Simultaneous Determination of Molecular Weight and Crystallinity of Recycled HDPE by Infrared Spectroscopy and Multivariate Calibration

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ABSTRACT: An attempt of correlating molecular weight (M_n) of recycled high-density polyethylene (HDPE) as measured by size-exclusion chromatography (SEC) with diffuse reflectance near and mid-infrared spectroscopy (NIR/MIR) was made by means of multivariate calibration. The spectral data obtained was also used to extract information about the degree of crystallinity of the recycled resin. Differential scanning calorimetry (DSC) was used as the reference method. Partial least-squares (PLS) calibration was performed on the MIR and NIR spectral data for prediction of M_n. Four PC factors described fully the PLS models. The root-mean-square error of prediction (RMSEP) obtained with MIR data was 360, whereas a RMSEP of 470 was achieved when calibration was carried out on the diffuse reflectance NIR data. A PLS calibration for prediction of degree of crystallinity was performed on the NIR data in the 1100–1900-nm region, but the ability of prediction of this model was poor. However a PLS calibration in the region 2000–2500 nm yield better results. Four PC factors explained the most of the variance in the spectra and the RMSEP was 0.4 wt %. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 321–327, 2002

Key words: polyethylene (PE); molecular weight distribution; differential scanning calorimetry (DSC)

INTRODUCTION

The physical properties and mechanical performance of recycled polymeric material depend on several structural factors such as molecular weight, degree of crystallinity, crystal structure, orientation, and degree of oxidation. These factors play a decisive roll in the future application of recycled material because they determine whether the material is worth reuse/upgrade, or should be disposed of in another way, for example, incineration for energy recovery. For quality control and quality assurance of recycled polymers assessment of these properties is indeed important.

Size-exclusion chromatography (SEC) is a well-established method for determination of molecular weight (M_w) and molecular weight distribution (MWD). However, SEC is a relative method because the results are evaluated upon calibration with linear polystyrene standards with narrow MWD. One of the disadvantages of SEC, intrinsic viscosity measurements and absolute methods such as membrane osmometry and light scattering is that sample preparation can be time consuming and inconvenient, especially when dealing with polyolefins due to their slow dissolution and hazardous character of the used sol-

vents. In addition, the analyzed sample cannot be reused.

Infrared spectroscopic methods are extensively used to analyze polymers due to their simplicity, rapidity, reproducibility, nondestructive character, and ease of sample preparation (very little or no sample preparation is required). Degree of crystallinity,[1] chain branching,[2] degree of oxidation,[3] density measurements,[4] quantification of additives,[3,5] end-group analysis,[6,7] and other physical/chemical properties have been studied using mid infrared (MIR) and/or near infrared (NIR). End-group analysis by means of infrared spectroscopy has been successfully used for determination of molecular weight of polymers obtained by step-wise polymerization, such as PBT and PET.[8,9]

The bands in the NIR spectral region arise from overtones and combinations of the fundamental vibration modes in the MIR region. Functional groups making up the hydrocarbon molecules, such as methyl, methylene, and vinyl groups, show characteristic peaks; the absorbtivity of these peaks is largely independent of the remainder of the molecule, which acts only as a diluent and can be related to the concentration of the absorbing groups. Mathematical relationships between band intensity/frequency and concentration of the above-mentioned functional groups have been found by Tosi and Pinto.[9]

Hyphenated techniques such as the combination of HPLC and SEC with infrared spectroscopy are finding great acceptance for study of deformulation of unknown samples, determination of compositional changes across the molecular weight distribution, compositional distribution of copolymers, and branching in polyolefins.[10–12] The utility of this technique has been enhanced by the availability of SEC-FTIR interfaces, which allow off-line solvent removal.[12] However, this is indeed a destructive method of analysis.

Besides MIR, there is a number of other techniques for characterization of crystal structure and degree of crystallinity of polymers such as dilatometric measurements, density measurements, Raman spectroscopy, X-ray diffraction (SAXS, WAXS), differential scanning calorimetry (DSC), being the last two the most used. Although these techniques yield different absolute crystallinity values due to the differences in their principles, the relative changes in crystal contents are comparable. It is important to remark that these methods often require extensive sample preparation and long analysis times. As a result, they cannot be used for rapid process analysis. When rapid analysis is desired NIR spectroscopy has shown to be a very effective technique, which allows accurate analysis on relative unprepared samples, such as meat,[13] wheat,[14] and bulk polymer.[5,15–19]

The objective of the present study was to develop NIR and MIR in combination with multivariate data analysis for material characterization. Calibration for simultaneous determination of molecular weight and degree of crystallinity is presented for a series of recycled blow-molding grade high-density polyethylene (HDPE).

EXPERIMENTAL

Material

Sixteen blow-molded high-density polyethylene (HDPE) jugs were collected at random from the waste plastic stream at the Lunda recycling plant located outside of Stockholm. Only noncolored items were used for these studies. The samples were washed with water at 60°C, dried at room temperature for a day and subsequently ground into flakes. The flakes were analyzed by diffuse reflectance near-infrared spectroscopy (NIR), size-exclusion chromatography (SEC), and differential scanning calorimetry (DSC). Thin films of approx. 100 μm were compression molded for ATR-MIR and DSC analysis.

Characterization Methods

Diffuse reflectance near-infrared (NIR) spectra were obtained using a NIRSystems 6500 (NIRSystems, Silver Spring, MD) supplied with a sample transport module NR-6511 and an elongated coarse sample cell. Data was obtained every 2 nm in the 1100 to 2500 nm region. Five replicates of each sample were analyzed and the obtained spectra were averaged. The sample transport module was designed for coarse irregular samples and provides sample averaging over the sampling area. The sample cell is moved up and down through the beam while scans are coadded, resulting in a representative spectrum.

Infrared spectra in the mid-region (FTIR) were acquired using a Perkin-Elmer FTIR-2000 equipped with a deuterated triglycine sulphate (DTGS) detector and attenuated total reflection (ATR) Golden Gate device with a diamond crystal as internal reflection element (IRE). Thirty-two

Table I   Molecular Weight Averages and Polydispersity of HDPE Samples Determined by GPC

Sample	M_w	M_n	M_w/M_n
Sample 1	255,000	15,900	16
Sample 2	194,000	10,600	18
Sample 3	178,000	16,100	11
Sample 4	189,001.5	10,800	17
Sample 5	161,000	10,600	15
Sample 6	224,000	9630	23
Sample 7	187,000	14,700	13
Sample 8	215,750	8535	25.75
Sample 9	209,000	10,900	19
Sample 10	186,000	14,900	12
Sample 11	198,500	12,825	15.5
Sample 12	178,000	10,600	17
Sample 13	175,000	13,500	13
Sample 14	197,000	15,700	13
Sample 15	167,000	8100	21
Sample 16	169,000	10,300	16

scans were averaged at 2 cm^{-1} resolution in the range of 400–4000 cm^{-1}. Samples were analyzed in duplicate. The spectral data was also used to calculate the crystallinity using the empirical equation given in the experimental part.

Crystallinity measurements were performed under a nitrogen atmosphere on a Mettler-Toledo 820DSC Differential scanning calorimeter calibrated with indium. About 7 mg of sample was heated to 200°C, subsequently cooled down to 25, held at that temperature for 3 min, and heated again to 200°C, the heating and cooling rate was equal to 10°C/min. The enthalpy of fusion (ΔH_f) of the first heating was used to calculate the mass crystallinity, which was defined as the ratio of enthalpy of melting of the sample and the enthalpy of melting of a 100% pure crystalline HDPE sample (ΔH_{100}). The ΔH_{100} was taken as 293.1 J/g.

Size-exclusion chromatography (SEC) was carried out by Rapra Technology Ltd. (Shawbury, UK). A Waters 150CV chromatograph equipped with a PLgel 2 × mixed bed-B, 30 cm, 10-micron column system and a refractive index (RI) detector was used. The solvent was 1,2-dichlorobenzene with antioxidant, and the analysis was performed at 140°C and a 1.0 mL/min flow rate. A single solution of each sample was prepared by adding 15 mL of solvent to 30 mg of sample and boiling gently for 20 min to dissolve. Each solution was then filtered through a fiber pad at 140°C, and part of each filtrate transferred to glass sample vials. The vials were then placed in a heated sample compartment and after an initial delay of 30 min to allow the samples to equilibrate thermally, injection of part of the contents of each vial was carried out automatically. Table I summarizes the results of the GPC analysis.

Unscrambler 4.0 from Camo AS, Norway, was used for multivariate data analysis. Principal component analysis (PCA) was performed on the spectral data and Partial linear square (PLS) calibration was carried out on this data, which was previously pretreated by multiple scattering correction (MSC) to compensate for baseline shift and possible physical differences between the samples, such as flake size, shape, and light scattering.

RESULTS AND DISCUSSION

Mid-Infrared

It was deduced that the recycled HDPE items (blow-molding grade) had been produced from HDPE made by the Phillips process. This was confirmed by the absence of absorbtion bands at 888 and 965 cm^{-1}, corresponding to unsaturations of vynilidene and vynilene type, respectively, which are common in PE produced by either Ziegler process or metallocenes.[20] Figure 1 shows MIR spectra in the region 1000–850 cm^{-1} for several samples. Another characteristic feature for Philips manufactured HDPE is its high weight-average molecular weight, high polydispersity, and two different chain ends, where one of them is a vinyl group and the other is a methyl group. It is known that the concentration of end vinyl groups can be estimated by measuring the
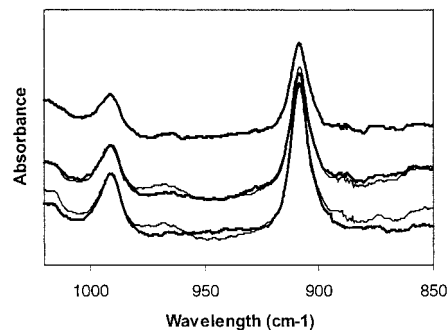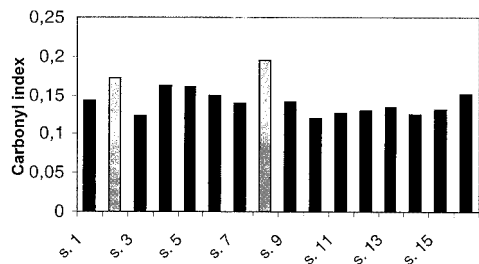

Figure 1   MIR spectra of several HDPE sample in the 1050–850 cm^{-1} region.
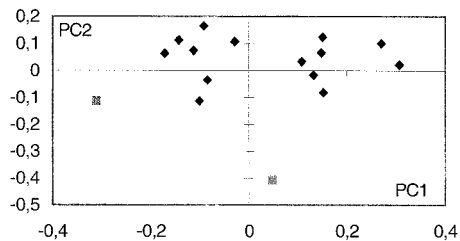
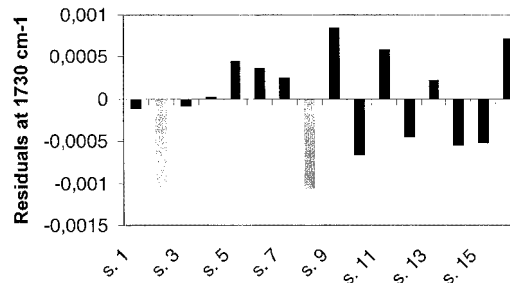**Figure 2** Score plot of PC1 and PC2 (outliers in gray).

Figure 4 Residual plot at 1730 cm^{-1} (outliers in gray).

intensity of the spectral band either at 910 or 990 cm^{-1}. The concentration of this end group is related to the molecular weight. In addition, two spectral regions are usable to detect the presence of CH$_2$ and CH$_3$ absorbances, namely the CH bending region (1350–1500 cm^{-1}) and the stretching region (2800–3000 cm^{-1}). This region has been used by some authors to determine CH$_2$ (2926 cm^{-1}) and CH$_3$ (2962 cm^{-1}) content in fractionated polyethylene.[10,11] The multivariate analysis and calibration in this work were, however, performed in the whole spectral range (600–4000 cm^{-1}) to extract the most information from the available spectral data.

PCA was done on the MSC-corrected MIR data. The MSC procedure was necessary to compensate for baseline variations between the spectra (presumably caused by scattering variations brought by variations in film condition) and multiplicative effects (primarily caused by small differences in the sample thickness). Four principal components (PC) fully explained the variation in the spectral data. Figure 2 shows the scores plot of the PC1 and PC2. Two presumable outliers were detected and excluded from further data analysis. Figure 3 shows the carbonyl index (CI) of all samples. The carbonyl index was defined as the absorbance ratio of the integrated carbonyl peak at 1740 cm^{-1} and the integrated CH$_2$ scissoring peak at 1463 cm^{-1}. An explanation for the presence of the out-

liers can be found in Figure 3. The CI of the outliers is much higher than that of the other samples. This statement is based on the analysis of residuals displayed in Figure 4, which showed high values at 1740 cm^{-1}, a band characteristic for carbonyl groups. Spectral residual analysis is a powerful tool for seeking outlier samples. In general, samples showing higher residuals than the rest of the samples in the training set may be considered outliers. Samples with small residual variance (or large explained variance) for a particular component are well explained by the corresponding model, and vice versa.

PLS calibration was performed on the MSC-corrected data and the number-average molecular weight data (M_n) measured by SEC. Eleven samples made up the calibration set, and the three remaining samples were included in a test set for validation of the model. The model was also validated by full crossvalidation. Four PCs were necessary to explain the most variation in the spectra (99.9%), which best described the molecular weight. Figure 5 depicts the PLS calibration model for prediction of M_n in HDPE. The root-mean-square error of prediction (RMSEP) is 360. Figure 6 depicts the loadings plot for the fourth PC factor. Analysis of the loadings plot showed two large upward peaks at 2926 and 2847 cm^{-1},

Figure 3 Carbonyl index of the HDPE samples (possible outliers are showed in gray).
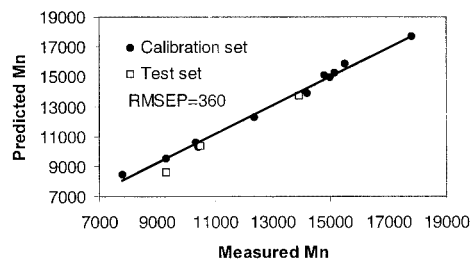
Figure 5 PLS regression model for predicting the molecular weight from MIR spectral data.
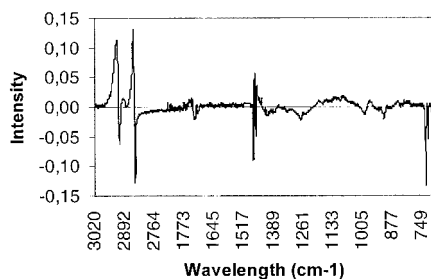
Figure 6 A loading plot of regression coefficients for the model shown in Figure 5.

Figure 8 NIR spectra after MSC correction in the 1000–2500-nm region.

ascribed to the methylene vibration modes in the stretching region and downward peaks at 1463, 1473, 1368, 730, and 720 cm^{-1}. The bands at 1473 and 730 cm^{-1} reflect the crystalline content of HDPE, whereas the band at 1368 cm^{-1} characterizes the methyl groups present at the chain ends and also the ends of the side chains (branches) along the main chain. This result suggests that PC four reflects variations in molecular weight, the higher the intensity of the upward bands, the higher the M_n.
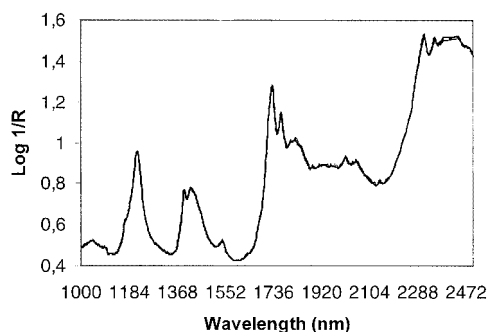
Two bands corresponding to the CH_2 bending mode, one at 1474 cm^{-1} due to the crystalline phase and the other at 1464 cm^{-1} representing the contributions from both crystalline and amorphous phases, were chosen to calculate the amorphous content (x), following the empirical formula given below:[21]

$$x = \frac{1 - (I_a/I_b)/1.233}{1 + (I_a/I_b)} \quad (1)$$

where I_a and I_b are the intensities of the bands at 1474 and 1464 cm^{-1}, respectively. The constant 1.233 represents the intensity ratios of these bands in the spectrum of a 100% crystalline polyethylene, and was derived using the factor group

splitting applied to a single polyethylene crystal.[22]

Figure 7 gives the relation between crystallinity determined by DSC, and MIR for all the studied HDPE samples is displayed. As expected, the absolute values are not the same; however, a linear correlation can be observed.

Near Infrared

Figure 8 shows the MSC-corrected NIR spectra of some HDPE samples in the 1000–2500 nm region. The sharp peaks at different wavelengths correspond to overtones or combination bands of the fundamental vibration modes of the methylene groups. However, additional bands related to the methyl groups have been identified at 1190, 1374, and 1698 nm.[23,24] The raw spectral data was MSC treated, and PLS was applied to make a predictive model for molecular weight determination. Calibration was performed in the range of 1100–1900 nm. The calibration set consisted of 11 samples and the test set was made up of three samples. Two PC factors fully described the model, and the M_n could be predicted with a RMSEP of 470. Figure 9 shows the calibration curve obtained.

Figure 7 Crystallinity calculated on MIR data vs. crystallinity measured by DSC.
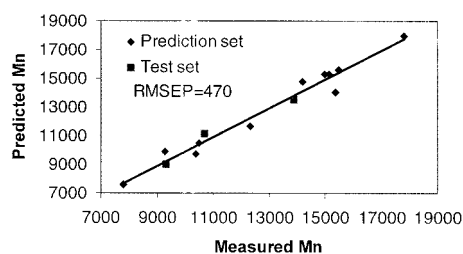
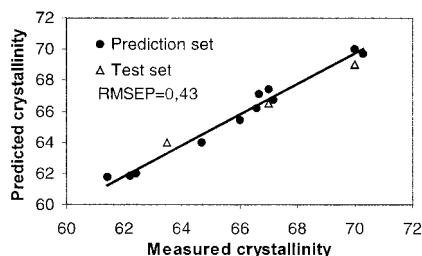**Figure 9** PLS regression model for predicting molecular weight from NIR data.

Figure 10 PLS regression model for predicting crystallinity from NIR spectral data.

A PLS calibration for prediction of degree of crystallinity was performed on the NIR data in the 1100–1900 nm region, but the ability of prediction of this model was poor. However a PLS calibration in the region 2000–2500 nm yield better results. Four PC factors explained the most of the variance in the spectra and the RMSEP was 0.4. The better results in this region can be explained with the presence of two spectral bands, at approx. 2310 and 2350 nm. The latter corresponds to a combination of the methylene symmetric stretching and scissoring bands, and the former is a combination of the methylene asymmetric stretching and scissoring bands. As was mentioned before, intensities of the scissoring bands are related to the crystalline content of PE. Figure 10 displays the calibration curve.

NIR has several advantages over MIR regarding sample handling. For instance, the necessity of preparing thin films for MIR analysis in the transmission mode brings additional changes to the structure of the material; additional thermal degradation of the material during this procedure cannot be discarded, because the already degraded material is subjected to high temperatures. In addition, the sample thickness cannot be readily controlled, and MSC might not be good enough to compensate for this variations. However, acceptable errors of prediction, comparable to that of the reference methods, were obtained with MIR data. On the other hand, better calibrations might be obtained if more accurate methods of molecular weight and crystallinity measurements were used. Thus, the use of light scattering or membrane osmosis and X-ray diffraction would possibly provide more reliable reference data.

The analyses have been carried out by HDPE produced using the Philips catalyst. The presence of HDPE produced by Ziegler-Natta may affect the calibration model because the vinyl end groups are not fairly distributed and side and *trans* (in backbone) unsaturations are also found. However, multivariate analysis tools, such as analysis of residuals, score plots, loading plots, normal probability plots, etc., make it possible to identify such "anomalous" samples. Once identified, these samples can be excluded from the calibration or the test set.

Even though the crystallinity of HDPE can be easily calculated from the FTIR-MID spectrum by rationing two peaks, the use of the whole spectrum becomes necessary to facilitate sample discrimination and outlier detection. In a calibration model outlying observations may be detrimental to the quality of the prediction. In the prediction such observations should be rejected to avoid erroneous results.

CONCLUSIONS

1. NIR and MIR spectroscopy worked well for fast determination of molecular weight and crystallinity of the recycled HDPE.
2. The use of PCA analysis and PLS calibration makes it possible to extract most of the information from the spectral data and detect small differences in it, which were related to the studied properties.
3. The accuracy of prediction of the reference methods is the limiting accuracy of the obtained calibration models.

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