Effect of High Molecular Weight Fraction in HDPE on Its Impact Properties: An HTSEC Study

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SYNOPSIS

Three commercial injection-molding-grade HDPE samples were evaluated for their properties. It was found that their impact property determined in the laboratory does not bear a simple correlation with the actual performance. The HTSEC study, undertaken to evaluate these samples, revealed that they differ significantly in z-average and $z + 1$-average molecular weights. This difference is attributed to the presence of a small amount of a very high molecular weight fraction and is responsible for the variation in the performance. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Molecular weight (MW) and molecular weight distribution (MWD) of a polymer are fundamental characteristics correlating its mechanical and performance properties. Different MW averages and their distributions are known to influence these properties.[1] The effect of number-average MW ($\bar{M}_n$) on brittleness and flow properties and that of weight-average MW ($\bar{M}_w$) on tensile strength and hardness is well documented.[2-5] However, the significance of other averages, i.e., z-average MW ($\bar{M}_z$) and $z + 1$ average MW ($\bar{M}_{z+1}$) has not been studied extensively. Since these averages are sensitive to the presence of small amounts of high MW polymer fraction, their contribution toward the polymer property is often difficult to judge.

The conventional method for the determination of $\bar{M}_z$ and $\bar{M}_{z+1}$, using the principles of sedimentation, has seldom been found to provide reproducible data.[6] Gel permeation chromatography, which separates molecules according to their hydrodynamic size in solution,[7] is widely used to calculate all these averages in a single experiment. In the present work, three commercial samples of high-density polyethylene (HDPE), suitable for producing large-size molded products such as crates and luggage shells,

were evaluated. Only one of these samples, however, passed in the field performance as indicated by the drop impact test, while the other two failed. To ascertain the reasons for failure, their physical and mechanical properties were determined in the laboratory and their molecular characteristics studied by high-temperature size-exclusion chromatography (HTSEC).

EXPERIMENTAL

Materials

The three injection-molding-grade commercial HDPE samples (nominal density 0.95–0.96 g/cm³) were obtained from different sources and designated as Samples #1, #2, and #3.

A broad MWD HDPE standard (Cat. No. PE105K) used for HTSEC calibration was obtained from American Polymer Standards Corp., U.S.A. 1,2,4-Trichlorobenzene (TCB; E. Merck, Germany) was used for dissolving the polymers for HTSEC measurements after filtration through a 0.45 micron Millipore filter (Millipore Corp., U.S.A.). Irganox 1010 (Ciba-Geigy, Switzerland) was added (0.2% w/v) to the polymer solution and mobile phase for the prevention of polymer degradation during its dissolution and chromatography.

HTSEC Equipment and Conditions

A Waters Model 150C ALC/GPC liquid chromatograph equipped with a bank of three Ultrastyragel columns (Waters Division of Millipore, U.S.A.) having a nominal porosity of 10^4, 10^5, and 10^6 Å were used. The mobile phase (TCB) flow rate of 0.8 mL/min at 145°C was maintained throughout the work. Resin samples (0.05% w/v) were dissolved in the solvent for 6–10 h at 145°C and kept in the HTSEC injector compartment for 1 h before injection. The calibration of HTSEC was carried out according to the method suggested by Purdon and Male.[8]

Testing of Resin Samples

Specimen Preparation

The test specimens of all three HDPE samples were injection-molded while maintaining the melt temperature of 190°C, injection pressure of 850 kg/cm², and mold temperature of 60°C.

Molding Conditions for Crates

The crates used to measure drop impact strength were molded under different molding conditions within the specified limits, i.e., melt temperature 185–200°C, injection pressure 800–1000 kg/cm², and mold temperature 60°C.

Density

The density of HDPE resins was measured by the density-gradient technique as per ASTM D1505-79.

Tensile Strength (TS)

The tensile strength of the samples was measured according to ASTM D638-82.

Flexural Modulus (FM)

The measurement of the flexural modulus was carried out as per ASTM D790-81 using 3 mm-thick test specimens prepared from a narrow parallel portion of molded tensile test dumbbells, i.e., type I (ASTM D638).

Izod Impact Strength

Impact measurements were made according to ASTM D256-81 using 3 mm-thick test specimens.

Differential Scanning Calorimetry (DSC)

The melting temperature of the resins was determined using a Mettler DSC Model TC2-25 while maintaining the heating rate of 10°C/min in a nitrogen atmosphere.

Melt Flow Index (MFI)

MFI was measured using an extrusion plastometer (Davenport, U.K.) under standard test conditions as per ASTM D1238-82.

Drop Impact Strength

The drop test was performed on molded crates of size 65.5 × 45 × 29 cm ($L \times W \times H$) by the fall of a 4.20 kg steel ball dropped from a height of 3 m, three times each on six gate points.

RESULTS AND DISCUSSION

The physical properties and molecular characteristics of the resins are given in Table I. It is observed that the test results are similar in magnitude except for izod impact strength, $\bar{M}_z$, and $\bar{M}_{z+1}$. These samples passed through all field performance tests except the drop impact test.

It is noteworthy that these commercial samples required different molding conditions for the productions of large-size crates due to variation in their MFI values. Hence, the crates used for the drop impact test were molded over the specified range of temperature and pressure. It was observed that Samples #2 and #3 always failed in the drop impact test whereas Sample #1 passed.

Table I Physical Properties and Molecular Characteristics of HDPE Samples

Characteristics	Sample #1	Sample #2	Sample #3
Density (g/cm³)	0.959	0.952	0.955
Melt index (g/10 min)	9.0	6.2	7.5
Melting temperature (T_m, °C)	136.8	131.5	133.5
Izod impact (kg cm/cm)	7.6	10.7	13.7
TS at yield (kg/cm²)	224	200	210
FM (kg/cm²)	8030	6300	8600
$\bar{M}_w$ ($\times 10^{-4}$)	8.99	8.68	8.69
$\bar{M}_n$ ($\times 10^{-4}$)	1.50	1.31	1.57
MWD ($\bar{M}_w/\bar{M}_n$)	6.00	6.60	5.50
$\bar{M}_z$ ($\times 10^{-4}$)	41.13	35.50	34.17
$\bar{M}_{z+1}$ ($\times 10^{-4}$)	152.00	70.60	74.2

In general, the specific properties of HDPE are governed by their density, MW, MWD, and a number of other factors. Sample #1, having the highest density, is expected to be the most crystalline. The lower izod impact strength of this sample is, therefore, in accordance with this observation. However, the failure of the other two samples (Samples #2 and #3) on the drop impact test, in spite of their superior izod impact strength and lower density, is rather unusual. It is noted that the impact strength of a material is merely a measure of its ability to resist breakage under specific loading conditions.[9] Since loading models are different in the tests conducted for assessing the field performance of the resin as compared to those in the laboratory (e.g., izod impact test), the values of latter can only be regarded as a qualitative indicator. In certain marginal cases, such as the present one, even qualitative agreement does not appear to hold good because the test bars and large-size molded products may have unmatched orientation characteristics, especially

near the surfaces.[10] Such variations are unavoidable due to the different molding conditions. Moreover, the energy application and its dissipation mechanism is different in the two tests and, hence, the values obtained in laboratory test may not reflect the actual behavior of a resin in field trials.

It is evident from the foregoing discussion that an average property such as density, melting point, and izod impact strength do not bear a simple correlation with the actual resin performance. These problems have led several workers[10-13] to the conclusion that MW is a very significant parameter in evaluating the end-use performance of polymers. Unfortunately, most of these studies have been conducted on narrow dispersity fractions, thus indicating only the absolute property difference. The studies on the actual contribution of a particular molecular species on performance is rather scarce in the literature. A study related to the poor performance of extrusion coating-grade low-density polyethylene (LDPE) toward its sealing behavior attributes it to
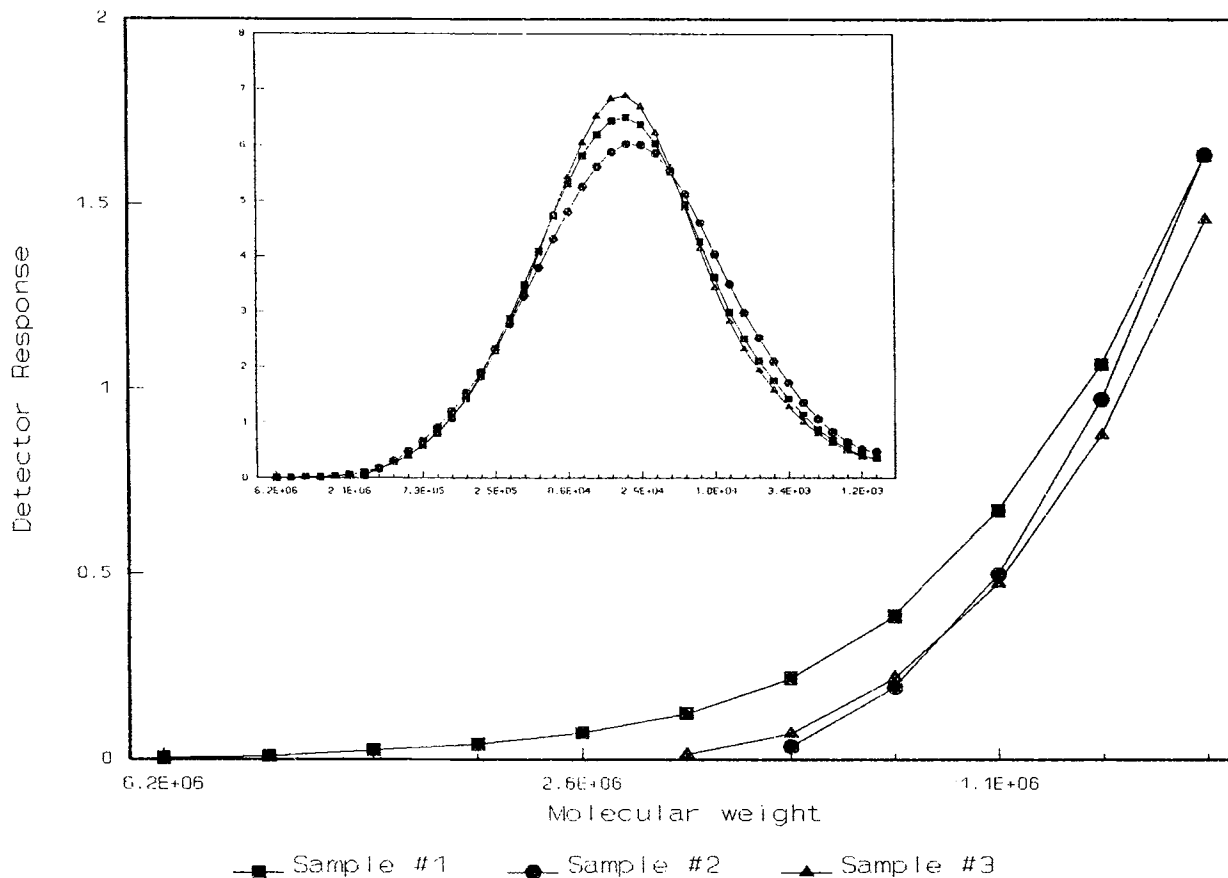

Figure 1   Enlarged relevant portion of the normalized chromatograms of HDPE samples showing the presence of very high MW fraction in Sample #1 (Inset: normalized chromatograms).

the variation in $\bar{M}_z$.[14] The other parameters related to sealing characteristics (such as long-chain branching and its distributions) have, however, not been discussed in this work. Hence, the contribution of molecular chains on solid-state properties is a complicated phenomenon and the interdependent variables, viz., crystallinity, orientation, crystal structure, and processing conditions, are influenced by MW and MWD of the material.

It is observed (Table I) that the samples studied have similar $\bar{M}_w$ and $\bar{M}_n$. Minor differences in these values could be within experimental variation. However, $\bar{M}_z$ and $\bar{M}_{z+1}$ have a vast difference which is due to the presence of small amounts of very high MW material present in Sample #1. Ward[15] also pointed out that the presence of a fraction of very large molecules can influence the physical and chemical properties of a polymer to a great extent. The normalized chromatograms of the three samples (Fig. 1) confirm this observation. It has been reported[16] that energy-to-break and breaking strength in a falling ball test significantly improve with increase in MW over a wide temperature range. Accordingly, it is inferred that the presence of traces of a very high MW fraction in Sample #1, as indicated by the values of $\bar{M}_z$ and $\bar{M}_{z+1}$, is responsible for its better drop impact behavior as compared to others.

CONCLUSIONS

(i) It is concluded from the present study that $\bar{M}_z$ and $\bar{M}_{z+1}$ averages, sensitive to the presence of a small amount of high MW material, significantly influence the drop impact strength of large molded articles.

(ii) Standard laboratory tests for impact strength measurement of the material studied do not bear a simple correlation with the product performance.

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