BEATA KOWALSKA

Lublin University of Technology
ul. Nadbystrzycka 36, 20-618 Lublin, Poland
e-mail: beatak@fenix.lublin.pl

Processing aspects of *p-v-T* relationship

RAPID COMMUNICATION

Summary — The pressure-specific volume-temperature (*p-v-T*) relationship of polymers are important for the analysis of injection molding process. In the study, the *p-v-T* data for polypropylene Malen P type J-400 were measured during slow isobaric cooling. From the results of these measurements, the *p-v-T* data of the amorphous and semi-crystalline phases were obtained. The crystallization kinetics of the sample was determined using DSC measurements and the results have been fitted to the Nakamura-Hieber model to obtain equation parameters. Then the *p-v-T* behavior corresponding to the high cooling rate used in molding process was obtained.

Key words: injection molding, *p-v-T* relation, Tait equation, Nakamura-Hieber model.

PRZETWÓRCZE WYKORZYSTANIE ZALEŻNOŚCI *p-v-T*

Streszczenie — Znajomość zależności ciśnienie-objętość właściwa-temperatura (*p-v-T*) dotyczących polimerów jest istotna w analizie procesu wtryskiwania. W ramach tej pracy wyznaczono zmiany *v* podczas powolnego izobarycznego ochładzania polipropylenu (Malen P typ J-400) stosując różne wartości ciśnienia z przedziału 0,1—160 MPa (rys. 1). Otrzymane wyniki opisano za pomocą równania Taita określając parametry dobierane odnoszące się do stanu ciekłego i stałego polimeru (tabela 1 i 2). Kinetykę krystalizacji próbek wyznaczano za pomocą pomiarów DSC (rys. 2), a wyniki opisano korzystając z modelu Nakamury-Hiebera (tabela 3). Za pomocą symulacji komputerowej określono zależność *p-v-T* odpowiadającą wysokim szybkościom chłodzenia polimeru, czyli takim jakie stosuje się w procesie wtryskiwania.

Słowa kluczowe: proces wtryskiwania, zależność *p-v-T*, równanie Taita, model Nakamury-Hiebera.

In recent years, the injection molding process has been widely studied experimentally and theoretically [1, 2]. The main purpose of these studies was to find the effect of molding conditions on the properties of the injection molding parts [3, 4]. The pressure-specific volume-temperature (*p-v-T*) relationships of polymers are important for the analysis of this process. Traditionally the *p-v-T* data are obtained at slow cooling rates, quite different that those in the injection molding process. In the study the *p-v-T* data at cooling rate characteristic for injection molding (fast-cool *p-v-T* data) were obtained.

EXPERIMENTAL

Material

The polymer used in the research was homopolymer — isotactic polypropylene, trade name Malen P type J-400, produced in Basell Orlen Polyolefins in Poland. Basic properties of the polypropylene were: density 905—917 kg/m^3, *MFR* (230 ^{o}C; 2.16 kg) = 2.5—3.5 g/10 min, stress at break 32 MPa, elongation at break ≥600 %.

Methods of testing

In the study, the *p-v-T* data were measured using a pvT 100 machine (SWO Polymertechnik GmbH). The measurements were done starting above the melting temperature (250 ^{o}C) with a cooling rate 5 ^{o}C/min at various pressures. The method of measuring and a structure of the apparatus were described elsewhere [5].

The crystallization kinetics was studied using Netsch DSC-204 differential scanning calorimeter (Garätebau GmbH Thermal Analysis). The nonisothermal crystallization was carried out at constant cooling rates of 5, 10, 20 and 40 ^{o}C/min, starting above the melting temperature (230 ^{o}C). Pure indium was used as a reference material to calibrate the temperature scale and the melting enthalpy. The relative crystallinity (θ) which developed up to time *t* was defined to be the fractional area confined between the rate-time curve and the baseline.

RESULTS AND DISCUSSION

The measurements of specific volume (*v*) of investigated polypropylene during cooling with rate 5 °C/min were carried out for six different values of fixed pressure (*p*). The results are presented in Fig. 1. Because the polypropylene is a fast crystallizing polymer, the specific volume values measured at low temperature for heating and cooling runs are similar [6, 7]. The course of curves obtained using different pressure are alike, but we can observe that higher pressure results at higher temperature of melting displayed in specific volume jump in the graph. Using these results, the *p-v-T* data of the amorphous and semi-crystalline phases were obtained.

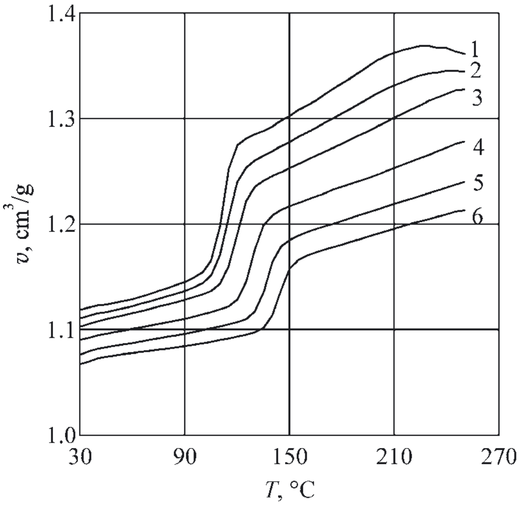

Fig. 1. Specific volume (v) of polypropylene Malen P type J-400 obtained at the isobaric cooling rate 5 °C/min; pressure: 1 — 0.1 MPa, 2 — 20 MPa, 3 — 40 MPa, 4 — 80 MPa, 5 — 120 MPa, 6 — 160 MPa

The empirical thermodynamic Tait equation of state was evaluated with regard to the prediction of *p-v-T* behavior of the polymer melts (fully amorphous) and solids (semi-crystalline). The *p-v-T* data (Fig. 1) allowed to determine the values of equation parameters. The Tait equation for solid phase was used in the following form [5, 8—10]:

$$v(p,T) = v_0\left[1 - C\ln\left(1 + \frac{p}{B}\right)\right] + v_p \tag{1}$$

where: $C = 0.0894$ — *empirical "universal" Tait constant,* v_0 — *specific volume at atmospheric pressure,* v_p — *specific volume at pressure p.*

The quantities occurring in eq. (1) can be determined by relations:

$$v_0 = b_1 + b_2\overline{T} \tag{2}$$

$$\overline{T} = T - b_5 \tag{3}$$

$$v_t = b_7\exp(b_8T - b_9p) \tag{4}$$

$$B = b_3\exp(-b_4\overline{T}) \tag{5}$$

Melting temperature T_m was evaluated by equation:

$$T_m = b_5 + b_6p \tag{6}$$

For the liquid state of polymer the Tait equation has the following form [6, 9—11]:

$$v(p,T) = v_0\left[1 - C\ \ln\left(1 + \frac{p}{B}\right)\right] \tag{7}$$

The Tait equation has been found to give good representation of the volume changes. The following errors were obtained for the whole range of measurements: standard deviation 0.48 %, maximum error 2.35 %. The values of fitting parameters b_1—b_9 estimated by approximation related to the solid state of polymer (with additional subscript "*s*") are shown in Table 1. The values of fitting parameters b_1—b_6 related to the liquid state (with additional subscript "*m*") are shown in Table 2.

Table 1. Values of Tait equation parameters for solid state of a polymer

Parameter	b_{s1}, m^3/kg	b_{s2} m^3/(kg °C)	b_{s3}, Pa	b_{s4}, 1/°C	b_{s5}, °C
Value	$1.495 \cdot 10^{-3}$	$3.382 \cdot 10^{-7}$	$3.97 \cdot 10^{8}$	$-5.7 \cdot 10^{-3}$	121,44
Parameter	b_{s6}, °C/Pa	b_{s7}, m^3/kg	b_{s8}, 1/°C	b_{s9},1/Pa	
Value	$1.51 \cdot 10^{-7}$	$1.3218 \cdot 10^{-4}$	0.2261	$4.226 \cdot 10^{-8}$	

Table 2. Values of Tait equation parameters for molten state of a polymer

Parameter	b_{m1} m^3/kg	b_{m2}, m^3/(kg · °C)	b_{m3}, Pa	b_{m4}, °C	b_{m5} 1/°C	b_{m6} °C/Pa
Value	$1.2817 \cdot 10^{-3}$	$8.1207 \cdot 10^{-7}$	$7.3849 \cdot 10^{7}$	$2.5 \cdot 10^{-3}$	121.44	$1.51 \cdot 10^{-7}$

To generate fast-cool *p-v-T* data, it is necessary to obtain *p-v-T* data for the amorphous and semi-crystalline (where relative crystallinity is 100 %) phases, using slow-cool measurements (Fig. 1). To obtain the amorphous phase behavior, the cooling data were extrapolated in the high-temperature range (above the melting temperature) down to room temperature.

For the semi-crystalline behavior, the cooling data in the low-temperature range were used. For the intermediate state of crystallinity, the specific volume was estimated using the following equation [6, 7]:

$$v = v_a(1 - \theta) + v_{sc}\theta \tag{8}$$

where: v_a — *specific volume of the amorphous phase and* v_{sc} — *that of the semi-crystalline state (100 % relative crystallinity),* θ — *relative crystallinity i.e. the crystallinity at time t to the crystallinity at the completion of crystallization.*

To determine crystallization kinetics of the polymer using DSC measurements, a nonlinear regression method was used for directly fitting nonisothermal crystallinity data using the Nakamura-Hieber model to obtain the equation parameters. This model can be represented by the following equations [12]:

$$\frac{d\theta}{dt} = nK(T)(1-\theta)\left(\ln\frac{1}{1-\theta}\right)^{\frac{n-1}{n}} \tag{9}$$

where: n — *constant equal 2.7 for isotactic polypropylene [11] and* K — *function of temperature in the following form [11].*

$$K(T) = \frac{1}{\exp\left(B_1 + B_2\tilde{T} + B_3\tilde{T}^2\right)} \tag{10}$$

where: $\tilde{T} = T - T_{sh}$, T_{sh} — *shift temperature according to the transition temperature at atmospheric pressure.*

The transition temperatures at different pressures are determined using *p-v-T* cooling data (Fig. 1). Using these data and equation

$$T_{sh} = B_4 p + B_5 p^2 \tag{11}$$

the fitting parameters B_4 and B_5 were determined.

The fitted values of parameters B_1—B_5 are listed in Table 3.

Table 3. Values of equation (10) and (11) parameters for polypropylene Malen P

Parameter	B_1	B_2 1/°C	B_3 1/(°C)^2	B_4 °C/MPa	B_5 °C/(MPa)^2
Value	9.3596	-0.2964	$1.9 \cdot 10^{-3}$	$1.157 \cdot 10^{-1}$	$-5.252 \cdot 10^{-5}$

The relative crystallinity versus temperature at atmospheric pressure, is shown in Fig. 2, where the experimental data are shown as symbols and the fittings are shown as the curves.

The cooling history for the selected point of the molding has been obtained using the simulation of injection molding process by means of simulation program Moldflow Plastics Insight ver. 4.1. At each instant along the cooling history the values of specific volume of amorphous (v_a) and semi-crystalline phases (v_{sc}) were calculated. At that time the crystallinity, using the Nakamura-Hieber equation, was obtained. Using v_a, v_{sc} and crystallinity values, the specific volume (v) at that instant was calculated [eq. (8)]. The fast-cool data thus generated for polypropylene are shown in Fig. 3. Values of Tait equation parameters obtained at fast cooling of a polymer are shown in Table 4.

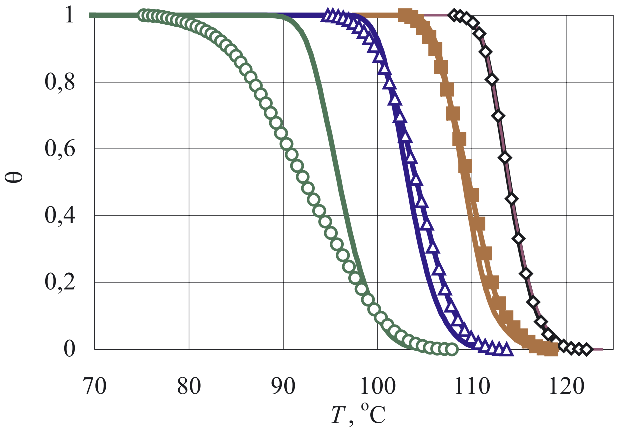

Fig. 2. Relative crystallinity (θ) versus temperature (T) for polypropylene Malen P type J-400 measured using DSC (symbols connected with line) and estimated by Nakamura- -Hieber equation (curves) at different cooling rates (◇ — 5 °C/min, ■ — 10 °C/min, Δ — 20 °C/min, ○ — 40 °C/min)

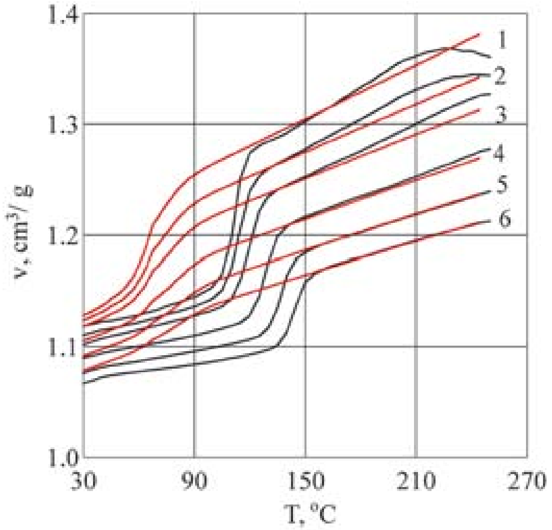

Fig. 3. Comparison of p-v-T diagrams at slow (black lines) and a fast (red lines) polymer cooling; curves mark as in Fig. 1

Table 4. Value of Tait equation parameters for solid state obtained at fast cooling rate of a polymer

Parameter	b_{s1} m^3/kg	b_{s2} m^3/(kg °C)	b_{s3}, Pa	b_{s4}, 1/°C	b_{s5}, °C
Value	$1.153 \cdot 10^{-3}$	$3.9 \cdot 10^{-7}$	$4.05 \cdot 10^{8}$	$5.5 \cdot 10^{-3}$	95.12
Parameter	b_{s6}, °C/Pa	b_{s7}, m^3/kg	b_{s8}, 1/°C	b_{s9}, 1/Pa	
Value	$1.51 \cdot 10^{-7}$	$9.427 \cdot 10^{-4}$	0.0934	$2.18 \cdot 10^{-8}$	

As can be seen from Fig. 3, the transition temperature shifts down 26 °C. The specific volume in the solid state increases with increasing cooling rate. It is clear that cooling rate has a decisive influence on *p-v-T* behavior.

It is necessary to use fast-cool *p-v-T* data in the simulations of injection molding process or process optimization calculations, especially for semi-crystalline polymers.

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