

Application of the temperature wave technique for the study of relaxation transitions in polymers

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Abstract

The paper describes the principles, theoretical calculation procedure, and apparatus used for the realization of the temperature wave technique. The efficiency of the technique for the studies of relaxation transitions in polymers when the thermophysical characteristics are in the complex form has been demonstrated. The temperature dependences of the moduli and arguments of thermophysical characteristics for different frequencies of temperature oscillations have been obtained for polyvinylacetate. The vibrational and configurational components of the heat capacity have been found. The effect of polymer plasticization and also of changes in the chemical composition of molecules on complex thermophysical characteristics has been shown using styrene–butylacrylate as an example. © 1997 Elsevier Science B.V.

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1. Introduction

All solids are characterized by the presence of not only the vibrational dynamics of atoms and molecules (relatively small vibrations of particles about the equilibrium position), but also of the fluctuational dynamics bumps of atoms, formation of vacancies and of other defects, migration of defects etc. The events of the fluctuational dynamics are often associated with variations in the particle energies. Therefore the fluctuational dynamics itself can affect the thermophysical characteristics of solids, such as heat capacity and thermal conductivity. Moreover, the consequences of the fluctuational dynamics (e.g.

changes in the free volume) can influence the characteristics of the vibrational dynamics (frequency, vibration amplitude), which in turn can affect heat capacity and thermal conductivity.

The fluctuational molecular mobility in polymers is in a specific form, that is, in the form of segmental mobility. It appreciably affects the thermophysics of polymers, especially in the region of relaxation transitions.

The theoretical estimates of the contribution coming from the fluctuational dynamics into the heat capacity of polymers have been performed by many authors [1–4]. However, the experimental separation of the thermophysical characteristics of polymers into the vibrational and configurational (fluctuational) components is a complicated task,

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and a few papers on this subject have been published [5,6].

This paper describes the technique which proved to be efficient for the detailed study of the thermophysical characteristics of polymers (the temperature wave technique) and gives the results of the use of this technique.

2. Theoretical relations

Because of the participation of the fluctuational processes in the molecular dynamics of polymers, the heat content and temperature vary asynchronously under nonstationary conditions (change of the thermal state of a solid).

Then such characteristics as heat capacity (C) and thermal conductivity (λ) can be represented by complex values:

$$C^* = C_0 \exp(i\delta_c) \quad (1)$$

where C_0 is the modulus and δ_c the phase shift between the heat content and temperature; and

$$\lambda^* = \lambda_0 \exp(i\delta_\lambda) \quad (2)$$

where λ_0 is the modulus and δ_λ the phase shift between the heat flow and temperature gradient.

It is important to emphasise that it is just the configurational component that gives rise to the phase shift, while the vibrational component has no phase shift (because of its 'inertialless' nature). Therefore the heat capacity, for instance, can be represented as a sum of the vibrational (C_{vibr}) and configurational (C_{con}) heat capacities. It has been shown [7] that:

$$C^* = C_0 \exp(i\delta_c) = C_{\text{vibr}} + C_{\text{con}} \frac{1 - i\omega\tau}{1 + (\omega\tau)^2} \quad (3)$$

where ω is the circular frequency of harmonic temperature oscillations, and τ the relaxation time, that is, the characteristic time of expectation for the fluctuational event of a corresponding molecular regrouping.

Thus the experimental task is defined as follows: to find the parameters of complex thermophysical characteristics, that is, the modulus and phase shift.

This problem can be solved by using the technique of plane temperature waves when their frequency is varied.

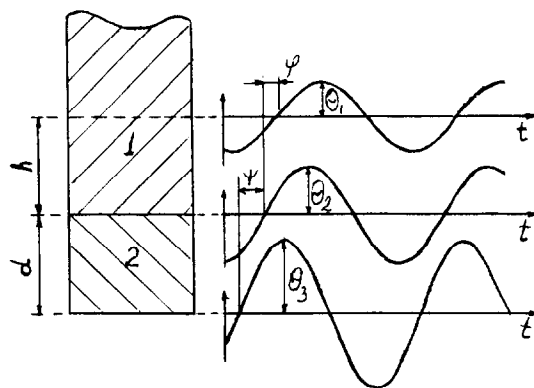


Fig. 1. The measuring unit and harmonic temperature oscillations in different cross section. 1 – sample under study; 2 – reference material.

In fact, this technique involves generation of temperature on the surface of a plane sample (a plate) which varies in time harmonically with frequency ω and measurement of harmonic oscillations of the temperature in the sample bulk at a certain distance h from its surface. Because of the finite velocity of propagation of heat front absorption of heat, the phase shift of temperature oscillations arises, and the amplitude of temperature oscillations decreases.

In practice, the temperature wave technique involves the use of measuring units of different types [6]. Fig. 1 shows schematically the unit which allows us to determine all complex thermophysical characteristics:

$$\text{temperature conductivity } a^* = a_0 \exp(i\delta_a)$$

$$\text{thermal conductivity } \lambda^* = \lambda_0 \exp(i\delta_\lambda)$$

$$\text{thermal activity } b^* = b_0 \exp(i\delta_b)$$

$$\text{heat capacity } c^* = c_0 \exp(i\delta_c).$$

The unit consists of the semi-finite solid (1) being studied which is in thermal contact with the reference plane sample (2). On down side of reference sample (Fig. 1), harmonic oscillations of temperature with amplitude θ_3 are generated. The reference sample is included in the measuring unit in order to determine the heat flow. After the measurement of amplitude and phase of oscillations of temperature at reference

sample surface and depth h in sample under study, the complex thermophysical characteristics are calculated from formulae [6]:

$$a_0 = \omega h^2 / [\varphi^2 + \ln^2(\theta_2/\theta_1)] \quad (4)$$

$$\delta_a = \pi/2 - 2 \arctg[\varphi/\ln(\theta_2/\theta_1)] \quad (5)$$

$$b^* = \frac{b_r[(\theta_3/\theta_2) \exp(i\psi) - \cos h(\sqrt{i\omega/a_r} \cdot d)]}{\sin h(\sqrt{i\omega/a_r} \cdot d)} \quad (6)$$

$$c^* = b^*/\sqrt{a^*}, \quad \lambda^* = b^*\sqrt{a^*} \quad (7)$$

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 depth h of the semi-infinite sample (Fig. 1), φ is the phase shift between the temperature oscillations with the amplitudes θ_2 and θ_1 ; ψ the phase shift between the oscillations with the amplitudes θ_3 and θ_2 (Fig. 1); d the thickness of the reference sample, and a_r and b_r are the known temperature conductivity and thermal activity of the reference sample. The reference sample was chosen so that the fluctuational dynamics did not manifest itself in the proper temperature region. In our experiments, ebonite was used as a reference sample. Temperature dependences of temperature conductivity and thermal activity for ebonite were determined by DSC and Temperature Wave Technique [5,6].

To fulfill the condition of semi-infinity of the sample studied, it was in the form of a plate of rather a large thickness, that is, 30–50 mm.

Thus expressions (4–7) allow us to analyze the results of temperature measurements and to find complex thermophysical characteristics of the objects under investigation.

3. Experimental

3.1. Apparatus

To measure complex thermophysical characteristics at temperatures ranging from 80 to 450 K at the frequencies of temperature oscillations from 10^{-3} to 1 Hz, an automated setup realizing the technique of plane temperature waves was developed and fabricated.

The source of temperature waves was a low-inertia plane ohmic heater, 30 mm in diameter. The non-uniformity of the temperature field on the surface of heater was not higher than 2%. The harmonic temperature oscillations on the heater surface that was in contact with the reference plate were produced by a generator of special oscillations of electric current. The amplitudes of harmonic temperature oscillations on both surfaces of the reference plate and at depth h in the sample studied, and also the phase differences between these oscillations were measured by differential manganin–constantan thermocouples connected to a computer assisted data acquisition system. Depth h was 0.5–1.5 mm; thickness of the reference sample d was 1 mm. The distances between the thermocouples were h and d .

The input amplitudes of temperature variations were varied in the range 0.05–5 K. The distortions of harmonicity did not exceed 3%.

The average temperature of the sample was maintained by a thermostat with the accuracy not poorer than 0.05 K, which was provided by an electronic monitoring system.

Measurements were performed at the intervals of 0.2–1.0 K during a continuous low-velocity (1–3 K/h) heating of the unit.

The measured values of temperature oscillation amplitudes were fed to a computer which computed the heat capacity and thermal conductivity from formulae (4–7).

The complex thermophysical characteristics were determined with the root-mean-square error of less than 2% for the modulus and 0.01 radian for the argument.

3.2. Objects

To demonstrate the efficiency of the temperature wave technique for the study of thermophysics of polymers, the following objects were used:

1. The amorphous polymer polyvinylacetate (PVAc) with the molecular weight $M = 120\,000$. The density at 293 K was $\rho = 1120 \text{ kg/m}^3$. The glass transition temperature was $T_c \approx 310 \text{ K}$.
2. Polyvinylacetate with $M = 800\,000$ and $\rho = 1127 \text{ kg/m}^3$, nonplasticized and plasticised by ethanol.

3. Copolymers of styrene-butylacrylate with ratios between concentrations of components 60:40 and 80:20. Molecular weight of copolymers was approximately 200 000.

4. Results

The results of determining the heat capacity for PVAc are shown in Fig. 2. The dependence of the temperature variation of modulus C_0 on the frequency of temperature waves can be seen in Fig. 2(a). It can also be seen that it is just in the glass transition region that the phase shift (nonzero value of argument δ_c) occurs (Fig. 2b). Thus in the glass transition region the heat capacity of PVAc indeed manifests itself as a complex value.

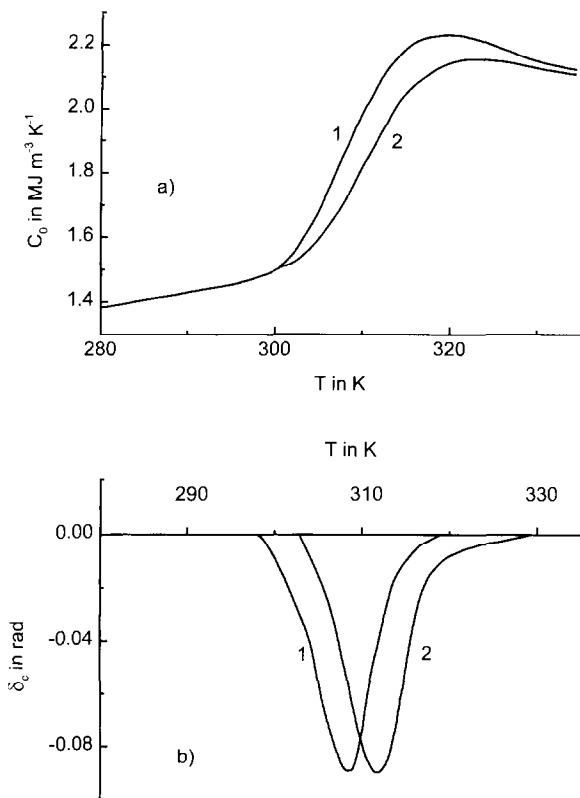


Fig. 2. Temperature dependence of the modulus C_0 (a) and argument δ_c (b) of the complex heat capacity of PVAc (molecular weight $M = 120\,000$) for different frequencies of temperature oscillations. 1 – 0.01 Hz; 2 – 0.1 Hz.

The ‘jump’ in the modulus ΔC_0 is nearly independent of frequency. Its magnitude $\Delta C_0 \approx 0.63 \text{ MJ/m}^3 \text{ K}$ is consistent with the data of [8], and also with our measurements of the dynamic heat capacity by the DSC technique.

As can be seen from Fig. 2(b), the values of argument δ_c are negative. Hence, the variations in the heat content in the steady-state harmonic process lag in phase of the temperature variations. This indicates that the heat content of the polymer is associated not only with the vibrational dynamics, but also with the configurational mobility.

From the data of Fig. 2 and using Eq. (3), the temperature dependences of the vibrational $C_{\text{vibr}}(T)$ and configurational $C_{\text{con}}(T)$ components of heat capacity, and also of the relaxation time $\tau(T)$ were calculated. These results are shown in Fig. 3.

It can be seen that in the region of polymer softening, its configurational heat capacity peaks and the vibrational component monotonically grows. Below the glass transition temperature, the configurational processes (segmental mobility) appear only slightly, and therefore C_{con} associates with them does not manifest itself. With unfreezing of the segmental mobility, C_{con} begins to increase. According to [9,10], the growth is due to an increase in the free volume (the number of ‘holes’) and an increase in the fraction of segments which are in the high-energy state (gauche conformations). The ‘hole’ component of the configurational heat capacity is proportional to the

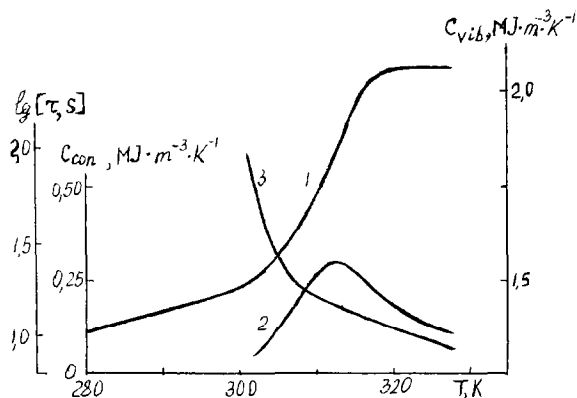


Fig. 3. Temperature dependence of the vibrational (1) and configurational (2) heat capacities and of the relaxation time (3) for PVAc ($M = 120\,000$).

temperature derivative of the hole concentration. This value sharply grows as the glass transition temperature is approached and then drops, because the concentration of holes tends to saturation with a further growth of temperature and transition of the polymer into a highly elastic state [4,9].

As far as the contribution of trans–gauche transitions into the heat capacity is concerned, the concentrations of trans- and gauche-conformers become equal after passing through the glass transition temperature and a further increase of temperature. Correspondingly, the contribution passes through the maximum and then drops.

The monotonical increase in the vibrational heat capacity with a plateau after T_c is mainly attributable, as supposed in [4], to a change in the anharmonicity of oscillations because of a strong increase in the thermal expansion of polymers in the region of devitrification.

Of interest in the resulting relation between C_{vibr} and C_{con} in the glass transition temperature region, where the dominating role of growth of C_{vibr} is seen. This quantitative problem needs further refinement and subsequent discussions.

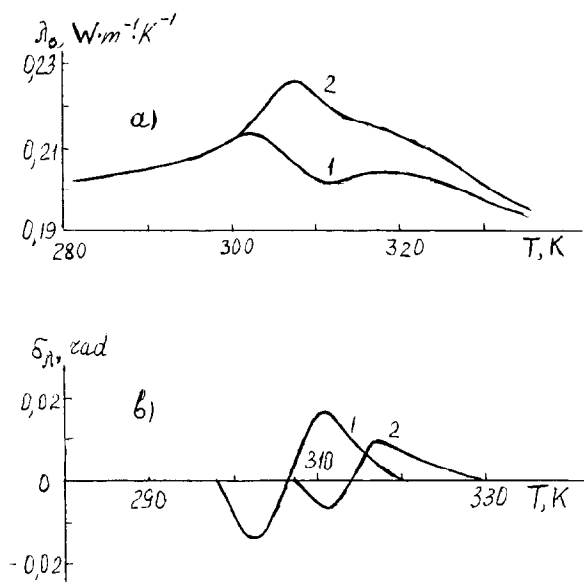


Fig. 4. Temperature dependence of the modulus λ_0 (a) argument δ_λ (b) of the complex thermal conductivity of PVAc ($M = 120\,000$) for different frequencies of temperatures oscillations. 1–0.01 Hz; 2–0.1 Hz.

The temperature dependence of the thermal conductivity of PVAc also shows a complex form of this characteristic (Fig. 4). The dependence of argument δ_λ on temperature turns out to be complicated: that is, it inverses the sign in the region of T_c . The modulus of thermal conductivity (λ_0) passes through the maximum in the region of T_c , consistent with the literature data [4,11]. It is likely that here the temperature behavior of thermal conductivity is also caused by the configurational processes.

The sensitivity of the technique to different changes in the state and structure of polymers can be seen using the following examples.

Fig. 5 shows the effect of plasticization of PVAc on the temperature dependences of the modulus and argument of heat capacity. It can be seen that the dependence shifts toward lower temperatures, which

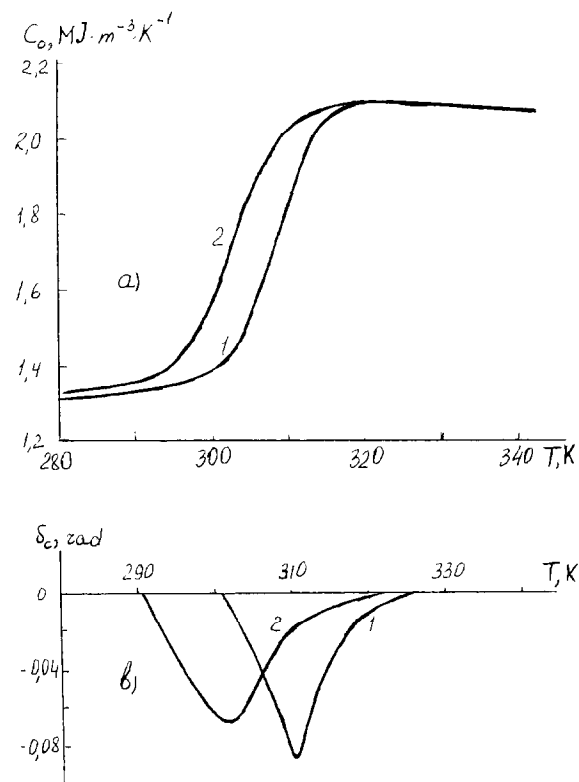


Fig. 5. Temperature dependence of the modulus C_0 (a) and argument δ_c (b) of the complex heat capacity of PVAc ($M = 800\,000$) for the frequency of temperature oscillations of 0.05 Hz. 1 – nonplasticized PVAc. 2 – plasticized by ethanol (~1% of weight).

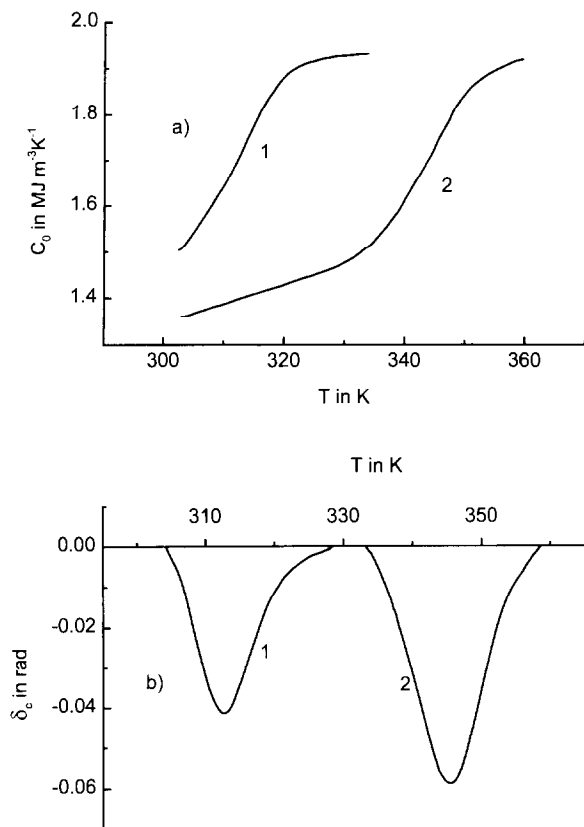


Fig. 6. Temperature dependence of the modulus C_0 (a) and argument δ_c (b) of the complex heat capacity of copolymer styrene–butylacrylate for the frequency of temperature oscillations of 0.05 Hz. 1–60% of styrene; 2–80% of styrene.

is the consequence of weakening of the intermolecular interaction.

Fig. 6 presents the temperature dependences of the modulus and argument of heat capacity of the copolymer styrene–butylacrylate for different ratios between the rigid and flexible fragments in macromolecules. An increase in the fraction of flexible fragments leads to a shift of the dependences toward lower temperatures.

5. Conclusions

Thus the temperature wave technique allows us to obtain a new and detailed information about the molecular relaxation processes in polymers. Of major interest is the possibility to separate the contributions of the vibrational and fluctuational dynamics into the thermophysical characteristics of polymers. A reliable identification of these contributions is one of the most important problems of the thermophysics of polymers.

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