Structure (and processing) dependent plasticity of isotactic polypropylene

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Polymer Technology

Structure (and processing) dependent plasticity of i-PP

D. Cavallo, H. Caelers, G.W.M. Peters, L.E. Govaert

Introduction
Isotactic polypropylene exhibits a rich polymorphic behavior, which depends on molecular features and crystallization conditions.\(^1\) For example the monoclinic structure (\(\alpha\)-phase), commonly found for mild crystallization conditions, is progressively replaced by a less-ordered mesomorphic structure with the increase of cooling rate.\(^2\)

The different polymorphs are expected to present a distinct mechanical performance, however, detailed characterization has been carried out for the most common \(\alpha\)-phase only. The present work attempts to fill this gap by:
- Reducing the amount of material required for mechanical properties characterization
- Crystallizing i-PP in controlled conditions to obtain differences in structure/morphology

Results and discussion

Compression molded thin films

Polypropylene films around 200 \(\mu\)m thick quenched at different rates were tested in tensile deformation.

![Figure 1. Comparison of a typical tensile test specimen with miniaturized one used in this study.](image)

![Figure 2 Stress-strain curves (left) and yield stress vs strain rates (right) of i-PP specimens cooled at different rates and measured at RT.](image)

The formation of mesomorphic phase with increasing cooling rate is accompanied by a decrease in the yield stress and a change in its strain rate dependence (Figure 2).

Two- processes Ree-Eyring equation:

\[
\sigma_i(T,\dot{\varepsilon}) = \sum_{x=12}^{x=12} k_T V_x \sinh^{\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0,x}} \exp\left[\frac{\Delta U}{k_B T} \right] \]

\(
\Delta U = \text{activation energy}
\]

\(V = \text{activation volume}\)

\(\dot{\varepsilon}_x = \text{rate constant.}\)

Samples crystallized in largely different conditions, leading either to monoclinic or mesomorphic structure differ only for the value of \(\dot{\varepsilon}_x\) (Figure 3).

![Figure 3. Correlation between rate constant and crystallinity for various materials.](image)

Samples solidified in the “Pirouette” dilatometer

The novel Pirouette dilatometer allows to process in controlled conditions a small amount of material (about 75 mg). Cooling rate (up to 100°C/s), applied pressure (up to 1.2kbar) and shear conditions (up to 180 s\(^{-1}\)) can be systematically varied to mimic real polymer processing. (Figure 4, left)

Dumbbell-shaped samples can be obtained (Figure 4, right), enabling the reproducible and accurate determination of deformation kinetics. (Figure 5).

![Figure 4. The “Pirouette” dilatometer (left). From ring to dog-bone sample (right)](image)

![Figure 5. Yield stress vs strain rate for i-PP samples solidified either in the PVT (blue symbols) or as compression molded films (red symbols).](image)

Conclusions
Correlation between structure and yield properties of i-PP samples solidified in monoclinic and mesomorphic phase have been established. The use of recently developed PVT tool will enable to extend this study towards crystallization conditions closer to processing applications (i.e., pressure, flow...).

References