Specific volume measurements at high cooling rates for semicrystalline polymers

Specific Volume Measurements at High Cooling Rates for Semicrystalline Polymers

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Introduction

In polymer processing the specific volume v is the key from processing characteristics to material properties. As v of semicrystalline polymers is severly 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 v is measured using the confining fluid technique [1] (fig.1, left). The maximum cooling rate achieved approximates $60[K/s]$ (fig.1, right).

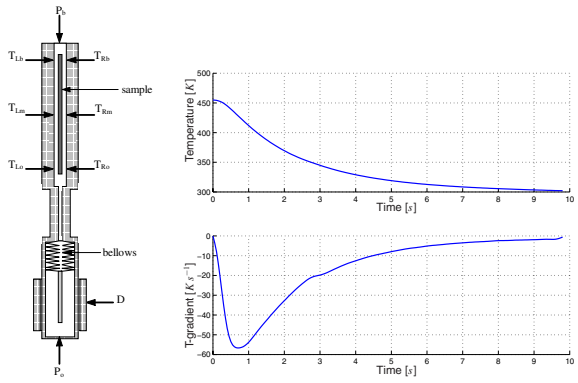


Fig. 1 *Basic outline of the setup (left) and measured temperature(-gradient) (right).*

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.

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

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

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

$$\frac{1}{v} = \xi_g V_\infty \frac{1}{v_c}(1+\Delta_c) + (1-\xi_g V_\infty)\frac{1}{v_a}(1+\Delta_a)$$

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).

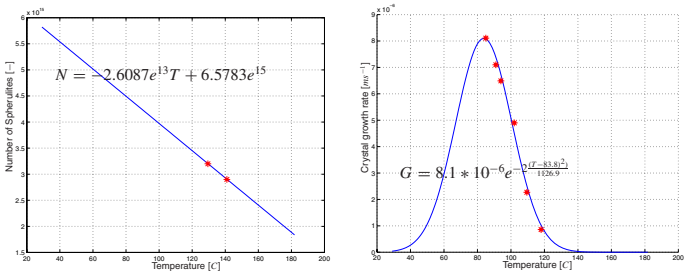
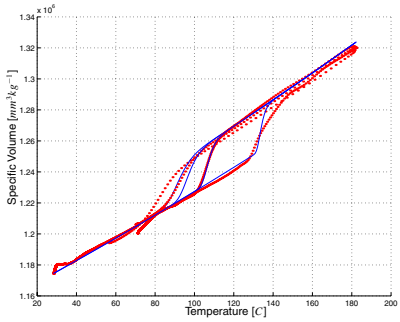


Fig. 2 *Data on the number of spherulites N (left) and crystal growth rate G (right) of the iPP K2Xmod.*

Results

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



$T_{ref} = 273$		$[K]$
$V_\infty = 0.16$		$[-]$
$\frac{\delta(1/v_a)}{\delta T} = -61e^{-5}$		$[m^3kg^{-1}K^{-1}]$
$\frac{\delta(1/v_c)}{\delta T} = -50e^{-5}$		$[m^3kg^{-1}K^{-1}]$
$v_a\|_{T_{ref}} = 1.1765e^6$		$[m^3kg^{-1}]$
$v_c\|_{T_{ref}} = 1.0526e^6$		$[m^3kg^{-1}]$

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.

References:

[1] P. Zoller, P. Bolli, V. Pahud, and H. Ackermann. Apparatus for measuring pressure-volume-temperature relationships of polymers to $350^o c$ and $2200kg/cm^2$. *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.