Trace Levels of Mechanochemical Effects in Pulverized Polyolefins

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ABSTRACT: This research investigated the structural changes that occur on different polyethylene polymer systems as a result of a novel pulverization process called solid-state shear pulverization (S³P). High-density polyethylene, low-density polyethylene, and two forms of linear low-density polyethylene were run through a pulverizer under high shear conditions as well as low shear conditions. The physical properties were examined before and after the pulverization via melt index, melt rheology, GPC, and DSC, techniques. The low shear pulverization did not noticeably alter the physical properties of the polymers. In contrast, high shear pulverization did result in an increase in viscosity as observed by melt index and oscillatory shear experiments, although solid-state and bulk properties as observed by DSC and GPC were not affected. These results indicate that a small amount of mechanochemically induced changes occur as a result of the pulverization process, including incorporation of a small amount of long-chain branches randomly placed on a few of the polymer chains. No evidence of short-chain branching resulting from S³P processing was found in these systems. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 671–679, 2001

Key words: polyethylene; rheology; branching; DSC; GPC

INTRODUCTION

Often in polymer processing, the polymer must undergo multiple processing steps that impart mechanical energy to the system. This energy may alter the structural, chemical, or physical appearance of the polymer, which, in turn, may alter thermal, physical, and rheological properties of the polymer. An understanding of how mechanical work may affect the polymer chains can be obtained by revisiting the field of mechanochemistry, wherein polymer chains are broken and the free radicals thereby created initiate other chemical reactions.[1–14]

A shearing force acting on the bulk polymer generates mechanochemical stresses. Internal stresses are distributed among the backbone bonds (intramolecular bonds) and between the chains (intermolecular bonds).[1–3] This distribution depends on the relative energies of the principal valency bonds in the chains and of the intermolecular interactions.[2] The applied stress can move the chains relative to each other (disentanglement) or result in direct scission of the chain (degradation). Chain rupture occurs if the stress applied exceeds some critical value.[1–3] If chains do experience primary scission, a radical exists at each of the two rupture sites.

Once the radicals are created, they behave so as to minimize their energy. Often the most stable course of action is termination. Radical termina-

tion may occur immediately after radical formation or after radical migration.[1–5,9,14] Termination is usually by combination, disproportionation, or a radical scavenger. If the radicals remain at the chain end and immediately recombine, they restore the linear chain architecture, and the system behaves as if degradation did not occur.[4] If a radical migrates before combining, then grafting or branching may occur elsewhere, in which case the original architecture of the chain is altered. Termination by disproportionation, in which the number of permanent chain scissions is equal to the number of bonds broken, reduces the molecular weight (MW) of the polymer.[4]

However, the most common reaction is the radical scavenging reaction. Here, a nonpolymeric species combines with the macroradical and stabilizes it or eliminates it through a series of reactions.[1–5] If the radical acceptor terminates the radical, there is a permanent reduction in MW, as is true with disproportionation. If a radical scavenger such as oxygen stabilizes the chain, then it initially forms a peroxy radical[2,4,5] that often turns into an aldehyde or ketone.[2] Polypropylene and polyethylene are examples of polymers very susceptible to forming peroxy compounds.[13] This emphasizes the importance of reaction media in mechanochemical reactions.

The creation of radicals as a result of mechanochemical action has been repeatedly verified, and under certain conditions, some researchers have been able to manipulate the phenomenon to create block or graft copolymers.[1,3,9–12] Further, industrial processes have been developed which make use of mechanochemistry via extrusion techniques to recycle post-consumer plastic waste.[15] However, it is difficult to control mechanochemical action, and undesirable changes such as a decrease in MW or a reduction of MW distribution can occur.[1–4,6] Changes in the chemical and physical structure of polymers can result in changes in melt rheology, which, in turn, complicate processing and mechanical properties of the solid and, hence, affect the performance of the polymer in service.

The process under consideration in this research is a pulverization process called solid-state shear pulverization (S³P). It resembles an extrusion process but, in addition, takes advantage of mechanochemical action. This technique is unique and differs from extrusion in that polymers are pulverized *in the solid state*. This continuous, one-step process shreds the polymer feedstock, which may be a single polymer type or a blend consisting of virgin and/or recycled polymers, into powders of controllable size ranging from coarse powders (10 mesh or 2540 μm) to ultrafine powders (200 mesh or 127 μm). The powder product can be useful in multiple applications such as compounding with additives, powder coatings, or direct injection molding. Further information on this process is given in refs. 17 and 18. Recent research indicates that the S³P process may compatibilize polymer blends, recycled or virgin.[16] It is known that S³P results in highly efficient, intimate mixing of immiscible blends,[17] and it is hypothesized that S³P may create compatibilizers *in situ* in the form of graft or block copolymers as a result of mechanochemical action.[7,8] Here, the research focused on only the virgin polyethylene homopolymer and examined the structural changes induced on the polymer system upon S³P processing of the polymer. The goal was to understand what modifications to polymer properties occur due to the pulverization and to ascertain the degree of branch formation associated with those modifications.

EXPERIMENTAL

Experiments were performed on a high-density polyethylene (HDPE), a low-density polyethylene (LDPE), and two linear low-density polyethylenes (LLDPE). The HDPE was LB 5620 from Equistar, Cincinnati, OH; the LDPE was NA 940 from Equistar; one LLDPE was GA 643-661 (ethylene–hexene copolymer) from Equistar; and the other LLDPE was NG 2432N (ethylene–octene copolymer) from Dow Chemical, Midland, MI. To differentiate between the two LLDPE polymers, they will be referred to as LLDPE-NG and LLDPE-GA. The equipment used for pulverization was a Berstroff PT-25 pulverizer consisting of a twin-screw device with a barrel diameter of 25 mm and an *L/D* ratio of 26. Cooling coils surround the barrel to maintain the processing temperature below the melting point (for a semicrystalline polymer) or glass transition point (for an amorphous polymer). Control of the feed rate, screw rpm, and shear/compression conditions (through screw design) optimize mixing and powder production. A more detailed description of the S³P equipment is given in ref. 17. Each polymer was run through the solid-state shear pulverizer under low shear conditions (a 23-mm-diameter screw in the 25-mm-diameter barrel) and under

high shear conditions (a 25-mm-diameter screw in the 25-mm diameter barrel). A screw speed of 300 rpm was maintained for both low shear pulverization and high shear pulverization.

Melt index (MI) experiments were performed using a constant pressure capillary flow device. The measurements were taken at 190°C under a constant load of 2.16 kg, in accordance with ASTM standard D 1238 Condition E. MI measurements were taken for each polymer in the virgin state as well as after high shear pulverization and low shear pulverization. All measurements are standardized to units of g/10 min. Six measurements were made for each of the 12 polymer samples.

The oscillatory shear experiments were conducted on a Bohlin VOR-melt rheometer using 25-mm parallel plates and a high-temperature torque head. Test samples were prepared by compression molding the polymer into disks 23 mm in diameter and 1.4-mm thick at 170°C under 4 tons force for 2 min and then immediately quenching in ice water. Samples were made for virgin, high shear, and low shear polymers of LDPE, HDPE, LLDPE-NG, and LLDPE-GA. Measurements were taken on three sample disks for each of the 12 types of polymer samples, accounting for a total of 36 samples used. Precautions were taken to ensure that no air bubbles were present in the test samples, and the parallel plates were cleaned between each run. The sample was placed between the plates of the apparatus that was then enclosed in an isothermal chamber and heated with hot air to 180°C. Excess polymer was squeezed out and removed at a gap of 1.1 mm. The gap was then reduced to 1.0 mm to obtain the slight bulge on the edge of the sample. Oscillatory shear rates of 0.063–0.63 s^{-1} were imposed at 100% amplitude, 0.63–18.8 s^{-1} at 50% amplitude, and 18.8–125.6 s^{-1} at 20% amplitude.

Molecular weight characterization of the polymers was determined by standard techniques on a Waters 150C gel permeation chromatography (GPC) at 140°C in trichlorobenzene (TCB) at a flow rate of 1.0 mL/min. Solution concentrations were 0.0026 g/mL without an added stabilizer, and the injection volume was 100 μL. Data were treated according to standard techniques. The samples analyzed by GPC were the virgin and high shear samples of LLDPE-NG, LLDPE-GA, and HDPE. All GPC experiments were courtesy of Dr. Francis Mirabella at Equistar Chemical.

Thermal characterization was performed using differential scanning calorimetry (DSC), and samples for DSC were prepared through solution crystallization. Two hundred milligrams of the polymer was added to 200 mL of *p*-xylene in a test tube. The mixture was held at 130°C in a large oil bath for approximately 3 h and the test tubes manually stirred to create a homogeneous polymer solution. The cooling was controlled by a Barnant temperature controller at a rate of 5°C/h until about 70°C, when the natural cooling rate of the oil bath fell below this rate. Virgin and high-shear samples of HDPE, LLDPE-NG, and LLDPE-GA were solution-crystallized in this manner, accounting for six solution-crystallized samples.

The crystallized polymer was recovered by filtration using filter paper and a glass funnel. The filtrate was vacuum-dried at room temperature for 3 days under 30 psi. Approximately 5 mg of the dried, solution-crystallized sample was sealed in a DSC aluminum pan. The samples were run in a Perkin–Elmer DSC 7 under nitrogen gas and using ice water to maintain the temperature. The samples were first heated from 10 to 160°C at a rate of 5°C/min and then held at 160°C for 20 min to erase the prior heat history. The samples were then cooled to 10°C at a rate of 5°C/min and subsequently heated to 160°C at 20°C/min. The samples were again maintained at 160°C for 20 min and then cooled to 10°C at a rate of 5°C/min. On the third heating, the samples were heated to 160°C at the fastest rate of 40°C/min. For the purposes of this research, T_m will be referred to as the peak of the melt endotherm.

RESULTS AND DISCUSSION

Changes caused by S³P processing were determined from changes in the melt rheology and crystallinity. These characteristics are affected by changes in the branching architecture of the polymer chain, which may occur as a result of mechanochemistry. Short-chain branches influence the morphology and solid-state properties of semicrystalline polymers,[19–29] whereas long-chain branches affect the melt rheology.[30–41] Based on this differentiation, the results are discussed in three categories: First is a discussion of the rheological changes as obtained from MI and oscillatory shear measurements, followed by a discussion on the MW distribution data obtained from the GPC experiments, and then a discussion of the crystallization and thermal property data obtained from DSC results. This section concludes

Table I Melt Index Data

| Sample	Virgin (g/10 min)	Low Shear (g/10 min)	High Shear (g/10 min)
HDPE	0.30	0.21	0.08
LDPE	0.25	0.21	0.32
LLDPE-GA	3.50	3.49	2.51
LLDPE-NG	4.00	3.91	0.91

All data have an error of ±0.02 g/10 min.

with some discussion on the results of preliminary spectroscopy work on the system.

The MI data are shown in Table I, and the viscosity versus frequency plots, in Figure 1. Based on the assumption that viscosity as a function of frequency in oscillatory shear rheometry is identical to viscosity as a function of shear rate as stated by the Cox-Merz–rule, $\eta(\dot{\gamma}) = |\eta^*(\omega)|_{\dot{\gamma}=\omega}$, the x-axis of these plots will be interpreted and discussed in terms of the log shear rate. The MI and oscillatory shear data complement each other and provide positive evidence for the limited creation of long-chain branches during high shear S³P processing. The HDPE and two LLDPE high-shear pulverization samples exhibit a lower melt index than that of the virgin polymer as well as a higher viscosity at low shear rates in the oscilla-

tory shear experiments. This indicates that under high shear conditions the minimum shear stress requirement for chain scission is exceeded, allowing for radical generation. The radicals created have the potential to migrate and recombine so as to cause structural changes such as long-chain branching that increase viscosity.[1,5,9,14] In contrast, the low-shear S³P processed samples do not show a significant change in the rheology, indicating that few, if any, structural changes occur. This implies that the stress applied at low shear does not exceed the critical shear stress required for chain scission and radical generation.

LLDPE-NG showed the greatest increase in apparent viscosity upon high shear pulverization, followed by LLDPE-GA and then HDPE. The explanation of this behavior relies on the structure of the virgin polymer. LLDPE has a greater number of short-chain branches along the polymer chain than does HDPE. These branch points act as defect sites for crystallographic packing, constantly forcing those chain segments into the amorphous phase and, hence, allowing the chain to act as a tie molecule at that point. Tie molecules are the most likely candidates to break upon exposure of mechanochemical stresses in semicrystalline polymers.[1–3] Because the virgin polymers are of high molecular weight, each is expected to have ample populations of tie molecules. Therefore, LLDPE, having numerous short-chain
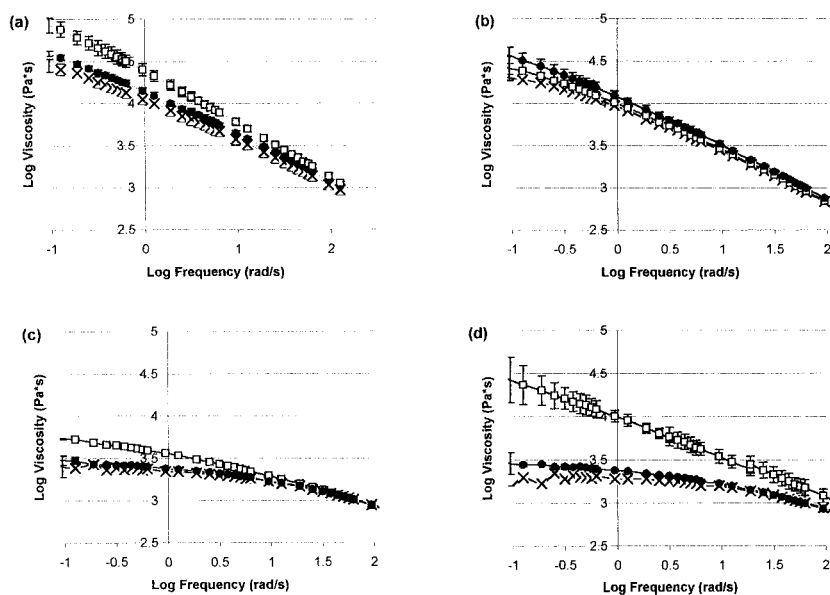
Figure 1 Oscillatory shear melt rheology of (a) HDPE, (b) LDPE, (c) LLDPE-GA, and (d) LLDPE-NG as (-**X**-) virgin polymer and polymer processed by S³P (-●-) at low shear and (-□-) at high shear.

branches, has a greater number of possible points of chain scission upon S^3P shearing than does HDPE, resulting in the creation of more radicals and more branching possibilities. The difference in the extent of viscosity change between the two LLDPEs could be due to the heterogeneous Ziegler–Natta catalyst used to make each polymer. Such catalysts create chains with a random distribution of branches and branch content.[31,34,42] Based on the extent of viscosity changes, it appears that the LLDPE-NG sample, having a greater viscosity increase upon high shear S^3P processing, has more branch points (and, therefore, more tie molecules), and it therefore undergoes greater mechanochemically induced structural changes upon pulverization.

These results are consistent with other results in the research literature. In the range of low shear rates, Yan et al.[31] verified that branched polyethylenes give higher viscosities than those of their linear counterparts. They found that long-chain branch densities lower than 0.2 branches per 10,000 carbons did not much influence the viscosity, but long-chain branch density of 0.44 per 10,000 carbons increased the viscosity sixfold. Hence, low levels of long-chain branching can exert a strong influence on the polymer rheological properties.

In contrast, LDPE, the only polymer sample with long-chain branches present along the chain before pulverization, defies the trends set by the other polymers. Upon high-shear pulverization, the MI of LDPE increases only slightly, indicating a small decrease in viscosity. Rheometry data confirmed this observation, as at low shear rates the LDPE subjected to high-shear pulverization has a lower viscosity than that subjected to low-shear pulverization. The LDPE data do not eliminate the possibility that more long-chain branches are added to LDPE upon high-shear pulverization. Various authors[35,37] reported a decrease in viscosity upon the addition of long-chain branches to LDPE. Mendelson et al.[35] noted that at constant MW and MW distribution increasing long-chain branches decreased both the zero shear rate viscosity and melt elasticity. Bersted[37] found similar results and concluded that the decrease was associated with a decrease in the radius of gyration of the polymer with increased branching. The addition of more random branches may alter the configuration of the polymer chain to more closely resemble a star polymer. In such a case, the viscosity of the star-

shaped polymer would be even lower than its more asymmetrically branched counterpart.

Qualitative information on polydispersity may be obtained by examining the shape of the viscosity–shear rate curves.[35,39] The high-shear pulverization LLDPE-NG and LLDPE-GA samples reach their Newtonian or zero shear rate plateau at a lower shear rate than did the respective virgin and low shear samples. The broadening of the transition from Newtonian behavior to power-law behavior as a result of high-shear pulverization is consistent with an increase in polydispersity as a result of branching.[39] For the HDPE and LDPE samples, neither the virgin not the sheared samples ever approached a zero shear rate viscosity plateau within the shear rates examined $(0.06–126 \text{ s}^{-1})$.

To obtain more accurate information on polydispersity changes, high-temperature GPC experiments were performed on six samples that showed significant rheological changes: the virgin and high-shear pulverization samples of LLDPE-NG, LLDPE-GA, and HDPE. The apparent molecular weights and polydispersities are shown in Table II, and the chromatograms for virgin and high-shear pulverized samples of HDPE and LLDPE-NG are shown in Figure 2. The MWs are apparent only as they must be relative to a linear polymer.

No pattern of significant changes in molecular weight is detected as measured by the GPC. Shearing slightly increases some of the molecular weight averages and slightly decreases others, with many changes being within experimental error. The number-average MWs (M_n) and viscosity average MWs (M_v) do not change significantly, indicating that the smaller chains remain unaffected. The weight-average MWs (M_w) are also little affected, except in the case of the HDPE, which shows a 25% increase after high-shear pulverization. In contrast, the z-average MWs (M_z) fluctuate considerably: M_z remains constant in one case, increases in another, and decreases in the third. However, M_z values are exceedingly sensitive to the baseline determination and therefore may not be completely reliable.

The similarity of the chromatography curves before and after pulverization indicates that the pulverization process leaves nearly all the material largely unaltered. This information does not contradict the findings of the melt-index and melt-rheology experiments, as not all measurement techniques are equally sensitive to branching.[31,43] Unlike those experiments, GPC is a di-

Table II GPC Data

Polymer	$M_w{}^a/M_n$	$M_n{}^b$ (Daltons)	$M_w{}^c$ (Daltons)	$M_v{}^d$ (Daltons)	$M_z{}^e$ (Daltons)	IV^f (dL/g)
HDPE-virgin	7.2	14,600	105,000	81,000	478,000	1.24
HDPE-shear	9.0	14,300	129,000	95,800	691,000	1.40
LLDPE-GA-virgin	6.1	12,600	77,600	63,300	298,000	1.04
LLDPE-GA-shear	4.7	17,800	84,400	69,600	283,000	1.11
LLDPE-NG-virgin	6.6	15,400	103,000	78,500	636,000	1.21
LLDPE-NG-shear	7.2	13,600	98,200	76,800	468,000	1.20

[a] Polydispersity.
[b] Number-average MW.
[c] Weight-average MW.
[d] Viscosity-average MW.
[e] z-average MW.
[f] Intrinsic viscosity.

lute solution experiment that measures macromolecular hydrodynamic volume. An increase in MW in a linear chain increases the polymer hydrodynamic volume, but an increase in MW by chain branching reduces the hydrodynamic volume.[38,39] Thus, if MW increases as a result of branching, the MI and oscillatory shear experiments would detect this increase through the viscosity increase, but the GPC data would not.

The lack of a substantial change in GPC data with solid-state shear pulverization, even though there were changes in the rheological behavior, may also be understood by reference to the literature where several authors[31,32,39] found it not unusual that two polymers with similar GPC results exhibit different melt-flow behavior. This difference is attributed to structural differences on individual polymer chains. Whatever changes

did occur as evidenced by viscosity was found by GPC not to be uniform among all the chains. Hence, the pulverization process does not affect all long chains in the same manner.

These results can be applied to suggest the structural changes that may accompany solid-state shear pulverization of the virgin HDPE and LLDPE systems studied here. The high-shear samples appear to have a threefold increase in viscosity at the lower shear rates, suggesting an addition of approximately 0.3 branches per 10,000 carbons according to the data reported by Yan et al. The low-shear pulverization samples do not show much viscosity change, so the branching is expected to be less than 0.2 long-chain branches per 10,000 carbons.

Differential scanning calorimetry was used to determine whether the apparently low levels of branching resulting from high-shear pulverization affect the crystallization and thermal properties of the LLDPE and HDPE samples. Several authors have also used DSC on carefully crystallized samples to obtain short-chain branching information analogous to that obtained by temperature-increasing elution fractionation.[19–22,24–29] In ethylene copolymers, short-chain branches longer than methyl are mostly excluded from the crystal, resulting in a reduction in the thickness of the crystal. This reduction is observable through a decrease in the melting point and percent crystallinity, and the extent of the decrease gives information on the type and degree of branching. Thus, an increase in short-chain branching content should decrease both the melting point and percent crystallinity. The authors[19–29] observed multiple peaks in the DSC
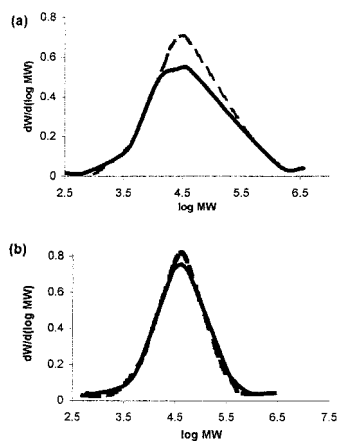
Figure 2 GPC chromatograms for (a) HDPE and (b) LLDPE-NG (----) before and (—) after pulverization.

Table III   DSC Data

| Polymer	Shear	Heat Enthalpy (J/g)	Melt Temperature (°C)	Crystallization Temperature (°C)
HDPE	Virgin	184 ± 13	140.1	120.1
HDPE	High	191 ± 13	140.8	120.6
LLDPE-NG	Virgin	154 ± 13	136.1	115.6
LLDPE-NG	High	155 ± 13	134.1	116.7
LLDPE-GA	Virgin	152 ± 16	135.5	117.2
LLDPE-GA	High	161 ± 14	136.1	117.2

The melt and crystallization temperatures were taken as the peaks of the melt endotherms and the crystallization endotherms.

endotherms, providing a profile of the relative amounts of material having different crystallinity: Each peak resulted from a crystal of particular thickness and, hence, particular comonomer type and concentration. However, such fine detail of the endotherm was not seen in this research.

Table III compiles the peak melt temperature (T_m) data and change in enthalpy data. Figure 3 shows the endotherms for both virgin and high-shear HDPE, LLDPE-NG, and LLDPE-GA at heating rates of 5, 20, and 40°C/min. The data reveal that the endotherms for virgin and high-shear samples are almost identical in the peak melt temperature as well as in the change in enthalpy upon heating. However, at the faster heating rate of 40°C/min, there is a slight difference between the virgin and sheared LLDPE-NG samples, with the high-shear pulverized sample exhibiting a T_m about 2°C lower than for the virgin sample.

At the slowest heating rate of 5°C/min, a multiple peak structure of the LLDPE endotherm is observed, but this structure is also seen with both the virgin and high shear S³P processed samples. The lack of change in the DSC endotherm upon shearing indicates that the pulverization process does not create a significant number of branch points. If branching were occurring, then a drop in both T_m and change in enthalpy would be observed. For example, HDPE (having few branch points) is 90% crystalline and has a T_m of about 135°C, whereas LLDPE (having several branch points) is 50% crystalline with a T_m range of 105–125°C and LDPE is also 50% crystalline with a T_m range of 110–115°C. Hence, an increase in branching content has obvious effects on the thermal and crystallization behavior of the polymer. Lack of significant changes observed by DSC rules out the possibility of additional short-chain branching as a result of pulverization.

In any case, the data are consistent with the fact that there may be a few additional branch-point defects during S³P processing but that there is not a significant increase in the amorphous content of the polymer; hence, long-chain branching is a possibility but short-chain branching is not. Yan et al.[31] showed that changes in the ther-
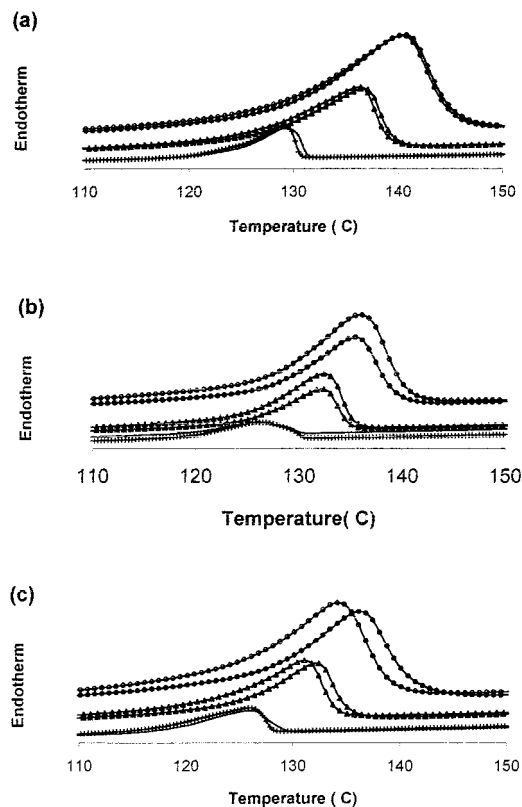
Figure 3 DSC endotherms of (a) HDPE, (b) LLDPE-GA, and (c) LLDPE-NG. The virgin and high-sheared sample for each polymer was run at different heating rates: (-✚-) high-shear pulverization at 5°C/min, (-△-) at 20°C/min, (-○-) at 40°/min, (----) virgin at 5°C/min, (-▲-) at 20°C/min, and (-●-) at 40°C/min.

mal behavior as a result of a small degree of long chain-branching are not expected to be significant. In their experiments, the melt temperature of PE decreased about 4°C for an increase in long-chain branch density of 0.44 branches per 10,000 carbons. Following the experimental findings of Yan et al., this research indicates that long-chain branching does increase upon high-shear pulverization; however, the increase is small and the long-chain branch density remains under 0.44 branches per 10,000 carbons.

To summarize, the rheometry experiments showed an increase in viscosity after high-shear pulverization in HDPE and both LLDPE samples, indicating changes in the polymer structure. However, GPC and DSC show that the distribution of the polymer chains as well as their thermal behavior is unaltered as a result of such shearing, indicating that the polymer structure is largely unchanged. This apparent discrepancy in results was observed by other researchers and can be attributed to the sensitivity of a given technique in detecting particular types of changes in the polymer. Because a very small amount of long-chain branching can create a significant rheological change, melt rheology experiments are more sensitive than are DSC and GPC for testing for the creation of long-chain branches. As this small degree of long-chain branching does not change solid-state properties, DSC is not sensitive to the addition. Further, GPC is not sensitive to the change because the chain structure is not altered substantially.

Numerous researchers[44–49] have successfully used NMR to analyze quantitatively the number of both long- and short-chain branches. Unique peaks have been identified for methyl, ethyl, propyl, butyl, and amyl branches. However, branches six carbons and longer share the same peak, and, hence, it is not possible to distinguish among branches longer than six carbons. Thus, NMR cannot provide evidence for additional, small levels of long-chain branching in the LLDPE samples under steady shear as the short-chain branches for these samples are six or eight carbons long.

While potentially less sensitive than NMR, preliminary work using Fourier transform infrared (FTIR) spectroscopy may indicate different structural changes that occur upon S³P pulverization.[23,28,29,47] For the systems considered here, the only substantial effect revealed by FTIR is that some oxygen is incorporated into the polymer chains as a result of high-shear pulverization:

Peaks arise at 1720 and 1730 cm^{-1}. These data implicate reactions between mechanochemically induced radicals and oxygen that readily stabilizes the radicals.[2,4,5,9,14] This might explain why relatively few radical-migration and radical-transfer events seem to occur. Because oxygen is incorporated into the polymer, it appears that termination by combination is more prevalent than is termination by disproportionation. The presence of oxygen is thus found to be useful as it prevents the occurrence of mechanodegradation and thereby maintains, to a large extent, the initial properties of the polymer.

CONCLUSIONS

Data presented here indicate that S³P processing leads to a small, but measurable, increase in long-chain branching. It is concluded that radical migration and then recombination form the few long-chain branches that originate upon high-shear pulverization. However, most of the radicals created by the mechanochemical scission events must be quickly stabilized by oxygen; subsequently, they terminate by combination in a manner that incorporates oxygen into the polymer chain.

The results of this study also lead to conclusions about the S³P process. Most important among these is that, while flow properties are altered, the process does not compromise the integrity of the polymer being sheared, that is, neither HDPE nor LLDPE are converted to LDPE by the S³P process, even though it is known that chain scission and radical formation commonly accompany this process. Significantly, this makes the S³P process viable for many industrial uses, ranging from continuous powder production to blending and recycling. Further research into the response of various polymer systems, including blends, to S³P processing is underway.

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