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EFFECT OF MODIFIED FIBRE GLASS ON THE STRUCTURE AND THERMOPHYSICAL PROPERTIES OF PENTAPLAST(PENTANE)

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The results of experimental investigations of the effects of ground fibre glass on the structural parameters and thermophysical characteristics of pentaplast(pentane) were assessed.

The degree of crystallinity, thermal conductivity, specific heat and density of pentaplast containing various amounts of modified fibre glass were determined experimentally.

The results obtained are discussed in terms of modern theories of the effects of fillers on the properties and structures of polymers.

Introduction

One of the most effective modifying factors, having a considerable effect on the structure of a polymer at practically all levels of its organization, is its filling with highly-dispersed agents [1, 2]. We have performed a complex investigation of the effects of an anisodiametric filler on the structure and thermophysical properties of polyether poly-3,3-bis(chloromethyl)oxacyclobutane, pentaplast (PTP).

Experimental

For the determination of specific heat (C_p) and heats of phase transition, a dynamic method of thermal analysis [3] with a heating rate of 0.04 deg/s was chosen. The limit of permissible error was 2.5% for the full temperature range (153–493 K).

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The temperature dependence of the thermal conductivity was also investigated in the dynamic regime by the Platunov method [4]. The limit of permissible error was 6–8%. The errors in both thermophysical methods were evaluated in accordance with the compulsory appendix to GOST 23630.1–79. The confidence probability was 0.95. A direct method of broad angle X-ray diffraction was chosen (BAXD) [5, 6].

Data decoding corresponds to that in [6]: the α-modification corresponds to angles 2Θ of 14°27', 21°31', 28°54', 31°24'; and the β-modification to 2Θ = 15°15', 15°33', 20°33', 25°06'.

As indirect methods of investigation of the structures of polymers, dilatometry and an acoustic method were used. Measurements of sample density were carried out by the method of hydrostatic weighing in accordance with the standard SAV 891-78 for plastics. The limit of permissible error was less than 0.5% at a confidence probability of 0.95.

Measurements of ultrasound velocity at 1 MHz were made by the method of impact excitation. The experimental technique and analysis of error are described in [8]. The relative error of measurement was 1.5% at a confidence probability of 0.95 in the entire range.

Samples obtained by compressing powdery industrial pentaplast (TU6-05-1422-71) were tested.

The viscosity of a 0.5% solution of polymer in cyclohexane at 293 K was 1.73 $\mathrm{dal \cdot g^{-1}}$, which corresponds to a molecular weight of 200 000 [9].

For the moulding of initial samples under pressure, a regime with technological parameters similar to those applied in the industrial processing of PTP was chosen. The method of sample preparation was that described in [15].

The characteristics of the finely-ground fibre glass are shown in Table 1. Particles of ground fibre glass have a considerable influence on the arrangement of the macromolecules, and lead to pronounced structural changes in both crystalline and amorphous regions of partially crystalline polymer [2]. The structural changes in the polymer matrix and the ability of the particles themselves to structure formation result in an altered specific heat exchange in composite materials.

Results and discussion

Compositions containing even a small amount of ground fibre glass agents undergo disintegration of the bonding agent. The increase in the specific volume of a polymer matrix at a 12% agent content is 0.5%.

Table 1 Characteristics of filler

Filler	$\rho\cdot10^{-3}$, kg/m^3	$C_p\cdot10^{-3}$, J kg K	λ, W cm K	Specific surface $S_{sp}\cdot10^{-3}$, m^2/kg	Particles size $d\cdot10^6$	Particles form
Fibre glass	2.25	0.71	7	0.16	10 × 200	Cylindrical

Table 2 Parameters of glass-transition of filled pentaplast

Filler content	T_c, K	$C\cdot10^{-3}$, J/(kg K)	ν	$E_h\cdot10^{-3}$, J/kg	$V_h\cdot10^3$, m^3/kg	Length of free path of phonons	$\alpha_m\cdot10^3$, K^{-1}	$\alpha_c\cdot10^3$, K^{-1}	$V_f\cdot10^3$, m^3/kg before annealing	$V_f\cdot10^3$ m / kg after annealing
0.06	278	0.197	0.057	39.4	0.078	0.202	0.355	1.138	0.112	0.109
2	278	0.192	0.085	40.1	0.79	0.224	0.355	1.136	0.112	0.109
4	280	0.189	0.100	40.5	0.080	0.237	0.353	0.120	0.113	0.110
6	282	0.180	0.140	41.2	0.082	0.265	0.349	0.115	0.114	0.111
12	283	0.175	0.167	42.0	0.083	0.339	0.332	0.085	0.115	0.113

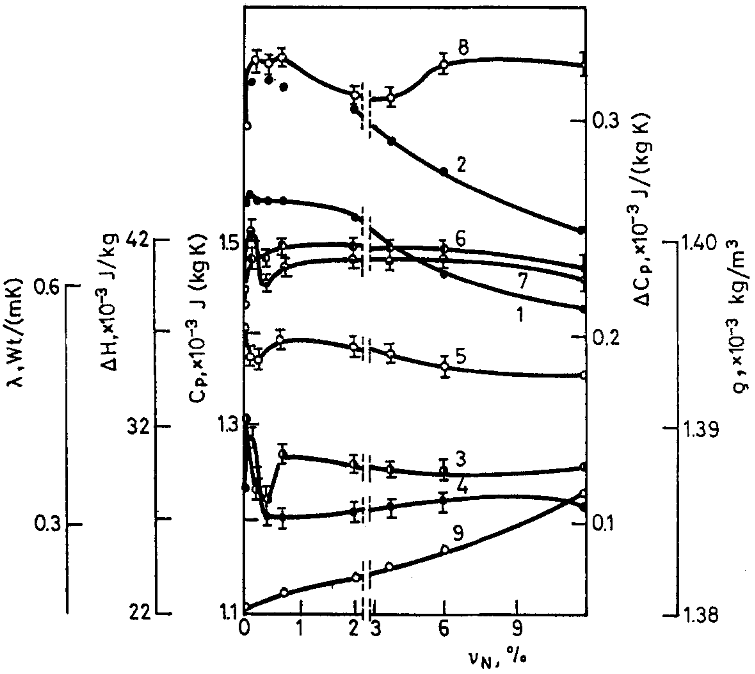

Fig. 1 Concentration dependences of density before (1) and after (2) annealing, of specific heat at 333 K before (3) and after (4) annealing; of specific heat jump at glass transition (5); heat of melt before (6) and after annealing (8-full endothermic effect, 7-responsible for general crystaline structure); of polymer matrix of pentaplast + fibre glass compositions. Thermal conductivity (9)

For comparison, an analogous cubic content (V_h) of aerosil in compositions based on PTP results in an increase in the specific volume (V) of the polymer matrix by 1.7–2.0%. At concentrations of fibre glass up to 2%, the density (ρ) of the matrix remains constant (Fig. 1).

A small concentration of fibre glass (less than 0.2%) somewhat increases the degree of crystallinity (chi) of the bonding, without causing a pronounced change in the α:β-modification ratio. With further increase of the filler concentration, the degree of crystallinity decreases, and at large concentrations the degree of crystallinity is practically zero.

The transition through the minimum of the concentration dependence of the specific heat jump (ΔC_p) at glassing takes place at a concentration of fibre glass of 0.2% (Fig. 1). At more than 0.7% of agents, this dependence decreases practically linearly, which is connected with the decrease in the polymer part which participates in atomic processes. A part from the basic process of the polymer being involved in the formation of transition layers, abnormally small values of ΔC_p at very small concentration are caused by the additional processes of structurization (cross-linking). The concentration dependence (C_p) is analogous. Consequent annealing at 445 and 413 K lowers C_p considerably in the concentration range 0.4–40%. In this range, the increase in enthalpy of the melt (ΔH_m) is maximum at the expense of cross-linking in amorphous regions of the polymer.

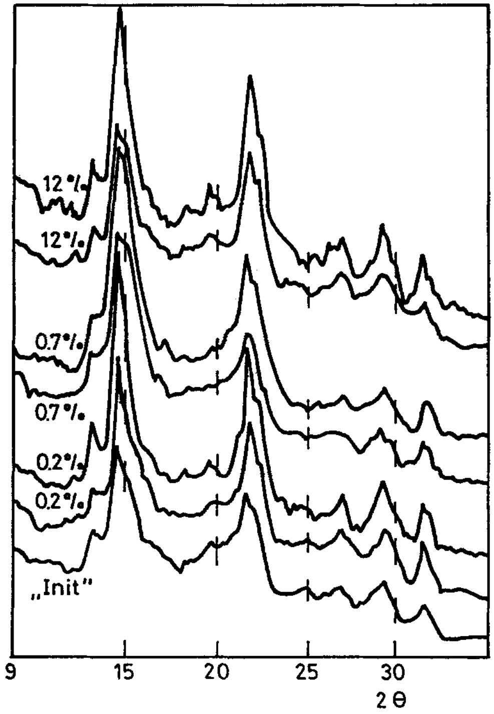

Fig. 2 Diffraction curves of pentaplast with various cubic content of fibre glass before and after (X) annealing

The increase in density during annealing decreases with increase of the filler concentration from 0.5%.

The mechanism of the transformations is as follows. Small concentrations of fibre glass induce additional cross-linking during crystallization, artificial germs of cross-linking being formed by the orientation of adjoining surface macromolecules in the melt. The thickening of the melt and the decrease in the molecular mobility of the chains, the links of which are adsorbed by the surface of the filler, both lead to the kinetic limitation of formation of the most perfect α-modification and give a chance for development of the β-structure.

With further increase of the concentration, with the practical formation of a transition layer, the process stabilizes. Annealing at 445 K favours the partial β-α transition and perfection of the basic crystalline structure. Subsequent thermal treatment at 413 K regulates the transition layers and amorphous region in response to the orienting influence of the filler surface.

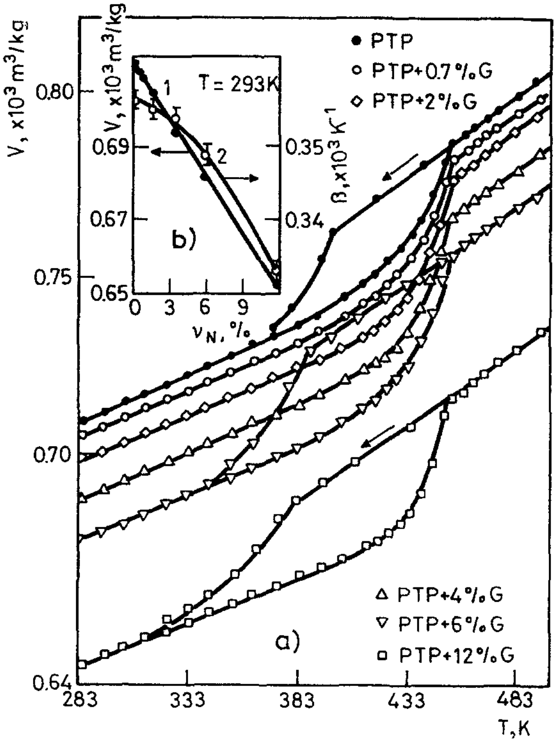

Fig. 3 a) Temperature dependence of specific volume of pentaplast with different cubic content of fibre glass. b) Concentration dependence of specific volume at 293 K (1) and concentration dependence of coefficient of volume expansion (2)

The temperature dependences of specific heat, specific volume and ultrasound velocity (V_{so}) are shown in Figs 3 and 4. The temperature of melting (T_m) of the compositions increases somewhat with increase of the concentration of the agent, and it exceeds the starting value practically throughout the concentration range. The temperature coefficient [C_p (T)] decreases practically linearly in the temperature range 203–393 K, with the exception of the glass-transition area, which agrees with the Tarasov non-interacting chain theory [11]. Deviations from linearity at lower than 203 K are caused by an increase in the interchain interaction role, and at higher than 293 K by the beginning of endothermic processes of melting of a metastable defective structure in low-ordering regions.

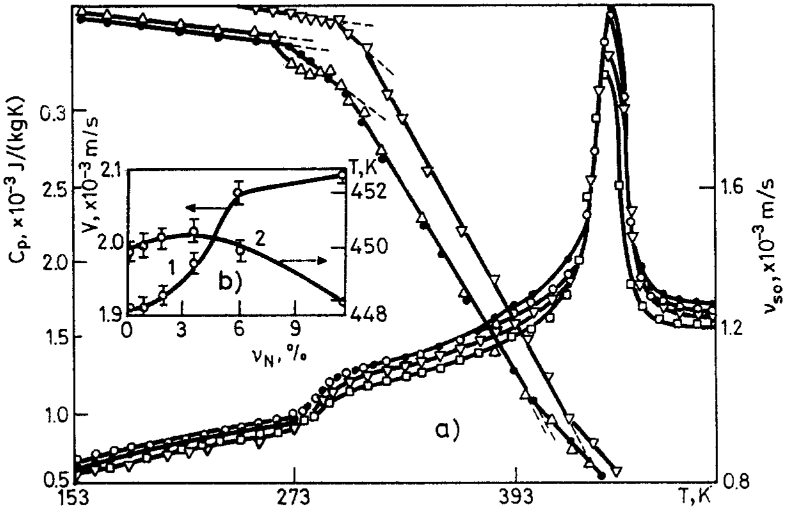

Fig. 4 a) Temperature dependence of specific heat and speed of ultrasound of pentaplast with different cubic content of fibre glass (● –0%, o–0.7%, Δ–2%, ∇–6%, □–12%). b)
b) Concentration dependence of speed of ultrasound at 298 K (1) and temperature of melt (2)

The specific character of the process of softening of compositions with anisodiametric particles is seen in the temperature dependence of the ultrasound velocity, and the temperature of the glass transition (T_g) in the volume and in layers connected with the filler surface varies (Fig. 2). The difference reaches T_c = 30 deg. With increase of the filler concentration, decreases occur in the proportion of the polymer, and in glassing in the volume, and T_c shifts to higher temperature. Softening of the transition layers takes place in the range 298–303 K. With increase of the filler concentration, the process of premelting is also delayed, which is seen in both the calorimetric and acoustic temperature dependences.

The concentration dependence of the ultrasound velocity increases exponentially up to 6% of fibre glass agent, but not on further increase of the concentration. This is connected with the begining of processes of disintegration of the polymer matrix. The temperature dependence of the specific volume of the compositions (Fig. 3) is linear up to 393 K for the initial material and up to 408 K at a fibre glass agent content of 12%. A considerable thickening of melt compositions of PTP occurs during crystallization at a constant rate of cooling of 0.15 deg/s. The maximum temperature of supercooling of the melt shifts from 403 K for unfilled PTP to 383 K for the composition with 12% fibre glass agent. Correspondingly, the temperature of the final stage of crystallization shifts from 368 to 323 K.

Some parameters of the process of glass transition of polymers can be evaluated approximately on the basis of conclusions of the theory of the liquid state. This theory states that many properties of liquids and amorphous bodies, including polymers, can be explained by the presence of free volume, which is a set of 'holes' of monomer size. The appearance of the holes has a fluctuating character, provoked by the thermal motion of the molecules, and is a result of the instability in the correct arrangement of the particles, due to the lack of harmony in their vibrations near the equilibrium position. The equilibrium number of 'holes' at a given temperature defines the free volume (V_f) of the liquid:

$$V_f = V(t) - V_o = V_o \exp[-E_h/(RT)] \tag{1}$$

where $V(t)$ and V_0 are the specific volumes at temperatures T K, and E_h is the 'hole' energy necessary to overcome the forces of cohesion. The specific volume of 'hole' is V_h. The process of disappearance and appearance of a 'hole' creates elastic deformation, which spreads with the speed of elastic waves, and preserves the dynamic equilibrium of 'hole' by means of phonons. Glass transition begins at the time the polymer reaches the free volume value, which at T_c is approximately identical for all polymers: 0.025 ± 0.003 [14].

Calorimetric investigations (Fig. 4) of the process of glass transition allow the determination of C_p and T_c, and calculation of E_h and V_h, using the formulae for the 'holes' theory:

$$\Delta C_p = \frac{E_c}{T_c} \cdot \frac{E_h}{RT_c} \exp[-E_h/(RT)] \tag{2}$$

$$V_h = (E_h \cdot V_c)/E_c \tag{3}$$

where E_c is the specific energy of cohesion at T_c, and V_c is the specific volume at the temperature of the glass transition.

Since PTP involves partially crystalline polymers, in calculations of the parameters of glass transition from the volume of polymer matrix the part due to the crystalline polymer was subtracted, which does not take part in the glass transition process. This was calculated from the BAXD data. That part of the polymer which was excluded from the process of glass transition by being involved in boundary layers was determined via the formula

$$\nu = (1-f) = 1 - \Delta C_p / \Delta C'_p \tag{4}$$

where ν is the proportion of 'excluded' macromolecules, f is the proportion of uncombined macromolecules, and C'_p is the thermal conductivity jump of the unfilled initial PTP.

The average length of the phonon path $(\bar{l})$ was obtained from the formula

$$\lambda = 1/3\,(C_p \rho\, V_{sou} \cdot \bar{l}) \tag{5}$$

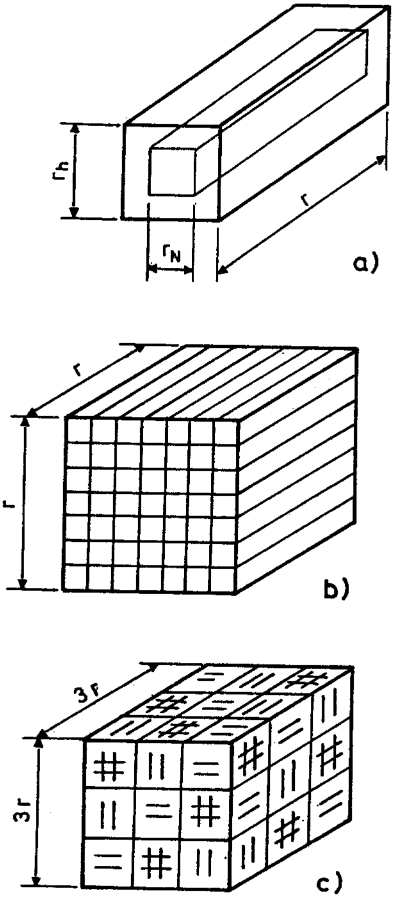

Fig. 5 Model of the composition structure with anisotropic form of filler particles: a) unit cell, b) unit with anisotropy, c) average isotropic unit

The value of V_0 for the polymer matrix was obtained by extrapolation of the temperature dependence of the specific volume of melt PTP to 0 K.

The coefficient of volume expansion at T_c is $0.59 \cdot 10^{-3}$ K^{-1} and $(\alpha_m - \alpha_c)$ $T_c = 0.121$. $\alpha_m T_c = 0.164$ $T/T = 0.625$ (α_c is the coefficient of cubic expansion below T_c, and α_m is that above T_c) and corresponds well to the general parameters for amorphous polymers.

Calculated values of the above parameters are given in Table 2.

Investigation of the concentration dependence of the thermal conductivity (λ) of compositions containing fibre glass shows that for the filler with anisodiametric particles in the entire concentration range the values considerably exceed the data obtained from calculations involving the theory of generalized conductivity [15] and correspondingly the values of the effective thermal conductivity of silicon-containing fillers with a quasispherical form of the particles (aerosil, quartz sand) [16].

For compositions containing anisodiametric agents with low thermal conductivity, the concentration dependence λ can be described by using a simple model (Fig. 5). Here, an anisodiametric particle with an area of r_H^2, enveloped by the polymer layer, makes an average unit that is a parallelepiped form with an area of r_n^2.

If it is assumed that $r_n = 1$, then the volume concentration of the filler $V_H = r_H^2 \cdot r/(r_n^2 \cdot r)$ and $r_H = V_H^{1/2}$. The thermal resistance of the unit in the direction OX is

$$R_{ox} = r/\lambda_{||} = [\lambda_H \cdot V_H/r + \lambda_n(1 - V_H)/r]^{-1} \tag{6}$$

where $\lambda_{||}$ is the thermal conductivity of the average unit parallel to the OX axis, and λ_H and λ_n are the thermal conductivities of the filler and the polymer, respectively. Hence

$$\lambda_{||} = \lambda_H \cdot V_H + \lambda_n(1 - V_H) \tag{7}$$

Let us arrange the units into a block with side r (Fig. 5b). In the OX direction, such a block possesses thermal conductivity, and in the direction perpendicular to OX we can calculate the thermal conductivity $\lambda_\perp$ according to the model suggested in [15]. For modelling of the structure of compositions, an initial unit with isotropic properties is necessary. Such a unit can represent a system of blocks which is a cube with side $3r$, with a definite arrangement of the blocks (Fig. 5c). The thermal resistance of such a system in the directions OX, OY and OZ is

$$R = 1/(\lambda_{eff} \cdot 3r) = \frac{1}{9}[1/(\lambda_{||} \cdot r) + r/(\lambda_{\perp} \cdot r)]$$

whence

$$\lambda_{eff} = 3\lambda_{||}\lambda_{\perp} / (\lambda_{\perp} + 2\lambda_{||}) \tag{8}$$

This relationship well describes the concentration dependence of series of compositions based on PTP (with fibre glass, titanium dioxide, boron nitride) with a small concentration of filler (up to 9% by volumen. The rapid increase in thermal conductivity at concentrations higher than 9% and the bend in the curve in the region of 4–5% are modelled very well. Concentrations higher than 9% by volume give low results.

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Zusammenfassung — Es werden die Ergebnisse der experimentellen Untersuchungen des Einflusses von gemahlenem Fiberglas auf die Strukturparameter und thermophysikalischen Eigenschaften von Pentaplast (Pentan) gewertet.

Der Kristallinitätsgrad, das Wärmeleitvermögen, die spezifische Wärme und die Dichte von Pentaplast mit verschiedenem Gehalt an modifiziertem Fiberglas wurde experimentell ermittelt.

Die erhaltenen Ergebnisse wurden hinsichtlich moderner Theorien über den Einfluß von Streckmitteln auf die Eigenschaften und die Struktur von Polymeren diskutiert.