

Ultraviolet-Induced Degradation of Ziegler-Natta and Metallocene Catalyzed Polyethylenes

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ABSTRACT: The metallocene revolution has aroused a storm of interest and associated questions regarding the performance and durability of polyolefins. This new technology has impacted the additives used to stabilize and process polymers. In this work, Ziegler-Natta and metallocene polyethylene (PE) samples were exposed to natural weather conditions under high doses of ultraviolet radiation, high temperature, and increased humidity. Weather-induced degradation of the two sets of PEs was studied using gel permeation chromatography, mechanical properties testing, differential scanning calorimetry, and Fourier transform infrared spectroscopy. The gel permeation chromatography analysis indicated the change in molecular weight distribution and molecular weights of metallocene PE to be more stable than conventional Ziegler-Natta PE. The tensile properties of metallocene PE are known to have higher values than Ziegler-Natta PE. The former exhibited a lower drop rate in mechanical properties when exposed to natural weather. Formations of nonvolatile carbonyl oxidation products, which absorb in the infrared region with a maximum absorbance level at 1742 cm^{-1} were determined. This indicated a higher rate of photo-oxidative and thermal degradation of Ziegler-Natta PE as compared with metallocene PE. The ultraviolet stabilization of metallocene PE may require different doses and a new kind of stabilizer system that can impart a longer useful lifetime and are cost effective for PE used for outdoor purposes. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1591–1596, 2000

Key words: Ziegler-Natta; metallocene; polyethylene; degradation; weathering

INTRODUCTION

Polyethylene (PE) is subjected to thermal stresses and high shear during their lifecycle starting from the thermo-oxidative degradation and high shear during conversion of the polymerization reactor product to high bulk density pellets. Conversion of PE to useful articles also involves high temperature and shear transformation in pro-

cesses such as blown film extrusion and injection molding. During these processing stages radicals are formed that act as chromophores absorbing ultraviolet (UV) radiation and become the initiating points for UV-induced degradation of PE. Many reviews^{1–5} have shown that degradation of polyolefins follow the free radical chain mechanism consisting of initiation, propagation, chain branching, and termination. In addition to the UV radiation, there are other weather parameters that contribute to the degradation of the polymers. They include total solar radiation, temperature and thermal cycling, humidity, environmental pollutants, abrasion, rain, wind, etc.⁶ PE has been used for outdoor applications since its

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discovery in 1930 and since then the scientific community and the business entrepreneurs have studied PE extensively. The origin of Ziegler catalysis and Ziegler-Natta catalysts in the mid-1950s revolutionized the polymerization process of ethylene to high molecular weight, linear polyethylene at low pressure. During the last four decades polyolefin catalysts have evolved with many improvements until the “metallocene revolution” by the mid-1980s.⁷ The significant difference in Ziegler-Natta and metallocene polyolefins is broad molecular weight distribution (MWD) in Ziegler-Natta as compared with narrow MWD in metallocene polyolefins. Uniform chain length, and lower bulk density of metallocene polyolefin is distinguished by nonuniform and high bulk density of Ziegler-Natta polyolefins.^{7,8}

Metallocene-based polyolefins have introduced materials that have unique properties that were not obtained with the Ziegler-Natta catalyst system. Polyolefins with uniform insertion of comonomers and different stereoregulation have been produced on a commercial scale by single site catalyst technologies. The densities and crystal morphology of these polymers have an effect on their solid state properties and behavior.⁹

Metallocene catalysts are considered new “precision” catalysts that provide manufacturing control over the molecular structure and properties of PE. They are significant in producing linear low density polyethylene (LLDPE) which can produce high tensile strength and high clarity film, appropriate for packing films application. It is estimated that more than 50% of all polyolefins within the next 10 years will be made by using metallocene catalysts, creating a new, dynamic, and challenging opportunity for polymer producers, processors, additive suppliers, compounders, molders, and end-users.⁹

The excellent mechanical and chemical properties that are offered by metallocene PE would provide an opportunity for its utilization in applications in which it is exposed to the outdoor environment. This work presents the performance results of Ziegler-Natta and metallocene LLDPE when exposed to natural weather conditions. The changes in molecular structure and performance properties are characterized and tested using standard techniques.

EXPERIMENTAL

Exposure trials were conducted for 3000 h in Dhahran that is an extreme weather location that

receives high doses of UV radiation and increased temperatures. The details of the Dhahran exposure site are presented in previous publications.^{3,10} Infrared spectra were recorded using a Perkin-Elmer FTIR Spectrophotometer Model 1700 (Norwalk, Connecticut, USA). Carbonyl absorbance was monitored in the region of 1700–1740 cm^{-1} . Crystalline melting temperature (T_m) and crystallinity of PE was determined using Perkin-Elmer differential scanning calorimeter attached to a System 4 microcomputer controller. An Instron Universal Testing Machine (Cambridge, MA, USA), Model 4301, was used to measure the change in tensile strength at 25°C according to ASTM standard D-882. The samples were not conditioned and the gauge length of the film samples was 25 mm. A long travel extensometer was used and a cross-head speed of 100 mm/min was maintained. The average molecular weights and MWD of the PE samples were determined using Waters gel permeation chromatograph (GPC) 150°C (Milford, MA, USA). The sample was dissolved at 135°C in 1,2,4 trichlorobenzene containing 0.05% 2,6-di-*tert*-butyl-4-methyl phenol antioxidant. The solution was periodically shaken without applying any high shear stirring. An aliquot of the hot PE solution was transferred into the vial of the auto-sampler and was injected into the instrument. The equipment was calibrated using polystyrene standards and the data were analyzed using Waters Millennium GPC software. The polystyrene-based calibration curve was converted into the universal one using the Mark-Houwink constants of polystyrene ($k = 0.000121$, $\alpha = 0.707$) and PE ($k = 0.000406$, $\alpha = 0.725$).¹¹ Table I presents the operating conditions for the GPC analysis. Commercially available Ziegler-Natta LLDPE from SABIC and metallocene PE from Dow were subjected to blown film extruder to produce 25-micron-thick film for this study.

Table I Operating Conditions for the GPC Analysis

Item	Operating Conditions
Sample concentration	0.1 % w/v
Injection volume	200 μL
Eluent	(TCB) with 0.05 % BHT
Flow rate	1.0 mL/min
Column type	Styragel HT3, HT4, and HT5
Column temperature	135°C
Pressure	30 bar
Detector	Differential refractometer

Table II Characteristics of Ziegler-Natta and Metallocene PE

Characteristic	Ziegler-Natta LLDPE	Metallocene PE
MI	0.82	1.1
Density (kg/m ³)	920	903
M_n	71,400	70,100
M_w	283,000	239,000
Melting Temperature (T_m) (°C)	128	123

RESULTS AND DISCUSSION

Table II presents the characteristics of the conventional Ziegler-Natta and metallocene PE. Molecular weight and MWD are the basic causes of having appropriate desirable properties of polyolefins. MWD of metallocene PE is found to be narrow as compared with the conventional Ziegler-Natta PE. Number-average molecular weight (M_n) and weight-average molecular weight (M_w) of metallocene PE is lower than that of conventional Ziegler-Natta PE. This can be attributed to the increased size of long branches in conventional PE. However, the mean size of long chain branches relative to M_n decreases with increasing M_n .¹² In most of the cases, degradation of polymers and a change in its major properties are directly related to the change in original molecular structure. The drop in M_n and M_w values shows the effect of UV-induced degradation on the molecular structure of PE samples (Table III). An approximate 30% increase in the polydispersity of Ziegler-Natta PE with exposure to UV radiation and other weathering factors indicates the broadness of MWD in PE. This is inherent to this PE as compared with metallocene PE. Conversely, UV irradiated exposure brought about a noticeable decrease (5%) in polydispersity for metallocene PE which indicates the sustainability of the narrowness of MWD in this type of PE. The drop in the M_n of conventional PE is slightly

higher than metallocene PE; however, M_w change in metallocene PE is higher than the drop in the conventional PE. Recombination of macro-radical products of photochemical scission for Ziegler-Natta PE may lead to larger molecular weights and hence an increase in MWD.

UV-induced degradation of PE is mainly caused by the presence of catalyst residue carry-over, hydroperoxide groups, carbonyl groups, and unsaturates introduced during polymerization, processing, and storage. These species play varying roles in the degradative photo-chemical reactions.¹³ The ultimate performance characteristic of polymer is its mechanical strength, which is of significance for practical applications. Figures 1 and 2 present the drop in mechanical properties of the Ziegler-Natta and metallocene PE when exposed to natural weathering conditions. Elongation at break is more important than stress at break in studying the degradation of polymers because the former can give an early indication of embrittlement. The degradation of mechanical properties of polymers is attributed to the chain scission and crosslinking reaction in the polymer matrix.¹⁴ Figure 1 shows that the elongation at break of unexposed metallocene PE is almost double that of Ziegler-Natta and the drop exhibited similar trends during the exposure period. In particular, percent of elongation at break dropped to zero after the first 2000 h of exposure for conventional PE. However, in the case of metallocene

Table III Molecular Weight Averages of the Unexposed and Exposed PE

Property	Ziegler-Natta Catalyzed PE		Metallocene Catalyzed PE	
	Unexposed	Exposed	Unexposed	Exposed
M_n	71,400	42,100	70,100	45,600
M_w	283,200	218,100	239,400	145,800
Polydispersity (MWD)	3.96	5.18	3.41	3.19

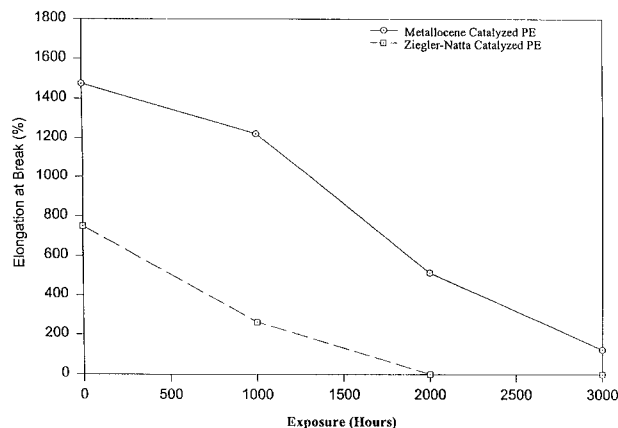


Figure 1 Change in elongation at break of metallocene and Ziegler-Natta catalyzed PE as a function of exposure duration.

PE, the drop was slow during the first 1000 h, then dropped drastically for the next 1000 h, only to change again to a gradual drop in the last 1000 h of exposure. Stress at break (shown in Fig. 2) has also shown that both PE samples have comparable values of stress at break. However, the Ziegler-Natta PE samples have exhibited a significant drop attaining a zero value at the first 2000 h of exposure as in the case of percent elongation at break. However, metallocene PE samples still retained about half of their initial value of stress at break until 3000 h of exposure. The loss in mechanical property, in part, is a consequence of the drop in M_w as discussed earlier. In particular, the greater drop in M_w for metallocene PE relative to the conventional PE should have resulted in a greater drop in mechanical proper-

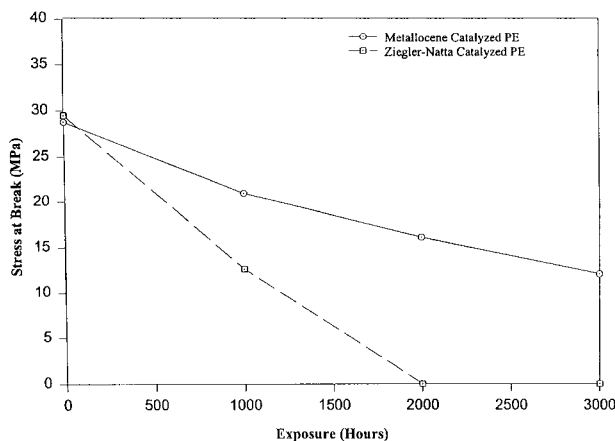


Figure 2 Stress at break of metallocene and Ziegler-Natta catalyzed PE as a function of exposure duration.

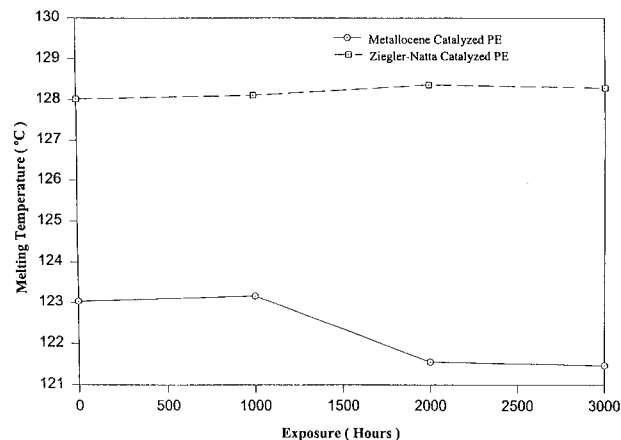


Figure 3 Change in crystalline melting temperature of metallocene and Ziegler-Natta catalyzed PE as a function of exposure duration.

ties. This mechanical behavior can be attributed to the easy cleavage of branching chains that resulted in the reduction of branching in metallocene PE and helps to retain chain stability to UV radiation and hence stress at break is considerable. The high tensile strength of unexposed metallocene PE can be attributed to its lower rate of drop with exposure time as compared with the conventional PE.

The thermal characteristics of unexposed and exposed PE samples are presented in Figures 3 and 4. Crystalline melting temperature (Fig. 3) of metallocene PE has shown a dip as a function of exposure time, whereas conventional PE has exhibited a constant trend. Percent crystallinity of the conventional PE sample has shown a contin-

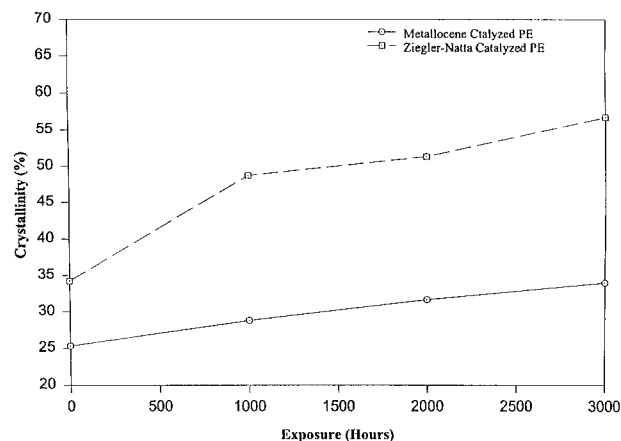


Figure 4 Change in percent crystallinity of metallocene and Ziegler-Natta catalyzed PE as a function of exposure duration.

uous increasing trend, which can be attributed to more embrittlement and a decrease in percent elongation at break. The processing stabilizers are also reported to interact with catalyst residue carryover.¹⁵ The crystallinity of the polymer has been shown to contribute in the blooming and solubility of characteristics of polyolefins.¹⁶ Changes in crystallinity also accelerate the thermal degradation effects in the polymers thereby degrading it at a faster rate. Because of the variety of single site systems in the metallocene catalysts, the interaction of catalyst and stabilizer system may vary and be less predictable than the Ziegler-Natta systems that are rather similar.¹⁵

The changes at molecular levels during the exposure trials are monitored by the growth of carbonyl group in the $1700\text{--}1750\text{ cm}^{-1}$ region of Fourier transform infrared spectra. The growth in carbonyl absorbance for Ziegler-Natta and metallocene PE as a function of exposure time is shown in Figure 5. Conventional PE has shown higher carbonyl growth as compared with metallocene PE. Carbonyl absorbance growth for metallocene PE is low and remained the same over the exposure period; however, it increased rapidly from about zero to 0.4 during 3000 h of exposure time. This growth is a clear indicator of photo-chemical degradation as shown in Figure 5. This indicates the greater stability of metallocene PE relative to Ziegler-Natta PE and is compatible with the variation observed in percent elongation and stress at break. The influence of UV on the stability of PE is not because of the direct absorption because pure polymers do not absorb in the UV range ($>290\text{ nm}$). The increase in carbonyl growth is

due to the absorbance of carbonyl and other degradation products formed during polymerization, processing, and storage (hydroperoxides or ketonic C=C moieties).¹⁷ Polymerization catalyst residues and charge transfer complexes between the polymer and oxygen also contribute in this process. In addition to carbonyl, there are other photoproducts such as hydroxyl, vinyl, acetaldehyde, and vinylidene groups that have shown similar trends of growth to that of the carbonyl group.¹⁸ Photooxidation can be initiated with hydroperoxide and ketones and photo-chemical hydroperoxide can decompose homolytically into alkoxy and hydroxy radicals having high quantum yield.¹⁹ The influence of higher ambient temperature during the exposure trials results in a higher rate of UV-induced degradation of PE and higher carbonyl growth. This is in agreement with the finding of Satato et al.²⁰ in a study conducted on the weathering of high density PE in a different altitude having different temperature profile.

CONCLUSIONS

The Ziegler-Natta PE has shown a higher rate of degradation and modification at the molecular level during exposure to the natural environment as compared with metallocene PE. Size exclusion chromatographic results as determined by GPC have shown higher narrowness of the MWD for metallocene-exposed PE. The broadness of MWD for the Ziegler-Natta PE is indicative of a higher degradation of this PE. The mechanical strength (tensile stress and strain) of unexposed metallocene PE samples by metallocene was superior than the conventional Ziegler-Natta PE samples and similar behavior was exhibited for the exposed samples. Thermal analysis indicated higher crystallinity for the conventional PE sample that can be attributed to crosslinking resulting in brittleness. Growth in carbonyl is observed to be higher for the conventional Ziegler-Natta PE as compared with metallocene PE. This complements the earlier results of higher degradation in former PE at the functional group level. It can be concluded that the stabilization and higher useful lifetime of metallocene PE will require new low levels of chemical stabilizers. Furthermore, this will open a new field of chemical stabilizer different than the conventional light stabilizers.

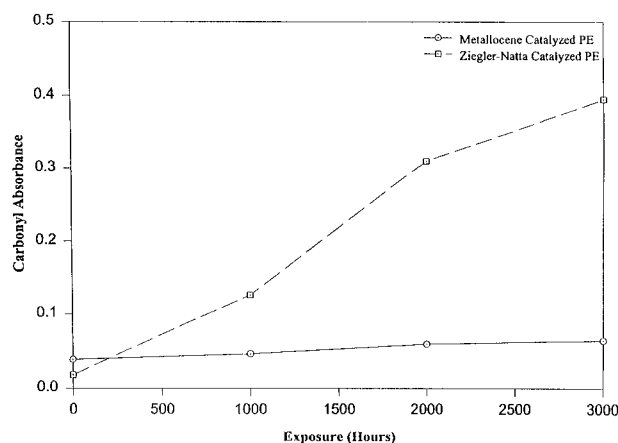


Figure 5 Growth in carbonyl absorbance of metallocene and Ziegler-Natta catalyzed PE as a function of exposure duration.

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