

On Relationship between PVT and Rheological Measurements of Polymer Melts

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ABSTRACT

The relation between PVT and rheological measurements of several polymer melts has been taken into investigation. A Doolittle relationship was modified and tested for connection of pressure-temperature dependent viscosities and PVT data. Proposed interconnection proved to be a good tool for linearization of PVT and rheological data.

INTRODUCTION

Melt viscosity is a crucial property in polymer processing. Its dependence on deformation rate as well as on temperature has been thoroughly described and considered in formulations and predictions of the flow behaviour. Pressure effects, on the other hand, are usually neglected, in spite of a large number of papers published over a long period. Possible reasons for such a situation are rather complicated determination and evaluation of pressure affected viscosity.

Almost a century ago Batchinski¹ presented a correlation between free space and flow properties of low-molecular-weight liquids. This approach was later extended to polymers by Doolittle^{2,3} by relation:

$$\eta = A_0 \exp \left(A_1 \left(\frac{v_0}{v_f} \right) \right) \quad (1)$$

where η is coefficient of viscosity, v_0/v_f means reciprocal relative free space

(considered to be a fractional rise in volume resulting from expansion of the liquid without change of phase), and A_0, A_1 are empirical constants.

“Free space” is currently interpreted in several ways. In view of these various interpretations Utracki^{4,5} modified Eq. 1 to a semi-empirical relation between temperature-dependent zero-shear viscosity, η_0 , and hole fraction, h :

$$\ln \eta_0 = B_0 + \frac{1}{h + B_2} B_1 \quad (2)$$

where B_0, B_1 are adjustable parameters and B_2 means an empirical value representing the excess of free volume required for linearization of the experimental data.

The term “hole fraction”, expressed by minimization of the Helmholtz free energy, was introduced by Simha and Somcynsky in the lattice-hole theory⁶ and it was evaluated through fitting PVT data into Simha-Somcynsky equation of state (SS EOS). This fit enables from PVT equilibrium melt data beside evaluation of scaling material parameters P^*, V^*, T^* (containing molecular characteristics of the system) also estimation of free volume fraction y .

Zero-shear viscosity, η_0 , used in former studies^{4,5} is difficult to measure during processing and further, the method of its extracting from the measured shear rate dependent viscosity might be a source of error^{5,7}. Therefore, it has been recently shown⁷ that η_0 can be effectively replaced

by a constant-stress viscosity, η_c , which can be obtained directly from experimental data.

The possibility to connect PVT data and pressure-temperature (P - T) dependent flow behavior thus offers an attractive way of viscosity estimation. Nevertheless, obtaining empirical coefficients in Eq. 2 from such a complex fitting seems to be a limiting factor for applying the obtained results into realistic process simulations.

The intention of this paper is to outline a possibility to estimate pressure influenced viscosity from the correlation of PVT and temperature dependent flow data. As the experimental background for this investigation, P - T dependent rheological⁸ and PVT data of various polymer melts (polyolefins, PS, and PC) were employed.

EXPERIMENTAL

Materials

The following injection molding grades of commercially available polymers were employed in the research:

- high-density polyethylene, **HDPE**
($M_w/M_n=3.12$, $T_m=134^\circ\text{C}$, $T_c=120^\circ\text{C}$),
- low-density polyethylene, **LDPE1**
($M_w/M_n=8.62$, $T_m=110.2^\circ\text{C}$,
 $T_c=100.2^\circ\text{C}$),
- low-density polyethylene, **LDPE2**
($M_w/M_n=6.49$, $T_m=109.4^\circ\text{C}$,
 $T_c=99.4^\circ\text{C}$),
- linear low-density polyethylene, **LLDPE**
($M_w/M_n=2.98$, $T_m=120^\circ\text{C}$, $T_c=110^\circ\text{C}$),
- polypropylene, **PP**
($M_w/M_n=3.21$, $T_m=160^\circ\text{C}$, $T_c=116^\circ\text{C}$),
- polystyrene, **PS**
($M_w/M_n=2.75$, $T_g=86^\circ\text{C}$),
- polycarbonate, **PC**
($M_w/M_n=2.26$, $T_g=117^\circ\text{C}$).

PC pellets were used predried; Memmert VO 500 vacuum drier was utilized for this purpose.

Rheological measurements

Rheological properties were measured using capillary rheometer (Göttfert 2001, Germany) modified by a backpressure device, which enabled evaluation of the pressure effect on viscosity⁸, and rotational rheometer (Rheometric Scientific ARES, United Kingdom) of 25-mm parallel-plate geometry. The more exact description of the capillary rheometer modified by an additional chamber can be found in⁸.

While for the determination of temperature sensitivity the tests were carried out at ambient pressure in steps of 20°C and range of 60°C (except of three measurements in steps of 10°C for PC), pressure effect was determined from measurements at various pressure levels (up to 70 MPa) at three constant temperatures. Using commercially available Compuplast software Flow 2000 the White-Metzner model modified by Barnes and Roberts⁹ was employed to fit the measured temperature and pressure dependent shear viscosity. The pressure and temperature effect was evaluated through coefficients β (GPa^{-1}) and α ($^\circ\text{C}^{-1}$), respectively, in this way.

The example of flow data supplemented by fits are shown in Fig.1.

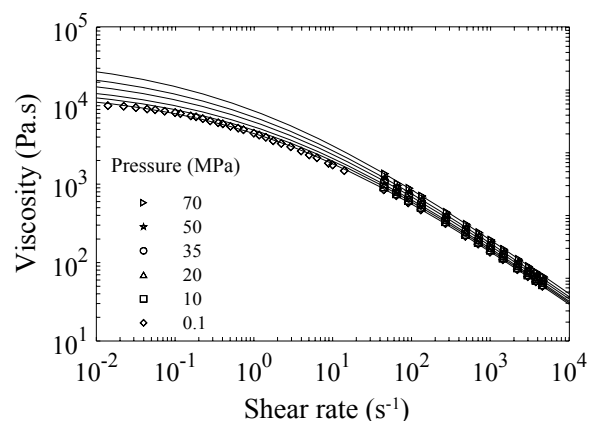


Figure 1. Pressure dependent shear viscosity vs. strain rate curves of LDPE1 at 170°C together with the modified White-Metzner model fit.

PVT experiments

PVT measurements were carried out on a fully automated PVT instrument (pvT 100 SWO, Germany). The data was collected in the pressure range of 15 to 70 MPa in steps of 5 MPa. Under isobaric conditions polymer melts were cooled at the rate of 2 K.min⁻¹. The temperature range, covering rheological testing temperatures, was chosen individually for each tested polymer. Specific volumes at the atmospheric pressure were determined via extrapolation by the help of the Tait equation using standard utility software (pvT, SWO Polymertechnik, Germany). The obtained values were further employed in fitting into SS EOS. The analysis of PVT data in a full range of pressure was carried out through an analytical approximation of the SS EOS proposed by Simha et al.¹⁰ and modified by Utracki and Simha¹¹. The accuracy of fitting LDPE1 can be seen in Fig. 2, where fits and measured data are shown only at the same pressure levels as the viscosity data was evaluated in order to avoid figure crowding.

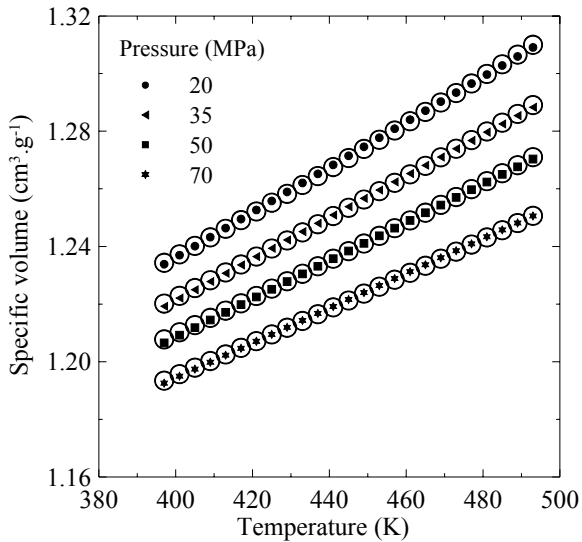


Figure 2. Specific volume of LDPE1 at various pressures as a function of temperature. The points represent experimental data, the surrounding circles mean values calculated through analytical approximation.

RESULTS AND DISCUSSION

Firstly, transformed Doolittle equation^{2,3}, presuming according to Utracki⁷ that coefficient of viscosity is proportional to viscosity constant-stress viscosity $\eta_c(P,T)$, or zero-shear viscosity $\eta_0(P,T)$, and relative free space is substituted by hole fraction $h(P,T)$, can be written:

$$\ln \eta = C_1 + C_2 \left(\frac{1}{h} \right) \quad (3)$$

Nevertheless, as it is clear from Fig. 3, it is not possible, with any adjustment of constants C_1 , and C_2 , to achieve any satisfying master curve if viscosity is directly related to the hole fraction. Therefore we modified Eq. 3 by the correcting factor, $h'(P,V,T)$, into the relation guaranteeing uniform and smooth master curves of all materials used (see Fig.

$$\ln \eta = C_1 + C_2 \left(\frac{h'}{h} \right)^3 \quad (4)$$

where C_1 is parameter equal to appropriate viscosity under condition of unlimited free volume, C_2 is factor proportional to activation energy¹², and h' is equal to:

$$h' = 1 - hC_3\tilde{Z} \quad (5)$$

where $\tilde{Z} = \frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{PV}{T} \cdot \frac{T^*}{P^*V^*}$ stands for reduced compressibility factor and C_3 is an empirical constant. The acceptable level of the Correlation Coefficient of Eq. 4 (Table 1,2 and 3) is observed when C_3 is equal to a unique constant value of 0.25.

Table 1. Values of parameters C_1 , C_2 , and CC evaluated from Eq. 4 for all tested materials at η_c ($\sigma_c=90$ kPa).

Material	$\ln C_1$ (-)	C_2 (-)	CC ² (-)
LLDPE	2.1886	0.394	0.9826
HDPE	3.6389	0.3703	0.9892
LDPE1	0.2799	0.8128	0.9877
LDPE2	0.4311	0.6363	0.9743
PP	-2.4891	1.062	0.986
PC	-6.2249	2.249	0.96
PS	-12.037	2.8318	0.9829

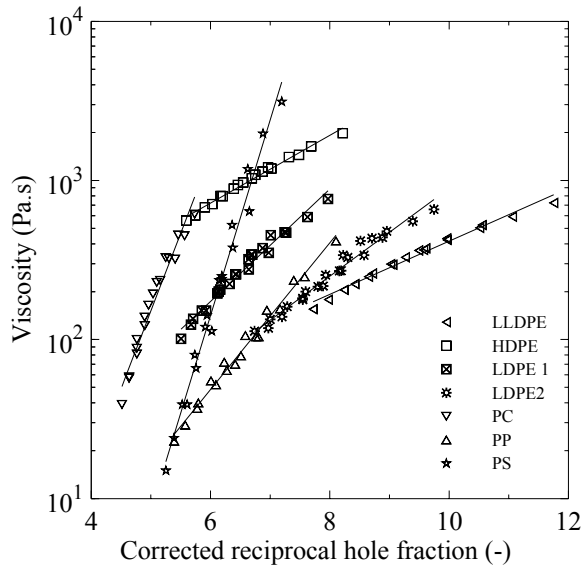


Figure 3. Constant-stress viscosity ($\sigma_c = 90$ kPa) as a function of the corrected reciprocal hole fraction of investigated materials at various pressures and temperatures conditions according to Eq. 4.

Values of parameter C_1 are primarily given by polymer characteristic and directly affected by shear stress at which η_c is determined (Table 2). The magnitudes of this parameter arise as this stress value is declined. The highest value of C_1 is obtained for η_0 .

Table 2. Values of parameters C_1 , C_2 , and CC of Eq. 4 evaluated for LDPE at different shear stresses.

Shear stress (Pa)	C_1 (-)	C_2 (-)	CC ² (-)
0	1.7946	1.0289	0.9929
45000	0.842	0.9236	0.989
90000	0.2799	0.8128	0.9877
120000	-0.54	0.7316	0.993

Magnitudes of C_2 parameter incoming from Eq. 2 are ranged as follows: PS>PC>PP>LDPE>LLDPE>HDPE. It is noteworthy, that this order corresponds to sequence of the pressure and temperature coefficients values taken from rheological measurements.

Very good linearization (see Table 1) of proposed relation for η_c was observed for all polyolefine types and PS having the simple polymer structure. Slightly lower

Correlation Coefficient, however still sufficient enough, was obtained for relatively complex molecules of PC. Also the master curves determined using η_0 (Table 3) proved very good validity for polymer melts tested in this study.

Table 3. Values of parameters C_1 , C_2 , and CC evaluated from Eq. 4 for all tested materials at η_0 .

Material	$\ln C_1$ (-)	C_2 (-)	CC ² (-)
LLDPE	3.2362	0.4614	0.9918
HDPE	5.6224	0.4101	0.9947
LDPE1	1.7946	1.0289	0.9929
LDPE2	2.9255	0.8169	0.987
PP	1.2828	1.0614	0.9954
PC	-5.9136	2.4823	0.9993
PS	-7.5255	2.9087	0.9953

As obvious from Fig. 4 the correcting factor, h' , decreases with pressure as well as with temperature. Nevertheless, the pressure effect is more distinguished. This factor, taking into account a distinct response of hole fraction and reduced compressibility factor at different conditions of pressure and temperature, corrects the corresponding calculated hole fraction, h .

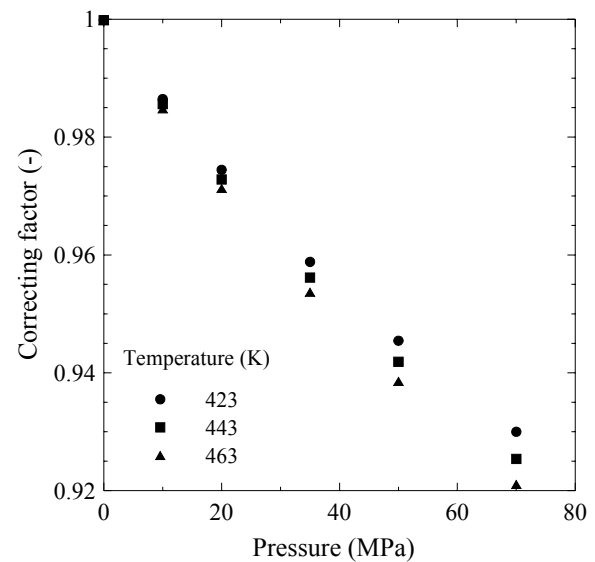


Figure 4. Pressure and temperature dependencies of the correcting factor, h' for LDPE1.

CONCLUSION

The presented relation (Eq. 4) indicates that the pressure effect on viscosity can be relatively accurately predicted only from the evaluation of temperature affected viscosity and PVT characteristics. The validity of the proposed equation has been successfully demonstrated on LDPE, LLDPE, HDPE, PP, PS, and PC.

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