Polymer orientation and crystallinity measurements by FT-IR and IR dichroism

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.

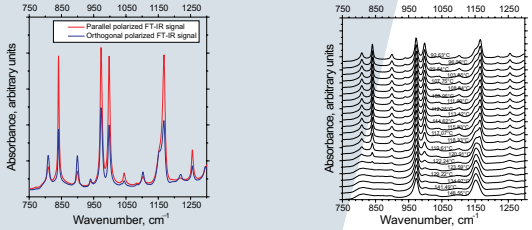

Figure 1 *Left: polarized FT-IR spectra from an iPP sample, Right: unpolarized FT-IR spectra collected during cooling*

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:

$$X_c = (a_{av}/a_{cr})\,(A_{cr}/A_{av})$$

A_{cr}, A_{av}: absorbancies, a_{cr}, a_{av}: absorptivities of crystalline fraction and of a peak insensitive to phase content respectively, (for iPP 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 $D_\nu = (A_\pi/A_\sigma)_\nu$, for iPP $K_{973} = K_{841} = 1$ [2]):

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

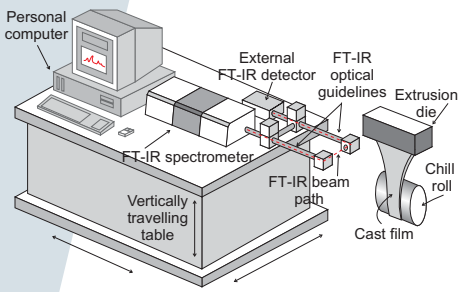

Figure 2 *The system developed at University of Salerno to gather transmission spectra during polymer film casting*

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].

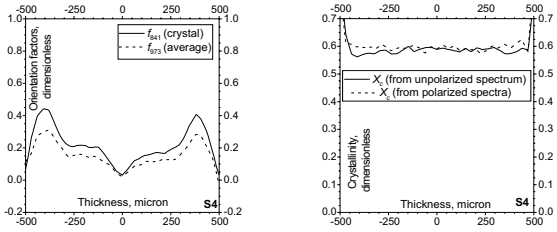

Figure 3 *Left: orientation distribution, Right: crystallinity distribution, both are obtained from injection moulded sample*

Future work

In principle, the techniques can be applied on a rheometer. Rheological responses (η, 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.

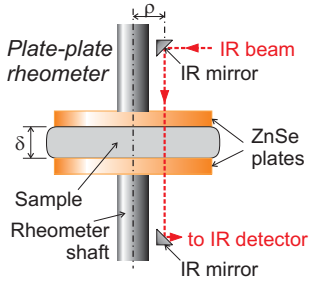

Figure 4 *The system under development at MATE/TUE to gather transmission spectra during rheology experiments*

Problems

- Two opposite needs on sample thickness: (i) Rheology: δ › 300 μm to avoid excessive forces, (ii) FT-IR: δ ‹ 150-200 μm to avoid saturated absorbancies
- Little room for IR mirror system positioning ($\rho \approx$ 1-2 cm)
- No reliable optical fibres available to gather the spectral region between 750-1000 cm^{-1}

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