At-line FTIR process monitoring

Determination of the composition of polypropylene-based materials

by Stefano Nascetti, Leonardo Contado, Michele Grazzi, Franco Rossi

The report describes an at-line FTIR spectrophotometer and the processing of the IR spectra suitable to determine the composition of moving films of different types of PP based-materials coming from an extruder. The whole device consisting of extruder, gel-counter and FTIR spectrophotometer can be placed in a "at-line building" and fed with polymer coming from the plant by a conveyor.

In the context of the global drive to reduce costs for the production of polyolefin, manufacturing companies have been substituting conventional analyses in quality control laboratories with on/at-line analyses. On-line involves the fully automated analysis on a continuous basis and sampling occurs directly in the process, without the sample being removed from the process. At-line consists of semi-automated analysis of samples that are removed from the process and conveyed to the analyzer that generally is located in a small building connected to the plant extruder. As on-line analyzers often require enclosures and special engineering to protect them from harsh environment and to prevent risks, at-line is often a cheaper monitoring system, especially if the same conveying and sample preparing system are used for multiple analyses, i.e. gel counting and composition determination. In fact, the polymer coming from the plant as pellets, nibs or powder can be extruded in film by a small extruder. The number of gels/specks and the composition of the film can be measured by a gel counter and a FTIR spectrophotometer placed after the extruder (Figure 1). The number and the dimension of gels are important characteristic of materials produced for packaging purposes and the composition affects both optical and mechanical properties of the polyolefins.

The present work was aimed at establishing the instrumental conditions and the spectra treatment in order to determine the comonomer (ethene) content in different types of polypropylene-based copolymers. For this purpose a FTIR spectrophotometer, suitable for collecting spectra of moving polymer films, was connected to a lab scale extruder.

The determination of the talc content, present in some type of materials, was also considered.

S. Nascetti, L. Contado, M. Grazzi, F. Rossi, Basell Polyolefin - Ferrara - R&D G. Natta - Piazzale Donegani, 12 - 44100 Ferrara - Italia - Stefano.Nascetti@basell.com.

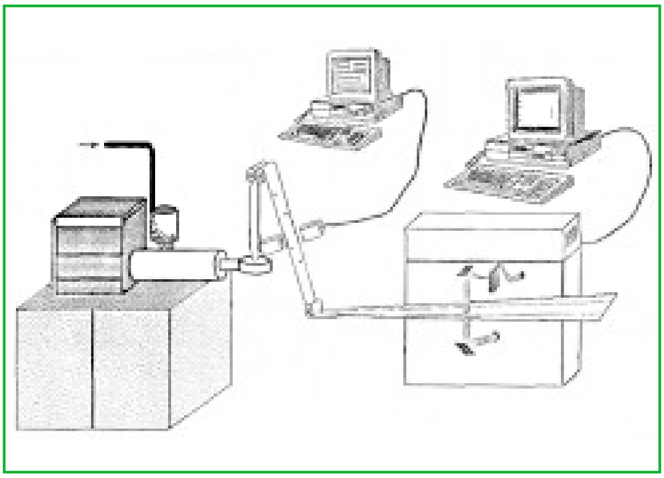

Figure 1 - Scheme of the apparatus consisting of: extruder, gel counter, FT-IR spectrophotometer

Experimental

All the copolymers were extruded in cast film with a Plasticisers MKII, a laboratory extruder with a 15 mm 22L/D screw. A flat die with a fixed gap of 0.2 mm and 80 mm width was used and films were quenched on a chill roll (25-30 °C). The proper melt temperature (240-260 °C) and the screw speed were chosen according to the different materials in term of melt flow rate (MFR) and composition. The films passed trough an Applairs, a FTIR Bomem MD100 spectrophotometer modified by OCS for measurements on moving film. The thickness was 70 micron in order to have the IR analytical bands below 1 AU even with high ethene content materials (about 30% by weight). The instrument collected background and film spectra with an air bearing-motor, which moved the infrared beam on

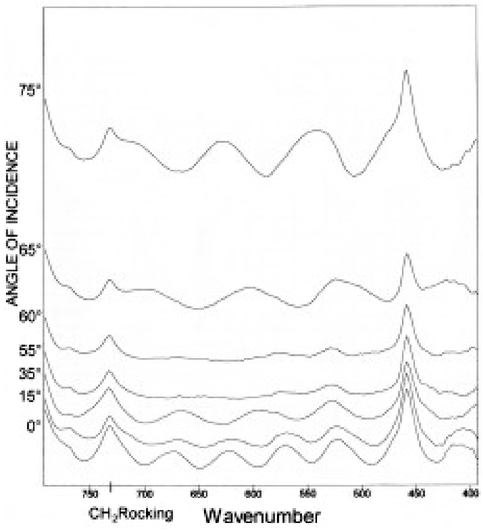

Figure 2 - Baselines between 800-400 cm^{-1} of spectra obtained at different angles of incidence of the polarized IR beam. Baseline at ϑ_{Br}=56.3 is free from fringes

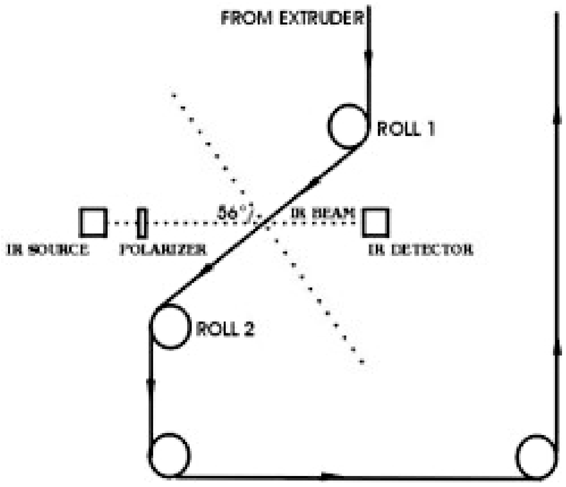

Figure 3 - Scheme of the device for fringe suppression

and off the film. This lateral movement was computer controlled. The background was collected every hour. A nitrogen or dry air purge was not necessary. To improve the baseline stability, the instrument started collecting spectra one hour before each composition analysis. Spectra acquisition time was set at 1.5 minutes (equivalent to 64 scans) at nominal resolution of 4 cm^{-1}. Each sample was extruded for at least one hour before starting the composition analysis and a spectrum was collected every 8 meters of film. Data collection and treatment were made by Lab-Calc software (Galactic). Lab-Calc array basic programs were written for automatic composition determination.

Fringe suppression

A proper apparatus was set up to avoid fringes in the spectra. Interference fringes arise from the constructive and destructive interference of the light beams generated from partial reflection of the infrared beam in the plane parallel surfaces of the extruded film. Fringes give rise to oscillations in the baseline of the IR spectrum. Such oscillations obscure small spectral absorptions and make the quantification difficult (Figure 2).

Fringes were avoided using polarized light incident at Brewster angle ϑ_{Br}. In fact, when a parallel polarized beam strikes the film surface at ϑ_{Br}, its reflectance is zero. Such result was obtained installing a KRS5 polarizer (Graseby-Specac) between the IR source and the film. The rolls that guide the film inside the optical bench were mounted on a dial. The dial was set to make the IR beam hit the film at ϑ_{Br} =arctg n, with the refractive index for polymers n≈1.5 and ϑ_{Br} =56.3 (Figure 3) [1-4].

Discussion

Ethene determination

Ethene propene semicrystalline copolymers show a band in the range 730-720 cm^{-1}, due to the rocking of $(CH_2)_n$ groups with n≥3, which is proportional to the ethene content.

At low ethene content, isolated units $(CH_2)_3$ prevail and the band maximum shows up at 732 cm^{-1} (Figure 4,A). On the other hand, at high ethene content, long sequences $(CH_2)_n$ (with n≥5) prevail and the band is split, due to crystallinity [5] (Figure 4,B). In both cases, the left shoulder of this band is affected by the band at 810 cm^{-1} due to $(CH_2)_1$ groups coming from the propene units. In order to improve the detection of low ethene content and to measure the area of the band respect to a baseline suitable for any content of ethene (from 0.6 to 35% molar ratio), the propene band was subtracted. The criterion applied in order to automate a correct digital subtraction, consisted in performing an iterative subtraction of an isotactic polypropylene homopolymer spectrum as a reference spectrum, with an increasing factor until a minimum in the range 790-730 cm^{-1} first occurs at 790 cm^{-1} [6]. This reference spectrum was collected once and stored in the computer disk. Afterwards, the area of the CH_2 rocking band was measured versus a linear baseline between 790-660 cm^{-1}.

As stated by the Lambert-Beer law, the absorbance of a band depends, both on the concentration of the absorbing chemical group and on the thickness of the sample. In order to avoid measuring the thickness of the extruded film, the area of the rocking band was divided by the height of the band at 4323 cm^{-1}. This band is a combination band associated with CH_2 groups and it is proportional to the thickness [7,8].

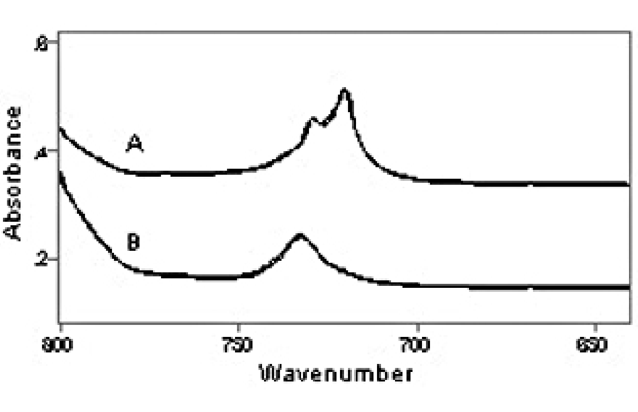

Figure 4 - CH_2 rocking of the IR spectrum of:
A - a copolymer with ethene 55% wt
B - a copolymer with ethene 2% wt

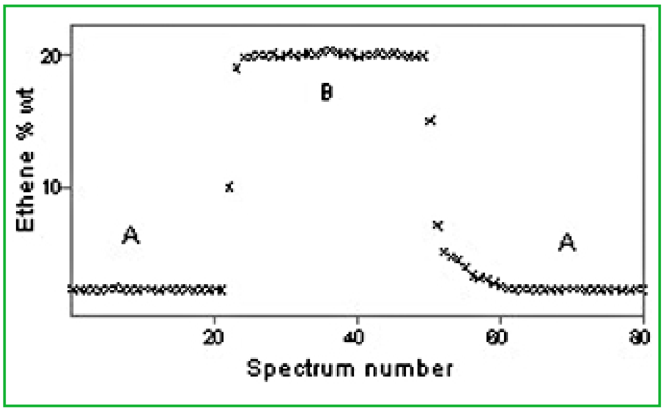

Figure 5 - Ethene %wt as function of time (a spectrum is collected every 1.5 minutes); Polymer A MFR=8g/10', Polymer B MFR=0.6g/10'. The hard material B pushes out the soft A quickly

The Lambert-Beer law was applied as follows:

$$A_{(790-660)} = k_{(790-660)} \cdot t \cdot C_E$$

$$A_{(4323)} = k_{(4323)} \cdot t$$

$$\frac{A_{(790-660)}}{A_{(4323)}} = \frac{k_{(790-660)}}{k_{(4323)}} \cdot C_E = k' C_E$$

Where A(790-660) is the area between 790-660 cm^{-1}, A(4323) is the height of the band maximum at 4323 cm^{-1}, k(790-660) is the integral absorptivity between 790-660 cm^{-1}, k(4323) is the absorptivity at 4323 cm^{-1}, C_E is the ethene molar fraction. The dimensions of the parameter k are [cm^{-1}]. A calibration was run by using standard copolymers with composition previously determined by 13C NMR [9]. Using the least squares method, the experimental points were interpolated by a straight line passing trough the origin. Concentration values were converted to % by weight for practical purposes.

Figure 5 reports the variation of the ethene content as function of the time when a copolymer A with ethene 2% by weight, MFR 8 g/10' and a copolymer B with ethene 20% by weight, MFR 0.6 g/10', were extruded in the order A, B, A. The slope of the curve at the change of the ethene content depends on the difference between the MFR values.

The Table reports the repeatability of the continuous "at-line method" compared with the standard method used in Basell quality control laboratories. In the Table, CI is the Confidence Interval (95% probability) for a single analysis

$$CI = \pm \frac{\sigma \cdot t}{\sqrt{N}}$$

(N=1)[9,10].

Where σ is the standard deviation of the population estimated from the standard deviation of the sample; N is the number of measurements and Student's t are $t_{(N=40)}$ =2.02, $t_{(N=10)}$ =2.26. The "at-line method" has comparable σ values, but better repeatability (smaller CI) than the standard method. The difference is due to the big number of measurements available using the at-line system.

Repeatability of the continuous "at-line method" compared with the standard method used in Basell quality control laboratories

Ethene content % by weight	*Standard Deviation "at line" (N=40)*	*CI*	*Standard Deviation std method (N=10)*	*CI*
2	0.046	0.09	0.039	0.09
10	0.160	0.32	0.190	0.44
20	0.180	0.36	0.250	0.57

Elimination of the interference due to talc and measurement of its amount

Some polypropylene-based materials are filled with talc in order to improve stiffness. In the mid IR spectra, talc shows a band at 669 cm^{-1}. Since the area of the band due to the ethene is measured between 790-660 cm^{-1}, the presence of talc causes a systematic error in the measured concentration of ethene. In order to avoid this, an automatic subtraction of the talc band was applied. A suitable criterion to automate a correct digital subtraction consisted in performing an iterative subtraction of a reference spectrum of talc (potassium bromide die pellet) previously collected and stored to the computer disk. The subtraction factor was raised until the absorbance value at 669 cm^{-1} (maximum) is ≤ to the absorbance value at 617 cm^{-1} (tail of the talc band)[12]. Figure 6 compares IR spectra of a ethene copolymer with no talc, filled with talc and after the automatic digital subtraction of the talc. Figure 7 shows the ethene % by weight of the respective extruded films. The subtraction of the talc band turned the ethene values into the correct ones. In addition, the amount (% by weight) of talc was determined using the subtraction factor FCR found in the routine described above. In fact the Lambert-Beer law can be written as:

$$A_{talc} = k_{talc} \cdot t \cdot C_{talc}$$

where A_{talc} is the absorbance of the band due to talc at 669 cm^{-1}, k_{talc} is the absorptivity at 669 cm^{-1}, t the thickness of the extruded film and C is the concentration of talc and

$$A_{talc,\, ref} = k_{talc} \cdot t_{ref} \cdot C_{talc,\, ref}$$

where $A_{talc,ref}$ is the absorbance of the band due to talc in the reference spectrum of the talc (in KBr pellet), t_{ref} is the thick-

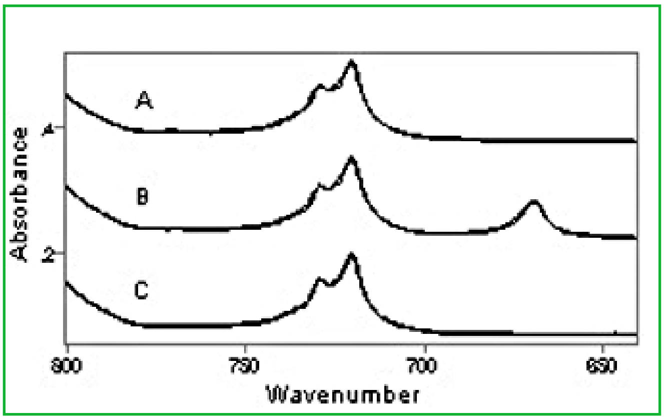

Figure 6 - Spectra of copolymer with no talc (A), with talc (B), after talc substraction (C)

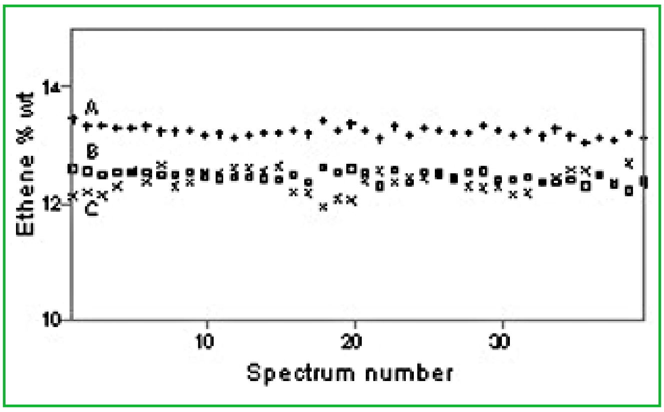

Figure 7 - Ethene % wt as a function of time (spectra are collected every 1.5 minutes).
In trace A, ethene values are systematically too high because of talc. After talc subtraction (trace C) the values are turned into correct ones represented by trace B)

ness of the pellet and $C_{talc,ref}$ is the concentration of talc in the pellet. When the FCR is set to the correct value:

$$A_{talc} = FCR \cdot A_{talc,\,ref}$$

$$k_{talc} \cdot t \cdot C_{talc} = FCR \cdot k_{talc} \cdot t_{ref} \cdot C_{talc,\,ref}$$

Then:

$$\frac{FCR}{t} = \frac{1}{C_{talc,\,ref} \cdot t_{ref}} \cdot C_{talc} = k'' \cdot C_{talc}$$

The thickness of the extruded film is substituted by A(4323) and a calibration FCR/A(4323)=k’’·C_{talc} obtained by using polymer sheets with known amounts of talc, allowed to monitor the talc content.

Conclusion

In the reported study, a commercial FTIR spectrophotometer was modified to avoid fringes in the spectra of a film coming from an extruder gel counter apparatus. Routines for treatment of the spectra were prepared to determine the ethene content of ethene propene semicrystalline copolymers in a fully automated manner. In the case of materials filled with talc, automatic routines were implemented to calculate its amount and to avoid its interference with the ethene determination.
The whole hardware/software device can be placed in a “at-line building” and fed with the polymer coming from the plant by a conveyor.

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