# Rheological Analysis of the Degradation of HDPE During Consecutive Processing Steps and for Different Processing Conditions

**Tim Kealy**

*Technical Department, Rheology Solutions P/L, Bacchus Marsh, Victoria 3340, Australia*

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**ABSTRACT:** Using a twin-screw extruder, HDPE has been processed six times consecutively under a range of processing conditions (changing barrel temperature, screw speed, and feed rate). After each pass, the product has been analyzed in terms of the melt flow index (MFI) and $G_C(\omega_C)$, the crossover point of the viscoelastic moduli as a function of the angular velocity at which it occurs. MFI data show changes in the structure of the HDPE after each processing step, but this information is limited in quality and quantity. $G_C$ data show the mechanism for degradation (side-chain branching and chain scission) and allow us to track relative changes in mean molecular weight (MMW) and molecular weight distribution (MWD). MMW and MWD both increase as a result of continued reprocessing. The apparent changes in MWD are substantial indicating significant chain scission initially, accompanied and followed during subsequent processing by a combination of side-chain branching and further chain scission. A relative measure of the polydispersity index (PI) of the melt is calculated and the PI increases as the HDPE is further reprocessed. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 639–648, 2009

**Key words:** high-density polyethylene; extrusion; degradation; rheology; processing conditions

## INTRODUCTION

Polyethylene (PE) has had considerable attention from the academic and industrial scientific communities, because of the high proportion of that polymer processed, in particular for packaging. Processing of PE is generally by extrusion at elevated temperatures, and the final product is usually injection molded, a cast or a blown film, depending on the application. Waste polymeric materials are an important environmental issue, and their reuse, reprocessing, and recycling have a high profile internationally.

Recent social and legislative trends have encouraged recycling and reprocessing of polymeric products, in particular those used for packaging. High-density PE (HDPE) is a frequently used material in this respect and is usually appropriately formed by thermal processes like extrusion. Continued, consecutive reprocessing of HDPE materials can cause degradation of the molecular architecture (chain scission and/or side-chain branching[1]), brought about by repeated exposure of the material to thermal and mechanical stresses. This degradation may adversely affect the packaged material,[2] or may simply cause undesirable changes in the physical or optical properties of the packaging itself.[3]

The flow pattern through a twin-screw extruder (TSE) occurs in a "figure-8" pattern, as in Figure 1.

The flow path is created by the intermeshing screws, which transfer the material from one screw to the other. Generally, much of the energy required to melt the material comes via the mechanical energy from screw rotation. High shear rates exist in the regions where the polymer is smeared between the screws and between each screw and the barrel wall. This combined with the thermal energy from the heated barrel is instrumental in the breakdown of the material structure.

There has been much work in the area of rheological testing for reprocessed and recycled HDPE.[1,3–5] These works have often used a single set of processing conditions, or have not examined the effects of multiple runs on process variables and flow properties simultaneously.

In the polymer processing industry, rheological analyses have been used to characterize HDPE packaging from a quality assurance and quality control (QA/QC) standpoint. One of the most frequently utilized QA parameters is the point at which the viscoelastic moduli—$G'$, Pa, the elastic (storage) modulus and $G'$, Pa, the viscous (loss) modulus—are

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*Correspondence to:* T. Kealy (timk@plantic.com.au).

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**Figure 1** Material flow through an intermeshing corotating twin-screw extruder.

equal, i.e., $G' = G''$ (the crossover moduli, $G_C$ and the associated angular velocity, $\omega_C$). Inexplicably, although this crossover has been mentioned in previous investigations,[3,6] in the literature, to this author's knowledge, it has not been explicitly used to compare data sets to examine the degradation of HDPE because of successive processing steps.

Traditionally, the melt flow index (MFI), has been a routine parameter for the polymer industry to obtain speedy QC data. This parameter is usually a single point measurement based on mass of polymer pushed through a narrow capillary by a standard weight (see for example ASTM D 1238). MFI measurements, though traditional and often very useful, can be potentially misleading because they represent only a small part of the complete flow behavior curve of the material.[7] In an absolute sense, the shear rates represented by the MFI test change slightly throughout the measurement as the height of the column above the capillary changes and also there may be issues with end effects and irregular flow patterns for the relatively short capillaries used in MFI tests. Moreover, the temperatures and (low compared with processing) shear rates may not correlate with processing conditions.

The following is an attempt to compliment other work by elaborating on the effects of changing independent process variables—temperature profile, $T$, screw speed, $S$, and extruder feed rate, $Q$—on residence time in the extruder, on the material MFI and on the dynamic rheological properties of the material ($G'$, $G''$, and, in particular, $G_C$).

## EXPERIMENTAL

Commercially available HDPE (HD0397UV, supplied by Qenos, of Altona, Australia), highly stabilized for UV, and used for injection molding applications, was used for these tests. The tests involved dynamic rheological analyses on a controlled stress rheometer (a Thermo Fischer HAAKE RheoStress 600) and a laboratory MFI tester (an SWO Polymertechnik Melt-Flixer MT), the die geometry of the MFI tester was 2.095 mm (diameter) × 8 mm (height). Tests were followed by reprocessing under air on a 16 mm, corotating, benchtop TSE (a Thermo Fischer PRISM EuroLab) with L/D of 25 : 1. Once extruded, through a strand die, the polymer strand was cooled in a water bath and pelletized for retesting and reprocessing. The procedure was repeated until the HDPE had been processed six times under each set of conditions (see Table I), with subsequent rheological analysis of each resulting product. Data collected from the extruder system were typical process data, heating zone temperatures, pressure at the die, torque, and rpm of the screws. The residence time in the TSE was measured by dropping a colored pellet into the feed throat of the extruder, then measuring the time taken for a color change at the die exit. The TSE screw segments were interchangeable allowing rearrangement for different applications. In this case, a high-energy configuration was chosen, Figure 2, with multiple, long mixing zones. The vents close to the center and die-end of the extruder barrel were sealed. Data collected by the rheometer were the viscoelastic moduli $G'$ and $G''$.

**TABLE I**
**Experimental Processing Conditions**

| Condition | Barrel temp. $T$ (°C) | Feed rate, $Q$ (kg/h) | Screw speed, $S$ (rpm) |
|---|---|---|---|
| A | 190 | 0.70 | 125 |
| B | 200 | 0.70 | 125 |
| C | 210 | 0.70 | 125 |
| D | 200 | 0.45 | 150 |
| E | 200 | 0.70 | 150 |
| F | 200 | 1.00 | 150 |
| G | 200 | 0.70 | 100 |

To maintain comparability between the flow properties of the different materials, the rheological analyses were all carried out under identical conditions, constant temperature of 190°C, constant applied stress of 1000 Pa (ensuring that testing was within the linear viscoelastic envelope, LVE, of each material) and in the angular velocity range 0.063–630 rad/s. MFI testing was at 190°C, 2.16 kg, as per the data sheet from the HDPE supplier, Qenos.

A range of independent processing variables ($Q$, $S$, $T$) was imposed to enable a better understanding, their impact both on residence time and the dynamic

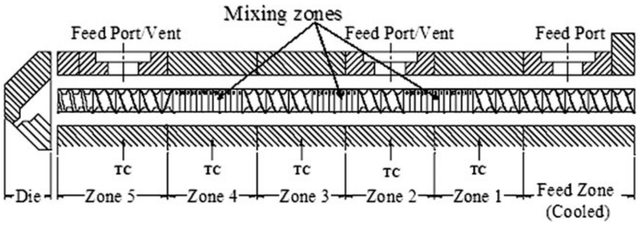

**Figure 2** TSE barrel and screw arrangement.

properties of the materials. The production conditions are shown in Table I. In each case, the temperature profiles along the extruder barrel were constant from the die through heating zones 2–5. Zone 1 was 10°C lower than the rest and the feedthroat of the TSE was cooled.

Table I shows the conditions used for the tests. Tests A, B, C examine the effects of changes in temperature; D, E, F examine the effects of changing feed rate; and B, E, and G examine the effect of changes in screw speed. Virgin HDPE was processed and then reprocessed under each set of conditions until a total of six passes had been completed and rheological data collected at the end of each pass.

## RESULTS AND DISCUSSION

The most immediate and obvious results available from these experiments are those generated by the output from the extruder instrumentation, and the residence time measurements. These are a critical element of this project, because in real terms, they dictate the processability and the comparative cost of reprocessing the degraded and virgin materials in the same extruder configuration and for different sets of processing conditions. Additionally, higher residence time will result in differing levels of HDPE degradation because of the increased exposure to thermomechanical energy in the extruder barrel and die.

Some of these results may be intuitive, but it is nonetheless an interesting exercise to display them. Figure 3 shows the effects on the residence time in the extruder of changing the process variables $Q$, $S$, and $T$. Virgin HDPE was used for these trials and the results do not differ significantly for reprocessed materials.

Keeping $Q$ and $S$ constant, and changing the temperature has no significant effect on the residence time for the range of processing variables tested here. TSE residence time is dominated by $S$ and $Q$. Increasing either of these parameters reduces the residence time for the material in the extruder. One might expect that $S$ and $Q$ would have this effect, because the TSE does not operate with the barrel completely filled, but the material is moved, in a "figure-8" shape through the extruder—increasing the screw speed pushes the material through the extruder more quickly. By increasing the feed rate, material is pushed forward more quickly by the material following it. Increases in process temperature lead to a decrease in HDPE shear viscosity, so increasing the ease with which it can be moved through the extruder. However, although the viscosity is reduced, the residence time remains largely unchanged because the volume of material displacing the material in front of it along the barrel is unchanged, as is the screw speed. Only in the case of a full screw would this change have a noticeable effect. Corotating TSEs are not generally designed to run full because of the "figure-8" design for mass transfer. The decrease in viscosity caused a decrease in the torque requirement for the extruder, and decreased the pressure at the die.

Traditionally, MFI has been the QC criterion of choice for the polymer industry. The limitations of this technique have been discussed earlier and elsewhere.[7] More recently, rheometric analyses, like steady shear viscometry using capillary viscometers and dynamic analyses using oscillatory measurements with a cone and plate type measuring geometries, have been used to provide better quality and quantity of information. After extrusion and subsequent pelletization, the HDPE was tested using these techniques with a view to comparing them, and

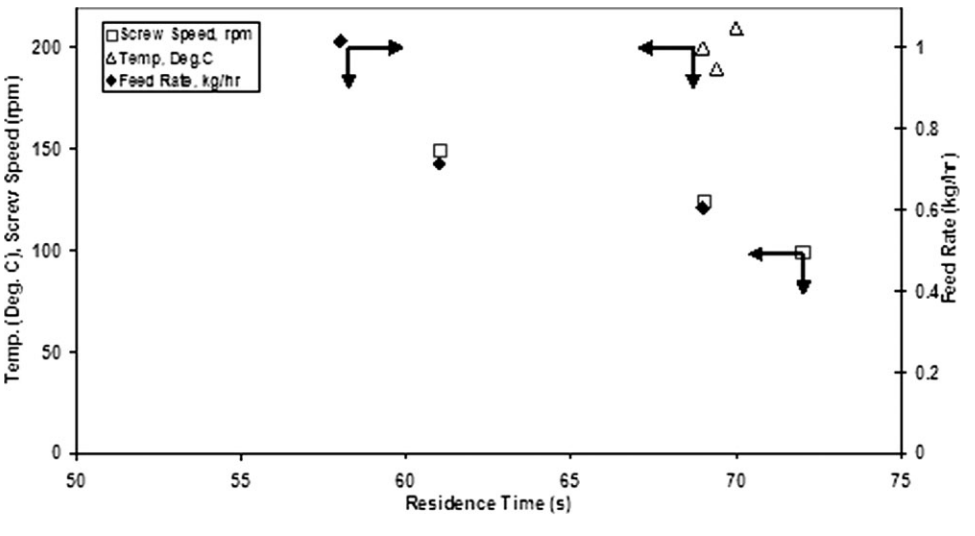

**Figure 3** Effect of $Q$, $S$, $T$ on the residence time in the extruder for virgin HDPE.

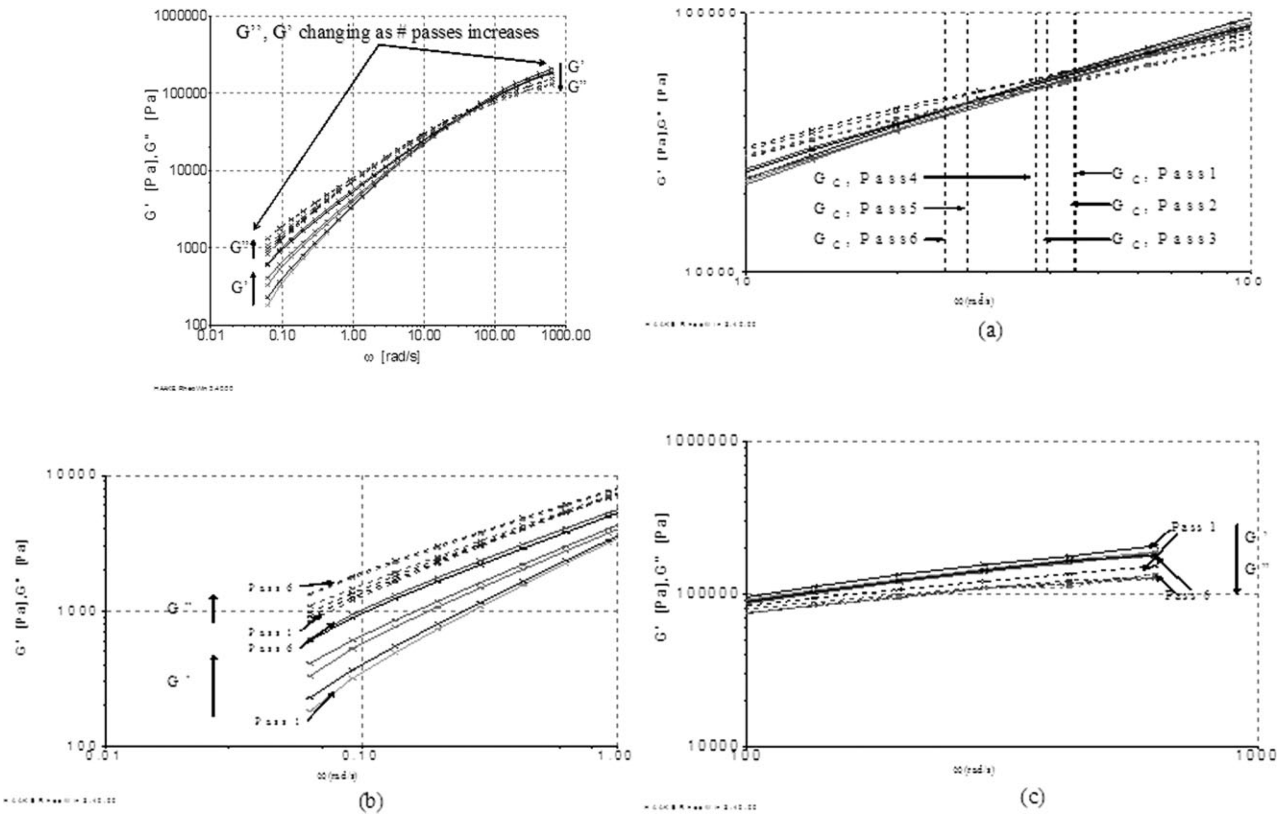

**Figure 4** Typical rheological oscillatory data for HDPE after consecutive passes through the TSE ($Q = 0.7$ kg/h, $S = 125$ rpm, $T = 190°C$). (a) $G_C$ detail (from Fig. 4) for HDPE after consecutive passes through the TSE ($Q = 0.7$ kg/h, $S = 125$ rpm, $T = 190°C$). (b) Low ω detail (from Fig. 4) for HDPE after consecutive passes through the TSE ($Q = 0.7$ kg/h, $S = 125$ rpm, $T = 190°C$). (c) High ω detail (from Fig. 4) for HDPE after consecutive passes through the TSE ($Q = 0.7$ kg/h, $S = 125$ rpm, $T = 190°C$).

using them to assess the nature of the changes in molecular architecture as a result of the series of reprocessing steps under the different conditions already described.

Typical rheological data are shown in Figure 4. The trends for this data were repeated for all of the subsequent tests using other combinations of $Q$, $S$, $T$. In Figure 4, $G'$, Pa, the elastic (storage) modulus and $G''$, Pa, the viscous (loss) modulus are shown for a series of processed and reprocessed HDPE at fixed $Q$ (0.7 kg/h), $S$ (125 rpm), and $T$ (190°C). The point at which $G'$ and $G''$ are equal is the crossover modulus, $G_C = G' = G''$ at the crossover angular velocity, $\omega_C$ is often used as a QC datum in the polymer processing industries.

There are several interesting aspects of Figure 4, which is qualitatively representative of all of the data sets collected for the different $T$, $S$, and $Q$ combinations used in this work. First, the crossover point, $G_C(\omega_C)$, magnified in Figure 4(a), changes as the number of passes increases, this will be discussed in more detail later. The trends at low [see Fig. 4(b)] and high ω [Fig. 4(c)] are opposite. At low ω, $G'$ and $G''$ increase as the number of passes increases. At high ω, $G'$ and $G''$ generally decrease as the number of passes increases. The differences in the moduli magnitudes at high ω are quite small, and in some cases, the order is altered slightly because of the similarity in the magnitudes of $G'$ and $G''$ for consecutive passes. That said this pattern is prominent through all of the data sets collected in this work. For polymeric systems, viscoelastic properties at low frequency usually relate to high molecular weight fractions. The thermomechanical forces in the extruder cause both chain scission and side-chain branching to occur.[4,6] Side-chain branching would result in bulkier (fatter) molecules, and these bulky molecules would have reduced ability to flow past one-another. As the number of passes increases, the number of side-chain branches also increases, causing increasingly bulky molecules, and increased difficulty for flow to occur at low frequency.

At high frequency, it is proposed that as a result of the increased molecular girth and molecular mass (side chain branching) but reduced length (chain scission), adjacent molecules move as a plug. High-frequency oscillation does not allow sufficient time for separation and flow of the individual elements of the plug, and so it reacts as a single entity with less resistance to flow because of the lubricating effect of

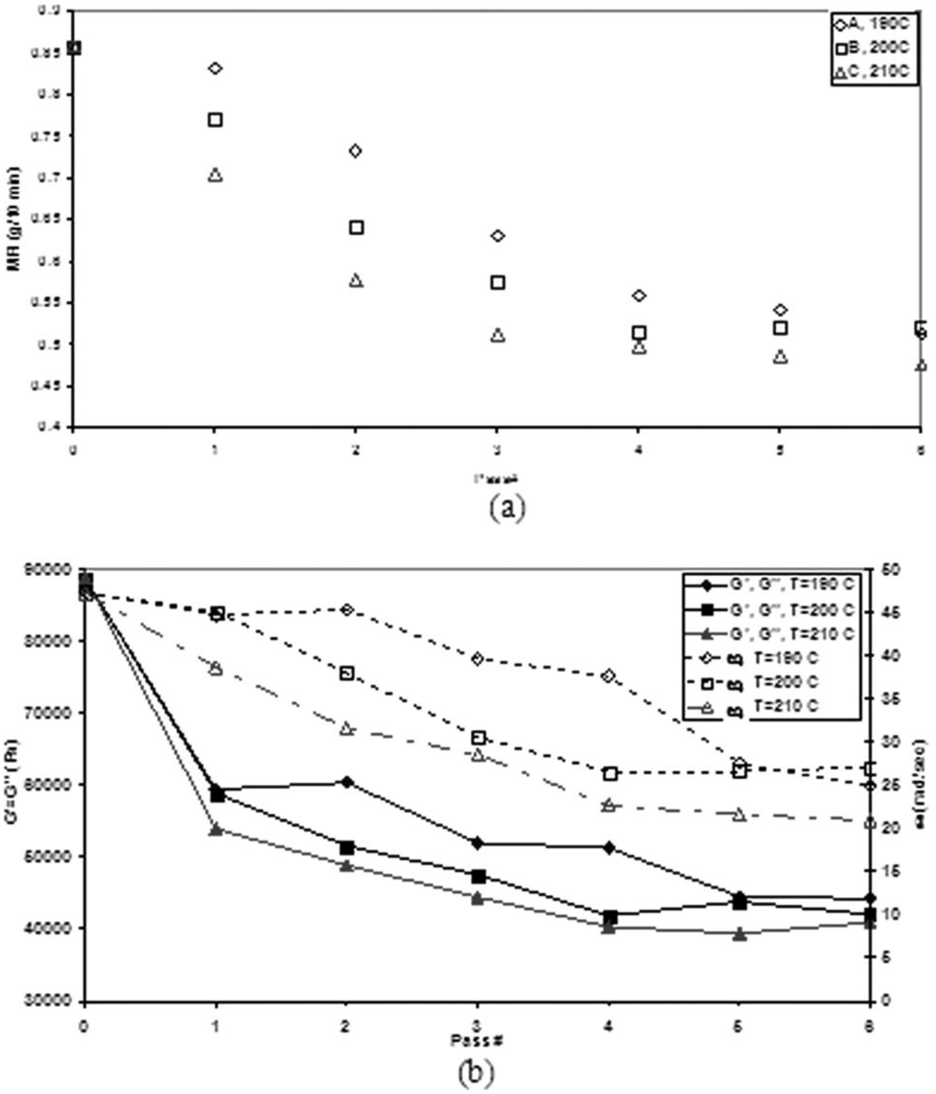

**Figure 5** Relationship between (a) MFI (190°C, 2.16 kg), (b) $G_C$, $\omega_C$, and changing temperature ($Q$ = 0.7 kg/h, $S$ = 125 rpm).

the remaining linear molecules and the smaller polymer strands around it, produced by chain scission.

Comparative MFI (190°C, 2.16 kg) and small amplitude oscillatory ($G_C$, Pa and $\omega_C$, rad/s) data are shown in Figures 5–7 for changes in $T$, $Q$, and $S$, respectively.

Figure 5 shows the effects of the changing process temperature on the measured variables. The trend for both is the same—at the same temperature, both the MFI and $G_C$ and $\omega_C$ decrease with increased processing (i.e., higher Pass#) and the MFI curves themselves are shifted toward lower values with increasing temperature. This pattern is repeated for the $G_C$ and $\omega_C$ curves. In general, MFI is regarded in the polymer industry as a measure of the molecular weight, and by association of degradation, of a polymeric material. From the standpoint of the MFI data presented, the reason for the observed trends is not immediately clear, and those uneducated in the art with HDPE might expect that increasing the temperature would decrease the viscosity, and so increase the MFI, shifting the curves upward, not downward. In addition, the changes in the MFI at individual temperatures reduce asymptotically after Pass#3.

The oscillatory data provide more useful information from a mechanistic viewpoint. Previous work[4,6] has suggested that alterations of the magnitudes of the crossover point can infer changing molecular architecture. These workers suggested that, for polymeric systems, reductions in the magnitude of $G_C$ correlate with increasing molecular weight distribution (MWD), and decreasing $\omega_C$ is the result of increasing mean molecular weight (MMW). An examination of the crossover point data reveals that, under the same processing conditions, both MWD and MMW increase.

Two mechanisms have been suggested for HDPE degradation during processing, chain scission, and side-chain branching. One would expect that side-chain branching should increase the MMW of the material, as the molecules change from quite narrow linear ones to broader ones. Chain scission should decrease MMW, but increase MWD as the polymer chains are randomly "chopped up" by the forces in the extruder. It is clear from the plots, that in every case, there is a step-change in the magnitude of $G_C$ after the first processing pass, followed by a more gradual decrease until an asymptotic value is approached. $\omega_C$ data show a more regular change throughout, until an asymptotic value is approached.

A mechanistic interpretation of the different behaviors for $G_C$ and $\omega_C$ data could be that, on the one hand, the virgin HDPE molecules are quite friable in the processing conditions encountered in the TSE. As shown previously (Fig. 2), a screw profile has been chosen with three mixing zones and the molecules experience significant mechanical as well as thermal energy input as they move along the barrel and through the die. As the molecular profile becomes more robust, "shorter and fatter," as opposed to the initial long and slender molecules, chain scission becomes more difficult, and the MWD does not change as quickly. Chain scission then proceeds at a similar, reduced rate after the first pass, slowing when the energy input cannot further reduce the chain length of the molecules. On the other hand, side-chain branching occurs simultaneously with scission in the barrel, but at a roughly even rate throughout the process. This indicates that the availability of branching sites and their utilization occur at a similar rate through the first few passes until an asymptotic value of $\omega_C$ is approached. Perhaps, sufficient side-chain branching propels the molecular size above a critical point, when they can be more easily broken down in the extruder, which in turn provides either more smaller, mobile molecules which can more easily become involved in branching, or/and access to more sites for branching. In this way, the branching and scission processes may reciprocate parasitically until steady state is reached between them at a given thermomechanical energy profile.

To summarize, increasing the number of passes increases the overall energy input, producing changes in polymer architecture essentially from relatively long and slender, to short and fat. Rheological data show the MMW and the MWD increasing as a result. It is suggested that these processes feed off one another until they reach steady state, when branching and scission proceed at the same rate.

These data and mechanistic explanations help to elucidate the apparently confusing MFI data. MFI depends not only on MWD but also on MMW and as a result, because of the increasing MMW and reduced flowability because of side-chain branching, bulkier molecules have more difficulty in flowing past one another and the MFI drops.

Elevating the process temperature profile in the extruder increases the level of the thermomechanical forces applied to the polymer during individual passes, increasing the opportunity for chain scission and side-chain branching. As a result, both the MFI and the crossover data curves are shifted downward. Increasing temperature profile increases the MMW and MWD of HDPE.

It is interesting to note that MFI measurements appear less sensitive than oscillatory measurements to changes in the molecular architecture. The relative changes in the MFI data for a single temperature appear to be less from Pass#3 onward, but the asymptotic values for the crossover data do not appear until around Pass#4. Similarly, the relative distinction between each curve is less for the MFI data (at high Pass#) than for the crossover data. This may be because MFI measurements themselves involve the application of thermomechanical forces—the polymer is exposed to moderate shear rates and process temperatures during MFI measurements—whereas oscillatory measurements do not offer the same opportunities for chain scission or branching because the small amplitude of the oscillation is within the linear viscoelastic envelope (LVE), and the structure of the material is unchanged during the measurement. Therefore, MFI measurements potentially influence molecular architecture during the measurement, whereas oscillatory ones (in the LVE) do not. Precisely, because of the changing molecular architecture, the material flows at a different flow rate through the capillary, meaning that the materials are being tested at quite different shear rates (it is quite common practice to compare steady shear viscosities at the same shear rate using a flow curve as a reference point). Previous work[7,8] has examined the relationship between flow curves and MFI measurements. A simple calculation[9] can indicate the range of different apparent shear rates encountered in the tests here:

$$\dot{\gamma}_a = 4V/\pi r^3 \tag{1}$$

where $\dot{\gamma}_a$ is the apparent shear rate, $V$ is the volume flow through the capillary per unit time, and $r$ is the capillary radius. Using eq. (1) allows the calculation of the range of $\dot{\gamma}_a$ encountered in the MFI measurements. The range is significant, 1108.2 (virgin material) to 536 $s^{-1}$ (six passes, conditions E).

In addition, because of the relatively primitive flow geometry and variable shear rate used in MFI measurements—a capillary of low aspect ratio, and

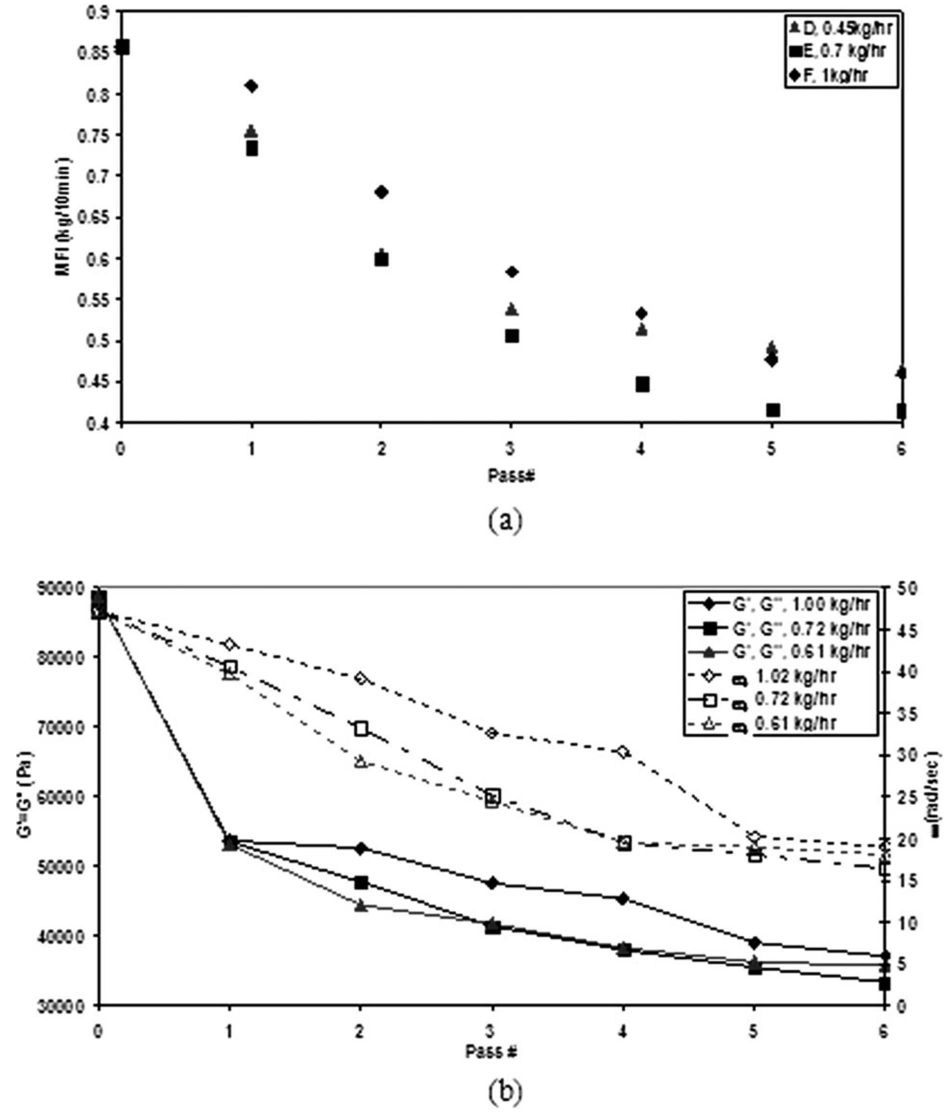

**Figure 6** Relationship between (a) MFI (190°C, 2.16 kg), (b) $G_C$, $\omega_C$, and changing feedrate ($S$ = 150 rpm, $T$ = 200°C).

changing mass above the capillary—flow irregularities and entry losses because of extensional flow are likely.

Figure 6 shows the effects of changing the process feedrate on the MFI and crossover points of consecutively reprocessed HDPE pellets. The pattern is similar to that seen for changing temperature (in Fig. 5), consecutive passes further degrade the molecular architecture, through decreasing MFI, $G_C$ and $\omega_C$. As before, the $G_C$ and $\omega_C$ data offer greater clarity regarding the mechanism by which the structure is being degraded. There is a significant initial drop in $G_C$, after the first pass, followed by a more gradual, nearly linear, change. $\omega_C$ changes more regularly throughout consecutive passes until an asymptotic value is approached. As discussed earlier, chain scission (changes MWD, seen through changing $G_C$) and side-chain branching (changes MMW, seen through $\omega_C$) are the mechanisms by which the HDPE molecules are degraded. Initially, the largest proportional changes are seen in the MWD (through the large initial proportional decrease in $G_C$) as the process cleaves the HDPE molecules in the high-energy zones of the extruder barrel and die. The MFI curves also approach an asymptotic value, but before the $G_C$ and $\omega_C$ data, probably for the same reasons discussed previously.

Figure 7 shows the influences of changing the extruder screw-speed for consecutively reprocessed HDPE pellets. From the evidence presented in the previous discussions, it is unsurprising that increasing the screw speed (resulting in higher energy levels and shear in the extruder barrel and through the die) causes increased chain scission and side-chain branching. As before, the HDPE is significantly degraded on the first processing step, primarily through high levels of chain scission and some side-chain branching, and more gradually thereafter by

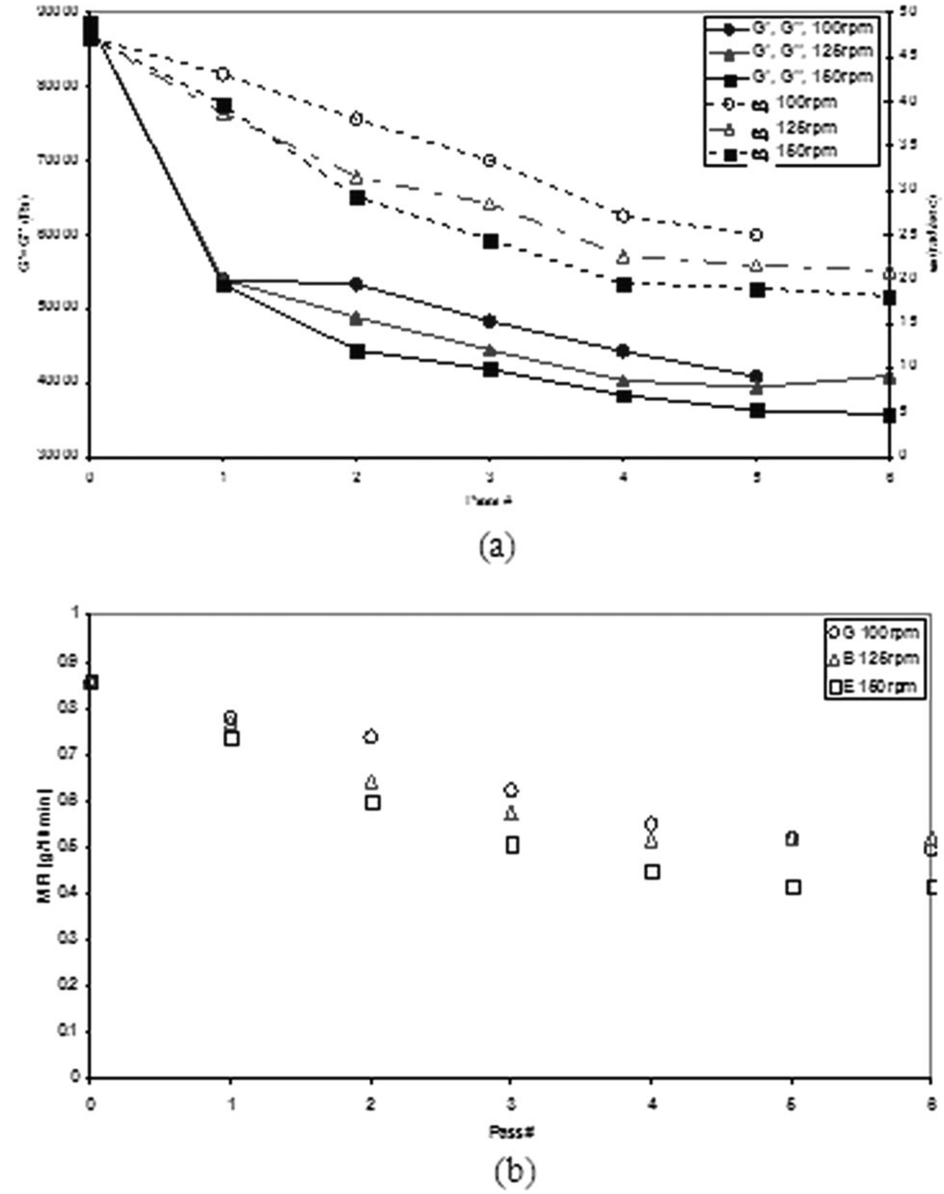

**Figure 7** Relationship between (a) MFI (190°C, 2.16 kg), (b) $G_C$, $\omega_C$, and changing screw-speed ($Q$ = 0.7 kg/h, $T$ = 200°C).

more steady levels of both scission and branching. As in the previous analyses, the oscillatory and MFI measurements show similar patterns, but more information is available from the oscillatory data. Overall, Figures 5–7 show similar trends. The first pass through the extruder causes a significant level of degradation through the increased opportunities for chain scission available in the more delicate virgin polymer, shown by the dramatic initial decrease in $G_C$. Afterward, the changes are more regular, trending to an asymptotic value for each set of process conditions. This suggests that the thermomechanical degradation of HDPE under a given set of processing conditions is a function only of the level of exposure of the polymer to them (in other words, the amount of time spent in the extruder). As discussed earlier, the actual mechanism for the gradual change may be one of the exposure-dependant chain scission creating more sites for branching and vice versa, or simply that each of the mechanisms can proceed independently at approximately the same rate in the extruder. This is the case until the energy available for scission and the available sites for branching approach equilibrium and further degradation can only be achieved by altering the processing conditions.

Figure 8 collates all of the $G_C$ data and shows that, after the initial large degradation steps, instigated by the first passes through the extruder, there is a direct relationship between $G_C$ and $\omega_C$ ($R^2$ = 0.97). This

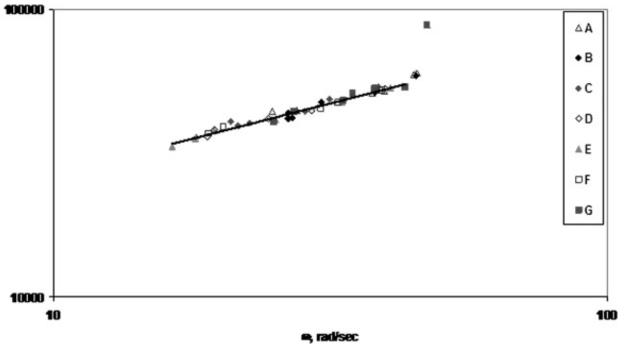

**Figure 8** Relationship between $G_C$ and $\omega_C$ for all data.

further indicates that as chain scission and branching proceed, so the opportunity for further side-chain branching and scission increases, because of the increased number of (shorter, more mobile) chains in the melt available for bonding with the bulkier molecules on the side-chain sites, which can in turn be cleaved.

$$G_c = 8588\omega_c^{0.49} \tag{2}$$

In the past, $G_C$ has been used to predict the polydispersity index (PI)—the ratio of the weight-average ($M_W$) to the number-average ($M_n$) molecular weight of polypropylene notably by Shang,[10] who found:

$$\mathrm{PI} = 10^6\mathrm{Pa}/G_c(\omega) \tag{3}$$

$$\text{where, } \mathrm{PI} = M_W/M_n, \tag{4}$$

$$\text{and } G_c(\omega) = G''(\omega) = G'(\omega). \tag{5}$$

Other workers[4,11,12] noted that although eq. (3) has been used to predict PI for some polyolefins, it has not been shown to hold specifically for PE and in particular in this case for HDPE. They used it to obtain comparative PI information for their data. Equation (3) will be used in the same way here, to compare the effects of process conditions and number of extrusion passes on relative changes in PI for HDPE.

After initial large-scale destruction of the macrostructure, a relationship between PI and $\omega_C$ appears to be present. Fitting a curve, shown in Figure 9, to this data reveals the relationship ($R^2 = 0.97$):

$$\mathrm{PI} = 11.6\omega_c^{-0.49} \tag{6}$$

As with the other data displayed, PI in Figure 9 shows a strong initial increase from its virgin state, as a result of large-scale molecular degradation. Given the relationships in eqs. (2) and (3), the curve-fit in Figure 9 [and eq. (6)] can be directly calculated. Equations (1) and (5) allow the direct prediction of a relative PI from rheological data for reprocessed HDPE for the conditions tested.

## SUMMARY AND CONCLUSIONS

Rheological data have been presented for six-times processed HDPE, under different processing conditions in a TSE (changing processing temperatures, $T$, screw speeds, $S$, and throughputs, $Q$). Data have been collected in terms of the traditional QC technique, MFI, and also with the increasingly common technique of dynamic rheometry.

Changing $T$, $S$, $Q$ influences the amount of thermomechanical energy acting on the HDPE macrostructure, causing the polymer to degrade. There is an initial step change in the MWD caused by the thermomechanical forces in the extruder, followed by a more gradual change. Changing MMW is a more regular function of the number of passes (the amount of energy input to degrade the polymeric structure, or analogously, the time spent exposed to a given set of operating conditions). This indicates that the initial degradation step is dominated by chain scission, though side-chain branching also occurs, thereafter both degradation mechanisms continue at a more steady rate, possibly feeding one another, diminishing as the opportunity for side-chain branching and scission diminish because of fewer sites or long chains, respectively.

The information presented has shown that dynamic rheological data, expressed in terms of the crossover point, $G_C(\omega)$ are more sensitive to changes in the molecular architecture than MFI, possibly because MFI measurements themselves influence the structure of the material. The shifting $G_C(\omega_C)$ data have shown that the polymeric architecture of HDPE is progressively degraded by the thermomechanical

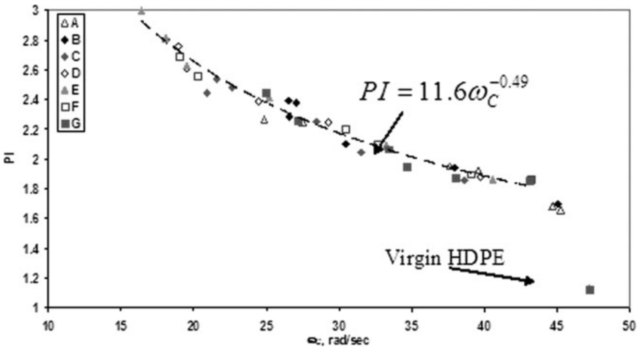

**Figure 9** Relationship between PI and $\omega_C$ for all data.

forces in the extruder during consecutive reprocessing, and that the mechanism for degradation includes both side-chain branching (resulting in increasing MMW) and chain scission (resulting in increased MWD). Both of these phenomena can be tracked using $G_C(\omega_C)$, and after the initial large-scale molecular degradation caused by the first processing step, a relative PI can be directly predicted from $G_C(\omega_C)$. Both $G_C(\omega_C)$ and PI are more descriptive measures of polymeric macrostructure than MFI.

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