing performance can only be obtained by changing its comonomer content, which for linear polyethylenes is the same as changing the polymer's density. Lowering the density (increasing the comonomer content) lowers the seal initiation temperature and has other detrimental effects such as higher extractables and increased blocking. Instead of being restricted to density and melt index as property control parameters, the new linear ethylene polymer technology described here provides new avenues for sealing performance optimization via modification of the molecular weight and composition distributions. By independently manipulating molecular weight and composition distribution, one is able to separately adjust the ability to process, the sealing performance, and the physical properties. This means that a polymer now can be optimized for a particular application rather than just choosing the melt index and density combination which gives acceptable performance.

Summary

The ability to control the molecular structure of polyolefins can lead to improved sealing performance. The first generation of a family of new linear ethylene polymers, with a unique set of sealing characteristics combining a low seal initiation temperature with high hot-tack strength, compares favorably with polymers typically used for sealing applications. Independent control of molecular weight and composition distribution can yield synergistic effects, producing both improved ability to process and improved sealing performance.□

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