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HEAT CAPACITY AND THERMAL CONDUCTIVITY PROPERTIES OF CRYSTALLINE AND AMORPHOUS POLYMERS

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Abstract: The article analyzes theoretically and experimentally the thermodynamic properties of crystalline and amorphous polymers, such as heat capacity, thermal conductivity and thermal expansion. The application of the Debye and Tarasov models to the heat capacity of polymers, especially their behavior at low temperatures, is considered. The influence of the degree of crystallization on thermal conductivity is also illustrated by the example of polymers such as polyethylene. The influence of low-frequency optical vibrations arising in amorphous polymers on heat capacity is emphasized. The article also provides theoretical formulas for determining the expansion coefficients of polymers and explains their physical meaning.

Key words: polymers, crystalline and amorphous structure, heat capacity, thermal conductivity, thermal expansion, Debye model, Tarasov model, low temperature physics, thermodynamic properties, degree of crystallization, polyethylene, optical vibrations.

Introduction

The thermal conductivity of polymers is much lower than that of other solids. $\lambda \rightarrow (0{,}2 - 0{,}3)\frac{J}{(kg \cdot K)}$ This is why polymers are considered thermal insulators. Due to the relative mobility of bonds and the change in conformation in polymers, they have a high coefficient of linear expansion. $\left(10^{-4} - 10^{-5}\right) \cdot K^{-1}$ have. Therefore, it can be assumed that they differ from materials with a smaller coefficient of linear expansion, such as metals and semiconductors. However, the high elasticity and relatively low operating temperatures of polymers allow them to be used as films on the surface of any material [1].

Very few experimental results on the heat capacity of polymers agree with those obtained by theoretical interpretation. The heat capacity of polymers in the solid state is expressed as:

$\mathrm{C} = \mathrm{C}_1 + \mathrm{C}_2 + \mathrm{C}_3$ in this: C_1– heat capacity of vibrating grates; C_2– characteristic oscillations, i.e., the heat capacity of individual links moving independently; C_3– heat capacity of an existing defect in the polymer [1].

At present, it is advisable to compare the experimental results of the heat capacity with the results of simpler theoretical models. As these models, the Debye and Tarasov models can be considered. For this purpose, one of the main issues is the issue of determining the limit of application of the Debye theory for polymers. During the propagation of long Debye waves in polymer chains, the chains interact based on the result of intermolecular forces. This, in turn, creates three-dimensional vibrations in polymers. As is known, three-dimensional vibrations can be explained by the Debye theory. During the propagation of short Debye waves, the main role in the spectra is played by vibrations directed along the polymer chain. As is known. In this case, the one-dimensional nature of polymer molecules is manifested. We know that this corresponds to the Tarasov model. The disadvantage of these models, namely, that they cannot calculate the heat capacity with high accuracy, is that they do not take into account the dispersion of Debye waves. It is known from the Debye theory that, $C \approx T^3$ Contact $T < \theta_D/12$, however, as a result of dispersion, this bond remains in the region of very low temperatures. The study of the dependence of heat capacity on temperature provides very important information about the nature of polymers and is a factor in creating a mechanism for theoretical assessment of the thermal properties of polymers [2]. Polyethylene is a partially crystalline polymer and forms an orthorhombic cell during crystallization. The repeating unit in PE consists of a methylene (H2) group, therefore its molar heat capacity $m = 14{,}03\ g$ belongs to the mass. Density of fully crystallized polyethylene $\rho_k = 0{,}999\ mg/m^3$, density of completely amorphous polyethylene $\rho_a = 0{,}8525\ mg/m^3$ will be [2].

A feature of amorphous polymers is that at low temperatures, their temperature-dependent changes in heat capacity are inconsistent with Debay's theory. Derived from Debay's theory in amorphous polymers at low temperatures C/T^3 =const Coupling fails, maximum hail occurs in the heat capacity graph near 5K temperature. This effect is explained by the presence of low frequency optical vibrations in the polymer. Jump to search For example, the thermal capacity of amorphous polyethylene is explained based on Tarasov's theory using a combination of frequency spectrum in the low temperature region [2].

Thus, the heat capacity of amorphous bodies moves away from the calculations of Debay's theory. This conclusion is especially evident in experimental experiments. For example; defined for polymethylmethacrylate and polystrone $f(T) = S/T^3$ In addition to acoustic vibrations, the effect of non-acoustic vibrations is also evident at temperatures close to liquid helium. At temperatures below 1.5K S/T^3 The amount decreases and tends to a limiting value. This change is clearly visible in ultrasonic measurements. For polymethylmethacrylate and polystyrene, the non-acoustic effect on the heat capacity is clearly noticeable in the helium temperature range [3].

An excessively high Debye heat capacity at low temperatures (explained by Einstein's theory) is one of the characteristic features of organic and inorganic amorphous substances. The vibrational spectra of ordered aggregates are discrete, and at low temperatures the formation of low frequencies occurs. This has a certain effect on the heat capacity and thermal conductivity of the system. This point of view is consistent with the modern molecular structure of amorphous polymers [4].

Research result

Thermal conductivity of crystalline and amorphous polymers. It is known that the degree of crystallization χ thermal conductivity of polymers (λ) is one of the characteristics that affect the thermal conductivity of partially crystallized polymers. Usually, the thermal conductivity of partially crystallized polymers is considered as a combination of the thermal conductivity of fully amorphous and crystalline polymers. The thermal conductivity coefficient of partially crystallized polymers is expressed as:

$$\lambda = \chi\lambda_K + (1-\chi)\lambda_A \qquad (1)$$

In this λ_K va λ_A Thermal conductivity coefficient of crystalline and amorphous polymers; χ – degree of crystallization.

Aerman expresses the effect of the degree of crystallization on thermal conductivity using the following formula::

$$\chi = \frac{2\lambda_A+\lambda_K+2\chi(\lambda_K-\lambda_a)}{2\chi_a+\lambda_K-\chi(\lambda_K-\chi_a)} \qquad (2)$$

In polymers, the x_k and x_a change significantly with temperature. In such cases, the polymers are amorphous. ρ_a and crystal ρ_K The density also changes. The degree of crystallization λ at room temperatures ρ_k and ρ_a can be calculated by. Formula (1.2) cannot be used as an exact analytical formula for all polymers. For polymers with a high degree of crystallinity, this formula cannot be considered appropriate. In this case, the use of formula (1.1) for the thermal conductivity of polymers gives a more accurate result [4].

The values of thermal conductivity calculated by theoretical methods for polymers differ significantly from the values calculated experimentally. Currently, there are more than 40 theoretical formulas for the thermal conductivity of polymers, but all of them are used as approximate calculation formulas. The creation of a single theory for the thermal conductivity of polymers requires many experimental studies [4].

Thermal expansion of crystalline polymers. The thermal coefficient of thermal expansion of crystalline polymers depends not only on volume and temperature, but also on the degree of crystallization of the polymer. If the polymer is neither completely crystalline nor completely amorphous, its specific volume V can be considered as the specific volumes V_1 and V_2 of the crystalline and amorphous polymers. If these volumes are at the same temperature and pressure, the following expression can be written:

$$V = \chi V_1 + (1-\chi)V_2 \qquad (3)$$

In this: χ – degree of crystallization of the polymer by mass; $\chi = m_1/m_2$ (m_1– mass of the polymer in the crystal sphere, $m_2 -$ its total mass).

Both parts of the above equation are equivalent to the specific gravity of a fully crystalline polymer. V_1^0 we divide by volume. Here T=0 K and R=0 let . We write the following equations by introducing dimensionless parameters:

$$X = \frac{V}{V_1^0};\ X = \frac{V_1}{V_1^0};\ X = \frac{V_2}{V_1^0}; \qquad (4)$$

These equations take the following form for specific volume::

$$X = \lambda X_1 + (1-\lambda)X_2 \qquad (5)$$

In this case, the thermal coefficient of expansion takes the following form::

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{X}\left(\frac{\partial X}{\partial T}\right)_p \qquad (6)$$

We can change this formula to the following::

$$\beta = [\lambda X_1\beta_1 + (1-\lambda)X_2\beta_2]/X \qquad (7)$$

The indices 1 and 2 in the formula refer to crystalline and amorphous polymers. Accordingly, the thermal expansion coefficient for crystalline and amorphous polymers takes the following form:

$$\beta_1 = \frac{1}{X_1}\left(\frac{\partial X_1}{\partial T}\right)_p; \qquad \beta_2 = \frac{1}{X_2}\left(\frac{\partial X_2}{\partial T}\right)_p; \qquad (8)$$

λ considering it as constant, (1.6) thermal coefficient of expansion from the equation β can be calculated. In this case β_1, β_2, χ_1 and χ_2 considering it permanent, (1.6) thermal coefficient of expansion from the equation β can be calculated.

In this case

$$P(X,T) = P_0(X) + g(X)T \qquad (9)$$

In this: *$R_0(X)$ – 0 K* pressure at temperature; *g(X)T* corresponding thermal effect at a given volume and temperature (R_T).

The shape of both functions in this formula depends on the relationship between the crystalline and amorphous domains of the polymer..

$(\partial P/\partial T)_X = \beta B_T$, $B_T =- X(\partial P/\partial X)_T$ Considering the last formula, the following expression follows:

$$\beta = \frac{PT}{(TB_T)} \qquad (10)$$

For crystalline polymers, formula (1.8) is often appropriate. Considering crystalline polymers as three-dimensional, their thermodynamic properties can also be calculated using other theoretical models. [5].

Conclusion

The study of the thermodynamic properties of polymers further expands their practical applications. According to the results of the study, crystalline and amorphous polymers have significant differences in heat capacity, thermal conductivity, and expansion coefficient. The degree of crystallization directly affects these properties. The temperature-dependent heat capacity and vibration spectra of polymers are explained by the use of the Debye and Tarasov models. Non-acoustic vibrations that occur in amorphous polymers, especially at low temperatures, demonstrate the uniqueness of thermal behavior. Also, the differences between theoretical models and practical applications require the development of more accurate models to improve the thermodynamic analysis of polymers**.**

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