Mathematical description of additional low temperature specific heat components for two fluoropolymers, PTFE and PCTFE

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Abstract. Our orthonormal polynomial expansion method (OPEM) is used here for describing the additional low temperature specific heat components of Polytetrafluoroethylen (PTFE) and Polychlorotrifluoroethylene (PCTFE). The temperature dependencies of the excess specific heat for the both semi-crystalline polymers are described mathematically up to 7-8 K in the present work. The peculiarity established earlier in C_p/T^3 vs. T of the PTFE and PCTFE manifested by a maximum appearing around 5 K for both fluoroplasts is hardly to be explained with the Debye model. This hump analyzed in our previous work was related to the additional low-frequency vibration modes (soft modes), localized together with lattice vibrations (sound waves) as it is postulated in the Soft Potential Model (SPM). The estimated excess specific heat data and approximating curves determined by the usual polynomial coefficients obtained by orthonormal ones in our OPEM approach, are presented too.

INTRODUCTION

The unique combination of physical, mechanical and electrical low-temperature properties of carbochain fluoropolymers, PTFE and PCTFE makes them very important materials to meet all requirements in new technical applications: in space, chemical engineering, electrical industry, electronics and cryogenics. The technology of preparation of these polymeric materials also needs knowledge of their thermodynamic characteristics. The unusual thermal properties concerning the low-temperature specific features of the heat capacities of the PTFE and PCTFE were considered in earlier papers [1, 2, 3]. The estimated excess specific heat [3] over Debye contribution below 10 K of these fluoroplasts was discussed in the frame of the recently developed Soft-Potential Model (SPM) which postulates an appearance of the proportional to T^5 specific heat contribution generated by the soft modes and connected with some kind of the material disorder. The investigated there temperature dependencies of the function $C_p^{SM(exc)}/T^5$ was proposed in the temperature range $(2.5 \div 7)\ K$ for PCTFE, as well as in two subintervals $(0.4 \div 2)\ K$ and $(2.5 \div 8)\ K$ for PTFE.

The present study is devoted to the mathematical description of the evaluated [3] additional (excess) low-temperature component $C_p^{SM(exc)}$ of the specific heat of these semi-crystalline polymers applying our Orthonormal Polynomial Expansion Method

(OPEM) [4]. The new type of weighting functions in the OPEM approximation involves the experimental errors in every point of the studied thermal characteristic. The investigated here temperature dependence of the function $C_p^{SM(exc)}$ is described in the low-temperature ranges $(2.5 \div 7)$ K and/or $(2.5 \div 8)$ K respectively for the two non-polar plastics PCTFE and PTFE. Numerical results of the deviations between the evaluated $C_p^{SM(exc)}$ data and their approximating values are given in the figures. The usual polynomial coefficients are calculated by orthonormal ones in our OPEM approach.

ADDITIONAL LOW-TEMPERATURE HEAT CAPACITY DATA

The previous work [3] clarifies several points concerning the heat capacity peculiarities found in the temperature dependencies of the scaled specific heat C_p/T^3 of the PTFE and PCTFE - a maximum appearing at $T_{max} = 4$ or 5 K correspondingly for PCTFE and PTFE (see the inset in the Figure 1). Analyzing the microscopic origin of the peak established in the low-temperature dependence of the scaled specific heat C_p/T^3 of the investigated polymers one can postulate the observed peculiarity as glass like behavior. This acceptance means that above 1 K these features in studied polymers also originate from the low-frequency vibrational (soft) modes. In accordance with the Soft Potential Model (SPM) [5, 6] the observed maximum $(C_p/T^3)_{max}$ in glasses is related to the softening of the lattice vibrations leading to an increase over Debye behavior of the density of states $g(\nu)$ of the harmonic oscillators with rising of their energy. Following the SPM, supposing a coexistence of acoustic phonons with quasi-localized low-frequency (soft) modes in glasses, successfully applied by us to some chalcogenide glasses [7, 8], the low-temperature $(T < 10$ K$)$ specific heat data for these fluoroplasts, were described [2, 3] by an equation

$$C_p = C_p^{TLS} + (C_p^D)^{acou} + C_p^{SM(exc)}. \tag{1}$$

The C_p components are:
i) $C_p^{TLS} = C_{TLS}T$ - a linear contribution, described by double-well potentials, conditioned by the thermal excitations of the tunneling state (TLS); for PTFE it was established [9] to predominate at $T \leq 0.2$ K.
ii) $(C_p^D)^{acou} = (C_D)^{acou}T^3$- a cubic Debye contribution, determined by the lattice vibrations (sound waves), evaluated in details in work [2].
iii) $C_p^{SM(exc)}$ - an excess specific heat (a soft mode) contribution of the quasi-harmonic excitations, described by single-well potentials.
Here, C_{TLS} was estimated by the C_p experimental data of Nittke et al [9], the true elastic coefficient $(C_D)^{acou}$ was calculated [2] by the macroscopic parameters of the investigated materials and the average sound velocity v_s, and $C_p^{SM(exc)}$ component was evaluated [2] by a difference between the measured specific heat C_p [1] and the sum $(C_p^{TLS} + (C_p^D)^{acou})$. The average sound velocity v_s was estimated [2] for PTFE (PCTFE) by the measurements of transversely and longitudinally polarized 10 (5) MHz ordinary sound waves available between 4.2 and 140 (180) K. The v_s for both polymers changes its value about 0.3 % below 10 K. This fact allows us to accept constant Debye coefficient

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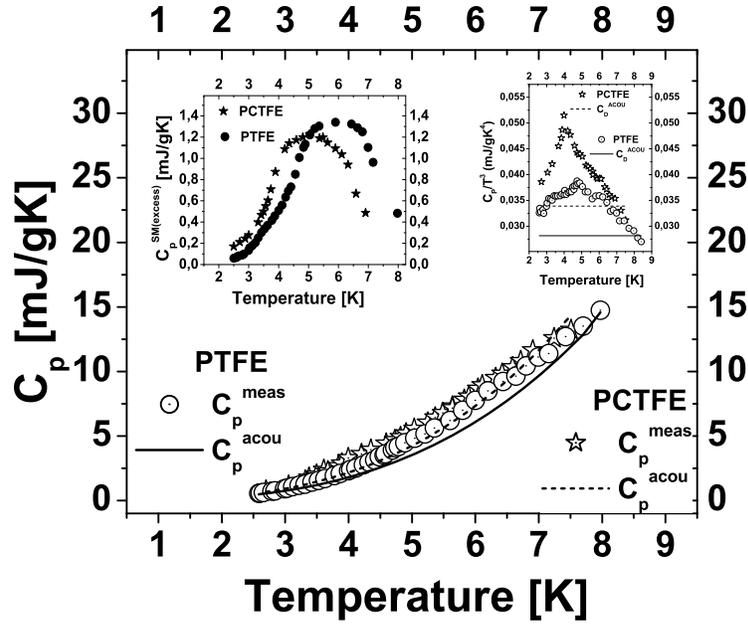
FIGURE 1. Temperature dependencies of the measured specific heat C_p^{meas} and the specific heat components defined in Eq. 1. Insets: temperature dependencies of the evaluated excess specific heat $C_p^{SM(exc)}$ of the PTFE and PCTFE and the scaled specific heat C_p/T^3 vs.T of the PTFE and PCTFE.

C_D of the the Debye specific heat contribution by acoustic measurements. Note that the quantities C_D up to 10 K and C_{TLS} are independent of the temperature.

The abbreviations of Two Level State, Debye and Soft Modes (excess) specific heat are marked with *TLS*, *D*, and *SM(exc)*, respectively. In the wider low-temperature range the temperature dependencies of the measured specific heat and the specific heat components defined in Eq. 1 as well as the evaluated excess specific heat $C_p^{SM(exc)}$ are presented, respectively in Figure 1 and in the inset of Figure 1. As it can be seen in the right inset of Figure 1, the SM delocalized at T=8 K for PTFE and at T=7 K for PCTFE.

MATHEMATICAL ALGORITHM

The mathematical algorithm of the OPEM is developed for applications in cryogenic thermometry in papers [4, 10]. Some important features of OPEM concerning cryogenic thermometry at the approximation of thermometric characteristics of different type low- temperature sensors are protected by a patent for an invention [11]. Our OPEM is a generalization of Forsythe [12] three-term relation for constructing orthogonal polynomials over a discrete point set with arbitrary weights in the term of the least square method. The one-dimensional recurrence for the generation of orthonormal polynomials $\{\Psi_k^{(0)}, k = 1, 2, \ldots\}$ and their derivatives $\{\Psi_k^{(m)}, m = 0, 1, 2, \ldots\}$, in OPEM is:

$$\Psi_{k+1}^{(m)}(q) = \gamma_{k+1}[(q - \alpha_{k+1})\Psi_k^{(m)}(q) - (1 - \delta_{k0})\beta_k \Psi_{k-1}^{(m)}(q) + m\Psi_k^{(m-1)}(q)] \quad (2)$$

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OPEM is a development of the Forsythe approach for receiving derivatives and integrals with a fourth term in the Eq. (2). The polynomials $\{\Psi_k^{(0)}\}$ satisfy the orthogonality relations over the point set $\{q_i, i = 1, 2, \ldots M\}$ with weights $w_i = 1/\sigma_i^2$, depending on errors σ_i in each point. The approximating values f^{appr} of the investigated function and its m-th derivative $f^{(m)appr}$ $\{m = 0, 1, ..\}$ are calculated by orthonormal and usual expansions:

$$f^{(m)appr}(q) = \sum_{k=0}^{N} a_k \Psi_k^{(m)}(q) = \sum_{k=0}^{N} b_k q^k. \tag{3}$$

The optimal degree N of the approximating polynomials in Eq.(3) is selected by the algorithm, combining the following two criteria. First, the fitting curve should lie in the error corridor of the dependent variable $(q_j, f_j^{exp} \pm \sigma_j, j = 1, ...M)$.

$$(f_j^{appr} - f_j^{exp})^2 w_j \leq 1. \tag{4}$$

Second, the minimum of normalized χ^2 should be reached:

$$\sum_{j=1}^{M} w_j (f_j^{appr} - f_j^{exp})^2 / (M - N - 1) \rightarrow min. \tag{5}$$

When the first criterion is satisfied, the search of the minimum χ^2 stops. The development of the algorithm in the biophysics with the total variance for involving the errors in both variables was published in a paper [13]. The last versions with obtaining of usual b_k coefficients from orthogonal ones a_k in Eq. (3) are developed in our works, [10, 13].

FITTING RESULTS

The temperature dependence of the $C^{SM(exc)}$ function is described by orthonormal polynomials in the temperature ranges $2.5 \div 8$ $[K]$, for PTFE, and $2.5 \div 7$ $[K]$ for PCTFE, using the new type of weights, $W^{C^{SM(exc)}}$.

By definition the weighting function $W^{C^{SM(exc)}}$ is $1/\sigma^2$, where σ^2 is a variance of the thermal characteristic $C^{SM(exc)}$ versus temperature T. In our investigation this variance is accepted to be, correspondingly square of the absolute heat capacity resolution (acr) $\Delta C_{acr}^{SM(exc)}$, determined by the experimental specific heat accuracy, equal to 5 %, as follows: $(\Delta C_{acr}^{SM(exc)})_i = 0.05(C^{SM(exc)})_i$ $[mJ/gK]$ for the PTFE and PCTFE given intervals. Here the weights, $W^{C^{SM(exc)}}$ are expressed by the relations:

$$(W^{C^{SM(exc)}})_i = 1/(\Delta C_{acr}^{SM(exc)})_i^2 = 400/(C^{SM(exc)})_i^2 \ [mJ/gK]^{-2} \tag{6}$$

for the approximating intervals of PTFE and PCTFE.

The deviations between calculated and approximating values of the excess specific heat are estimated in each point by the expression: $(\Delta C^{SM(exc)})_i = (C^{SM(exc)})_i^{calc} - (C^{SM(exc)})_i^{appr}$. The temperature behavior of the calculated differences, the overall characteristics: the root mean square deviations RMS^C and the mean absolute deviations
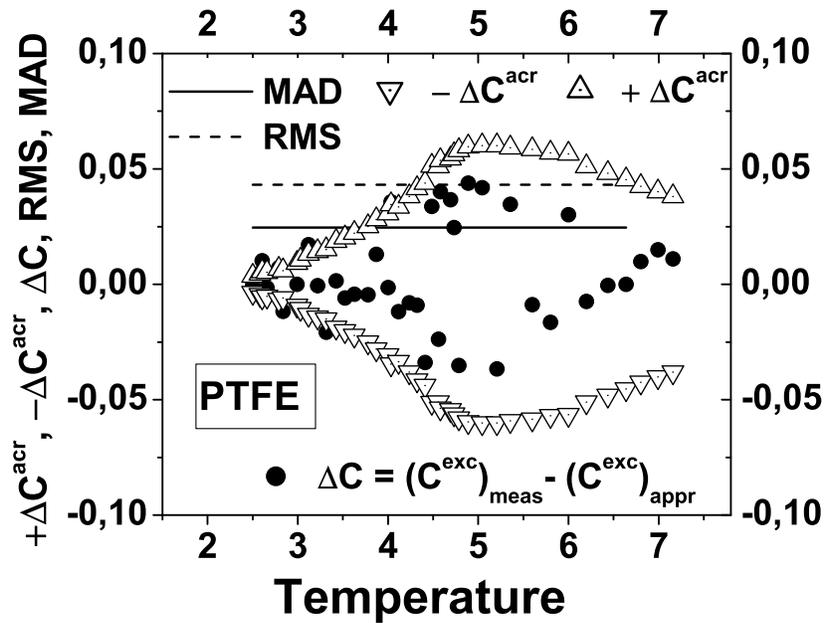
FIGURE 2. Temperature dependencies of $\Delta C^{SM(exc)}$, $(\Delta C^{SM(exc)})_{acr}$, the overall characteristics $MAD^{C^{SM(exc)}}$ and $RMS^{C^{SM(exc)}}$ of the PTFE for the approximating temperature range.

TABLE 1. Usual coefficients $\{b_k\}$ for OPEM approximation of C_p^{excess} $[mJ/gK]$ vs. T

					PTFE					
b_0	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	b_9	b_{10}
-3859.	9028.	-9317.	5584.	-2152.	557.8	-98.43	11.68	-.8930	.03973	-.0007
					PCTFE					
b_0	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	b_9	b_{10}
.1824	-.6679	.9978	-.7691	.3205	-.0680	.0056	-	-	-	-

MAD^C respectively for PTFE and PCTFE excess specific heat approximations, are shown in Figs.2 and 3. The RMS and MAD deviations are defined in our previous papers [4, 10]. Following the cited criteria in Eqs.(4,5) the deviations $(\Delta C^{SM(exc)})_i$ are in the error corridor (see Figs.2,3). As a result of our mathematical description, the polynomial optimal degree N for the $C^{SM(exc)}$ vs. T approximation of the $C_p^{SM(exc)}$ function for PTFE within $2.5 \div 8$ K is $N = 10$ while the one for PCTFE within $2.5 \div 7$ K is $N = 6$. Calculation of usual coefficients $\{b_k\}$ from orthonormal ones $\{a_k\}$ using extended OPEM and applied for $C_p^{SM(exc)}/T^5$ vs. T approximation, is developed and discussed in our paper [3]. Here, the calculated usual coefficients $\{b_k\}$ of the $C_p^{SM(exc)}$ polynomial description are presented in Table 1.
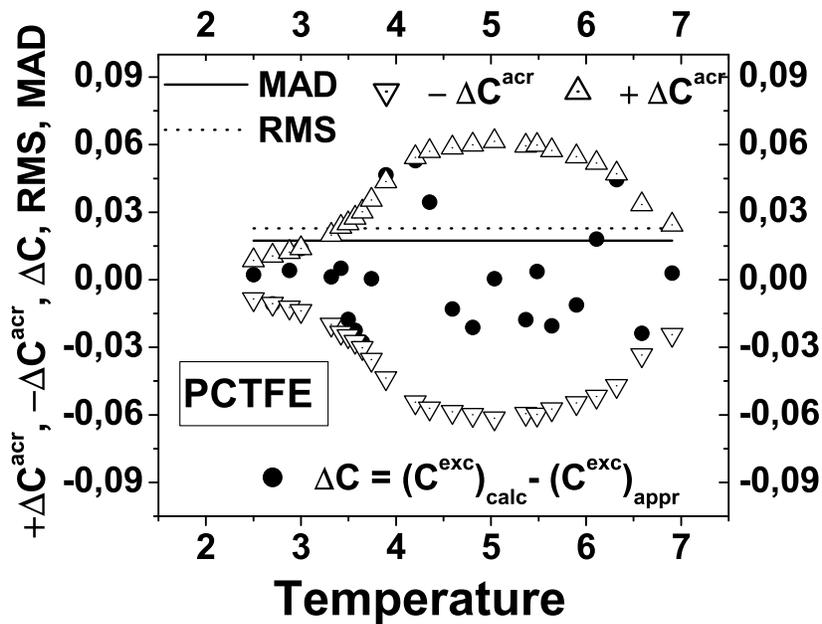
FIGURE 3. Temperature dependencies of $\Delta(C^{SM(exc)})$, $(\Delta C^{SM(exc)})_{acr}$, the overall characteristics $MAD^{C^{SM(exc)}}$ and $RMS^{C^{SM(exc)}}$ of the PTCFE for the approximating temperature range.

In conclusion, the additional low-temperature contributions to the specific heat of the PTFE and PCTFE, related to the low-frequency vibrational modes (soft modes), localized together with lattice vibrations (sound waves) as it is postulated in the SPM, are examined mathematically. Our OPEM is used for describing the excess low-temperature heat capacity components of the both semi-crystalline polymers. The approximation parameters of the studied thermal characteristic were determined by the usual polynomial coefficients, obtained from orthonormal ones in our OPEM approach, satisfying the first criterion (Eq.(4)) for the fitting curve to remain in the error corridor.

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