PEER REVIEWED

A batch light-scattering study of microgel formation in film resins

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ABSTRACT

A comprehensive set of techniques has been developed in a study to determine whether or not microgels form in hot melt extrusion. Using rheology techniques to comparing zero-shear viscosity measurements with high-shear viscosity measurements can indicate the presence of microgels. Temperature rising elution fractionation (TREF) experiments further indicate the presence of microgels. With gel permeation chromatography (GPC), microgels tend to be filtered out by the columns and are not detected. The batch light-scattering technique can measure the total molecular weight content of the sample, including both the separated polymer molecules and the gelled molecular weight species.

Application:

Knowledge gained from using these techniques will aid pelletizing engineers in polymer fabrication processes involving hot-melt extrusions.

COMMERCIAL POLYETHYLENE resins are extruded with a hot melt extruder into pellet form for shipment. In the transformation from polymer fluff to pellets, the melt index drops. How does the polymer structure change with this drop in melt index?

The formation of a microgel has been thought to be the main mechanism, although there has been no proof. This microgel hypothesis is supported on one hand by rheology data that show an increase in the zero-shear viscosity for the pellets. The hypothesis is contradicted on the other hand by the gel permeation chromatography (GPC) data that show decreases in the values of molecular weight and the z-average molecular weight (1).

SAMPLE MATERIAL AND GENERAL METHODS

The sample used in the study was a blown-film polyethylene resin that had a high density of 0.945. The six samples in the study set consist of the original polymer fluff, or the base resin, and the pellet products for the first through the fifth extrusion passes.

To maximize the effect of thermal degradation in these test samples, we did not use antioxidants in the pelletizing process. Without the antioxidants, there is a better chance of establishing a trend for the effect of hot extrusion with repeated extrusions. The compounder we used to prepare the samples was a co-rotating, twin-screw design that is commonly employed in commercial polyolefin plants.

INITIAL GPC EXPERIMENTS

Background and experimental procedure

GPC is a liquid chromatographic technique that separates polymers by their hydrodynamic volumes. Normally, linear polymer species are used to perform the calibration. Therefore, when linear molecules are analyzed, the true molecular weight distribution can be obtained (*2*).

As branching occurs within the polymer network, however, the ratio of polymer size to molecular weight starts to decrease. In other words, the material becomes more densely packed, and the true value of molecular weight is systematically underestimated when column size separation is used.

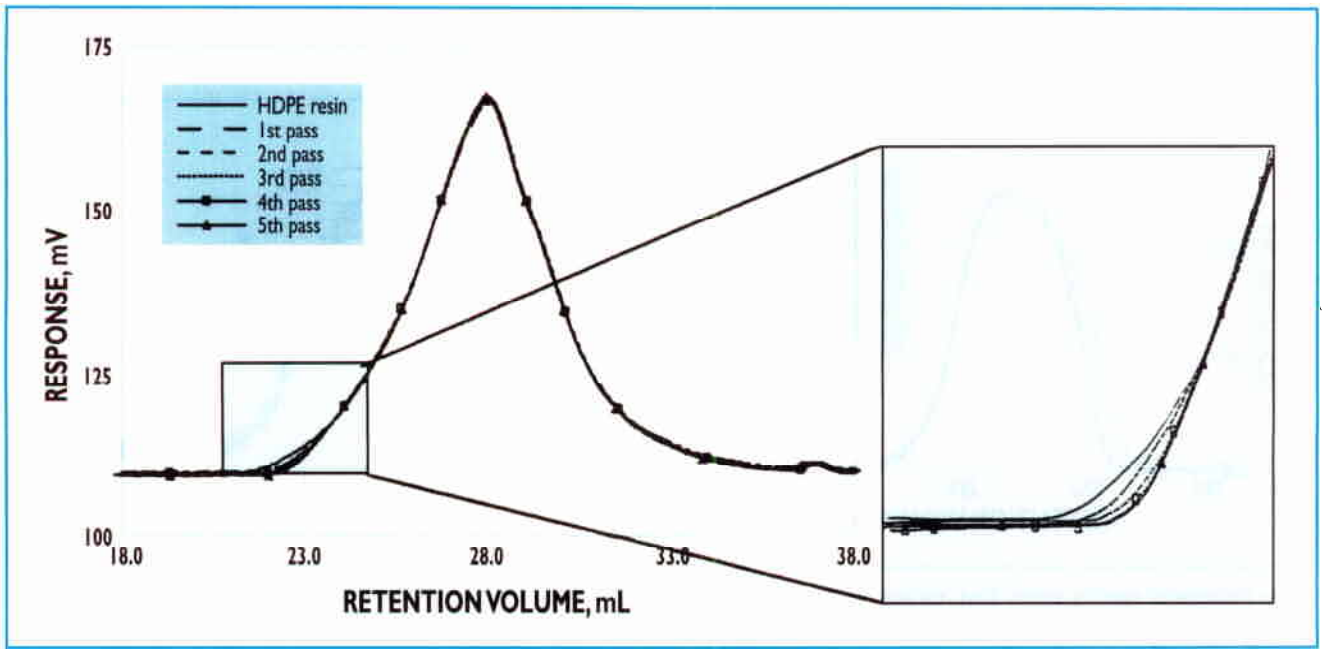
In this study, conventional chromatography was completed on a Waters Corp. 150C High Temperature Chromatograph equipped with an internal refractometer. The four-column set was obtained from Polymer Laboratories. The solvent used was 1,2,4-trichlorobenzene, and concentrations were 2.5 mg/mL. The injection volume was 400 µL, and the flow rate was 0.7 mL/min. Data were collected and processed with Viscotek TriSEC GPC software, Version 3.0.

Results and discussion

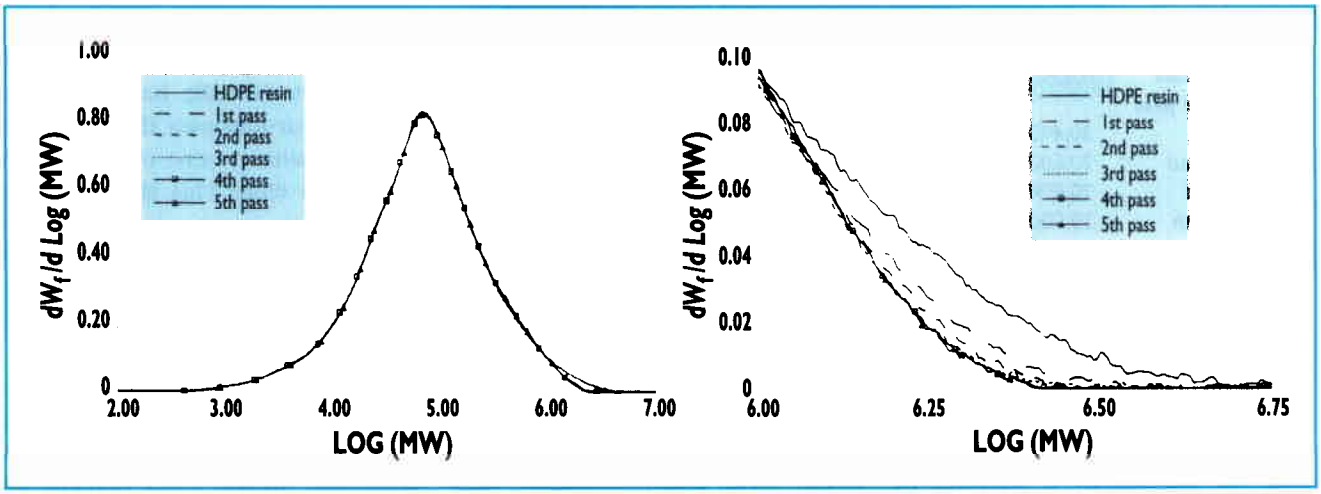
Figure 1 is an overlay of GPC refractometer curves of the five extruded samples along with the base resin. Recall that the species of highest molecular weight will elute earliest from a chromatography column. As the enlargement in the figure shows, the base resin elutes earliest. The first-pass sample is next, followed by the second-pass sample. The volume profile for the third-pass sample is indistinguishable from the profiles of the fourth-pass and fifth-pass samples. Nevertheless, this profile separation in the high-molecular-weight regime of the polymer peak indicates that the molecular weight is slightly degraded with successive passes through the extruder.

The graph on the left in **Fig. 2** shows the conventional GPC molecular weight distributions as calculated for these samples.* This area overlay shows the apparent decrease

*The area of the differential molecular weight distribution is equivalent to one. The differential molecular weight distribution is the first derivative of the cumulative molecular weight distribution.



1. The overlay of the refractometer measurements of extruded samples shows that the molecular weight is slightly degraded with successive extruder passes.



2. Overlay of the calculations of conventional molecular weight distribution, with an expanded view of the region of high molecular weight.

in molecular weight through the multiple-pass extrusion experiment. In the graph on the right, the view is expanded for the region of high molecular weight. The apparent differences between the distributions are related only to the contents of those species having the highest molecular weights. Since separation actually depends on molecular size, the molecules of greatest size are breaking apart during the extrusion process. Apparently, the most extensive fracturing occurs in the first extrusion pass.

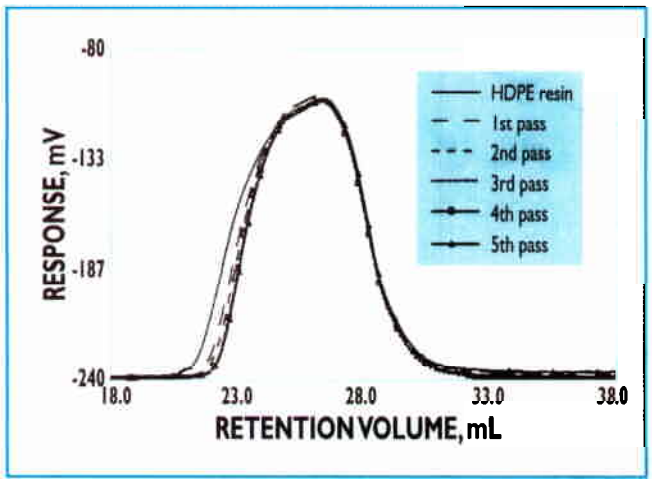
The most notable differences between the extrusion samples are shown as differences between the base resin, the first pass, the second pass, and the third pass. After the third extruder pass, the change in the molecular weight distribution starts to approach the sensitivity limit of the measurement.

The molecular weight data obtained from the conventional calibration technique are given in Table I. The apparent molecular weight, MW(apparent), decreases as a function of the number of extruder passes and approaches a limiting value. The apparent number-average molecular weight, MW_n(apparent), remains virtually unchanged. The apparent z-average molecular weight, MW_z(apparent), which is weighted to the high end of the distribution, decreases rapidly. Furthermore, the amount of polymer with molecular weight greater than 1,000,000 apparently decreases from 2.5% to 1.8% across the extrusion process.

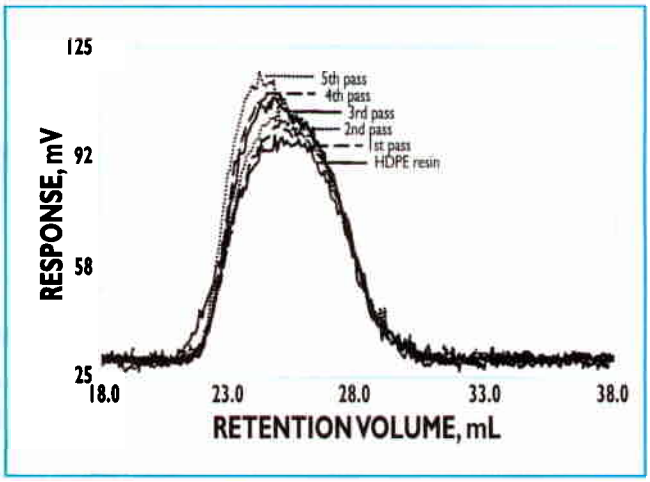
GPC WITH LIGHT SCATTERING AND VISCOMETRY

Background and experimental procedure

To examine the polymer degradation process more fully during extrusion, we added light-scattering and viscometer detectors to the system. This technique is commonly referred to as "TriSEC" (*3*). The light-scattering detector is sensitive to the product of molecular weight and concentra-



3. The viscometer overlay shows that intrinsic viscosity is reduced with repeat extrusion processing.



4. The light-scattering overlay shows that molecular weight increases with repeat extrusion processing.

	MW_N	MW	MW_Z	D	POLYMER PERCENT,* <10^4	>10^6
HDPE resin	20,300	157,600	827,000	7.76	9.7	2.5
Extruder pass						
First	20,400	148,600	618,000	7.28	9.2	2.0
Second	20,600	147,000	562,800	7.14	9.2	1.9
Third	20,800	146,300	549,000	7.03	9.2	1.8
Fourth	20,500	145,700	537,000	7.11	9.3	1.8
Fifth	20,300	143,000	533,900	7.04	9.5	1.8

*Percent of polymer with molecular weight less than 1000 or greater than 1,000,000.
D = polydensity = MW/MW_N

I. Apparent molecular weight distribution as a function of extrusion on HDPE resin

tion. The viscometer is sensitive to the product of intrinsic viscosity and concentration.

Branching increases the molecular weight and thus increases the result of the light-scattering measurement. For the viscometer, in contrast, branching increases molecular compactness and decreases intrinsic viscosity (*4*), contrary to its general effects on melt viscosity. If intrinsic viscosity is plotted as a function of molecular weight (referred to as a "Mark-Houwink" plot), an increase in branching shows up as a decrease in intrinsic viscosity at any point of molecular weight (*5*).

Run conditions were duplicated from the conventional GPC runs. The additional detectors used were the Model 150R Wheatstone-Bridge viscometer from Viscotek Corp. and the Model 2040, high-temperature, dual-angle light-scattering detector from Precision Detectors. Data from the 15° angle from the light-scattering detector were collected and processed using TriSEC software from Viscotek.

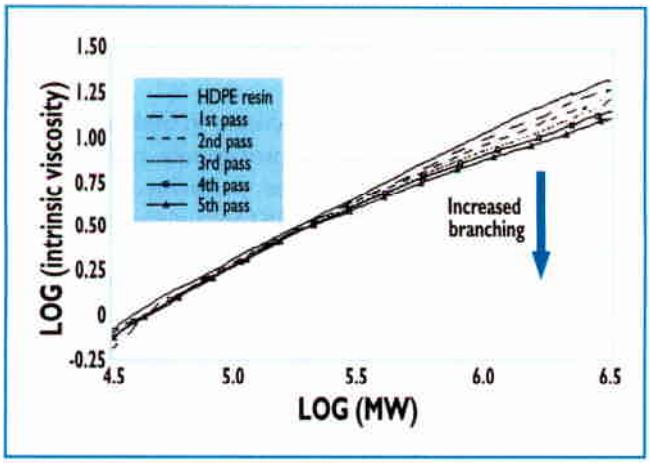
Results and discussion

Figure 3 is a GPC-viscometer overlay of five extruded samples along with the base resin. The graph indicates an apparent increase in molecular density (mass per unit volume), as depicted by the decreasing viscometer signal (volume per unit mass). This decrease is most notable between the base resin and the first extruder pass. However, the decreasing trend is visible up to the third extruder pass.

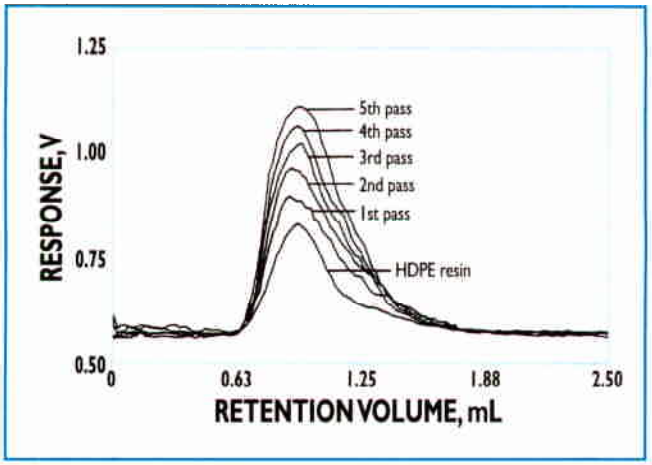
Figure 4 is an overlay of the GPC-light-scattering results for the five extruded samples along with the base resin. The light-scattering signal increases with each extruder pass, indicating an apparent increase in molecular weight (mass per unit molecule). Between the base resin and the first extruder pass, there is a shift in the elution volume of the earliest species to elute. This shift indicates that the most extended molecules have broken up. After this shift occurs, the height of the light-scattering peak increases with each extruder pass.

Table II gives the calculation results for the TriSEC analysis. With each pass through the extruder, the molecular weight rises (except for the initial pass). The *z*-average molecular weights are included to illustrate the increase in molecular weight at the high end of the molecular weight distribution. The overall polymer molecule becomes more compact in solution, as shown by the decreasing values of intrinsic viscosity. These decreasing values mean that somewhat branched polymer molecules are replacing their linear forms.

However, the table shows a contrast between the state of the base resin and the state after the first pass of the extruder. The table shows that the true molecular weight drops at the on-set of extrusion. The intrinsic viscosity also drops significantly from the base resin to the first extruder pass. At this point, there may be microgels being formed. However, the



5. The Mark–Houwink overlay shows that the molecular density increases with repeat extrusion processing.



6. The batch light-scattering measurements indicate greater percentage increases in molecular weight than indicated in Fig. 4 by the GPC technique.

microgels may be filtered out by the chromatography columns and may not be detected by the light-scattering detector.

The Mark–Houwink plot in **Fig. 5** shows the effect of plotting intrinsic viscosity with molecular weight. The graph makes it possible to rapidly sort out the structural heterogeneity within the extrusion processes. As the figure shows, the high-molecular-weight species (in solution) are the species most greatly compacted during the extrusion process. The overall molecular size of the polymer molecules decreases, as reflected in the conventional GPC overlay of Fig. 1. However, when measured by the light-scattering technique, the molecular weight apparently increases, producing molecules that are more compactly packed, as illustrated in the viscometer overlay of Fig. 4. A plausible explanation of this phenomenon is that the molecular weight species that get fragmented during the extrusion process form free radicals and quickly splice together, forming molecular species that are branched and that probably have long chains (*6*).

BATCH LIGHT SCATTERING FOR MICROGEL DETECTION

Background and experimental procedures

The moderately branched polymer molecules can be monitored by the TriSEC technique as long as the molecule size distribution stays within the size separation window of the GPC column. As the molecules grow with even further branching, the chromatography columns can begin to filter out these highly branched molecules or microgels.

To evaluate the amount of microgels suspended in the polymer solution, we can remove the column set from the chromatography system and inject the sample through a length of holdup tubing that leads directly into the light-scattering device. The resulting light-scattering peak area will be equivalent to the weight-average molecular weight, *MW*(true), of the polymer solution and will include the microgel content multiplied by the concentration of each respective species (polymer plus microgel) (*7*).

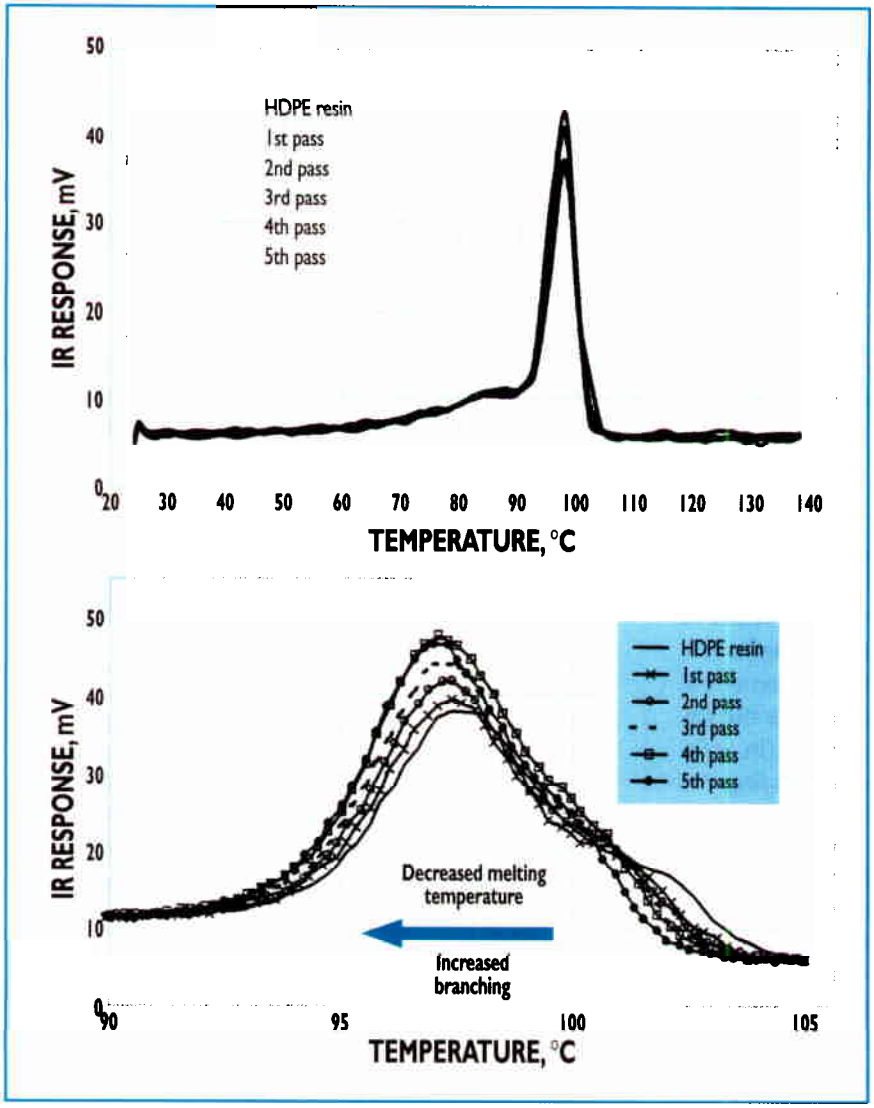
	MW	MW_z	Intrinsic viscosity, dL/g
HDPE resin	159,600	1,155,000	2.31
Extruder pass			
First	149,100	712,300	2.16
Second	151,300	759,000	2.11
Third	156,000	778,900	2.07
Fourth	157,100	831,000	2.03
Fifth	165,800	867,000	2.00

II. TriSEC molecular weight by light scattering as a function of extrusion on HDPE resin

	Melt index	High load melt index
HDPE resin	0.227	15.567
Extruder pass		
First	0.064	11.810
Second	0.031	9.482
Third	0.019	8.437
Fourth	0.008	6.965
Fifth	0.006	5.802

III. Decrease in the sample melt index with extrusion on HDPE resin

The batch light-scattering technique was completed with an Eppondorf Column Heater; a Wyatt Technology Dawn-F, high-temperature light-scattering instrument; a Shimadzu HPLC Pump; and a Foxboro infrared detector that was used to monitor sample concentrations. To delay the polymer peak, we used ten feet of tubing with an inner diameter of 0.05 cm. The solvent was 1,2,4-trichlorobenzene, the concentrations were 2.5 mg/mL, the injection volume was 400 µL, and the flow rate was 0.5 mL/min. Data were collected and processed with Viscotek TriSEC GPC software.



7. TREF overlay for the extrusion processing experiment. The lower graph is an enlargement that shows the downward shift of the melting temperature.

Results and discussion

Figure 6 is a batch light-scattering overlay of five extruded samples along with the base resin. The curves indicate increases in molecular weight between all samples with increasing amounts of extrusion. Note that the percentage increase in area is much greater than the increase shown in Fig. 4 for TriSEC chromatography. For example, the increase in area between the first extruder pass and the last extruder pass for the TriSEC analysis was 22%, whereas the batch light-scattering area increased by almost two-fold. This additional increase in light-scattering area can be accounted for by the formation of microgels that are filtered out by the GPC process.

CORRELATION WITH MELT INDEX MEASUREMENTS

Background and experimental procedure

Melt index is generally considered to be inversely correlated with molecular weight to the 3.5 power for polyethylene resins (*8*). Therefore, the measurement of melt index is especially sensitive to microgels and is somewhat less sensitive to the underlying molecular weight distribution of the polymer. Consequently, the formation of a large crosslinked species within a resin should be accompanied by a decrease in melt index. The melt index procedures and determinations were performed in accordance with ASTM guidelines.

Results and discussion

Table III gives the results of the melt index measurements for the base resin along with the five extrusion passes. The decreasing values of melt index indicate a significant increase in MW(true) and MW_z(true) with each sample extrusion pass.

In the TriSEC analysis, MW and MW_z increased with each extruder pass with the exception of the first pass. In the first pass, there was a significant drop in MW and MW_z. However, the batch light-scattering data indicated that there is an increase in MW with each pass *including* the first pass.

The melt index measurements correlate strongly with the batch light-scattering measurements in this regard. This discrepancy between the TriSEC data and the batch light-scattering data is evidence that microgels are forming. The discrepancy also indicates that these microgels are much bigger than single polymer molecules and that the microgels are filtered out by the chromatography columns.

The implication is that there are two categories based on size. The first category is for molecules of a size approximately the same as that of the linear polymer molecules. Molecule weights in this category are detectable by both the TriSEC and the batch light-scattering techniques. The second category is for molecules that are much bigger. These molecules are microgels that filtered out by chromatography but are detected with the batch light-scattering technique.

CORRELATION WITH TREF MEASUREMENTS

Background and experimental procedure

Molecules with more branching than others tend to melt more at lower temperatures. The TREF technique (temperature rising elution fractionation) separates polymer molecules

on the basis of melting temperature.

The sample is placed in solution at an elevated temperature. The mixture deposits on a nonporous column bed, which is cooled to allow the deposit to crystallize. A flow rate is established, and the temperature is increased steadily. Polymer species elute from the TREF column as they melt and become solubilized by the solvent (*9*). Commonly, an infrared detector is placed after the TREF column to detect the concentration of the emerging species (*10*).

The mobile phase for the TREF work was 1,2,4-trichlorobenzene. The TREF unit was modified from a Waters 150C High Temperature Liquid Chromatograph. Data were collected and processed using in-house software.

Results and discussion

Figure 7 is a TREF-IR overlay of five extruded samples along with the base resin. The upper graph shows that the samples are relatively close to each other in terms of overall profiles for melting temperature. Short-chain branching attributable to some comonomer groups on this resin gives rise to a broad low-melting population near 85°C.

When the plot is scaled across a more narrow temperature region, as presented in the lower graph, the small differences in melt temperature profile become more evident. In accordance with the other types of measurements, the trend is toward lower melting temperatures (and more highly branched molecules) as a direct function of the number of extrusion passes.

The fraction with the most linear molecules and the highest melting temperature (eluting at 103°C) is shown to have the highest percentage of the base resin. This peak deteriorates rapidly at the onset of extrusion. By the fifth extrusion pass, this linear component has almost completely vanished, indicating that virtually all of the polymer molecules possess at least a small amount of branching (short or long chain).

CONCLUSIONS

The set of polymer characterization techniques we have developed is a solid package for characterizing thermal or shear degradation in polymers. Our results demonstrate the value of using all of the various techniques to study the thermal degradation effect in polyethylene.

The addition of the batch light-scattering technique allowed us to directly detect the presence of microgel for the first time. This new technique will be found useful as well in other studies of microgel-related problems in polymer film processing. Between GPC, TriSEC, and batch light scattering, we should be able to determine the origins of ordinary microgel problems in polymer films, such as how to distinguish the "unmelt" versus the true crosslinked type of microgel in films.

The TREF technique has the resolution necessary to show the effect of branching caused by hot-melt processing. The entire TREF profile shifts toward lower melting temperatures with repeated processings. This observation shows that branching is widely spread throughout the sample and is not just limited to the formation of microgels.

Of course, it is nice to have this conclusion further supported and demonstrated in the TriSEC data. The TriSEC data do not show microgel content, because the GPC column screens out these species. Nevertheless, the fact that the light-scattering detector signal increases with repeat processings is a firm validation of the conclusion derived from the TREF data.

While the increase in TriSEC light scattering shows the broad branching effect across the main polymer constituents, a much larger increase in the batch light-scattering signal is observed for the same samples. This increase in the signal provides a novel tool for separating the effect of microgels from the effect of general branching behavior.

In summary, the results of our study confirm that polymer microgel structures form in hot-melt extrusion if the antioxidant is insufficient to protect the polymer from thermal degradation. The thermal degradation effect is not limited to the extremely high-molecular-weight components that lead to microgels in the samples. Some degree of branching occurs within the bulk of the polymer sample across almost the entire molecular weight distribution.

This finding means that polymer properties are going to be affected beyond the effects of microgel alone. How much effect will this broad distribution of branching have on processibility and performance? This question will be an interesting one to explore in future studies. **TJ**

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