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Relation between *PVT* measurements and linear viscosity in isotactic and syndiotactic polypropylenes

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Abstract

Pressure–Volume–Temperature (*PVT*) data of an isotactic and a syndiotactic PP are fitted to a modification of the Simha–Somcynsky equation of state (S–S), to calculate characteristic parameters, such as V^*, T^*, P^* and the solubility parameter δ. The hole fraction of the S–S model and the free volume are deduced from these parameters. The application of a modified Doolittle equation and a modified Berry–Fox equation to estimate viscosity, leads to extract novel conclusions on the differences between both types of PPs. An equation which accounts for the effect of temperature on the characteristic ratio of syndiotactic PP is presented.

Keywords: Characteristic ratio; Free volume; Syndiotactic polypropylene

1. Introduction

The knowledge of *PVT* behaviour is important, because many features of polymers depend on pressure and on the associated changes in volume. Besides the technical importance of determining the specific volume as a function of pressure and temperature in injection moulding process, *PVT* data allow to obtain reduced equations of state, cohesive energy, internal pressure and free volume, contemplated in the theories of molecular liquids. The pioneering work of Batschinski [1] showing the variation of viscosity with specific volume is one of the basis for well known papers, like those of Doolittle [2], Williams et al. [3] and Hildebrand [4], devoted to correlate viscosity and free volume. This subject currently deserves a substantial interest in the field of polymer melts [5–12].

In the particular case of polypropylene (PP), the recent use of metallocene or single site catalysts lets to produce highly syndiotactic samples. The almost perfect stereoregularity reached, gives rise to a peculiar viscoelastic response; in particular syndiotactic polypropylenes (sPP) exhibit Newtonian or linear viscosities about 10 times larger than isotactic samples (iPP) [13,14].

On the other hand, few papers refer to *PVT* measurements of syndiotactic PPs. Some experimental *PVT* data are given in the literature [15–18], but, as far as we know, only two papers [19,20] take advance of a equation of state model to obtain the characteristic parameters P^*, T^* and V^*, from which the cohesive energy and the solubility parameter δ can be determined: in both papers the Flory–Orwoll–Vrij free volume theory [21] is used. We also remark that a PALS (positron annihilation lifetime spectroscopy) study [22] gives data of the mean local free volume of syndiotactic PP, although these are not combined with *PVT* data.

This work is organised as follows: *PVT* data of an isotactic and a syndiotactic PP are analysed using the Simha–Somcynsky equation of state [23], modified by Utracki and Simha [10], which allows to calculate V^*, T^*, P^* and δ. From this model we also obtain other thermodynamical parameters, such as the hole fraction of the Simha–Somcynsky [23] model and the free volume. Both the parameters are used to determine the linear

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viscosity, applying, respectively, a modified Doolittle equation [12] and a modified Berry−Fox equation [11]. Novel conclusions on the differences between both types of PPs are attained from the application of these models.

2. Experimental part

A syndiotactic polypropylene from Fina, as well as a commercial isotactic polypropylene provided by Repsol YPF have been investigated. The molecular characteristic of the samples are presented in Table 1.

PVT behaviour was measured in a *PVT* apparatus of the piston die technique made by Haake. Measurements were carried out using the isobaric cooling mode procedure in the pressure range of 200−1600 bar using a cooling rate of 5 °C/min. The test was repeated for number of times necessary to make sure a volume difference ≤0.05% between two measurements.

Dynamic or oscillatory measurements in the linear viscoelastic regime were carried out in a ARES (Advanced Rheometric Expansion System) in the temperature range 130−190 °C at ambient pressure. The experimental error was checked by repeating the measurements at least four times: the repeatability was within 3%.

The real part of the complex viscosity η', plotted as a function of frequency, at different temperatures, is displayed in Fig. 1. The well-known Briedis−Faiteĺson model was used to calculate the Newtonian viscosity η_0:

$$\eta' = \eta_0/(1+(\omega\tau_0)^{\alpha}) \quad (1)$$

where η_0 is the linear or Newtonian viscosity, τ_0 a relaxation time and α a non-linearity index. The standard deviation was $\sigma < 0.005$.

Table 1
Molecular characteristics of the investigated polypropylenes

	M_w (g/mol)	M_w/M_n	mmmm%	rrrr%
iPP	22,4300	4.2	93	
sPP	18,1300	3.95		77

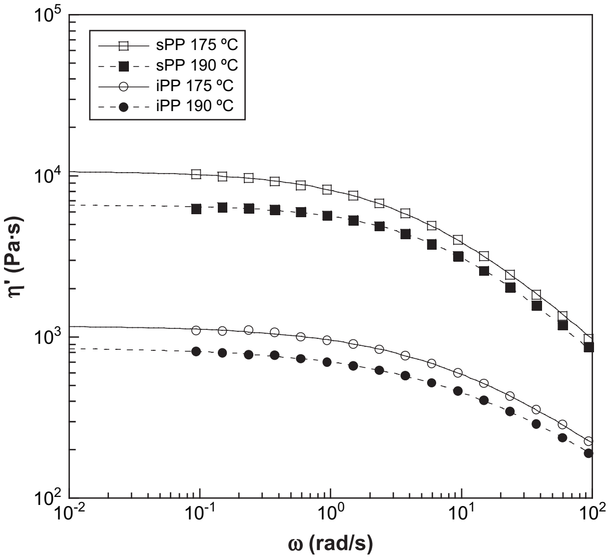

Fig. 1. The real part of the complex viscosity as a function of frequency at $T = 175$ and 190 °C (circles are used for iPP and squares for sPP). The lines correspond to the Briedis−Faiteĺson model (see Section 2). Similar results are obtained for the rest of temperatures ranging from 130 to 190 °C.

3. Results and discussion

Fig. 2 shows the specific volume as a function of temperature, at a constant pressure $P = 400$ bar. The glass transition temperature and the crystallization process of both, isotactic and syndiotactic PPs, are observed. For the purposes of our work, the relevant data are those obtained in the molten state. Similar results are obtained in isobaric cooling experiments at different pressures (see Section 2), which allow to determine the specific volume at atmospheric pressure, via extrapolation of the Tait equation [24].

The specific volume at atmospheric pressure as a function of temperature is included in the inlet of Fig. 2. Experimental data are fitted to Simha−Somcynsky approximation at zero reduced pressure [23]:

$$\ln \tilde{V} = a_0 + a_1\tilde{T}^{3/2} \quad (2)$$

where $\tilde{V} = V/V^*$ and $\tilde{T} = T/T^*$ are reduced variables defined according to the equation of state models for dense liquids [21]. According to recent results obtained by Utracki and Simha [10], the following values are taken for the adjustable parameters: $a_0 = -0.10346$ and $a_1 = 23.854$. The characteristic volume V^* and the characteristic temperature T^*, obtained from the fitting to experimental values of Fig. 2, are presented in Table 2. The Simha−Somcynsky equation of state in the full range of pressures is used to evaluate the characteristic pressure P^*, also shown in Table 2:

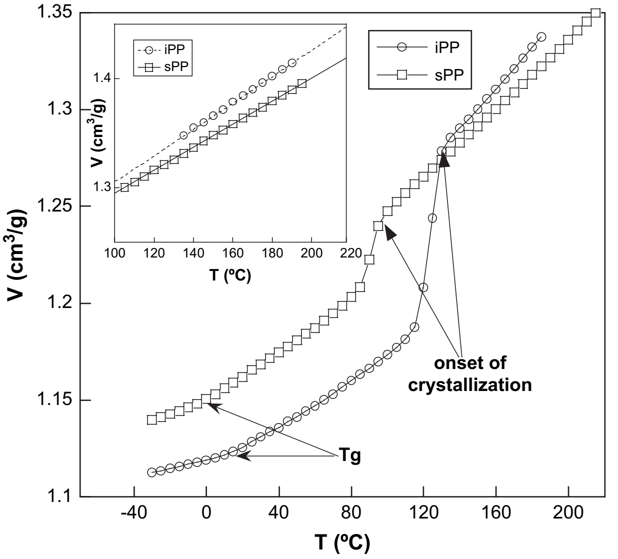

Fig. 2. The specific volume as a function of temperature at a pressure of 40 MPa. The glass transition and crystallization temperatures are marked. The specific volume at the atmospheric pressure, determined via extrapolation of the Tait equation and adjusted to the Simha−Somcynsky model (see Section 3), is shown in the inlet. Same symbols as in Fig. 1.