

Analysis of equations of state for polymers

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Abstract

In the literature there are several studies comparing the accuracy of various models in describing the PvT behavior of polymers. However, most of these studies do not provide information about the quality of the estimated parameters or the sensitivity of the prediction of thermodynamic properties to the parameters of the equations. Furthermore, there are few studies exploring the prediction of thermal expansion and compression coefficients. Based on these observations, the objective of this study is to deepen the analysis of Tait, HH (Hartmann-Haque), MCM (modified cell model) and SHT (simplified hole theory) equations of state in predicting the PvT behavior of polymers, for both molten and solid states. The results showed that all equations of state provide an adequate description of the PvT behavior in the molten state, with low standard deviations in the estimation of parameters, adequate sensitivity of their parameters and plausible prediction of specific volume, thermal expansion and isothermal compression coefficients. In the solid state the Tait equation exhibited similar performance to the molten state, while HH showed satisfactory results for amorphous polymers and difficulty in adjusting the PvT curve for semicrystalline polymers.

Keywords: equation of state, PvT behavior, polymer.

1. Introduction

The study of the thermodynamic behavior of polymers is essential to analyze the physical transformations that occur during processing, *e.g.* injection molding or extrusion, and to predict the properties of the final products. Polymers in melt state or in solution can be represented correctly by an equation of state (EoS) because these can be considered equilibrium states for polymers. Conversely, the solid state is at least one quasi-equilibrium state, because the properties depend on the conditions of solidification, as the cooling rate and pressure, which difficulties their description by means of EoS^[1].

Numerous equations of state have been developed to describe the PvT (pressure-volume-temperature) behavior of polymers. In literature, there are several studies comparing the fitting accuracy of various models for PvT data of polymers^[1-7]. These studies are focused mainly in the analysis of the fitting accuracy of the specific volume in the molten state, employing usually the method of least squares^[2,3,6,8-20] for the parameter estimation step. They showed that the theoretical equations based on cell-and-hole models and the Tait and the Hartmann-Haque (HH) empirical equations are those which provide more accurate fitting of the experimental data.

On the other hand, little information is available in the literature on at least two important aspects that are essential for the use of the referred equations in process simulation: quality of the estimated parameters as a function of the model employed and fitting accuracy of the models for thermal expansion and isothermal compression coefficients.

The isobaric thermal expansion coefficient (β) and isothermal compressibility (κ) are defined by:

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P \quad (1)$$

$$\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T \quad (2)$$

where the negative sign indicates the volume decrease with pressure increase^[21].

These coefficients are important for the simulation of polymer processing operations, because they are present in the governing equation of energy conservation. However, to the best of our knowledge, the only studies on their prediction from EoS are those of Utracki^[22,23], in which the prediction of thermal expansivity and compressibility by hole models is analyzed.

Based on these observations, the objective of this study is to deepen the analysis of Tait, HH, MCM (modified cell model) and SHT (simplified hole theory) equations of state in prediction of PvT behavior of polymers, in both molten and solid physical states. The EoS were analyzed with respect to: (i) quality in the estimation of its parameters by the method of least squares, (ii) sensitivity of their predictions to each of its parameters, (iii) quality of the prediction of the specific volume, and (iv) quality of the prediction of isobaric thermal expansion coefficient and isothermal compressibility.

2. Equations of State Analyzed

2.1 Tait equation of state

This equation is purely empirical, and was originally proposed for water. Presently, through various modifications, it is applied to a wide variety of substances, being possibly one of the equations of state most used to model the PvT behavior of polymers^[3]. For some authors, it is not a true equation of state, but an isothermal compressibility model

(i.e., a volume-pressure relationship). Tait equation can be written as^[3]:

$$v(T, P) = v_o(T) \left[1 - C \ln \left(1 + \frac{P}{B(T)} \right) \right] + v_l(T, P) \quad (3)$$

where for polymers in the molten state, i.e., above the liquid-solid transition temperature:

$$v_o = b_{1m} + b_{2m} (T - b_5) \quad (4a)$$

$$B(T) = b_{3m} \exp[-b_{4m}(T - b_5)] \quad (4b)$$

$$v_l(T, P) = 0 \quad (4c)$$

and for polymers in solid state, i.e., below the liquid-solid transition temperature

$$v_o = b_{1s} + b_{2s} (T - b_5) \quad (5a)$$

$$B(T) = b_{3s} \exp[-b_{4s}(T - b_5)] \quad (5b)$$

$$v_l(T, P) = b_7 \exp\{[b_8(T - b_5)] - (b_9 P)\} \quad (5c)$$

The liquid-solid transition temperature, which is the glass transition temperature for amorphous polymers and the melting or crystallization temperature for semicrystalline polymers, can be calculated by

$$T_l(P) = b_5 + b_6 P \quad (6)$$

In these equations, v is the specific volume of the polymeric material; the coefficient C is a constant equal to 0.0894; v_o is the specific volume at zero pressure; v_l is the specific volume corresponding to crystalline phase; B is the sensitivity to pressure of material; b_1 at b_9 are parameters of model, obtained by fitting of PvT diagram. The parameters b_{1m} to b_{4m} and b_{1s} to b_{4s} describe the dependence on pressure and temperature in the molten and the solid state, respectively; b_5 and b_6 are parameters that describe the change of transition temperature with pressure; b_7 to b_9 are particular parameters of semicrystalline polymers that describe the form of the state transition^[24].

2.2 HH equation of state

Hartmann and Haque^[10] developed an empirical equation of state combining the thermal pressure function of Pastine and Warfield, the zero-pressure isobar presented by Somcynsky and Simha, and the empirical dependence of volume with the thermal pressure. HH EoS describes the PvT behavior of polymers in the molten and solid states. It is given by:

$$\tilde{P}\tilde{v}^5 = \tilde{T}^{3/2} - \ln\tilde{v} \quad (7)$$

where the dimensionless variables \tilde{P} , \tilde{v} and \tilde{T} for molten polymers are defined as:

$$\tilde{P} = \frac{P}{B_{0m}}; \quad \tilde{v} = \frac{v}{v_{0m}}; \quad \tilde{T} = \frac{T}{T_{0m}} \quad (8)$$

and for solid polymers as:

$$\tilde{P} = \frac{P}{B_{0s}}; \quad \tilde{v} = \frac{v}{v_{0s}}; \quad \tilde{T} = \frac{T}{T_{0s}} \quad (9)$$

where B_0 , v_0 and T_0 are the characteristic parameters. T_0 and v_0 are defined as temperature and specific volume, respectively, extrapolated to zero pressure, while B_0 is identified as the isothermal bulk modulus extrapolated to zero temperature and pressure.

2.3 MCM equation of state

The modified cell model equation of state was developed by Dee and Walsh^[2], starting from the formalism presented by Prigogine et al.^[25]. In the cell model, the compressibility and thermal expansion of the structure are explained only by changes in the cell volume. Dee and Walsh^[2] introduced a numerical factor that scales the hard-core cell volume in the free volume term, disconnecting the theory from the specific geometry. This factor, q , was found to be constant for numerous polymers and equal to about 1.07. MCM EoS can be written as:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 0.8909q} - \frac{2}{\tilde{T}} \left(\frac{1.2045}{\tilde{v}^2} - \frac{1.011}{\tilde{v}^4} \right) \quad (10)$$

The reduced parameters \tilde{P} , \tilde{v} and \tilde{T} are defined as:

$$\tilde{P} = \frac{P}{P^*}; \quad \tilde{v} = \frac{v}{v^*}; \quad \tilde{T} = \frac{T}{T^*} \quad (11)$$

where P^* , v^* and T^* are characteristic parameters.

2.4 SHT equation of state

The hole theory introduces empty cells in the cell model^[26], based on the concept that the thermal expansion of liquid is mainly due to holes (h), i.e., the empty cells, while volume changes of the cells are also allowed. Zhong et al.^[27] simplified the hole theory through the use of an exponential function to the fraction of occupied cells. SHT EoS is derived as:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{(y\tilde{v})^{1/3}}{(y\tilde{v})^{1/3} - 0.9165y} + \frac{2y}{\tilde{T}(y\tilde{v})^2} \left(\frac{1.1394}{(y\tilde{v})^2} - 1.5317 \right) \quad (12)$$

where \tilde{P} , \tilde{v} and \tilde{T} are reduced parameters defined by Equation 11, y is the fraction of occupied cells, being defined by:

$$y = 1 - e^{-0.52/\tilde{T}} \quad (13)$$

3. Methodology

The experimental PvT data used in this work were taken from the literature^[7,21,28-32] as shown in Table 1. For each polymer, the available data were subdivided in two sets: one used for parameter estimation (DATA1) and other for validation (DATA2). The construction of these subsets was based on random selection of points.

Differently from specific volume data, the isobaric thermal expansion and isothermal compression coefficients are hard to obtain experimentally. Thus, the EoS were only qualitatively analyzed with relation to the prediction of these

Table 1. Relevant information about the experimental PvT data used^a.

Polymer	Amorphous						Semicrystalline					
	PS	PC	PMMA	PCHMA	PnBMA	PoMS	iPP	LPE	PEO	PA6	PLA	PBS-B
Reference	28	29	30	30	30	31	29	32	7	21	32	32
Pressure range (MPa)	0.1-200	0.1-200	0.1-180	0.1-180	0.1-180	0.1-180	0.1-200	0.1-200	0.1-200	0.1-190	0.1-200	0.1-200
Temperature range (K)	280-468	313-603	353-423	357-453	285-355	302-470	313-573	313-493	313-493	364-586	313-493	313-493
Initial temperature of analysis (K)	468	313	353	357	285	302	313	313	313	364	313	313
Initial pressure of analysis (MPa)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Number of experimental points in solid state used for parameter estimation	33	26	36	30	29	25	28	41	27	35	56	16
Number of experimental points in molten state used for parameter estimation	28	30	20	26	22	26	25	29	43	17	21	20
Number of experimental points in solid state used for the analysis of the prediction accuracy	33	24	-	30	-	-	28	-	-	35	-	15
Number of experimental points in molten state used for the analysis of the prediction accuracy	28	32	-	26	-	-	24	-	-	17	-	19
Experimental data variance (σ_{exp}^2)	0.0003	0.001	0.0004	0.0004	0.0004	0.0004	0.001	0.002	0.002	0.0003	0.002	0.002

^aData obtained by the method of confining fluid in isothermal mode, except for polystyrene, for which the experiments were conducted in isobaric mod.

coefficients, taking as basis of comparison their theoretically expected behavior. The estimation of parameters was conducted by the least squares method, using the *lsqnonlin* function already implemented in MatLab® software, with the following objective function (*FObj*):

$$FObj = \sum_{i=1}^n (\hat{v}_i - v_i)^2 \quad (14)$$

where $(\hat{v}_i - v_i)$ is the residual between predicted (\hat{v}_i) and experimental (v_i) values and n is the number of points considered.

The parameters of the equations of state were estimated simultaneously, as suggested by Hartmann and Haque^[10]. For the Tait EoS, firstly, b_5 and b_6 were estimated from data of transition temperature at different pressures. The melt parameters (b_{1m} , b_{2m} , b_{3m} and b_{4m}) and solid parameters (b_{1s} , b_{2s} , b_{3s} , b_{4s} , b_7 , b_8 and b_9) were estimated separately from data corresponding to the respective states^[33]. Likewise, for HH EoS, the experimental data were divided into two states: molten and solid state. The parameters of the MCM and SHT EoS were estimated only with molten state data.

The quality of the estimated parameters for each model was analyzed in terms of their covariance matrix (V_α), evaluated using a routine developed in MatLab®, according the following expression^[34]:

$$V_\alpha = H_\alpha^{-1} G_\alpha \sigma_y^2 G_\alpha^T (H_\alpha^{-1})^T \quad (15)$$

where σ_y^2 is the experimental data variance, H_α is the Hessian matrix of *FObj*, and G_α is the matrix that represents the derivative of the gradient of *FObj* with relation to the experimental values v_i .

The normalized parameter sensitivity matrix was used to evaluate the sensitivity of the predictions of the considered EoS to parameter variations. The coefficients of this matrix are given by:

$$S_{ij}^* = \frac{\partial \hat{v}_i}{\partial a_j} \left(\frac{a_j}{\hat{v}_i} \right) \quad (16)$$

where a_j is the parameter of the equation analyzed. These coefficients were calculated using a MatLab® function, according to the following central-difference approximation:

$$S_{ij}^* = \frac{v_i(\alpha_j + h) - v_i(\alpha_j - h)}{2h} \left(\frac{\alpha_j}{v_i} \right) \quad (17)$$

with h equal to 10^{-4} . In this way, the parameter sensitivity of the specific volume predictions was analyzed in a wide temperature range, at different pressures, for polycarbonate and linear polyethylene.

To appraise the fit and prediction quality of each model, the mean relative deviation (MRD) and the regression coefficient (R^2) were calculated:

$$MRD = \frac{100}{n} \sum_{i=1}^n \frac{|v_i - \hat{v}_i|}{v_i} \quad (18)$$

$$R^2 = 1 - \frac{\sum_{i=1}^n (v_i - \hat{v}_i)^2}{\sum_{i=1}^n (v_i - \bar{v}_i)^2} \quad (19)$$

where \bar{v}_i is the arithmetic mean of experimental specific volumes.

Additionally, F-tests were performed to assess the suitability of the considered models. The value of F_0 used in the comparison with the critical value of F ($F_c = F$ distribution value corresponding to 95% confidence) was defined as the ratio between the model (σ_{eos}^2) and the experimental (σ_{exp}^2) variances, according to the following expression:

$$F_0 = \frac{\sigma_{eos}^2}{\sigma_{exp}^2} = \frac{\sum_{i=1}^n (v_i - \hat{v}_i)^2}{n - np} \frac{np}{\sigma_{exp}^2} \quad (20)$$

where np is the number of estimated parameters. The experimental variances are shown in Table 1.

4. Results and Discussion

4.1 Fitting and prediction of specific volume

As mentioned previously, the comparison of the EoS under analysis with relation to the fitting of specific volume data has already been extensively studied by other authors^[2,3,6,8-20]. Therefore, in the present work, the analysis corresponding to the fitting stage will be focused only in the quality of the estimated parameters, aspect for which there is little information available in the literature.

The values of parameters estimated from data set DATA1 and their respective standard deviations are presented in Tables 2 and 3, for the amorphous and semicrystalline polymers, respectively. The low values of the standard deviations indicate that the fitting were adequate. The parameters of equations of state showed a higher standard deviation for semicrystalline polymers, in both physical states. The fitting of Tait and HH EoS were better in molten state, both to amorphous and semicrystalline polymers. In general, Tait equation exhibited the lowest values of standard deviations (below 2%) except for the parameter b_6 in the cases of the polymers iPP and PLA, for which the linear dependence between transition temperature and pressure described by Equation 6 is not obeyed. For all equations of state, the greatest deviations were found for the parameters related to pressure, what can be explained by the wide range of pressure analyzed.

For the evaluation of the prediction capability of the studied models, calculations of specific volume for the conditions corresponding to each experimental data of data set DATA2 were performed using the values of parameters estimated with data set DATA1 (Tables 2 and 3). The values of F_0 , MRD and R^2 obtained are presented in Table 4, together with the respective values of F_c used in the F-test to 95% confidence. As can be seen in Table 4, all the four EoS provided predictions not significantly different from the experimental data ($F_0 < F_c$), showing their adequacy in the prediction of the PvT behavior of the considered polymers. It is observed that Tait equation exhibited the lowest relative deviation module mean and the highest regression coefficient in most cases. However, the other equations of state studied also presented satisfactory results, with values close to those obtained with Tait EoS. The only exception was in the prediction of specific volume of semicrystalline

Table 2. Estimated parameters (a_i) and percentage standard deviation (σ_{ai}) for amorphous polymers.

EoS	Parameter	PS		PC		PMMA		PCHMA		PnBMA		PoMS		Mean
		a_i	σ_{ai} (%)	a_i	σ_{ai} (%)	a_i	σ_{ai} (%)	a_i	σ_{ai} (%)	a_i	σ_{ai} (%)	a_i	σ_{ai} (%)	
Tait	b_{1m} (cm ³ /g)	0.9767	0.0015	0.8590	0.0025	0.8603	0.0024	0.9318	0.0017	0.9469	0.0014	1.0046	0.0013	0.0018
	b_{2m} (cm ³ /gK)	0.000506	0.0461	0.000553	0.0392	0.000511	0.1042	0.000596	0.0477	0.000628	0.0532	0.000547	0.0492	0.0566
	b_{3m} (MPa)	154.65	0.0672	151.39	0.1062	277.56	0.1512	161.98	0.0629	192.89	0.0998	184.57	0.0882	0.0959
	b_{4m} (1/K)	0.0030	0.2749	0.0034	0.2218	0.0075	0.6696	0.0052	0.1845	0.0047	0.4290	0.0062	0.2388	0.3364
	b_{1s} (cm ³ /g)	0.9748	0.0015	0.8575	0.0035	0.8625	0.0007	0.9303	0.0014	0.9479	0.0011	1.0045	0.0018	0.0017
	b_{2s} (cm ³ /gK)	0.000213	0.1116	0.000192	0.2435	0.000275	0.1665	0.000248	0.1118	0.000376	0.3084	0.000232	0.0996	0.1736
	b_{3s} (MPa)	275.87	0.0645	249.21	0.1005	257.75	0.0303	255.61	0.0486	223.53	0.0373	276.20	0.0649	0.0577
	b_{4s} (1/K)	0.0018	0.6080	0.0021	0.7384	0.0045	0.3877	0.0038	0.3082	0.0036	0.8858	0.00067	1.2603	0.6981
	b_5 (K)	370.86	0.0026	417.06	0.0059	375.30	0.0034	383.84	0.0030	296.66	0.0039	401.21	0.0028	0.0036
	b_6 (K/MPa)	0.3924	0.0211	0.2687	0.0885	0.3485	0.0692	0.2665	0.0441	0.2225	0.0528	0.3361	0.0350	0.0518
HH	B_{0m} (MPa)	2953.3	1.3157	3470.2	2.6453	5238.2	5.0184	3115.0	1.3573	3654.1	2.5917	3154.5	2.1292	2.5096
	v_{0m} (cm ³ /g)	0.8753	0.6226	0.7413	1.3425	0.7570	0.7592	0.8192	0.7058	0.8431	0.6388	0.8917	0.6503	0.7865
	T_{0m} (K)	1602.1	0.2884	1471.8	0.6255	1464.9	0.7126	1471.8	0.3327	1256.7	0.4040	1631.2	0.3724	0.4559
	B_{0s} (MPa)	4278.5	3.6067	3858.2	7.8331	3867.7	3.2444	4172.8	3.7264	3499.0	3.3230	4251.8	4.6353	4.3948
	v_{0s} (cm ³ /g)	0.9218	0.5102	0.8107	1.4375	0.8158	0.5568	0.8785	0.6056	0.8891	0.7577	0.9399	0.6413	0.7515
	T_{0s} (K)	2552.0	0.4872	2914.7	1.3898	2592.6	0.4136	2656.6	0.5196	1863.6	0.4846	2453.5	0.7396	0.6724
MCM	P^* (MPa)	532.04	0.4534	707.66	0.9018	1017.5	2.1312	594.83	0.8393	656.45	0.6733	616.17	0.9196	0.9864
	v^* (cm ³ /g)	0.8690	0.0822	0.7357	0.1447	0.7463	0.2813	0.8101	0.1353	0.8392	0.1177	0.8745	0.1612	0.1537
	T^* (K)	6933.9	0.3985	6441.5	0.5280	6178.8	1.1607	6298.7	0.5389	5427.0	0.5621	6704.6	0.6911	0.6466
SHT	P^* (MPa)	420.57	1.0068	675.78	2.1852	887.13	6.4028	518.74	2.1551	506.85	1.3689	577.23	4.3201	2.9065
	v^* (cm ³ /g)	0.9242	0.1769	0.7620	0.3835	0.7798	0.8736	0.8491	0.3381	0.8937	0.2329	0.9032	0.7175	0.4538
	T^* (K)	4009.2	0.8431	3353.9	1.3560	3311.9	3.4399	3425.4	1.3222	3168.3	1.1022	3429.9	2.7175	1.7968

Table 3. Estimated parameters (a_i) and percentage standard deviation (σ_{ai}) for semicrystalline polymers.

EoS	Parameter	iPP		LPE		PEO		PA6		PLA		PBS-B		Mean
		a_i	σ_{ai} (%)	a_i	σ_{ai} (%)	a_i	σ_{ai} (%)	a_i	σ_{ai} (%)	a_i	σ_{ai} (%)	a_i	σ_{ai} (%)	
Tait	b_{1m} (cm ³ /g)	1.3082	0.0021	1.2532	0.0022	1.2301	0.0018	1.0002	0.0030	0.8875	0.0043	0.8837	0.0035	0.0028
	b_{2m} (cm ³ /gK)	0.0010	0.0378	0.000957	0.0509	0.000932	0.0304	0.000659	0.0873	0.000712	0.1455	0.000622	0.0788	0.0718
	b_{3m} (MPa)	66.84	0.0438	93.68	0.0769	113.12	0.0577	132.00	0.0860	100.68	0.1041	152.55	0.1278	0.0827
	b_{4m} (1/K)	0.0048	0.1116	0.0046	0.2521	0.0044	0.1411	0.0029	0.5355	0.0047	0.5810	0.0040	0.4383	0.3433
	b_{1s} (cm ³ /g)	1.1804	0.0033	1.0669	0.0030	1.1666	0.0975	0.9600	0.0020	0.8553	0.0025	0.8361	0.0109	0.0199
	b_{2s} (cm ³ /gK)	0.000517	0.0743	0.000453	0.1063	0.000780	1.1831	0.000489	0.0396	0.000372	0.0695	0.000525	0.2850	0.2930
	b_{3s} (MPa)	110.82	0.0765	228.35	0.0825	173.63	1.3530	125.96	0.0496	148.00	0.0902	198.59	0.3480	0.3333
	b_{4s} (1/K)	0.0064	0.1556	0.0023	0.5972	0.0029	3.0337	0.0078	0.0830	0.0064	0.1984	0.0057	1.1048	0.8621
	b_5 (K)	452.86	0.0055	405.47	0.0061	365.09	0.0068	501.95	0.0020	440.44	0.0056	385.88	0.0064	0.0054
	b_6 (K/MPa)	0.0057	4.1917	0.2107	0.1129	0.2043	0.1164	0.0835	0.1127	0.0048	4.9477	0.1254	0.1897	1.6119
	b_7 (cm ³ /g)	0.3644	0.2083	0.4848	0.1569	0.0565	1.9711	0.0406	0.0709	0.0327	0.1187	0.0133	2.7994	0.8876
	b_8 (1/K)	0.1429	0.1600	0.2893	0.1153	0.0210	1.4194	0.0890	0.0718	0.4684	0.2048	0.1785	1.4186	0.5650
	b_9 (1/MPa)	0.1133	0.2824	0.0762	0.1072	0.0074	0.5776	0.0029	0.2204	0.0081	0.2998	0.0111	1.3604	0.4746
HH	B_{0m} (MPa)	1877.2	0.9060	2514.9	1.5167	2581.2	1.3639	4330.2	2.6157	3235.6	1.6826	3648.7	3.1454	1.8717
	v_{0m} (cm ³ /g)	1.0864	1.5161	1.0496	1.4684	1.0605	1.1865	0.8137	1.5780	0.7196	1.8242	0.7573	1.8053	1.5631
	T_{0m} (K)	1370.7	0.3162	1273.9	0.4684	1277.8	0.4502	1437.2	0.7388	1242.7	0.6546	1327.6	0.8649	0.5822
	B_{0s} (MPa)	2689.0	3.2847	5508.9	5.8402	5242.2	2.0723	5634.4	1.7457	4112.4	4.1033	6393.9	9.2255	4.3786
	v_{0s} (cm ³ /g)	1.0241	1.4413	0.9064	1.0336	0.9097	1.6756	0.7828	0.5857	0.7426	1.0285	0.6945	2.0437	1.3014
	T_{0s} (K)	1574.8	0.9417	1284.6	0.9761	830.57	0.5881	1396.3	0.3584	1576.0	0.9510	1170.2	1.4734	0.8815
MCM	P^* (MPa)	406.30	1.4660	497.88	1.7795	516.67	0.9554	882.19	1.3540	668.30	3.7141	717.11	1.6693	1.8231
	v^* (cm ³ /g)	1.0656	0.1957	1.0435	0.2740	1.0492	0.1417	0.8110	0.1867	0.7141	0.5219	0.7510	0.2474	0.2612
	T^* (K)	5825.1	0.5207	5601.7	0.8363	5521.4	0.4740	6392.2	0.4969	5457.8	1.3499	5774.1	0.8529	0.7551
SHT	P^* (MPa)	445.72	3.5869	509.45	4.7145	509.45	2.4290	922.41	3.4977	714.20	9.5570	678.21	4.2874	4.6788
	v^* (cm ³ /g)	1.0880	0.5217	1.0730	0.7374	1.0836	0.3770	0.8285	0.4958	0.7288	1.3734	0.7783	0.6555	0.6935
	T^* (K)	2929.4	1.3930	2864.6	2.2278	2855.9	1.2422	3209.4	1.3034	2737.2	3.5220	3016.0	2.2253	1.9856

polymers in solid state, where a higher difference between Tait and HH equations occurred.

Figure 1 shows the residual plots for each equation of state. It is possible to observe that the predominately random nature of the errors distributions for both molten and solid state data, with the predictions of the HH EoS

for molten iPP as only relevant exception. These results support the statement of good suitability of the EoS tested.

As example of the general behavior described in the previous paragraph, Figure 2 shows the variation of MRD with the temperature for an amorphous polymer, PC, and with the pressure and temperature for a semicrystalline one, iPP. It can be seen that the HH EoS presented a high relative

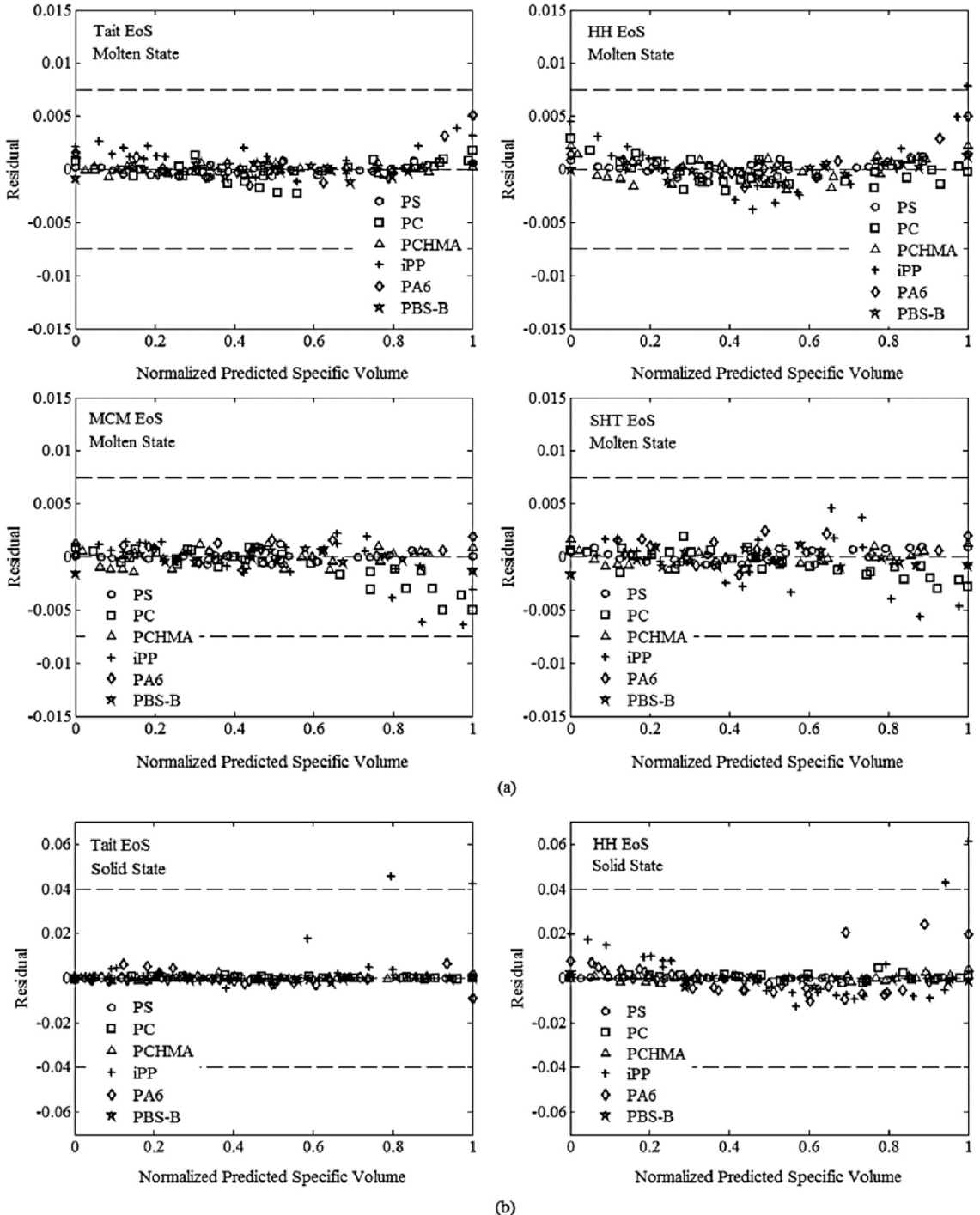


Figure 1. Residual plots of specific volume predictions for all EoS tested: (a) Molten and (b) Solid state polymers.

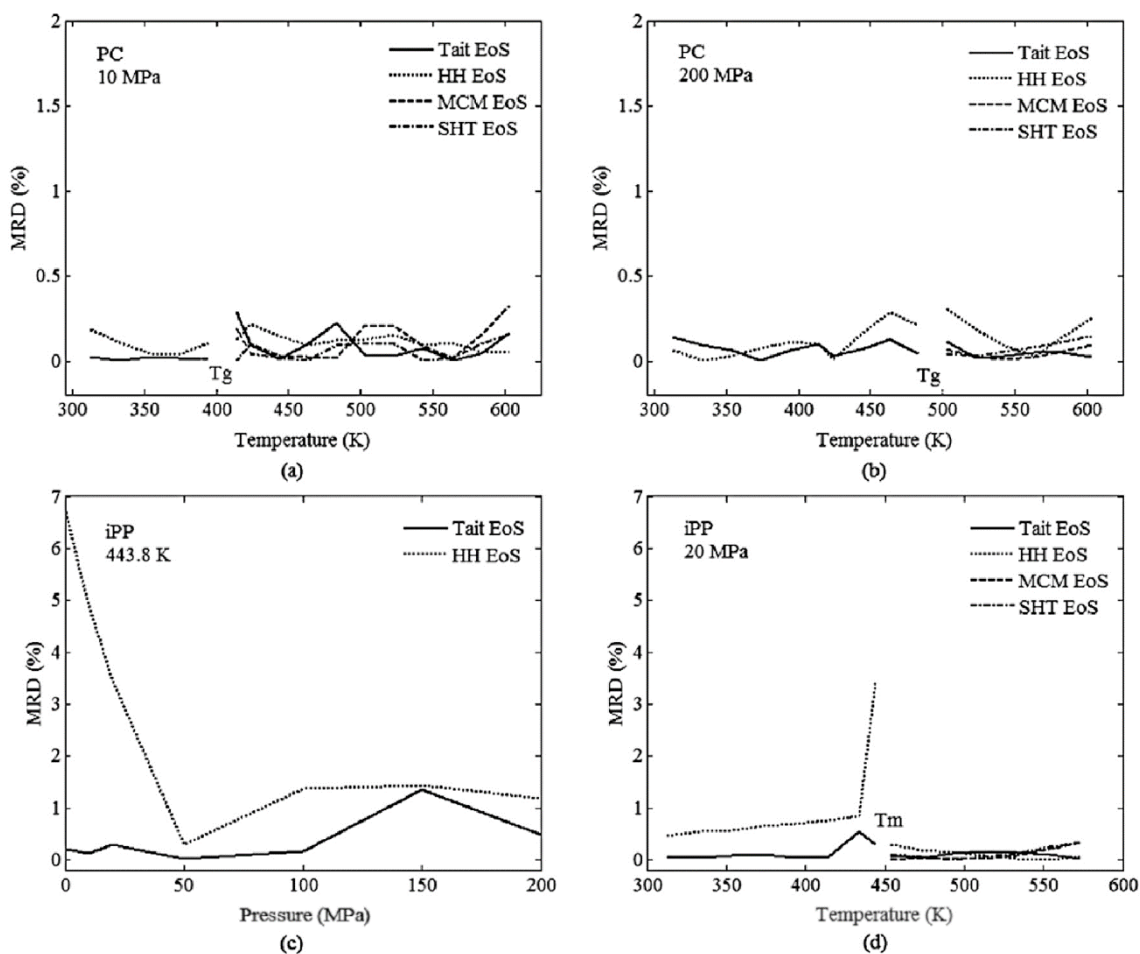


Figure 2. MRD (%) in specific volume prediction: (a) PC in 10 MPa, (b) PC in 200 MPa, (c) iPP in 443.8 K and (d) iPP in 20 MPa.

deviation in solid state, especially at low pressures near the transition temperature (Figures 2c and 2d).

4.2 Sensitivity analysis

The sensitivity of the prediction of specific volume with relation to each parameter of HH, MCM and SHT EoS is shown in Figure 3. The sensitivity of parameters showed similar behavior for all these EoS, both to amorphous and semicrystalline polymers. Besides the highest sensitivity corresponds to the volume related parameters, the sensitivity to each parameter was nearly constant in the whole ranges of pressure and temperature analyzed.

For the Tait EoS, the behavior of the sensitivity to the parameters was somewhat different, as shown in Figure 4. The sensitivity to the parameters b_1 and b_2 varied continuously and complementarily with the increase of the temperature (Figures 4b and 4c), with increase of the sensitivity to b_1 and decrease of the sensitivity to b_2 . Moreover, it is perceived that there was an abrupt change in the sensitivity of the parameters of Tait EoS near the transition temperature of linear polyethylene in the solid state. The sensitivities of parameters b_{1s} and of term v_i (b_7 , b_8 and b_9) of Tait equation were modified near the transition region. It is

found that there is a correlation between the sensitivities to the parameters b_{1s} and b_7 , both related to the specific volume. All parameters of the v_i term (b_7 , b_8 and b_9) reveal sensitivity close to the transition regions, stating that they are within linked in modeling this region. Thus, this transition region has fundamental importance for the estimation of the parameters of the Tait EoS.

4.3 Isobaric thermal expansion and isothermal compression coefficients prediction analysis

Figure 5 shows the isobaric thermal expansivity calculated from the PC, PoMS, iPP and PLA by equations of state. It is observed that all the EoS predict similar values of this coefficient and are in qualitative agreement with the theory in the sense that the thermal expansion coefficient of a polymer melt is always greater than that of the corresponding amorphous and semicrystalline solid^[35,36]. However, Tait EoS, unlike the other equations, predicts a reduction of this coefficient with the increase of the temperature, contrarily to theoretical expectations^[35], revealing a limitation of the model. Moreover, in the case of semicrystalline polymers, Tait equation of state presented an abrupt increase in thermal expansion coefficient in the

crystalline transition region. This occurs because Tait EoS describes satisfactorily sudden change in specific volume due to destruction/growth of crystallites, which does not happen with the HH equation. The theoretical equations of state, MCM and SHT displayed the same curve shape.

Figure 6 shows the isothermal compressibility predicted from the PC, PoMS, iPP and PLA by equations of state.

It appears that the equations predict values near. The curves exposed by EoS are consistent with the theory^[35,36], coefficient gradually increases with temperature and decreases with pressure. Again, as in the case of predicting thermal expansivity, Tait equation of state exhibited an abrupt reduction of isothermal compressibility in the crystalline transition region.

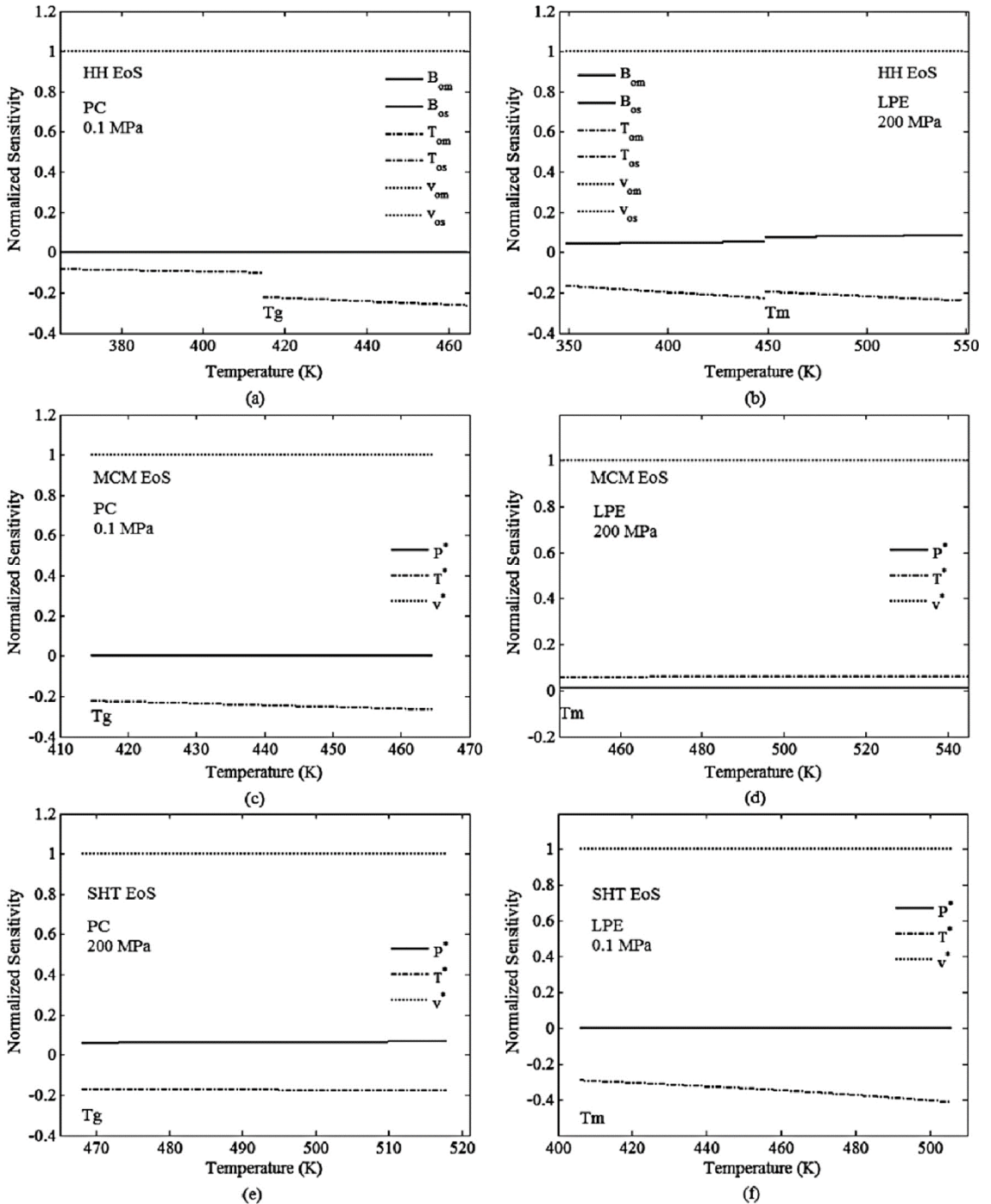


Figure 3. Normalized sensitivity of specific volume relative to the parameters of: (a) HH EoS to PC in 0.1 MPa, (b) HH EoS to LPE in 200 MPa, (c) MCM EoS to PC in 0.1 MPa, (d) MCM EoS to LPE in 200 MPa, (e) SHT EoS to PC in 200 MPa and (f) SHT EoS to LPE in 0.1 MPa.

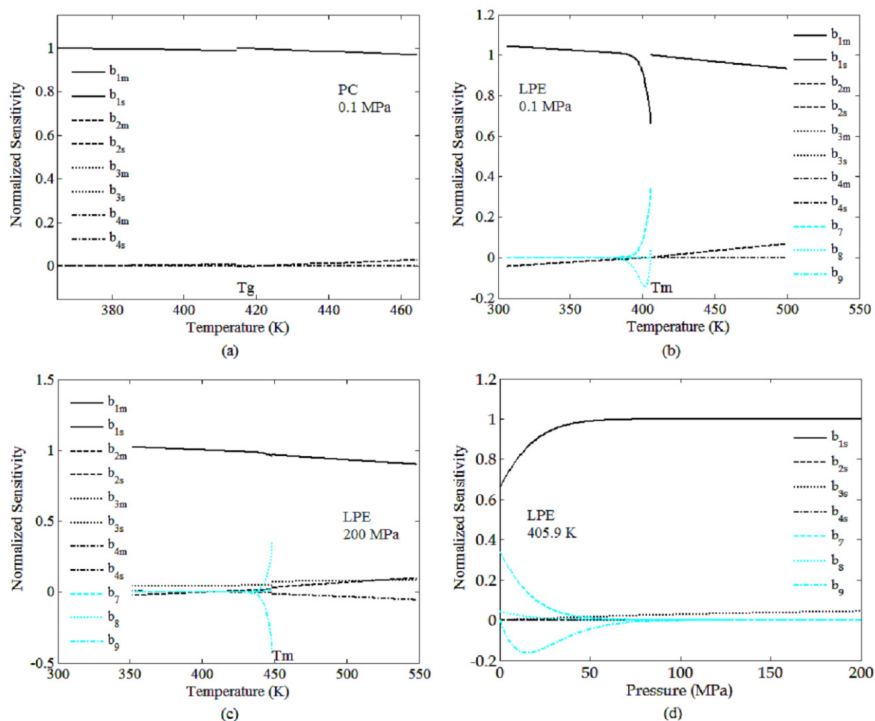


Figure 4. Normalized sensitivity of specific volume of polymers relative to parameters of Tait equation of state: (a) PC in 0.1 MPa, (b) LPE in 0.1 MPa, (c) LPE in 200 MPa and (d) LPE in 405.9 K.

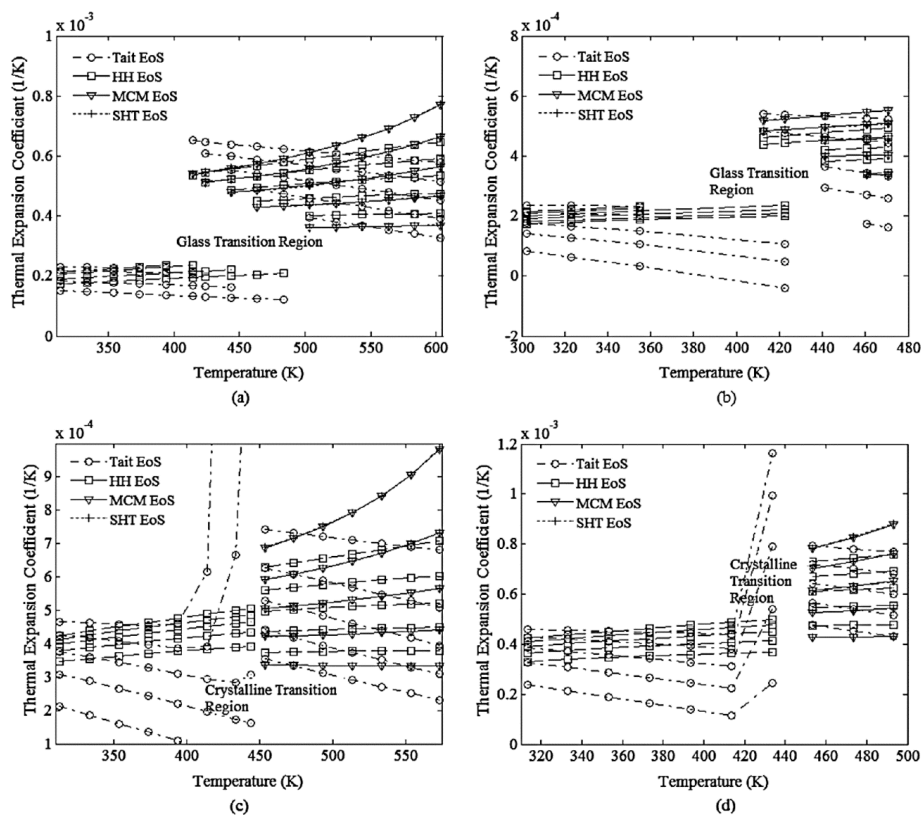


Figure 5. Isobaric thermal expansion coefficient predicted by EoS: (a) PC, (b) PoMS, (c) iPP and (d) PLA.

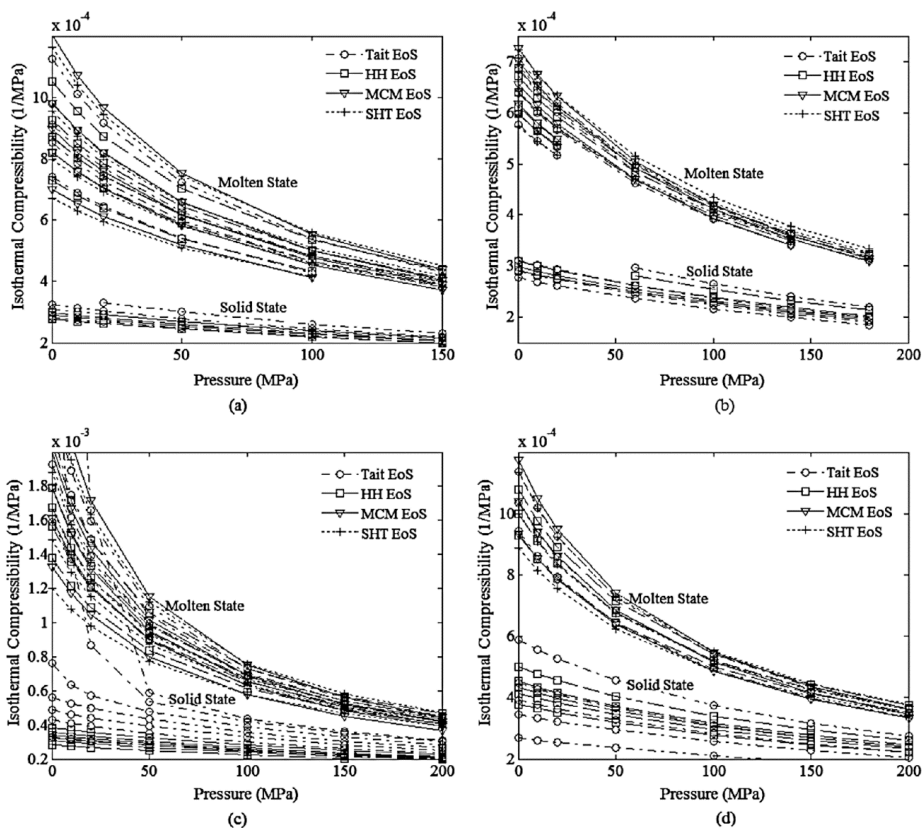


Figure 6. Isothermal compressibility predicted by EoS: (a) PC, (b) PoMS, (c) iPP and (d) PLA.

5. Conclusions

The Tait, HH, MCM and SHT equations of state were evaluated in prediction the PvT behavior of polymers, for both molten and solid physical states.

In the analysis of the PvT behavior of melt polymers, all equations of state studied showed adequate fitting of specific volume data, with light advantage of the Tait equation. No significant differences among them were observed in terms of quality of the estimated parameters, sensitivity of the predictions to the parameters, and of prediction of the thermal expansion and compression coefficients. Then, all EoS studied are appropriate in modeling the molten state.

In the analysis of the PvT behavior of solid polymers, Tait and HH equations exhibited differences in sensitivity analysis and specific volume prediction, justified mainly because HH EoS does not describe correctly the crystalline transition. The parameter estimation in both equations was adequate, with low values of standard deviations. Thus, the Tait equation of state is the most appropriate for modeling solid polymers, except for the prediction of the isobaric thermal expansion coefficient, property for which the values predicted with this equation are not in qualitative agreement with theoretical expectations.

Based on these results, the Tait equation of state can be indicated as the most appropriate for modeling the PvT behavior during processing of polymers.

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