

Determination of percent polyethylene in polyethylene/polypropylene blends using cast film FTIR techniques

Application note

Energy and chemicals; Materials testing

Author

Frank Higgins

Agilent Technologies
Danbury, CT, USA



Introduction

Polyethylene (PE) is the most common group of thermoplastic polymers due to its low cost and versatile physical properties. PE is blended with polypropylene (PP) to improve physical properties, such as low temperature impact performance. The composition of these blends is important with regard to performance, and the correct mixing of the pure homopolymers (PE and PP) can eliminate the need for costly synthesis of new block copolymers. Knowing the composition of these blends is also critical to the recycling and regeneration of polyolefins in waste and scraps.

In this application note, we demonstrate a method for rapidly determining the PE:PP ratio in blends using the Agilent Cary 630 FTIR spectrometer.



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Experimental

Calibration standards of PE/PP blends in the 35–85% PE range were prepared by dissolving different ratios of the polymers in hot (110–120 °C) tetrachloroethylene (perchloroethylene), making a roughly 3% polymer to solvent solution.

The dissolved polymer mixture was then used to cast films on either PTFE coupons or KBr plates for analysis by FTIR. In the case of KBr plates, approximately 0.3 mL of the polymer solution was evenly placed on the plate. The plate was then placed on a ~70 °C hotplate until all the solvent evaporated. The coated KBr plate was allowed to cool and analysis was carried out using the Cary 630 FTIR spectrometer, equipped with a transmission sampling accessory. The ratios of the methyl IR bands (mainly PP) and the methylene CH₂ bands (both PE and PP) were used to accurately measure the weight % PE in the blend. The thickness of the film was controlled to ensure that the strongest absorbance in the 1500–1200 cm⁻¹ region did not exceed 1.2 absorbance units (AU) and remained in the preferable 0.3–1.0 AU range (Figure 1, Y-axis). Infrared spectra recorded on these salt plate cast films consisted of 74 co-added interferograms measured at 4 cm⁻¹ resolution. Total measurement time was 30 seconds.

We developed a second, novel procedure for measuring the PE:PP blend ratio. This procedure used the same calibration solutions, but rather than salt plates, the solutions were applied to a smooth piece of PTFE. After drying in an oven at 70–80 °C, the resulting 20–50 μm thick films were easily peeled off the still warm PTFE. These self-supporting polymer cast films were then analyzed by the Cary 630 FTIR equipped with the DialPath (or TumbIR) accessory using the 100 micron pathlength cell. The polymer films easily slide between the cell windows, allowing for convenient repositioning and analysis of multiple areas of the film. This makes finding the optimal thickness (0.3–1 AU) faster, since larger pieces of polymer film can be sampled in many locations. Infrared spectra recorded of these self-supporting films consisted of 74 co-added interferograms measured at 4 cm⁻¹ resolution. Total measurement time was 30 seconds.

The new DialPath method can be used on the Agilent 4500 and 5500 FTIR spectrometers as well as the Agilent Cary 630 FTIR. The 4500 is a portable, battery operated FTIR spectrometer available with the DialPath technology. The 5500 is a dedicated, benchtop FTIR spectrometer also available with the DialPath sample interface. These instruments have the same reliable performance and patented interferometer technology as the Cary 630 FTIR, but allow for onsite and near line analysis.

A calibrated method was developed and added to the Cary 630 FTIR methods library so that future unknown samples can be analyzed. The method enables an automatic calculation of the PE:PP ratio, and the numerical value and spectra of the unknown is automatically displayed and/or printed.

Results and discussion: PE/PP blend cast film FTIR calibration

The salt plate cast film FTIR procedure is consistent with ASTM D3900-05a (Rubber-Determination of Ethylene Units in Ethylene-Propylene Copolymers (EPM) and in Ethylene-Propylene-Diene Terpolymers (EPDM) by Infrared Spectrometry). To correct for film thickness, the absorbance of a variable component peak (in this case, PP) is measured as a ratio to another matrix peak (in this case, PE). Both the novel PTFE and the original salt plate cast film method use the same peak height ratio of the 1376 cm⁻¹ to the 1462 cm⁻¹ bands (Figure 1) to determine composition. The new cast film method, based on the DialPath accessory linear regression calibration plot yields R²=1.000 (Figure 2) and the salt plate cast film method yields the identical calibration and R² value.

Fringing patterns are sometimes observed when smooth polymer films are measured in the mid infrared region. Fringing appears as a baseline sine wave pattern in the spectra and arises from internal reflection of the IR light inside smooth polymer films. The techniques described in this application note do not produce fringing in the areas of interest by either the salt plate or the DialPath transmission methods. In the latter case, the concave/convex matching cell window design of the DialPath and TumbIR minimizes fringing, while providing an easy to open and clean optical cell with precise pathlength reproducibility.

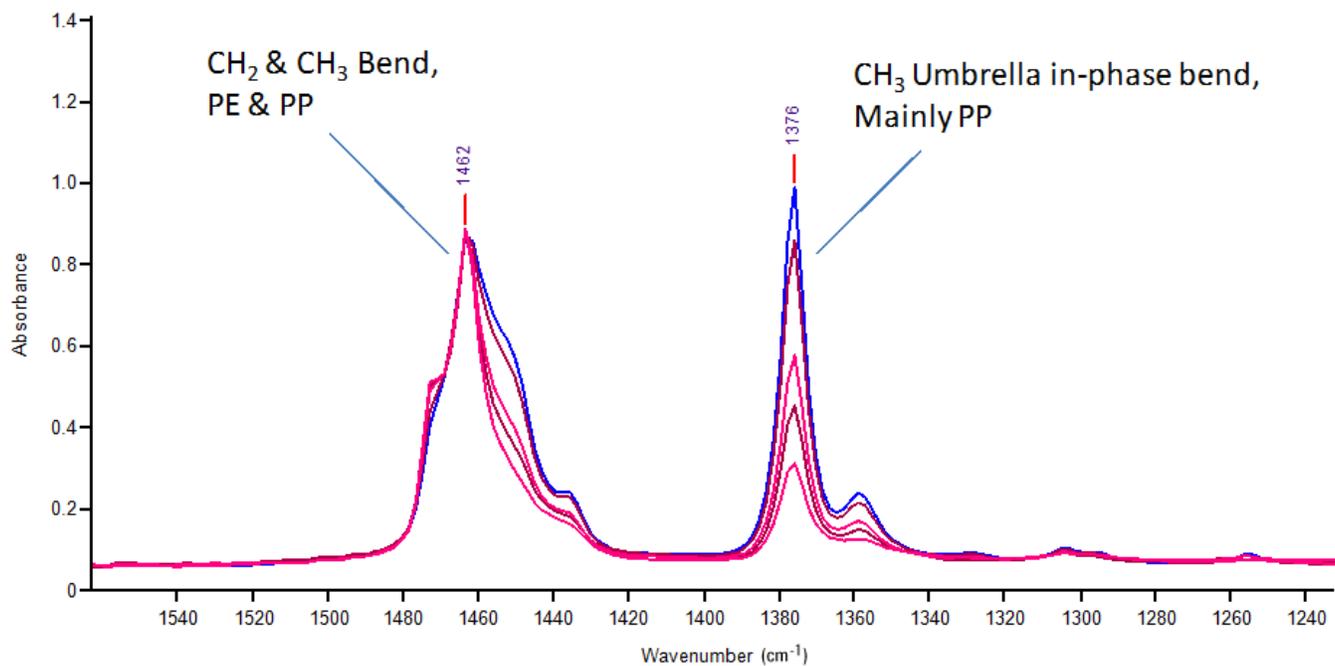


Figure 1. The overlaid aliphatic bend region of the FTIR PE/PP blend calibration spectra. The quantitative method for %PE uses a ratio of the methyl 1376 cm⁻¹ (mainly PP) to the 1462 cm⁻¹ (methyl and methylene bend) band.

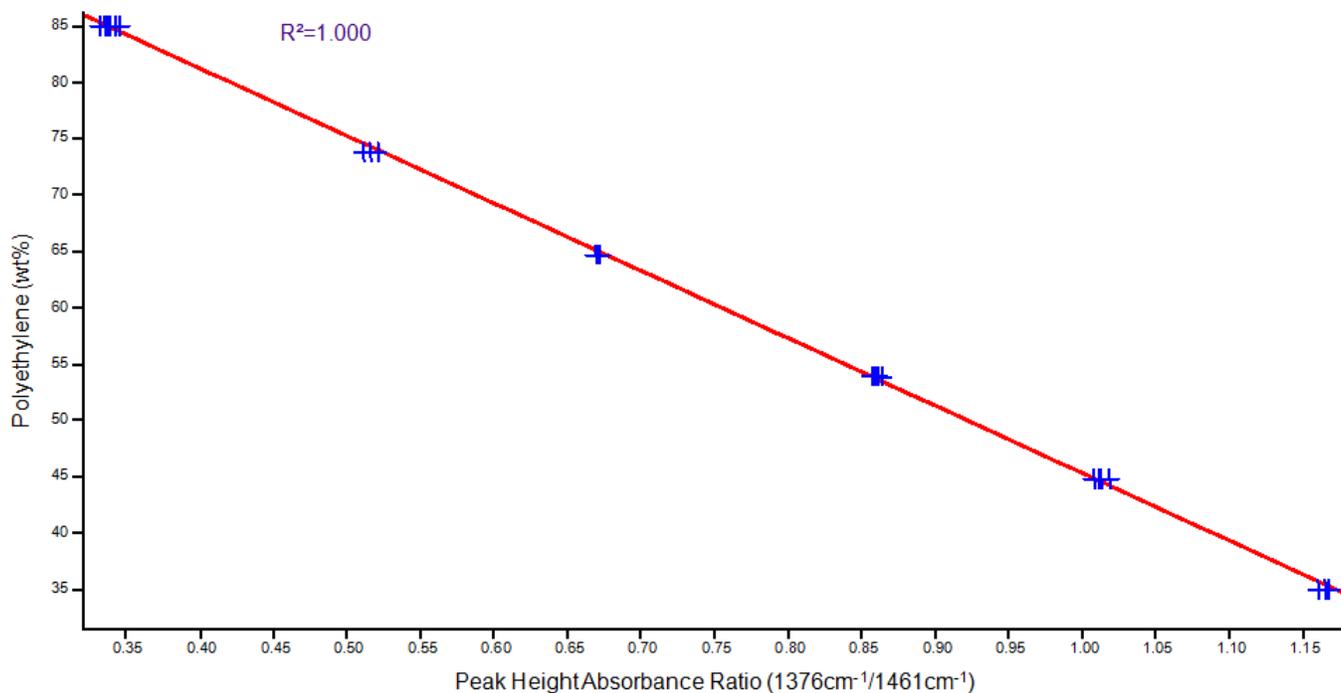


Figure 2. The calibration plot of PE/PP blends prepared as cast films, and analyzed using the Tumbler or DialPath on the Agilent Cary 630 FTIR. The same calibration with traditional transmission compartment (film cast in salt plate) yields similar calibration results. The calibration uses the ratio of the PP band at 1376 cm⁻¹ to that of the 1462 cm⁻¹ band in both PE and PP.

Conclusions

The FTIR analysis of 35–85% PE concentrations in PE/PP blends is now easier than ever using the versatile Agilent Cary 630 FTIR spectrometer. An excellent calibration was developed using the same cast film technique and IR peaks as the ASTM D3900 PE/PP copolymer method. The Cary 630 FTIR standard transmission compartment is used for the measurement of these cast polymer films on salt plates.

A second, novel method has been developed using the Cary 630 FTIR DialPath transmission accessory, which is easier and more versatile, because larger pieces of self-supporting films can be analyzed in a short amount of time. The polymer films can be repositioned and measured in multiple regions without opening the cell, thus allowing the analyst to find the ideal film thickness for the measurement.

Both methods yielded the same excellent calibration and identical R^2 value. The PE:PP calibration is now part of a method that has been added to the Cary 630 FTIR software, allowing the polymer ratio in unknown samples to be instantly calculated and displayed.

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