

Thermomechanical Degradation in the Preparation of Polyethylene Blends

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Polymer Degradation and Stability, 2000, Vol 68(3), 381-392

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ABSTRACT

A Haake Rheocord 90 melt blender was used to prepare several types of commercial polyethylene samples intended for studies on blends as well as to condition the pure components. The objective was to assess whether thermomechanical degradation of polyethylenes was occurring during the “conditioning” process and, if so, to characterize its nature and to find ways to prevent the degradation. There was no significant evidence of molecular breakdown but, rather, abundant evidence for chain buildup and possible gel formation. Without mechanical stress, no degradation occurred.

Melts were conditioned in the blender at temperatures in the range 190° - 220°C. Samples were characterized by dynamic viscosity (η') as well as by average molecular weight and MWD from GPC analysis, both before and after the blender experience. The rheological and GPC analyses were complemented by NMR, DSC, and TREF testing. The study included "conditioned" resins with and without additional antioxidants; results were compared to the properties of as-received polymers. The different techniques combine to explain: the modifications that can occur due to melt blending of polyethylenes; relationships to the polymer molecular structure; and possible means for detection and prevention of degradation. Addition of *adequate* amounts of antioxidant is successful in prevention of degradation.

Ziegler-Natta and metallocene LLDPE mixed with LDPE at different temperatures showed different levels of degradation depending on blender conditions. Enhancement of η' of "conditioned" resins over that of the as-received resins was the best indicator of degradation and correlated with branch content of the LLDPE, with metallocene LLDPE showing highest susceptibility to degradation.

Keywords: degradation; polyethylene; melt blender; cross-linking; viscosity enhancement

INTRODUCTION

The conditions for melt processing of polymers, namely high temperature, the presence of oxygen, and substantial mechanical stresses, can cause chemical reactions to occur. Even a small extent of reaction can have an enormous effect on the physical properties of the polymer¹. The buildup or breakdown of polymer chains can considerably influence the liquid and solid-state properties of the polymer.

Degradation is often a complex process involving combinations of different mechanisms^{2,3}. The rates of oxidation of various polyolefins such as linear polyethylene (HDPE), LLDPE, and polypropylene depend on details of their chemical structure. The susceptibility to oxidation increases with the increase in the number of branch points. At those points, weakly bound hydrogens are likely points for initiation of oxidative degradation, and consequently LLDPE is less stable to oxidation than is HDPE² (see Figure 108 of reference²). The extent to which hydrogen at branch sites in LDPE promotes oxidation, however, decreases at higher temperatures⁴. These differences in resistance to oxidation are reflected in the amounts of stabilizers required to provide protection to these polymers. In general, LDPE needs less antioxidant than LLDPE under the same conditions and HDPE needs very little. The mechanisms of polyethylene oxidation have been reviewed and described as free radical chain reactions^{5,6}.

Various analytical techniques have been employed to detect and quantify degradation, but among those differential scanning calorimetry (DSC) may not be useful. DSC is not expected to show any significant shifts in T_g or T_m which are relatively insensitive to moderate changes in \bar{M}_w resulting from oxidative degradation⁷. Similarly, tensile strength shows only a weak response to changes in \bar{M}_w . However, melt viscosity

measurements are highly sensitive to \bar{M}_w changes so we expect melt rheology to provide useful tools for tracking degradation.

In the past, different techniques were used to study the degradation of polyethylene in the presence of *foreign* materials (mostly peroxide initiators). For example, Konar and Ghosh⁸ reported that the extent of oxidation of LDPE, as well as the nature of the oxidative degradation products vary with catalyst cation. Konar et al.⁹, using DSC, observed small differences in melting peak temperature (2-4 degrees) and in percentage crystallinity (~2%) between as-received LDPE, and degraded LDPE. Ghosh et al.¹⁰ observed enhancement of the low-shear melt viscosity η_0 and a reduced shear rate ($\dot{\gamma}$) for onset of pseudoplastic flow behavior, both associated with \bar{M}_w increase. This arose as a result of mild cross-linking in LDPE due to peroxide action. The melts of conditioned LDPE and modified LDPE (oxidized) both showed an extended range of pseudoplastic flow behavior^{10,11}.

Depending on the polymerization technology^{1,12} (ZN or Phillips) and even the catalyst used to produce it, HDPE may undergo many radical reactions; chain scission and chain branching leading to cross-linking are generally favored. Furthermore, the oxidation rate of HDPE and LDPE melts was found to depend on the nature of the metal (and metal-containing compounds) with which they had been conditioned^{13,14}. El'darov et al.¹⁵ observed that in the presence of the stabilizer Ionol, the \bar{M}_w of HDPE decreased at a constant rate, while in the absence of the stabilizer the \bar{M}_w of HDPE either increased or decreased depending on the oxygen concentration of the processing environment. Moreover, heterogeneity of oxidation was observed in photo-oxidized γ -irradiated

LLDPE films, which may result from, for example, limited oxygen diffusion or non-uniform initiation¹⁶.

The results for different studies of structural modifications in polymer reactive extrusion may appear to conflict if the effects due to different flow geometry are not taken into account¹⁷. In reactive extrusion experiments, Polance and Jayaraman¹⁷ reported that LLDPE was significantly more reactive than the LDPE. Their shear viscosity measurements showed an order of magnitude increase at low shear rates but much less at higher rates. [i.e., η_0 is more sensitive to \bar{M}_w and MWD than is the shear-thinning $\eta(\dot{\gamma})$]. In another study, Wasserman and Foster¹⁸ observed increase in the viscosity of unstabilized LLDPE; flow activation energy was noticed to increase dramatically with the number of extrusions. Moreover, the peroxide action was found¹⁹ to broaden the MWD of HDPE, especially towards the higher molecular weight end (strongly affecting \bar{M}_w and \bar{M}_z). The low molecular weight end of the MWD, which affects mainly \bar{M}_n , remained virtually unchanged at all temperatures (180°-200°C).

Batch blenders (e.g., Brabenders, Haake Rheocord 90) are widely used in polymer research laboratories, yet little consideration (in the public literature) has been given to thermomechanical degradation of polymers in these devices. Research has focused on degradation during melt processing in extruders. Furthermore, most of these latter degradation studies were carried out by introducing a *foreign* material. Thus, the present study of the possible thermomechanically-induced degradation in the Rheocord 90 batch melt blender represents a novel contribution.

In all processes and research that involve melt “conditioning” (either in an extruder or in a batch blender) care should be given to prevent degradation of polymers

during the conditioning process. Here, as part of a larger study^{20,21} a Rheocord 90 melt blender was used to prepare samples to study the rheology and miscibility of HDPE, different LLDPEs and LDPE blends as well as to condition the pure components. Consequently, the question of stability of all polyethylenes in the melt blender was investigated as a preface to the later investigation.

The objective of the study reported here was to make sure that degradation of polyethylenes was prevented during the conditioning process. Different techniques were employed to examine the stability of polyethylenes in the melt blender. Small-strain dynamic oscillatory measurements of viscoelastic properties (η') in a Rheometrics Mechanical Spectrometer 800 (RMS) as well as \overline{M}_w and MWD from GPC analysis were used to assess the stability of samples of LLDPE and LDPE in the melt blender. The rheological and GPC analyses were supported by NMR, temperature rising elution fractionation (TREF), high pressure liquid chromatography (HPLC), and DSC testing.

The study included samples with and without additional antioxidants; results were compared to the properties of as-received samples. Results of using the different techniques can be integrated to explain: (a) the modifications that can occur due to melt blending of polyethylenes; (b) relation to the polymer chemistry; and (c) possible means for detection and prevention of degradation.

EXPERIMENTAL

Materials

Most polyethylene resins used in this study were supplied by Nova Chemicals Ltd. (and are here designated with sample codes "S"). One HDPE sample (Q-HDPE) and one LLDPE metallocene resin had other origins. Molecular weight (from GPC), branch

content (NMR and FTIR), and melt index (M.I.) characterizations of the samples are given in Table 1. The MI characterization of as-received samples was provided by resin manufacturers. Q-HDPE, S221 (HDPE), S229 (butene LLDPE), and S237 (hexene LLDPE) were Ziegler-Natta products. The metallocene resin was a butene LLDPE. S216 was a LDPE made by high-pressure gas polymerization. All polyethylene samples used were commercial resins and contained antioxidant (AO) with the exception of S216 (LDPE) that had no AO, yet was found to be very stable.

The mixture of antioxidants used in this study was a 50/50 blend of the primary AO Irganox 1010 {Phenol B, tetrakis[methylene 3-(3',5'-di-t-butylphenol) propionate]methane, $M_w=1178$ } and a secondary AO Irgafos 168 {P-1, tris[2,4-di-t-butylphenol] phosphite, $M_w=646$ }. The primary and secondary antioxidants are made by Ciba-Geigy. Normally, 0.1% (1000 ppm) or less of primary and secondary antioxidants are used commercially for polyolefins⁷. The optimal composition of the stabilizer formulation depends most critically on the temperature selected for melt processing^{22,23}.

Melt Conditioning in the Blender

The Haake Rheocord 90 is designed for use as a computer-controlled torque rheometer, which can also be operated as an extruder or a mixer. The latter configuration, featuring a sample bowl containing 60 mL of melt, was used for conditioning different polymers at constant temperature and rotor speed, and for a fixed time. The LDPE and LLDPE resins used in this study were conditioned in the melt blender at 50 rpm for 10 minutes. The influence of the blender mixing temperature (T_{mix}) on the degradation was investigated by tests at $T_{mix}=190^\circ\text{C}$ and 220°C . The effect of AO on degradation was examined by mixing the polymer(s) with and without (w/o) additional AO. The influence

of a nitrogen atmosphere on the degradation process was examined, too. The “conditioned” samples were then removed from the mixing bowl, air-cooled, and characterized by different techniques. The as-received resins were used in this study as control samples.

Mechanical Spectroscopy

The RMS was employed for ω -sweep measurements (ω =angular frequency) of dynamic properties at 190°C. A shear strain amplitude (γ°) of 10% was used, after a strain sweep showed that this γ° was sufficiently small to produce sinusoidal torque responses and dynamic properties independent of γ° (i.e., linear properties were obtained). The ω -sweep was carried out in the range 10^{-2} to 10^2 rad/s. A cone-and-plate (CP) geometry of 25-mm diameter platens with cone angle of 0.1 radian with a 53 μm truncated apex was used for the dynamic shear measurements, while a parallel plate geometry was employed for the temperature sweep tests. All measurements were conducted using nitrogen, obtained from a nitrogen cylinder, as the convection-heating medium to alleviate possible oxidative sample degradation during the sweep tests. The RMS testing was carried out on disc specimens molded either from the as-received resins or from samples of the air-cooled mixer-conditioned resins. Sample preparation and test procedure are explained elsewhere²⁴.

NMR Spectroscopy

NMR spectroscopy was carried out in Bruker DPX 300 or Bruker AC200 instruments. ¹³C NMR was used to study the influence of the blender experience on the branch content ($\text{CH}_3/1000 \text{ C}$) of conditioned resins.

Thermal Analysis

Samples of 5-10 mg were sliced from the as-received and conditioned resins then compressed into aluminum sample pans for testing in a TA Instruments DSC 2910 equipped with a Thermal Analyst 2200, and a nitrogen gas flow established from a nitrogen cylinder; this further protected the samples from oxidation. A scan rate of 10°C/min was used to heat the samples from 30°C to 160°C in nonhermetic pans.

TREF Analysis

TREF analysis was performed using a custom-built apparatus described elsewhere²⁵. Polymer sample (~ 5 mg) was dissolved by immersion in o-xylene at 125°C for 4 hours, followed by slow cooling to -8°C at a cooling rate of 1.5°C/h. The crystallized sample was then filtered into a TREF column containing 100 mesh glass beads. The TREF process was then initiated with passage of another solvent (o-dichlorobenzene) through the column as the column temperature was raised in order to extract the branched species from linear species according to their different solubilities as temperature changed. The temperature of the packed column was ramped at a rate of 1°C/min up to 125°C with a solvent flow at 1 mL/min. The eluting solution was passed through an IR detector to measure the amount of material eluting at a certain temperature.

GPC Characterization

The molecular weight distributions were obtained from GPC measurements in dichlorobenzene at 140°C and interpreted with calibrations utilizing near-monodisperse HDPE standards obtained from NIST. Molecular weights obtained in this way for the branched species in LDPE and LLDPE can be only approximate, but the pseudo-linear

structure of the copolymers in LLDPE allows the GPC technique to be quite accurate for them too.

HPLC Analysis

WATERS 2690 HPLC System with WATERS 996 Photodiode Array Detector was used to identify active and degraded antioxidant.

RESULTS AND DISCUSSION

The influence of the blender conditioning process on the possible degradation of polyethylene was studied initially by using the linear chains of HDPE as model polymers. Q-HDPE and S221 (HDPE) were used. Next, LLDPE (S229) and LDPE (S216) were used to complete the investigation.

The study of the degradation of HDPEs in the melt blender was limited to rheological and HPLC characterization. Viscosity temperature sweep (160°-260°C) testing on Q-HDPE in the RMS showed (Figure B.15 of reference²¹) agreement of $\eta^*(T) = \eta' - i \eta''$ or $\eta'(T)$ measurements for as-received and conditioned resin (with and w/o added AO; at 180°C, 50 rpm for 10 minutes). Hence, it was considered that "conventional" melt conditioning in the blender causes no structural modifications in commercial HDPE. This further confirms the stability of the linear PE^{2,4}.

Parallel results emerged from study of Nova S221 (HDPE), conditioned at 50 rpm for a longer time (23 minutes) with the same temperature ramp (from 160°C to 260°C). Samples from three different batches were analyzed by HPLC for residual AO at the end of the conditioning experiment. The HPLC analysis was carried out by Nova Chemicals in Calgary. Results (see Table 2) showed the residual presence of more than 93% active AO, demonstrating that the AO had not been "used up" (by oxidation), which would have

left the resin unprotected. Although this experiment has helped to validate the reproducibility of previously reported torque data²⁶, its other important significance is to indicate that the AO is essentially not consumed regardless of the high T (average T=210°C) and residence time (23 minutes). This analysis demonstrates the stability of stabilized HDPE during melt conditioning particularly when performed at *lower* temperatures and/or for *shorter* times (i.e., the blending conditions of 50 rpm, 190°C and 10 minutes employed in the latter part of the larger study²⁰). For LDPE and LLDPE, five different techniques were used to study the possible degradation. Results will be discussed below.

Dynamic Mechanical Spectroscopy

The RMS was used to examine the degradation of LLDPE and LDPE that might have occurred in the melt blender. ω -sweep testing (0.01-100 rad/s) was employed rather than steady shear to avoid any sample modifications that could result from the large strains inherent in the latter. All tests were carried out using the CP test geometry, and strain amplitude (γ°) of 10% was selected following γ° -sweep test. All tests were performed under N₂ at 190°C. Initially, the two polymers investigated were S216 (LDPE) and S229 (butene LLDPE). Subsequently, two more LLDPEs were examined for degradation: a hexene Ziegler-Natta resin (S237) and a butene metallocene resin.

Figure 1 displays the ω -sweep test results for S216 (LDPE) conditioned at 190° and 220°C without additional AO. Only at very low ω is there a tendency for the case of T_{mix}=220°C to show $\eta'(\omega)$ exceeding slightly η' for the case of T_{mix}=190°C. Results for the as-received resin are plotted as well. The dynamic viscosity measurements, $\eta'(\omega)$, showed excellent agreement between results obtained at 190° or 220°C and that of the as-

received resin, suggesting no influence of the conditioning process on the LDPE. These results indicate that LDPE was very stable and did not undergo degradation despite the fact that it contained no extra AO. To check the reproducibility of the data, the ω -sweep test was repeated on a sample prepared in Calgary at Nova Chemicals Ltd. Excellent, if not perfect, agreement was obtained (Figure B.16 of reference²¹).

The rheological characterization of S229 (LLDPE) was examined after conditioning under different blender conditions. These conditions included the use of added AO (1000 ppm) in the absence of N₂ as well as under a N₂ blanket without adding extra AO (indicated in the following Figures as “no AO”). Results for S229 mixed at 220°C in the presence of extra AO and under N₂ blanket are displayed in Figure 2 as $\eta'(\omega)$. The $\eta'(\omega)$ curve for the “control” sample showed a Newtonian behavior at low ω with $\eta_0 \sim 10^4$ Pas. Measurements obtained for the resin conditioned in the absence of both extra AO and N₂ blanket (the norm in commercial melt blending) showed enhancement of viscosity at low ω by up to a factor of 7 over the range $\omega = 0.01$ to ~ 10 rad/s without showing a Newtonian limit at low ω . For high ω (10 to 100 rad/s), the curve matched that of the as-received resin. On the other hand, measurements obtained for S229 conditioned under N₂ blanket in the absence of added AO showed less enhancement in viscosity ($\eta_0 \sim 1.4 \times 10^4$ Pas) but did not eliminate degradation. Results obtained in the presence of extra AO without using N₂ agreed with the as-received measurements over the whole ω -range. The effect of T_{mix} was examined by comparing $\eta'(\omega)$ for S229 conditioned at 190°C and 220°C, in the absence of both extra AO and N₂. At low ω , $\eta'(\omega)$ data showed (Figure 3) higher viscosities at higher T_{mix} with excellent reproducibility for samples taken from the same batch (Run #1 and Run #2).

An attempt was made to separate the effects of heat and torque on the oxidative degradation of S229 (LLDPE). The as-received polymer was placed in a preheated oven for 10 minutes at 220°C (same time and T as with the melt blender). Rheological characterization of the “statically” heated samples showed (Figure 4) essentially the same $\eta'(\omega)$ and $G'(\omega)$ as the as-received resin. This result suggests the significance of the combined effect of stress and heat in the melt blender on the degradation process; the absence of stress reveals that temperature alone is ineffective, so stress plays a vital role in the degradation in the blender.

The adequacy of the amount of the AO was checked by mixing S229 with an extra 2000 ppm of AO at 190° and 220°C. Results (Figure 5.3 of reference²¹) showed no difference from the case of 1000 ppm of extra AO which was therefore adequate to prevent polymer degradation.

The above observations of degradation in S229 (butene) motivated the investigation of another LLDPE. This time S237 (hexene) was used. Results on $\eta'(\omega)$ for S237 samples mixed with and w/o additional AO at different temperatures are given in Figure 5. A behavior similar to that of S229 was obtained. Again, $\eta'(\omega)$ for the resin conditioned at 220°C with 1000 ppm additional AO matched that of the as-received sample. The conditioning at 190° and 220°C in the absence of extra AO resulted in enhancement of viscosity at low ω , with greater increase in $\eta'(\omega)$ as T_{mix} increased. Further assessment of these $\eta'(\omega)$ data was made by comparison with non-Newtonian viscosity $\eta(\dot{\gamma})$ obtained by running a steady shear test on as-received samples of S237. Results that show the excellent match of $\eta(\dot{\gamma})$ and $\eta'(\omega)$ [Cox-Merz rule] for as-received resin at low $\dot{\gamma}$ (or ω) are given elsewhere (Figure B.18 of reference²¹). This implies that

the results shown here for $\eta'(\omega)$ as indicators of degradation or the absence of it are valid for $\eta(\dot{\gamma})$ in commercial processing conditions as well.

The enhancement of the viscosity of S237 (hexene) at 190°C relative to the as-received resin was less than that of S229 (butene), at the same temperature, by a factor of $\sim 5/2$. If the two polymers were prepared under similar conditions and had the same original dose of extra AO, then these differences could be related to post-reactor processing or to possible differences in susceptibility to oxidation with different branch types. Regardless, for both ZN LLDPEs 1000 ppm of extra AO was sufficient to prevent degradation.

The rheological investigation of degradation in LLDPEs was then extended to the metallocene resin. Results for $\eta'(\omega)$ are shown in Figure 6 for the metallocene resin obtained after conditioning the polymer at 190°C without extra AO and at 220°C in the presence of 1000 ppm of extra AO. The measurements indicated a significant enhancement in the low- ω viscosity over that of the as-received polymer, with less difference in the high- ω regime. The low- ω viscosity of the metallocene resin (conditioned at 190°C without extra AO) increased by a factor of ~ 15 , while that obtained for the ZN LLDPE (S229) (at the same conditions) increased by a factor of only ~ 5 (see Figures 2 and 3 by comparison to the as-received resins). Furthermore, the addition of 1000 ppm of AO to the metallocene polymer did not prevent degradation as it did with the ZN resins (S229 and S237). The rheologies of metallocene and ZN polyethylenes have been reported previously to be different^{27,28}. Possible explanations for the substantially greater enhancement of the low- ω viscosity for the metallocene LLDPE are:

1. The higher content of unstable branches in the metallocene resin (36.2) compared to ZN resins S237 (17.2) and S229 (21.5). This possibility is reinforced by the correlation shown in Figure 7 [Enhancement factor = $(\eta'_{\text{conditioned resin}}/\eta'_{\text{as-received}})_{\omega \rightarrow 0}$]. Previous reports^{2,4} suggested the increase in susceptibility of LLDPE to degradation with increased branching, but didn't show a quantitative correlation.
2. The different metal residues of catalysts in ZN and metallocene resins could result in different influences on the degree of degradation.
3. Possible differences in the unsaturation levels (double bonds) of the polymer molecules produced by different catalysts.

It is clear that conditioning for LLDPE under standard conditions (i.e. no additional AO and no N₂) can lead to a substantial increase in viscosity at low ω , both alone and during blending with LDPE. Since low- ω data are often used to assess the miscibility of polymer blends, the conditioning process that takes place in the melt blender can strongly influence the interpretations of blend miscibility data if an adequate amount of extra AO is not added.

The enhancement of viscosity at low ω was observed when LLDPEs (S229, S237, and metallocene resins) were conditioned without adding extra AO. It was also observed that the enhancement was less at high frequencies, which are less sensitive to long relaxation times associated with larger and cross-linked molecules. Similar observations were reported for LLDPE and LDPE and their blends^{10,29} where degradation was induced by reactive processing (adding peroxides) and cross-linking was assumed to take place. Hinsken et al.¹² suggested that the increase in MI (because of multiple extrusions)

of HDPE (Cr-catalyst) might be caused by chain scission. However, the enhancement of viscosity or the decrease in MI were caused by cross-linking^{1,10,12,17}.

In the current study, no foreign material was added and the mixing device was different than in the previous studies; however, similar behavior was obtained. The enhancement of viscosity at low ω or $\dot{\gamma}$ (sensitive to structural modifications) could result from cross-linking (chain buildup) which would lead to increase in branching or molecular weight, and hence an increase in viscosity. Rheology is known to be sensitive to very low levels of long chain branching³⁰.

The above rheological characterization revealed the structural modifications that can occur in LLDPEs due to the conditioning in the melt blender. It was also observed that the low-shear viscosity increased with T_{mix} , signaling the influence of temperature-enhanced chemical reactions.

NMR Spectroscopy

The NMR analysis for S229 (LLDPE) was carried out by Nova Chemicals in Calgary. The resin was conditioned in the melt blender under different temperatures (190° and 220°C) with and without AO. Five such “conditioned” samples were analyzed for branch content and compared to as-received resin. The six NMR spectra are shown elsewhere (Figures B. 19 to B.24 of reference²¹). The branch content for the six samples is given in Table 3.

The NMR data show no difference in branch content between the as-received resin (21.5) and that mixed at 190°C in the presence of extra 1000 ppm of AO (21.9), indicating no modifications in the structure of the LLDPE. On the other hand, samples mixed at the same temperature (190°C) but without additional AO, resulted in lower

branch content (17.8 CH₃/1000 C), which could be due to loss of short branches or cross-linking or long chain branching. The short branch content at 220°C was lower (16.6 CH₃/1000 C) than that at 190°C for samples conditioned without extra AO, suggesting the sensitivity to temperature of the reactions. Since both cross-linking and chain scission are occurring simultaneously, a temperature change could shift their relative importance, making branch content increase or decrease slightly. The effect of T_{mix} and added AO on NMR data followed the same trend described above for the rheological characterization. First, in both cases the degradation (lower short branch content) at 190°C was prevented by adding 1000 ppm of AO. Second, the low- ω viscosities as well as the loss of branches increased with increasing conditioning temperature.

Samples conditioned at 220°C in the presence of 1000 and 2000 ppm of AO showed less loss of short branches (content 18.8 and 19.9, respectively) than those mixed w/o additional AO (content 16.6). Higher amounts of AO resulted in lesser loss of short branches and hence a better protection against degradation. Higher amounts of AO may be needed to compensate for the influence of high temperature on the degradation reactions as well as the partial loss of the low M_w AO by volatilization^{3,7}.

Under these mixing conditions stress, residual ZN metals in the polymer, and heat act to initiate (in the absence of AO) free radicals that attack the H-C bond on the tertiary carbon atoms in ZN LLDPE and possibly form ethylene or cross-link through intramolecular hydrogen transfer reactions³¹. The NMR analysis has also shown that the frequency of long chain branches (calculated from the NMR Spectra) in all samples after conditioning was < 1 branch/1000 C, indicating light cross-linking on the side groups. Cross-linking could be responsible for the apparent drop in branch content. Further,

support for long chain branching was obtained from TREF analysis (see following). Therefore, the NMR results and the low- ω rheology data could both be results of long-chain branching due to cross-linking.

The stability of pure LDPE under similar conditions can be explained by the absence of ZN metals, since ZN catalysis is not used in polymerization. However, this opens the possibility that LDPE might degrade in those blends wherein it is mixed with LLDPE components containing ZN metals. The stability of LDPE could also be linked to its saturation level since unsaturated LDPEs can easily be cross-linked³².

DSC and TREF Analyses

The DSC analysis was carried out after conditioning samples of S229 (190°C) and S216 (220°C), with and w/o added AO. In both cases, results were compared to those of the as-received resin. All samples were heated in the DSC under N₂ from 30° to 160°C at a scan rate of 10°C/min. DSC data were analyzed for possible differences in the melting peak (T_m) and the weight fraction crystallinity (X_c). A comparison of S229 (LLDPE) conditioned with and w/o additional AO is given in Figure 8.

The summary of T_m and X_c for both polymers is given in Table 4. It is relevant to note that our previous oxidation experiments on Dowlex 2045 (LLDPE) stabilized and unstabilized resin indicated that added AO by itself had no influence on X_c or T_m .

Table 4 suggests no change in the melting peak of S216 due to conditioning with or w/o added AO and the values of T_m were very close to that of the as-received resin ($\Delta \leq 0.5^\circ\text{C}$). This result indicates the stability of the LDPE and supports the previous rheology data. Similar behavior was obtained in comparison of the T_m between the as-received LLDPE (S229) and that conditioned at 190°C with additional AO ($\Delta T_m = 0.2^\circ\text{C}$).

On the other hand, the melting peak of LLDPE (S229) conditioned w/o additional AO at 190°C showed an increase of T_m (to 124.1°C, $\Delta T_m = 1.3^\circ\text{C}$). Similar increases in T_m were reported by Konar et al.⁹ for chemically degraded LDPE. The increase in T_m of degraded LLDPE could be explained by the possible increase in the lamellae thickness (as shown in Figure 59 of reference³³) that results from the long chain branching (Rheology and NMR data).

In general, the DSC results on T_m support the previous rheology and NMR data with regard to the stability of the LDPE and the degradation of the LLDPE when conditioned in the absence of additional AO. Again, the degradation of LLDPE was prevented by the addition of 1000 ppm of AO as shown by the rheology, NMR and DSC data.

The percent crystallinity is anticipated to increase in branched polymers if the branches are getting longer⁹ (see Figure 60 of reference²). However, in our case X_c slightly decreased from 40-41% to 38% and a “shoulder” in the DSC curve was more visible (see Figure 8) in S229 conditioned w/o additional AO. It is clear that the influence of melt conditioning on the percent crystallinity is somewhat difficult to resolve by DSC. The rise of the shoulder indicates the presence of a different molecular structure. The "shoulder" was better resolved in the TREF profile (Figure 9) of S229 conditioned w/o additional AO.

Figure 9 shows the TREF profiles for S229 conditioned with and w/o additional AO. The curves were offset vertically for clarity. The bimodal distribution (common characteristic of ZN LLDPE which is known to contain chains of linear and others of short-branched character) was composed of a narrow peak at high temperature and a

broad peak at lower temperature^{34,35}. The high temperature peak measures the concentration of homopolymer of ethylene (linear chains), while the low-temperature peak relates to the concentration of methyl groups at the ends of branches^{25,36}. The high temperature peak was well defined in the sample conditioned with extra AO with a TREF profile typical of undegraded ZN LLDPE³⁴. In comparison to the profile for the sample conditioned with additional AO, the TREF profile for the sample w/o AO shows the following differences:

- i. decreased intensity of the homopolymer peak
- ii. multimodality of the copolymer (branched) peak
- iii. modification of branches eluted at $\sim 30^{\circ}\text{C}$ (the kink), which could be due to long chain branching.

All of the above differences clearly suggest that structural modifications (in a form of new branch types and altering of old ones) had taken place as a result of melt conditioning w/o additional AO. This observation could be used to support the rheology and NMR data that suggested long chain branching and/or cross-linked gels in LLDPE resins conditioned w/o extra AO.

GPC Characterization

The GPC characterization was performed on S229 (LLDPE) and S216 (LDPE) after conditioning at 190°C and 220°C without additional antioxidants. The as-received polymers were characterized, too, and used as control samples for comparison purposes. If degradation is to take place, then M_w will either increase (chain buildup) or decrease (chain breakdown) and the polydispersity (PD) will be broadened^{1,12}. Four measurements were carried out for each of the six samples. Results are shown in Table 5. The M_w and

PD of the four different measurements were averaged and the standard deviation (S_D), given in parenthesis, was calculated for each case.

Statistical decision theory was used to test the significance of the differences in M_w and PD (reported in Table 5) between the conditioned and as-received resins. The null hypothesis is $H_0: \mu_1 = \mu_2$ (where μ can be either M_w or PD from the two different populations we are comparing). This is the hypothesis that the two means (M_w or PD) are equal and the samples (represented by the two sets of four data points) were withdrawn from the same population. A 95% confidence level was chosen and the t-test was performed. Even for small sample size, the t-test is usually relatively accurate³⁷.

For 95% confidence level, if the value of t_o (defined by equation 1) is *less than or*

$$t_o = \frac{y_1 - y_2}{S_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \quad (1)$$

equal to 2.447 then the null hypothesis is true and the differences are not significant.

In equation 1, y_1 and y_2 are the sample means, n_1 and n_2 are the sample sizes (here $n_1 = n_2 = 4$), and S_p^2 is an estimate of the common variance computed from:

$$S_p^2 = \frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2} \quad (2)$$

where S_1^2 and S_2^2 are the two individual sample variances.

Otherwise, the hypothesis is rejected and one concludes that the samples represent two different populations. The values of t_o calculated for the conditioned polymers in comparison with as-received resins are reported in Table 5. Values that are *less than or*

equal to 2.447 are shown in boldface representing the cases where the null hypothesis is true.

The results show that M_w and PD for S216 (LDPE) conditioned at 190°C are (with 95% confidence) the same as those of the as-received resin. For S216 conditioned at 220°C, the analysis of PD suggests no significant difference between conditioned and as-received resins, while that of M_w predicts an increase in M_w . This rather misleading latter finding is not a surprise for GPC analysis¹². Furthermore, the PD is more reliable than M_w measurement³⁸. Moreover, the predicted increase in M_w is not substantiated by the low- ω viscosity measurements shown in Figure 1 and hence rejected on physical grounds. Therefore, we conclude from the GPC evidence that S216 (LDPE) did not undergo any detectable degradation, which agrees with the previous rheological and DSC characterization.

However, all the results displayed in Table 5 for S229 (butene LLDPE) suggest that the conditioning at 190°C and 220°C produced significant differences between the conditioned and as-received resins. This observation supports the previous rheology, NMR DSC and TREF characterization.

What could happen in the absence of additional AO?

This is the primary question that confronts one when studying the properties of blends. To answer this question, we first followed the normal practice of preparing melt blends and hence no extra antioxidants were added. Blends of S229 (LLDPE) and S216 (LDPE) as well as the 'pure' resins were conditioned in the melt blender at 190° and 220°C and 50 rpm for 10 minutes. The LLDPE concentration in the blends was 10, 30,

50, 70, 80 and 90% by weight. $\eta'(\omega)$ ω -sweep testing on blends and as-received resins was carried out in the RMS at 190°C and 240°C and $\gamma^0=10\%$.

As noted earlier, the high-pressure LDPE (S216) did not contain any AO; however, the polymer was very stable and tests on samples prepared from different batches showed excellent reproducibility (“batch reproducibility”; Figure B.16 of reference²¹). The reproducibility of the $\eta'(\omega)$ data for LLDPE (S229) samples prepared from the same batch was excellent, too (Figure B.17 of reference²¹). On the other hand, the reproducibility of $\eta'(\omega)$ for LLDPE was poor for samples prepared from different batches (see Figure 10). To check the batch reproducibility of $\eta'(\omega)$ for blends of S229 and S216, a blend of 80% S229 was studied. Samples from three batches prepared under the same blender conditions were used. One of the batches was prepared by Dr. Kam Ho of Nova Chemicals in Calgary. The rheological characterization of the 80% LLDPE blend produced significant differences among the three batches in the low- ω viscosity. Results (given in Figure 5.7 of reference²¹) show values of η' that are different by a factor of up to ~ 3 . It is clear that the batch reproducibility of the degraded samples is very poor, and hence this test could be used as a quick check for degradation. Furthermore, the poor batch reproducibility could be the reason behind the observed peculiar behavior of $\eta'(\phi)$ curves that will be discussed below.

The ω -sweep for η' data obtained for the blends of different compositions of S229 (LLDPE) and S216 (LDPE) as well as for the ‘pure’ resins were analyzed and plots of $\eta'(\phi)$ ($\omega=0.1$ rad/s; $T=190^\circ\text{C}$) are given in Figure 10 (Batch # 1; because ω is so low, Figure 10 is essentially a plot of η_0 vs. ϕ). The solid straight line that connects points for the ‘pure’ resins represents the expected behavior of the blend if a linear additivity rule

were followed (which would suggest miscibility across the entire ϕ -range). The linear additivity rule was approximately followed for $\phi \leq 50\%$ LLDPE, while negative deviation behavior (NDB) was observed for $50 < \phi < 100\%$ LLDPE where immiscibility could be suspected. The NDB and the minimum in $\eta(\phi)$ and $N_1(\phi)$ curves were previously reported for HDPE-PS blends which are known to be immiscible³⁹.

The NDB for immiscible melt blends has been explained by interlayer slip⁴⁰ or through a free volume approach^{41,42}. However, the data displayed in Figure 10 could be simply explained by looking into the influence of degradation on the batch reproducibility of these results. The values of η' for the 80% LLDPE from the second and third batch (prepared under the same conditions as batch # 1) are both displayed in Figure 10. While η' for batch # 2 supports that of batch # 1 (circles) and shows NDB, the batch # 3 value is far above the linear additivity line, suggesting a positive deviation behavior (PDB). Moreover, all blends data on the plot would look like showing a PDB if the data point for the stabilized LLDPE was used as a reference. NDB was also observed in $\eta'(\phi)$ and $G'(\phi)$ curves for the same blend at $\omega=1$ rad/s.

Previous reports that examined HDPE/LDPE melt blends⁴³ reported enhancement in the viscosity, $\eta(\dot{\gamma})$, of pure components due to melt conditioning. This observation had significantly influenced the interpretations of the blend viscosity and resulted in NDB when the conditioned pure components were taken as reference. The thermomechanically-induced modifications were explained in terms of intermolecular interactions induced through the extra entanglements generated by the shearing forces^{44,45}. It is valid to question whether the observed modifications were due to extra entanglements or simply a result of degradation that could have been prevented by adding

extra AO, taking into consideration the long conditioning time and the high temperature (20 minutes and 190°C in the Manero et al.⁴³ study).

Conclusions

In summary, HDPE was found to be stable during melt blending in agreement with previous reports^{2,4}. However, LLDPE was shown by the rheology, NMR, DSC, TREF and GPC analysis to degrade because of combined torque and heat in the melt blender. The degradation in LLDPE was prevented by adding 1000 ppm of AO; no advantages were observed with 2000 ppm of AO. On the other hand, LDPE (which did not contain any additional AO) was very stable; although this is known³² not to be the case for unsaturated LDPEs (copolymers of ethylene and 1,9-decadiene that results in terminal vinyl groups).

The above mentioned techniques collectively show the following:

- a. The degradation in Nova ZN LLDPEs (conditioned at 50 rpm for 10 min. at temperatures up to 220°C) could be prevented by adding 1000 ppm of AO. However, this amount was not enough to prevent degradation in the metallocene resin under the same blender conditions.
- b. Preliminary results show that the susceptibility of ZN LLDPEs to degradation could be correlated to branch content.

These observations integrate to support a degradation model involving the formation of long chain branching or light cross-linking¹² that could be promoted by oxidation but only in the presence of stress. The thermomechanically-induced degradation was demonstrated to be similar to the chemically induced degradation.

The above analysis also shows very important observations that strongly influence the interpretation of the polyethylene blend rheology data. These observations could be summarized as follows:

- a. lack of ‘batch reproducibility’, specially at different T_{mix} , could be a sign of degradation in one (or more) of the blend components. The reproducibility test might be introduced as a routine check for degradation.
- b. it is difficult to conclude anything about the implication of blends data if one (or more) of the components is undergoing degradation.
- c. It is important to check the influences of melt conditioning or sample preparation steps on the ‘pure’ polymers before proceeding with melt blending.
- d. Comparison of the dynamic shear rheology before and after conditioning proved to be helpful in detecting the influence of the melt blender on the polymer(s).

Acknowledgements

Financial support in the form of grants from Nova Chemicals Ltd. and the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged, as is a University of Alberta Scholarship for one of the authors (IAH). In addition, we thank Nova Chemicals Ltd., Quantum Chemicals and Dr. William Tchir of Dow Chemicals for providing polyethylene samples.

We would like to thank: Mr. Mingqian Zhang for performing the TREF analysis and Ms. Naiyu Bu for the GPC characterization. We are also grateful to Professors William C. McCaffrey and Sieghard E. Wanke for valuable discussions.

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Table 2: HPLC analysis for residual AO in S221 (HDPE) after conditioning*

Batch #	Active Primary AO (ppm)	Active Secondary AO (ppm)	Degraded Secondary AO (ppm)	Total active AO ×100%
				<u>(Total active+Degraded) AO</u>
1	2408	2412	356	93.1
2	2485	2474	345	93.5
3	2508	2525	347	93.6

*ramp from 160° to 260°C @ 5°C/min and 50 rpm

Table 3: NMR Characterization of S229 (LLDPE)

Blender Conditions	Branch Content (CH ₃ / 1000 C)
None (as-received)	21.5
Conditioned at 190°C with 1000 ppm of added AO	21.9
Conditioned at 190°C w/o added AO	17.8
Conditioned at 220°C w/o added AO	16.6
Conditioned at 220°C with 2000 ppm of added AO	19.9
Conditioned at 220°C with 1000 ppm of added AO	18.8

Table 4: DSC Characterization of S216 (LDPE) and S229 (LLDPE)

Blender Conditions	T_m , °C	X_c , %
S216: none (as-received)	110.1	41.0
S216: with 1000 ppm of added AO	109.6	40.0
S216: w/o added AO	109.7	38.0
S229: none (as-received)	122.8	39.7
S229: with 1000 ppm of added AO	122.6	41.3
S229: w/o added AO	124.1	37.7

Table 5: GPC Characterization of S216 (LDPE) and S229 (LLDPE)

Blender Conditions	$M_w (S_D^*)$	t_o	PD (S_D^*)	t_o
S229: none	105,313 (1285)	–	3.57 (0.07)	–
S229: $T_{\text{conditioning}} = 190^\circ\text{C}$	95,794 (1750)	8.770	3.32 (0.10)	4.096
S229: $T_{\text{conditioning}} = 220^\circ\text{C}$	93,530 (2163)	9.367	3.39 (0.22)	4.097
S216: none	99,464 (902)	–	6.45 (0.36)	–
S216: $T_{\text{conditioning}} = 190^\circ\text{C}$	100,255 (1818)	0.78	5.98 (0.14)	2.434
S216: $T_{\text{conditioning}} = 220^\circ\text{C}$	108,934 (1696)	9.86	6.48 (0.56)	0.090

* S_D = standard deviation

Legends for Figures:

Figure 1. Effect of T_{mix} on η' for S216 (LDPE). Here, a CP geometry was used

$$(T_{\text{test}}=190^{\circ}\text{C}, \gamma^{\circ}=10\%).$$

Figure 2. Effect of blender conditions on η' for S229 (LLDPE), ($T_{\text{mix}} = 220^{\circ}\text{C}$,

$$T_{\text{test}}=190^{\circ}\text{C}, \gamma^{\circ}=10\%).$$

Figure 3. η' for S229 mixed at 190° and 220°C (Check for reproducibility within the same batch).

Figure 4. $\eta'(\omega)$ and $G'(\omega)$ for as-received and statically heated S229 (LLDPE), (CP,

$$T_{\text{test}}=190^{\circ}\text{C}, \gamma^{\circ}=10\%).$$

Figure 5. Effect of AO and T_{mix} on η' for S237 (hexene, LLDPE), (CP, $T_{\text{test}}=190^{\circ}\text{C}$,

$$\gamma^{\circ}=10\%).$$

Figure 6. Effect of blender conditions on η' for the metallocene resin ($T_{\text{test}}=190^{\circ}\text{C}$,

$$\gamma^{\circ}=10\%, \omega=0.01-100 \text{ rad/s}).$$

Figure 7. Enhancement of low- ω viscosity for ZN and metallocene LLDPEs ($\gamma^{\circ}=10\%$,

$$T_{\text{test}}=190^{\circ}\text{C}; T_{\text{mix}} = 190^{\circ}\text{C}, \text{w/o extra AO}).$$

Figure 8. DSC melting curve for S229 (LLDPE) with and w/o added AO ($T_{\text{mix}} = 190^{\circ}\text{C}$;

$$\text{sample size}=5.6 \text{ mg}, \text{heating rate}=10^{\circ}\text{C}/\text{min}).$$

Figure 9. TREF profiles for S229 (LLDPE) conditioned with and w/o AO (at T_{mix}

$$=190^{\circ}\text{C} \text{ and } 50 \text{ rpm for } 10 \text{ min}).$$

Figure 10. $\eta'(\phi)$ for blends of LLDPE and LDPE ($T_{\text{mix}}=220^{\circ}\text{C}$, w/o added AO;

$$T_{\text{test}}=190^{\circ}\text{C}, \gamma^{\circ}=10\%, \omega=0.1 \text{ rad/s}). \text{ Ordinate represents essentially } \eta_0.$$