

Polyethylene degradation: effect of polymerization catalyst

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Metallocene catalysis yields a polyethylene resin of superior chemical stability during melt processing.

Polyethylene (PE) degradation may occur at any stage, from manufacture to end use. However, for most applications, the melt-processing stage is characterized by the most rapid degradation. Mechanical shear and temperatures between 180 and 280°C are experienced during melt processing. In closed conditions (such as within an extruder barrel), oxygen dissolved in the polymer enables thermo-oxidative¹ and thermo-mechanical degradation.^{2–5} Different industrial methods for PE production considerably influence the latter.

Chemical composition also affects PE degradation. Considering PE as simply a long alkane chain without either unsaturated species or catalyst residues is a gross oversimplification. Although the spent catalyst is removed after polymerization, traces often remain. Such impurities may initiate premature oxidation. It is also difficult to entirely prevent unsaturated-species formation in PE chains during synthesis. Although the concentration of such species is very low, their presence can affect oxidation rate. The degree of branching may also be significant in relation to the polymer-chain structure and could affect PE degradation rate. Indeed, branched PEs oxidize more readily than linear polymers because of the relatively labile tertiary hydrogen atoms at the branch points.

Different polymerization routes lead to differences in type and relative concentration of vinyl, transvinylene, and vinylidene unsaturated species. These variations interfere with the primary degradation mechanism, which involves chain scission and branching, followed by crosslinking.^{6–8} Although chain scission and crosslinking occur simultaneously, one may predominate, depending on such factors as molar mass, shape of molar-mass distribution, polymerization catalyst system (and associated residues), and branching level. Melt viscosity increases or decreases, depending on whether scission or crosslinking predominates.⁹

We used several PE resins—e.g., high-density PE (HDPE), using a Phillips (Ph) metal-oxide catalyst, and linear low-density PE (LLDPE), based on Ziegler-Natta (ZN) and metallocene catalyst technology (see Table 1)—to acquire insights into the effect of different

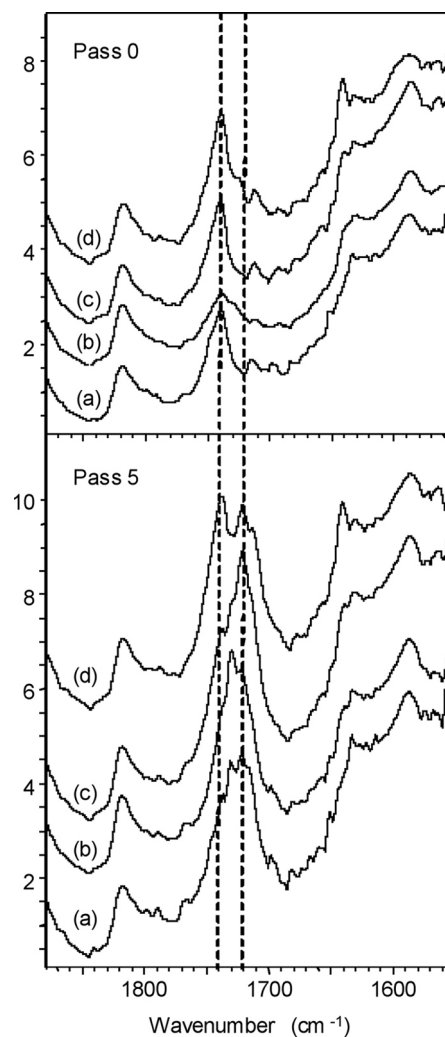


Figure 1. Transmission Fourier-transform IR spectra illustrating the carbonyl region of (a) metallocene medium-density polyethylene (PE), (b) metallocene linear low-density PE (LLDPE), (c) Ziegler-Natta LLDPE, and (d) Phillips high-density PE. The absorbance was normalized to the internal standard at 2018cm⁻¹. Upper group: Pass 0 samples. Lower group: Pass 5 samples.

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Table 1. Properties of polymers investigated for our degradation study. MDPE, HDPE: Medium-, high-density polyethylene. Cr, Zr, Ti: Chromium, zirconium, titanium. ISO: International Standards Organization.

Polymer	Phillips HDPE	Metallocene MDPE	Metallocene LLDPE	Ziegler-Natta LLDPE
Supplier	Atofina	Atofina	Repsol	Borealis
Grade	Finathene 5502	Finacene EF 2277	PLM 130	FG5190
Catalyst/residual metal	Phillips/Cr	Metallocene/Zr	Metallocene/Zr	Ziegler-Natta/Ti
Abbreviation	Ph-HDPE	m-MDPE	m-LLDPE	ZN-LLDPE
Density (23°C) (ISO 1183 test method)	0.954	0.927	—	0.919
Melt-flow index (deg/min) (190°C/2.16kg)	0.2	0.9	—	1.2

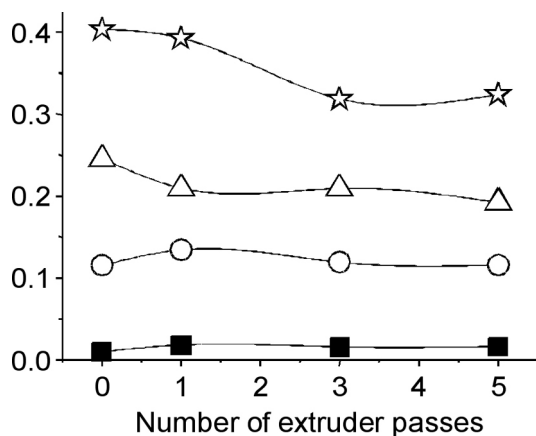


Figure 2. Normalized vinyl-group absorbance— Abs_{908}/Abs_{2019} —versus the number of extruder passes for m-MDPE (squares), m-LLDPE (circles), ZN-LLDPE (triangles), and Ph-HDPE (stars).

polymerization catalyst systems on degradation-product formation during melt processing. We used color measurement, IR spectroscopy, hydroperoxide determination, and melt-flow-rate measurements to monitor degradation as a function of the number of passes through a twin-screw extruder.^{10, 11}

Relative to a range of additive-free PEs (see Table 1), we recorded unusually good thermo-oxidative stability during melt processing for PEs produced by means of the metallocene route, especially medium-density PE. We attribute this relatively high stability to low levels of noxious metal-catalyst residues, as well as very low vinyl-unsaturation content. The relatively high melt stability of the metallocene PEs was manifested as a weak tendency to chain extend/crosslink and the lowest recorded rate of carbonyl-group formation (see Figure 1). In contrast, Ph-HDPE had a strong tendency to chain extend/crosslink and oxidize because of the abundant vinyl groups in this polymer. Vinyl groups are

the origin of chain extension/crosslinking by addition of macro-radicals (see Figure 2).

The relative ease of melt oxidation of Ph-HDPE led to high hydroperoxide production levels, despite the presence of chromium catalyst residues that are believed to decompose hydroperoxides into free radicals. This results in acceleration of the auto-oxidation process. On the other hand, we observed significantly reduced hydroperoxide production within the metallocene and ZN PEs. This was entirely consistent with the carbonyl-index trends, since these PEs generally featured less carbonyl growth during multipass extrusion.

We recorded an increase in yellowness index with increased number of extruder passes for all PEs examined (see Figure 3). The increase was most and least significant for, respectively, ZN-LLDPE and

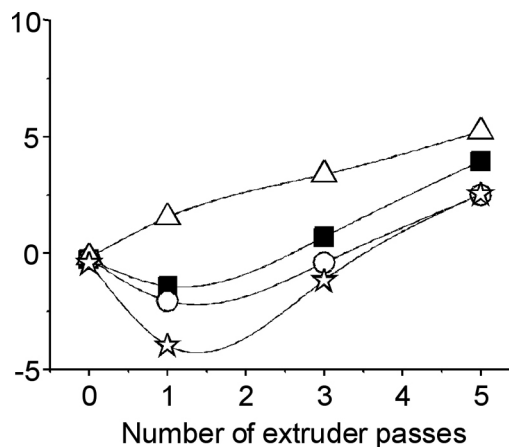


Figure 3. Yellow index versus the number of extruder passes for m-MDPE (squares), m-LLDPE (circles), ZN-LLDPE (triangles), and Ph-HDPE (stars).

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metallocene LLDPE and Ph-HDPE. Previous work¹² indicates that the increased color development in ZN-LLDPE may be caused by chelation of the titanium catalyst residues. In the other polymers, discoloration may be attributed to extensive formation of conjugated systems consisting of transvinylidene unsaturation and carbonyl groups.

We will next examine the effect of catalyst type on melt-stabilization performance of single antioxidants, antioxidant combinations, melt-processing oxidation-product chemiluminescence, and the largely neglected area of the effect of stabilizer type on the production of low-molar-mass (volatile) oxidation products.

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