

Specific volume measurements at high cooling rates for semicrystalline polymers

Citation for published version (APA):

Zuidema, H., Peters, G. W. M., & Meijer, H. E. H. (1999). *Specific volume measurements at high cooling rates for semicrystalline polymers*. Poster session presented at Mate Poster Award 1999 : 4th Annual Poster Contest.

Document status and date:

Published: 01/01/1999

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Introduction

In polymer processing the specific volume ν is the key from processing characteristics to material properties. As ν of semicrystalline polymers is severely influenced by the crystallisation process in the polymer during processing, it has to be related to pressure p , temperature T , cooling rates \dot{T} and ordered state of the molecules (crystals) [2].

Objective

- Measuring and modelling the specific volume of semicrystalline polymers at high cooling rates.

Methods

The specific volume ν is measured using the confining fluid technique [1] (fig.1, left). The maximum cooling rate achieved approximates $60[K/s]$ (fig.1, right).

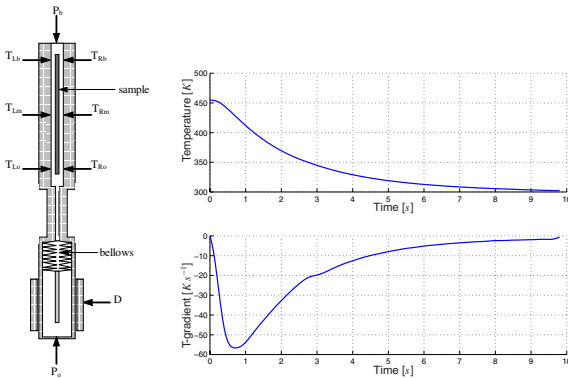


Fig. 1 Basic outline of the setup (left) and measured temperature(-gradient) (right).

Modelling the degree of crystallinity ξ is done using Avrami-Schneiders rate equations [2] in which N is the number of crystals and G the crystal growth rate.

$$-\ln(1 - \xi_g) = \phi_0, \quad \phi_i = G^{-1} \dot{\phi}_{i-1}, \quad \phi_3 = 8\pi N$$

A crystallinity dependent model for the specific volume is used, in which V_∞ the maximum degree of crystallinity:

$$\Delta_c = \frac{\delta(1/\nu_c)}{\delta T}(T - T_{ref}), \quad \Delta_a = \frac{\delta(1/\nu_a)}{\delta T}(T - T_{ref})$$

$$\frac{1}{\nu} = \xi_g V_\infty \frac{1}{\nu_c}(1 + \Delta_c) + (1 - \xi_g V_\infty) \frac{1}{\nu_a}(1 + \Delta_a)$$

References:

- [1] P. Zoller, P. Bolli, V. Pahud, and H. Ackermann. Apparatus for measuring pressure-volume-temperature relationships of polymers to $350^\circ C$ and $2200 kg/cm^2$. *Rev. Sci. Instrum.*, 47(8):948–952, 1976.
- [2] H. Zuidema, G.W.M. Peters, and H.E.H. Meijer. An experimental-numerical investigation of flow-induced crystallisation of polymers. *To Appear*, 2000.

Materials

The material used is an isotactic polypropylene (K2Xmod) with known number of spherulites N (fig.2, left) and crystal growth rate G as a function of temperature (fig.2, right).

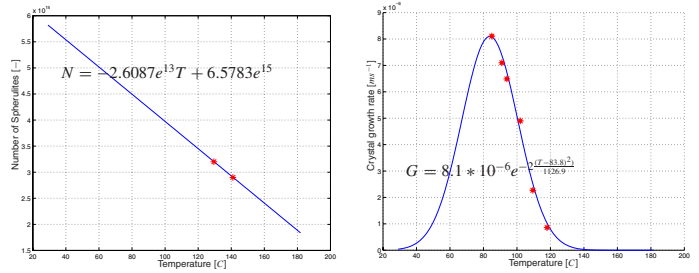


Fig. 2 Data on the number of spherulites N (left) and crystal growth rate G (right) of the iPP K2Xmod.

Results

Results show the very good correlation between experiments (•) and simulations (—) (fig.3) at small cooling rates. At high rates the correlation is good.

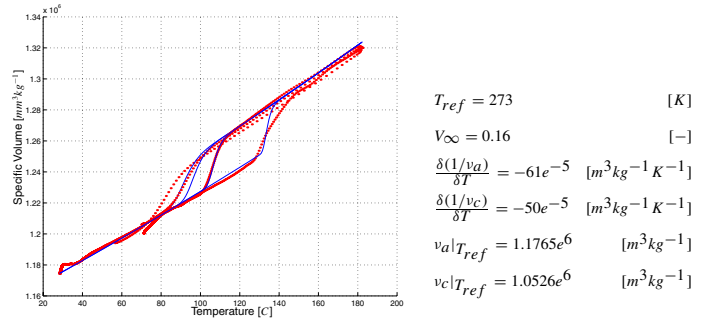


Fig. 3 Results and used model parameters.

Discussion

Although the results at atmospheric pressure are promising, high pressure measurements have to be done to confirm this. The small deviation from the experimental data at high cooling rates can be a result of a different crystal structure.

Conclusion

Modelling the crystallisation process accurately, results in accurate predictions for the specific volume.