Abstract
Comparison of diffuse reflectance and direct transmission measurement of polymer pellets

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Introduction

Although diffuse reflectance can provide the convenience of spectral collection for solid samples, it has also drawbacks that can negatively influence the accuracy of quantitative analysis. The resulting spectra may represent chemical information related to the characteristics of only the sample surface, rather than to those of the whole sample, because the penetration depth of NIR radiation into a sample is small, compared to the size of the granular sample. In addition, the penetration depth is affected by diverse factors, such as wavelength, refractive index, and morphology of the samples. Because of these factors, largely uncontrollable variability is usually associated in a diffuse reflectance spectrum. Several studies have shown that the accuracy of NIR measurement could be improved with the use of direct absorbance spectra, rather than diffuse reflectance spectra. The objective of this study was to investigate the possibility of improving the accuracy for density determination of polyethylene (PE) pellets through direct transmission measurement, instead of diffuse reflectance. Apparently this feasibility has not been thoroughly investigated so far in polymer analysis.

Materials and methods

Twenty-five polyethylene (LLDPE: linear low density polyethylene) pellets were obtained from a petrochemical company in Korea. The group of samples was composed of three different grades: 1-butene (12 samples), 1-octene (9 samples) and homo (four samples). The density of the samples ranged from 0.918 g cm^{-3} to 0.961 g cm^{-3}. The shapes of the 1-butene and 1-octene grade pellets were disk-like, while the homo grade pellets were relatively more spherical. Diffuse reflectance NIR spectra were collected using a Foss NIRSystems model 6500 spectrometer equipped with a quartz halogen lamp and four PbS detectors, to collect diffused radiation from the samples. The spectrometer was equipped with a sample moving system which allowed scanning of large areas of approximately 16 cm vertically, by continuously moving the sample cell with a fixed radiation source and detectors. The NIR spectra were collected by putting the samples into a sample

cell (size of window: 3.5 cm × 26 cm) without any pretreatment. Transmission NIR spectra were collected using a Nicolet FT-NIR spectrometer equipped with a tungsten–halogen source and InSb detector. The small circular aperture of 0.85 mm (diameter) was used to minimise the spectroscopic deviations from the round surface of a pellet. NIR spectra were collected over 9000–4500 cm^{-1} range with the resolution of 8 cm^{-1}.

Results and discussion

Figure 1 (left plot) shows NIR absorbance spectra (9000–4500 cm^{-1} range) of all PE pellets collected by transmission.

As shown, the baselines are fairly variable because of the round surface of samples, as well as variation of shapes. The bands observed correspond to –CH overtone and combination bands. The most significant spectral variation related to the change of density was observed in the 6100–5300 cm^{-1} range as shown in the right-hand plot. For clarity, the baselines of NIR spectra were corrected at 6100 and 5300 cm^{-1}, and the peak area under the 6100–5300 cm^{-1} range was calculated. Then, each baseline corrected spectrum was divided by the corresponding peak area. Through this type of normalisation, the possible peak intensity variations resulting from changes in sample shape and/or thickness could be minimised. Using PLS, the resulting prediction accuracy of density was 0.0008 g cm^{-3} using direct absorbance spectra; while it was 0.0011 g cm^{-3} with the use of diffuse reflectance spectra. The spectral features obtained by direct transmission contain whole chemical information rather than the near-surface information recorded by diffuse reflectance. This fact led to the improved prediction accuracy.

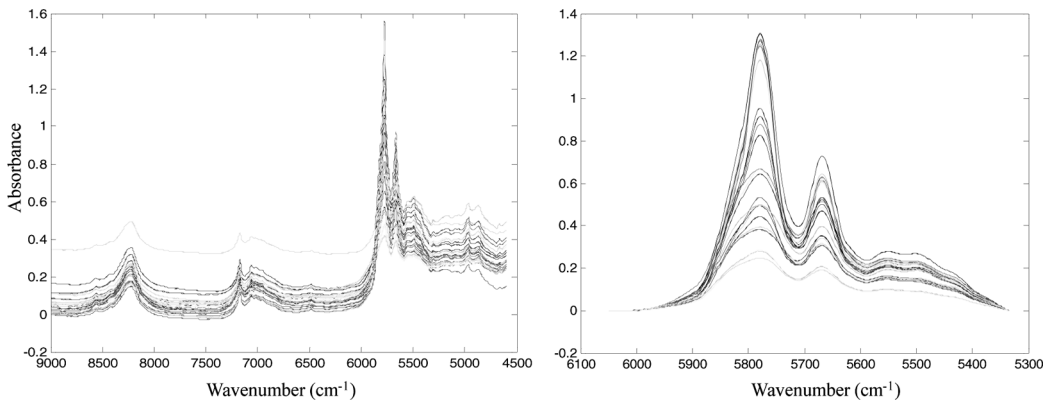

Figure 1. NIR spectra of 25 PE pellets collected by direct transmission of NIR radiation through each pellet.