INVESTIGATION OF THE THERMOPHYSICAL PROPERTIES OF POLYMERS BY THE TEMPERATURE WAVE TECHNIQUE

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The technique of temperature waves to measure the complex thermophysical characteristics of materials has been proposed. The relations for the moduli and arguments of these characteristics for the case of plane temperature waves have been calculated. The temperature dependences of the moduli and arguments of complex thermophysical characteristics of polyvinylacetate (PVAc) at different frequencies and also the temperature dependences of its vibrational and configurational heat capacities have been determined. It has been shown that the vibrational heat capacity of PVAc in the region of softening grows sharply and its configurational heat capacity goes through a peak. The segmental mobility has been found to affect the heat transfer in the polymer in an ambivalent way causing both a decrease and increase of thermal conductivity.

Keywords: heat capacity, polymers, polyvinylacetate, temperature wave technique

It is known [1] that a change in the heat capacity of polymers in the glass transition region (a 'jump' of heat capacity) is caused by their vibrational and configurational heat capacities. The configurational capacity is the sum of the hole and conformational heat capacities and is associated with segmental mobility. Finding out the temperature dependences of the vibrational and configurational heat capacities is a complicated theoretical and experimental problem which has not yet been solved.

For this reason, there is no correct definition for the relation between the contributions of these components to the jump of heat capacity.

The role of segmental mobility in heat transfer remains even less clear. The data on the temperature dependence of thermal conductivity in the region of softening given in the literature are highly contradictory [2–6].The studies of thermal conductivity employ mainly stationary techniques, but unfortunately these techniques give little information on the role of segmental mobility (fluctuational dy-

namics of molecules) in heat transfer. At the same time, the nonstationary techniques give typically erroneous data [7–9], because their theory does not take into account the time dependences of the thermophysical characteristics.

Hence, further studies of heat capacity and thermal conductivity of polymers in the glass transition region are required.

It is most attractive to study the laws of heat transfer and absorption associated with the fluctuational (configurational) dynamics of macromolecules by using harmonic temperature oscillations [10]. However, the AC calorimeters used for this purpose are not effective. They are unable to define all complex thermophysical characteristics (CTPC) and have shortcomings which impede the measurements and lower the accuracy of determination of the complex heat capacity.

In this paper we discuss the applicability of the technique of plane temperature waves for measuring CTPC (complex thermal diffusivity $a^* = a_0 \cdot \exp j\, \delta_a$, complex thermal activity $b^* = b_0 \cdot \exp j\, \delta_b$, complex thermal conductivity $\lambda^* = \lambda_0 \cdot \exp j\, \delta_\lambda$, and complex heat capacity per unit volume $C^* = C_0 \cdot \exp j\, \delta_c$) associated with segmental mobility in polymers. The major advantages offered by this technique were listed in [11–13]. In addition, this technique allows the dependences of CTPC on temperature and frequency of temperature oscillations to be readily obtained. It can also be used to reveal the variations of CTPC during annealing, glass transition or softening, crystallization or melting, to distinguish between the influence of nonlinear and hereditary effects on CTPC, and to study the thermal relaxation processes near the equilibrium state. An undoubtful advantage of this technique is also the possibility to use the linear theory of thermal conductivity for the determination of CTPC in the phase and relaxation transition regions, because the amplitudes of temperature oscillations can be made fairly small.

Theoretical relations

For this work, the theory of the technique of plane temperature waves was developed. It has been assumed that the velocity of heat transfer is finite [14, 15], and the thermophysical characteristics can be complex-values. As a result the relations were found for a steady-state harmonic process for three most preferential measuring units (Fig. 1).

For instance, from the solution of a one-dimensional uniform linear problem of thermal conductivity for propagation of plane temperature waves in an isotropic semi-infinite solid (Fig. 1a), the expressions calculated for modulus a_0 and argument (phase) δ_a of complex temperature conductivity are

$$a_0 = \frac{\omega h^2}{\ln^2(\theta_2/\theta_1) + \varphi^2} , \qquad (1)$$

$$\delta_a = \frac{\pi}{2} - 2\cdot\arctan\left[\frac{\varphi}{\ln\left(\theta_2/\theta_1\right)}\right]$$ (2)

where ω is the circular frequency of temperature oscillations, θ_2 and θ_1 are the amplitudes of temperature oscillations on the input surface and at depth h of a semi-infinite body, respectively, and φ is the phase shift between these oscillations.
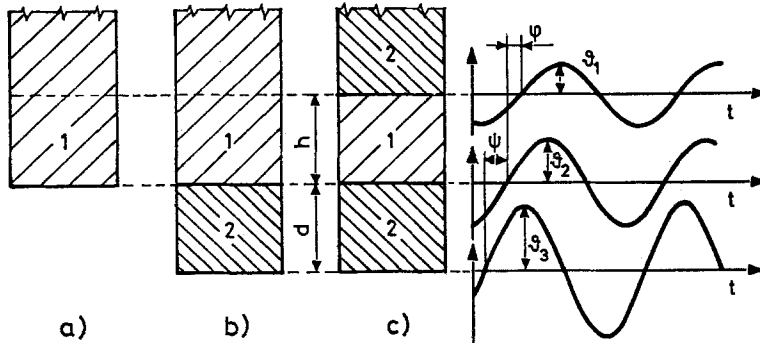

Fig. 1 Measuring units and harmonic temperature oscillations in different cross sections, 1 – sample under study, 2 – reference material

The semi-infinite solid is a body in which the plane wave almost fully decays at the distance equal to its length. The distance L_N at which the amplitude of the temperature wave decreases by a factor of N will be given by

$$L_N = \frac{\ln N}{\sqrt{\omega/a_o}\cdot\cos\left(\pi/4 - \delta_a/2\right)}$$

In case of complex thermal diffusivity, the effect of heat exchange through the lateral surface of the sample on its value cannot be taken into account by using expressions from [11]. Therefore, we have derived the relation $a_o / \cos \delta_a = \omega h^2 / [2\varphi \ln (\theta_2 / \theta_1)]$. If the relation is satisfied, the heat exchange may be neglected, and, hence, expressions (1) and (2) are applicable for the calculation of complex thermal diffusivity.

The advantage offered by the measuring unit shown in Fig. 1a is the possibility to analyze easily the relationship between the complex thermophysical characteristics being determined and the values measured.

For the determination of all CTPCs, the relative method of plane temperature waves, which is superior in many respects to the absolute method, is most suitable [12]. Figure 1b shows schematically the measuring unit used for definition of all CTPCs. The unit consists of a semi-infinite body under test, which is in thermal contact with a reference infinite plate. On the lower surface of the plate harmonic

temperature oscillations with amplitude θ_3 are generated. In this case CTPC is calculated from expressions (1) and (2), and also from

$$b^* = \frac{b_r \left[\left(\dfrac{\theta_3}{\theta_2} \right) \exp j\,\psi - \cosh\left(\sqrt{j\,\omega/a_r} \cdot d \right) \right]}{\sinh\left(\sqrt{j\,\omega/a_r} \cdot d \right)} , \tag{3}$$

$$\lambda^* = b^* \sqrt{a^*} \quad \text{and} \quad C^* = b^* / \sqrt{a^*} \tag{4}$$

where $j = \sqrt{-1}$, a_r and b_r are thermal diffusivity and thermal activity of the reference material, respectively, d is the reference plate thickness, and ψ is the phase shift between the temperature oscillations with amplitudes θ_3 and θ_2.

For both measuring units considered above a semi-infinite body (L ~ 30–50 mm) prepared of the material to be studied is required. The same holds for the unit shown in Fig. 1c. In this the sample in the form of a thin plate is placed between the reference semi-infinite body and the reference plate and is brought into thermal contact with them. On the opposite surface of the reference plate, harmonic temperature oscillations with amplitude θ_3 are generated. The calculated expressions in this case are given by

$$(b^*)^2 = b_r^2 \cdot \frac{\left\{ (\theta_2/\theta_1) \cdot (\exp j\,\varphi) \cdot \dfrac{(\theta_3/\theta_2) \cdot (\exp j\,\psi) - \cosh\left(\sqrt{j\,\omega/a_r} \cdot d\right)}{\sinh\left(\sqrt{j\,\omega/a_r} \cdot d\right)} \right\}^2 - 1}{(\theta_2/\theta_1)^2 \cdot (\exp j\,2\psi) - 1}$$

$$\tag{5}$$

$$\exp\left(\sqrt{j\,\omega/a^*} \cdot h\right) =$$

$$= \frac{(\theta_2/\theta_1) \cdot (\exp j\,\varphi) \cdot \left\{ (b^*/b_r) + \dfrac{\left[(\theta_3/\theta_2) \cdot (\exp j\,\psi) - \cosh\left(\sqrt{j\,\omega/a_r} \cdot d\right) \right]}{\sinh\left(\sqrt{j\,\omega/a_r} \cdot d\right)} \right\}}{(b^*/b_r) + 1}$$

$$\tag{6}$$

where θ_2 and θ_1 are the amplitudes of temperature oscillations on the surfaces of the plate of thickness h.

The analysis of expressions (3)–(6) has shown that to obtain the highest accuracy in definition of CTPs, it is necessary that $b_r \leq |b^*|$ and $|\tan h\left(\sqrt{j\,\omega/a^*} \cdot h\right)| \approx |\tan h\left(\sqrt{j}\,\omega/a_r d\right)| \approx 1$

Experimental

Apparatus

To measure CTPCs in the temperature range 80 K–450 K at frequencies from 10^{-3} Hz to 1 Hz, an automated setup based on the relative method of plane temperature waves was developed. The setup measured the moduli and arguments of CTPCs with mean-square errors less than 2% and 0.01 rad, respectively. The high accuracy was achieved by applying the methods described in [16, 17] which allow for the effect of monotonously varying the average levels of harmonic infralow frequency signals on the accuracy of defining the amplitudes and phase differences between these signals. In addition, the setup allowed the thermophysical characteristics to be defined for different amplitudes of the alternating component of temperature.

The harmonic temperature oscillations were produced by the generator of temperature oscillations. The generator was an electronic monitoring system. The source of plane temperature waves was a law-inertia plane ohmic heater. The generator of temperature oscillations produced harmonic variations with nonlinear distortions less than 3% and amplitude from 0.05 K to 5 K in the frequency range from 10^{-3} Hz to 1 Hz on the surface of the sample or reference plate (depending on the type of the measuring unit). The nonuniformity of the temperature field on the entire surface did not exceed 2% in this case.

The amplitudes of the harmonic temperature oscillations on the surface of the reference plate and the plate under study, and also the phase differences between these oscillations were measured by differential manganin-constantan thermocouples and a computer assisted data acquisition and measuring system [18, 19]. The CTPCs were computed from expressions (1)–(4) or (5) and (6), depending on the type of the measuring unit. The results of measurements and calculations were fed to the printer or plotter.

Objects

We studied the thermophysical properties of polyvinylacetate (PVAc) with M =120 000, density 1 120 kg/m^3 (at 293 K), and T_c =301 K determined by the penetration technique. The studies were carried out in the temperature range 280–340 K. In this temperature range, PVAc which is a typical amorphous polymer, passes from the glassy to the rubber-elastic state. As known, the transition is accompanied by an intensive unfreezing of the segmental mobility. For comparison, the thermophysical properties of ebonite, which is a tightly cross-linked polymer, were also studied. At the temperatures mentioned above, ebonite does not exhibit segmental mobility [20]. The moduli and arguments of the complex thermophysical characteristics were measured during continuous heating of the sample at a rate of 2–3 K/hour at 0.5–1 K intervals.

Results and discussions

The experiments have shown that the thermophysical characteristics of ebonite are independent of the frequency of temperature oscillations and the arguments of these characteristics are zero. Thus, the thermophysical characteristics of ebonite are real-valued. This indicated that the thermal relaxation processes associated with segmental mobility are indeed absent in ebonite in the temperature range studied. The measured temperature dependences of the heat capacity and thermal conductivity of ebonite are shown in Fig. 2. Note that they are in good agreement with the data reported in literature [21].
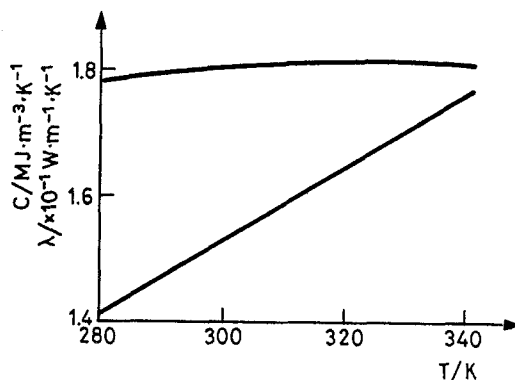

Fig. 2 Temperature dependence of the heat capacity (1) and thermal conductivity (2) for ebonite

These dependences exhibit quite a different behaviour for PVAc (Figs 3, 4). For instance, modulus C_0 of the complex heat capacity in the region of softening increases sharply with increasing temperature and its magnitude depends on the frequency of temperature oscillations. At the same time, the magnitude of the modulus ΔC_0 jump observed during the polymer transition from the glassy to the rubber-elastic state is almost independent of the frequency of temperature oscillations. The magnitude of ΔC_0 is about 0.63 MJ/(m^{3}K) and is in a good agreement with the data reported in [8], and also with the values obtained by a differential scanning microcalorimeter. It is also shown by Fig. 3 that the argument of the complex heat capacity in the region of softening has nonzero magnitudes and depends on the frequency of temperature oscillations. In addition, the argument values are negative in this case, and, therefore, the variations in the enthalpy of the steady-state harmonic process lag in phase behind the temperature oscillations. This is attributable to the fact that the enthalpy of the polymer is associated not only with the vibrational modes, but also with segmental mobility.

From the dependences shown in Fig. 3, using the relation

$$C^* = C_0 \cdot \exp j\, \delta_c = C_{\text{vib}} + C_{\text{con}} \cdot \frac{(1 - j\,\omega\,\tau)}{1 + (\omega\,\tau)^2} \qquad (7)$$

the temperature dependences of the vibrational C_{vib} and configurational C_{con} heat capacities and also of the relaxation time (Fig. 5) were obtained for PVAc. Relation (7) was obtained using the equivalent circuit of heat capacity of a polymer proposed in [10]. It was assumed there that C_{vib}, C_{con} and τ are functions of the temperature alone and are independent of the frequency of temperature oscillations $f = \omega/2\pi$.
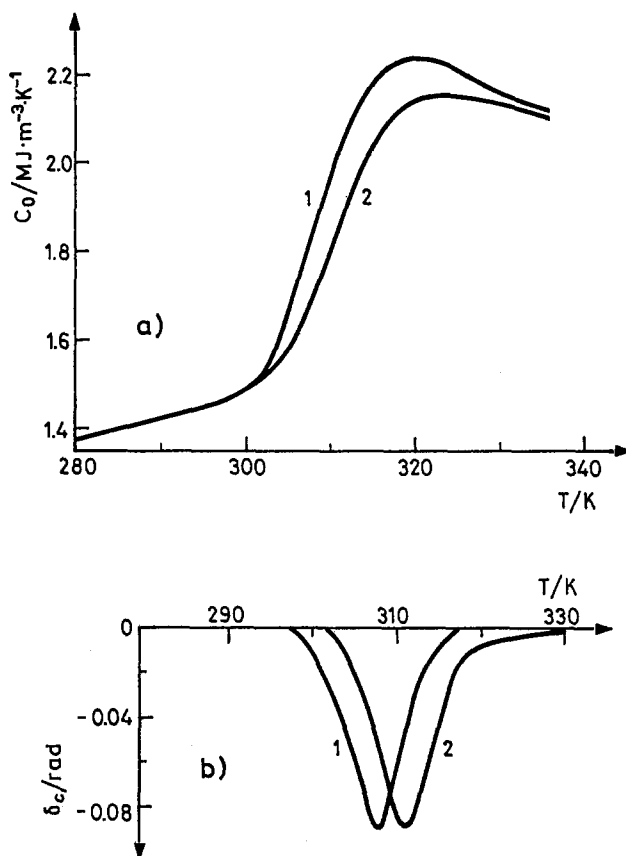

Fig. 3 Temperature dependence of the modulus C_0 (a) and argument δ_c (b) of the complex heat capacity of PVAc for different frequencies of temperature oscillation:
1 – 0.01; 2 — 0.1 Hz

It is seen from Fig. 5 that the vibrational heat capacity of PVAc in the region of softening grows markedly (by ~ 40%), and its configurational heat capacity

goes through a peak. At $T < T_g$, the segmental mobility manifests itself only slightly and therefore C_{con} associated with it is close to zero. With unfreezing of the segmental mobility, C_{con} begins to grow. Its growth is due both to an increase of the free volume (of the number of holes), and an increase of the fraction of segments that are in high-energy (gauche) state. The growth is observed up to temperature T_m which corresponds to the largest difference between the number of transitions of segments from the low-energy (trans-) to high-energy state and back. It should be noted that the obtained maximum C_{con} is close to the conformational heat capacity found experimentally for an individual macromolecule [22].
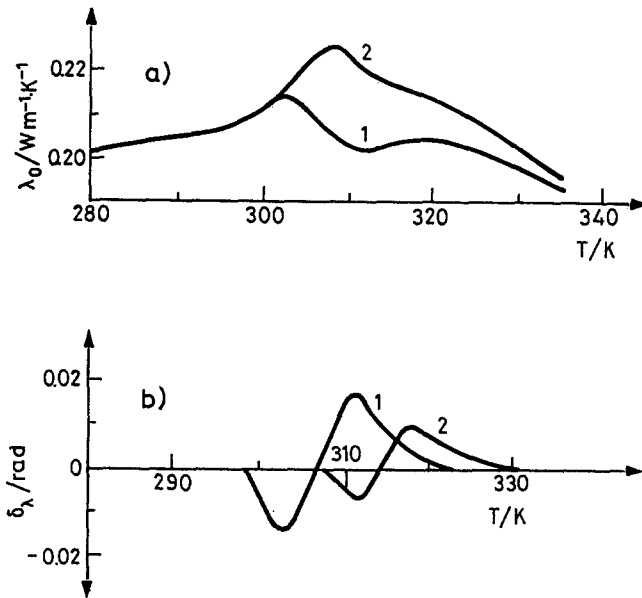
Fig. 4 Temperature dependence of the modulus λ_0 (a) and argument δ_λ (b) of the complex thermal conductivity of PVAc for different frequencies of temperature oscillation: 1 – 0.01; 2 – 0.1 Hz

A sharp increase of the polymer vibrational heat capacity (which is a sum of the interchain C'_{vib} and intrachain C''_{vib} vibrational heat capacities) in the region of softening is a new and somewhat unexpected fact. It can be assumed that the observed growth is attributable primarily to the increase of the interchain vibrational heat capacity. This hypothesis is confirmed both by the rough estimates (Fig. 5) and by the measurements of the thermodynamic (macroscopic) β_t and intermolecular β_i coefficients of thermal linear expansion of PVAc carried out by dilatometric and X-ray diffraction techniques, respectively, [23]. The measurements revealed that in the region of polymer softening β_i grows sharper than β_t, and the ratio $\beta_i/\beta_t \approx 5$–6.
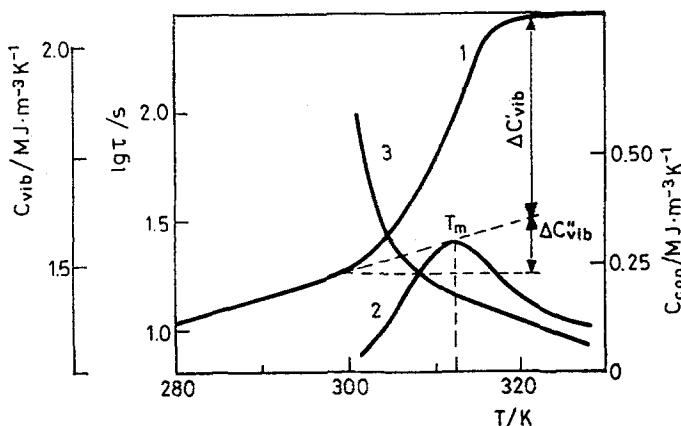
Fig. 5 Temperature dependence of the vibrational (1) and configurational (2) heat capacities, and of the relaxation time (3) for PVAc. C''_{vib} and C'_{vib} are variations of the intrachain and interchain vibrational heat capacities in the glass transition region

Figure 5 also shows that the relaxation time increases sharply with decreasing temperature and reaches at T_g the typical value of 100 s. From this figure we can estimate the contributions of C_{vib} and C_{con} to the jump of the modulus of the complex heat capacity and also the effective activation energy for the structural relaxation process.

The temperature dependences of the modulus λ_o and argument δ_λ of the complex thermal conductivity (Fig. 4) in the glass transition region exhibit a more complicated behaviour than the temperature dependences of C_o and δ_c. For instance, the sign of δ_λ depends on the temperature and its temperature dependence has not only a minimum, as for δ_c, but also a maximum. In the region of softening, λ_o and δ_λ depend on the frequency of temperature oscillations. Specifically, an increase of frequency by an order of magnitude gives rise to a 10% growth of λ_o at 310 K and also to a displacement of the extrema of δ_λ and λ_o by 5–8 K towards higher temperatures. Thus the obtained temperature dependences at different temperature oscillation frequencies show that the segmental mobility affects the heat transfer in polymers, causing both an increase and decrease of the modulus of complex thermal conductivity. The resulting effect depends both on the absolute temperature and frequency of temperature oscillations. Such an ambivalent effect of the segmental mobility on the heat transfer is apparently due to the following reasons. First of all, the unfreezing of segmental mobility leads to an increase of the free volume, and thus the energy exchange between neighbouring molecules is inhibited. However, the intensity of the fluctuational motion of macromolecular segments grows in this case, and additional channel for heat transfer can appear. Special studies are necessary to understand better the mechanism of the thermal conductivity of polymers. For instance, the segmental mobility can be in-

tentionally varied by modifying the polymer under study, i.e. by changing the molecular weight of the polymer or by introducing a plasticizer.

Thus, the use of the temperature wave technique for studying the complex thermophysical characteristics of the polymer allowed the determination of the temperature dependences of its vibrational and configurational heat capacities and estimation of the contributions of these heat capacities to the jump of the modulus of complex heat capacity observed during the polymer transition from the glassy to the rubber-elastic state. The studies also revealed the relaxation nature of heat transfer in polymers.

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Zusammenfassung — Zur Bestimmung der komplexen thermophysischen Eigenschaften von Stoffen wurde eine Temperaturwellentechnik vorgeschlagen. Für den Fall zweidimensionaler

Temperatur-wellen wurden die Verhältnisse von Moduli und Argumenten dieser Eigenschaften berechnet. Die Temperaturabhängigkeit von Moduli und Argumenten der komplexen thermophysischen Eigen-schaften von Polyvinylacetat (PVAc) bei verschiedenen Frequenzen und auch die Temperatur-abhängigkeit seiner Vibrations- und Konfigurations-Wärmekapazitäten wurden bestimmt. Es wurde gezeigt, daß die Vibrations-Wärmekapazität von PVAc im Erweichungsbereich scharf zunimmt und die Konfigurations-Wärmekapazität durch einen Peak geht. Man fand, daß die Segment-Mobilität den Wärmetransport im Polymer auf eine ambivalente Weise beeinflußt, in dem die Wärmeleit-fähigkeit entweder gesenkt oder angehoben wird.