Polymer Orientation and Crystallinity Measurements by FT-IR and IR dichroism

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Introduction
Final properties of a polymeric product are determined by its morphology that was developed as a consequence of processing conditions. Measurement of crystallinity and orientation is of importance for process optimization [1].

Experimental: FT-IR spectra analysis
Three IR spectra have to be collected (Fig. 1): non-polarized, polarized parallel and perpendicularly to the flow direction.

Crystallinity
Considering a crystalline peak and a peak insensitive to phase content, and starting from Lambert and Beer’s law, crystallinity $X_c$ can be evaluated as follow:

$$X_c = \left( \frac{a_{av}}{a_{cr}} \right) \left( \frac{A_{cr}}{A_{av}} \right)$$

$A_{cr}$, $a_{cr}$, $a_{av}$: absorbancies, $a_{cr}$, $a_{av}$: absorptivities of crystalline fraction and of a peak insensitive to phase content respectively, (for iPP $a_{av} = 973$ cm$^{-1}$, $cr = 841$ cm$^{-1}$ and $a_{973}/a_{841} = 0.79$ [2]).

Orientation
The orientation factor can be obtained from Fraser’s theory (dichroic ratio $D_\nu = (A_{\parallel}/A_{\perp})_\nu$, for iPP $K_{973} = K_{841} = 1$ [2]):

$$f = \left[ \left( \frac{D - 1}{D + 2} \right) \left( \frac{D_0 + 2}{D_0 - 1} \right) \right] = K_\nu \left( \frac{D - 1}{D + 2} \right)_\nu$$

Case histories
- Quenched polypropylene films [2] and film casting products [1] were analysed off-line (UNISA).
- On-line measurements were performed during film casting by a dedicated apparatus (UNISA, Fig. 2) [1].
- Injection moulded samples have been investigated by a FT-IR microscope (TUE, Fig. 3) [3].

Future work
In principle, the techniques can be applied on a rheometer. Rheological responses ($\eta$, $G'$, $G''$) can directly be related (being measured during the same experiment) to morphology ($f$, $X_c$). A set-up like the one sketched in Fig. 4, is under development.

Problems
- Two opposite needs on sample thickness: (i) Rheology: $\delta > 300 \mu$m to avoid excessive forces, (ii) FT-IR: $\delta < 150-200 \mu$m to avoid saturated absorbancies
- Little room for IR mirror system positioning ($\delta \approx 1.2$ cm)
- No reliable optical fibres available to gather the spectral region between 750-1000 cm$^{-1}$

References: