Introduction

The mechanical and optical properties of semi-crystalline polymers are largely determined by the crystalline structure. This structure in its turn is greatly influenced by the processing conditions, such as flow, cooling rate and pressure the material is subjected to. Both these relations (flow-structure and structure-properties) have to be accurately described by a modeling framework for polymer processing. (Fig. 1)

A vital step in developing this framework is being able to measure the structure, as knowledge about this structure is required both for validation of nucleation models and as input for structure-property models. Directly probing this structure requires tedious and/or expensive experimental techniques, due to the small scales involved. Our goal in this study is to investigate the capability of rheometry to obtain information about this structure by applying an accurate structure-property model to rheology data.

A suspension-based structure-property model

A polymer crystallizing in quiescent conditions consists of a melt with a number of growing spherical crystalline structures, which we model as a suspension of spherical soft particles using the Generalized Self-Consistent Method (GSCM).

Results

The performance of the GSCM in describing a crystallizing polymer melt is validated with RheoDSC experiments on HDPE. Fig. 3 shows comparison between experiments and simulations of the hardening function $\Gamma$, given by

$$\Gamma(\xi, \omega) = \frac{|\eta^*(\xi, \omega)|}{|\eta^*(\xi = 0, \omega)|}$$

where $\eta^*$ denotes the dynamic viscosity, $\xi$ space filling of the crystalline structures and $\omega$ oscillatory frequency. Experiments and simulations agree very well, indicating that the behavior of crystallizing HDPE is indeed suspension-like.

Conclusions

We have applied a model describing suspension-like behavior to a crystallizing polymer melt. Validation with experiments on HDPE show the model accurately describes the rheological properties. By analyzing rheometry data, we can now measure space filling and number of spherulites with an ordinary rheometer without the need for hot stage microscopy or DSC apparatuses.

References

