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INFLUENCE OF ANHARMONIC EFFECTS ON THE STRUCTURAL-MECHANICAL AND THERMOPHYSICAL PROPERTIES OF FILLED POLYMER SYSTEMS

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The force constants of anharmonicity, the total energy, and the force of interaction between structural elements of PVC systems are determined from the values of the quasielastic constants of filled polymer systems.

Within the region of elevated temperatures and/or force actions, in addition to harmonic effects [1, 2], anharmonic components of the potential energy of interaction between structural elements of polymer systems [3] should be taken into account. In this case it is important to determine the effects of various ingredients on the value of the interaction potential.

We studied systems based on polyvinylchloride (PVC) with MW = $1.4 \cdot 10^5$ and Fickentcher constant equal to 65, obtained by suspension polymerization and refined by reprecipitation from the solution. Industrially fabricated phosphogypsum (PG) and BZh-1 phenolformaldehyde tar were used as PVC fillers [1]. Thermophysical and structural-mechanical properties were determined according to the method published in [2].

We consider a structural element of the polymer in the shape of a linear chain whose anharmonicity is described by the single force constant q (q') of the third order that holds for the two nearest neighbors. In this case q (q') are equal to $\beta/d(\kappa/d)$ in order of magnitude [4], where d is the interatomic distance, and $\beta(\kappa)$ are the corresponding force constants of the interaction.

As is shown by results of calculations, the value of q in the PVC+PG system depends on the phosphogypsum content in the system. Thus, in the content region up to 4% (Fig. 1) a nonmonotonic character is observed for the variation of the value of q. At a filler concentration φ equal to 1 – 2 vol.% PG the value of q attains its maximum. Within the region of filler concentrations 4–10 vol.% PG no substantial variations are observed in the q value. Within the range of 10 vol.% $< \varphi <$ 22 vol.% PG a monotonic increase in q is observed.

The dependence of the value of q' on φ is more complex. Thus, within the region of PG content 0.3–0.5 vol.% a minimum is observed for q'. Within the region of 0.5 vol.% $< \varphi <$ 10 vol.% the value of q increases insignificantly, and q' = const upon change in concentration of PG from 10 to 20 vol.%. At $\varphi \geq$ 22 vol.% PG the value of q' tends to increase.

The temperature dependence of q shows that the value of the constant decreases monotonically with increase in T (Fig. 1). The dependence of q' on T possesses the same character. However, within the temperature region 313–323 K a deviation from linearity is observed in the dependence $q' = f(T)$. For the PVC+PG system the dependence $q(T)$ is characterized by a sharp decrease in the value of q within the temperature region 293–353 K and by insignificant variations within the region $T \sim$ 353–403 K. The dependence of q' on T is similar.

Thus, the values of the anharmonicity constants of PVC systems depend not only on the type of filler and the temperature but also on its content in the composition as well. Suppose that the law of the force interaction between the structural elements is as follows:

$$F = -\beta x + qx^2 . \tag{1}$$

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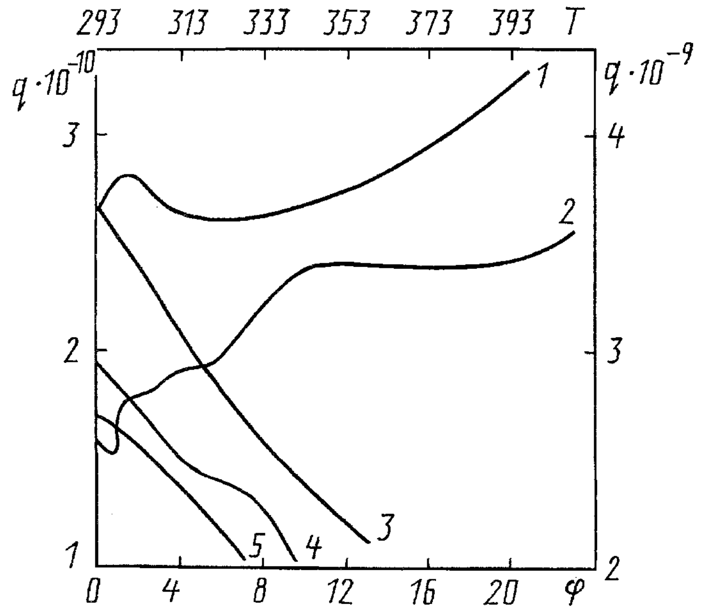


Fig. 1. Concentration (1 and 2) and temperature (3, 4, and 5) dependences of q (1, 3, and 5) and q' (2 and 4) of filled polymer systems: 1) and 2) PVC+PG; 3) and 4) PVC + 3 vol.% PG; 5) PVC + 3 vol.% BZh. q (q'), $\mathrm{N \cdot m^{-2}}$; φ, vol.%; T, K.

TABLE 1. Concentration Dependence of the Interaction Forces and the Energy of Structural Elements of the PVC+PG System

φ, vol.%	$F_{\min_1} \cdot 10^{10}$, N	$F_{\min_2} \cdot 10^{11}$, N	$F_{\min_3} \cdot 10^{12}$, N	$U \cdot 10^{20}$, J	$U_p \cdot 10^{20}$, J	(A_3-A_4), J/kg·K^2
0	1.56	2.05	3.52	3.73	1.78	2.012
0.1	1.56	2.13	3.77	3.88	1.94	1.510
0.3	1.68	1.91	3.52	3.94	1.98	1.510
0.5	1.69	2.00	3.52	3.99	1.99	1.510
1.0	1.69	2.22	4.05	4.06	2.03	1.510
2.0	1.67	2.22	4.05	4.02	2.01	1.510
3.0	1.56	2.32	4.05	3.80	1.90	1.510
5.0	1.59	2.32	4.05	3.88	1.94	1.514
10.0	1.61	2.71	4.85	4.01	2.02	1.505
20.0	1.98	2.71	4.85	4.78	2.70	1.504

Then for PVC systems $F_{\min_1} = -\beta^2/4q$ (in the case of the C–C bond) and $F_{\min_2} = \kappa^2/(4q')$ (in the case of H–Cl and H–H bonds). In the case of thermodynamic equilibrium ($F = 0$) we determine $x = x_0$ as $x_0 = \beta/q$.

As is shown by the results of calculations the maximum increase in the harmonic component of the interaction force is observed in the case of the C–C bond at $x = 0.8$ Å. For the H–H bond this quantity is 0.5 Å, and for the H–Cl bond it equals 0.9 Å. It should be noted that with a change in the filler type and concentration and in the temperature the value of x_0 is practically unchanged. Equality between the components βx and qx^2 is observed correspondingly at 1.6 Å (C–C bond), 1.0 Å (H–H bond), and 1.8 Å (H–Cl bond).

An analysis of the dependence of the force $F_{\min_1}$ on φ (Table 1) demonstrates that its values depend on the filler concentration. Thus, within the region $\varphi = 0.3$–2 vol.% PG the values of $F_{\min_1} \simeq$ const. Only at $\varphi \geq 10$ vol.% PG is an increase in $F_{\min_1}$ observed. For the concentration dependence of $F_{\min_2}$ ($F_{\min_3}$), constancy of the force value is observed at $\varphi = 1$–5 vol.% PG. An increase in the values of $F_{\min_2}$ and $F_{\min_3}$ is observed within the region of concentrations 5–10 vol.% PG, and at $\varphi \geq 10$ vol.% PG these quantities are unchanged. This

TABLE 2. Temperature Dependence of the Interaction Forces and the Energy of Structural Elements of Filled Polymer Systems

T, K	PVC+3 vol.% PG					PVC+3 vol.% BZh				
	$F_{\min_1}\times 10^{10}$, N	$F_{\min_2}\times 10^{11}$,N	$F_{\min_3}\times 10^{12}$, N	$U\cdot 10^{20}$,J	$U_p\times 10^{20}$, J	$F_{\min_1}\times 10^{10}$, N	$F_{\min_2}\times 10^{11}$, N	$F_{\min_3}\times 10^{12}$, N	$U\cdot 10^{20}$,J	$U_p\cdot 10^{20}$,J
293	1.56	2.32	4.05	3.19	1.90	1.13	1.40	2.45	2.52	1.26
303	1.39	2.18	3.77	2.85	1.72	0.99	1.38	2.44	2.40	1.20
313	1.23	1.96	3.52	2.52	1.53	0.93	1.33	2.44	2.25	1.16
323	1,05	1.91	3.24	2.17	1.33	0.73	1.33	2.44	2.24	0.80
333	0.94	1.74	2.97	1.92	1.20	0.59	1.29	2.44	1.82	0.72
343	0.81	1.55	2.69	1.68	1.03	0.55	1.29	2.44	1.66	0.55
353	0.71	1.38	2.44	1.46	0.91	0.49	1.25	2.16	1.44	0.55

character of the dependence of $F_{\min_1}$, $F_{\min_2}$, and $F_{\min_3}$ on φ bears witness to the fact that upon introduction of the first portions of the filler 0.1–0.5 vol.% PG the boundary layer formation process proceeds intensely in the system, which leads to an increase in the anharmonic force component of the interaction. At $\varphi \geq 20$ vol.% PG a further increase in the component $F_{\min_1}$ is observed. This points to the fact that for C– C at high filler concentrations and small deviations from the quasi-equilibrium position the harmonic component of the interaction force plays a leading part.

The temperature dependence of $F_{\min_1}$, $F_{\min_2}$, and $F_{\min_3}$ (Table 2) for the system PVC + 3 vol.% PG shows that the values of the interaction forces decrease with increase in the temperature. This is a consequence of the fact that the action of the temperature field leads to more intense manifestation of anharmonic effects in the composition. For the system PVC + 3 vol.% BZh the presence of temperature regions on the temperature dependences of $F_{\min_1}$, $F_{\min_2}$, and $F_{\min_3}$ for which the force values vary only slightly is characteristic (Table 2).

It should be noted that the values of the forces $F_{\min_1}$, $F_{\min_2}$, and $F_{\min_3}$ also depend on the filler type. Thus, for the system PVC + 3 vol.% PG these values are greater than those for the system PVC + 3 vol.% BZh. Therefore the anharmonic effects manifest themselves more distinctly in the PVC+PG system. A comparison of the corresponding values of the interaction forces in the PVC+PG systems with the values for the original PVC shows that they are close to each other and somewhat higher than those for the PVC+BZh composition.

Knowing the values of the anharmonicity constants q and q' and assuming that the deviation of the structural elements from the quasi-equilibrium position is equal to the interatomic distance ($x \simeq d$) we determine the component of the potential energy as

$$U = \frac{qx^3}{3} + \frac{q'x_1^3}{3} + \frac{q'x_2^3}{3}. \tag{2}$$

An analysis of the concentration dependence of U (Table 1) shows that it possesses its maximum value at $\varphi = 1$ vol.% PG, whereas within the region $2 < \varphi < 10$ vol.% PG the values of U change insignificantly. At $\varphi \geq 10$ vol.% PG an increase in observed again in the anharmonic component of the potential energy of the interaction. The temperature dependence of U for both of the systems PVC + 3 vol.% PG and PVC + 3 vol.% BZh shows that the total potential energy of the anharmonic component decreases with increase in the temperature (Table 2). It is characteristic that within the region of the temperature-induced α-transition [5, 6] ($T_c \sim 353$–363 K) the character of the $U = f\,(T)$ dependence changes.

With the effects under consideration taken into account, the potential energy of the interaction of the structural elements in the PVC composition for the C–C bond is

$$U_{p_1} = \frac{1}{2}\beta x^2 - \frac{1}{3}qx^3, \tag{3}$$

and, correspondingly, for the H–Cl bond

$$U_{p_2} = \frac{1}{2}\kappa_1 x_1 - \frac{1}{3} q' x_1^3 \tag{4}$$

and in the case of the H–H bond

$$U_{p_3} = \frac{1}{2}\kappa_2 x_2 - \frac{1}{3} q'' x_2^3 . \tag{5}$$

Then the total energy of interaction of the structural elements is determined as

$$U_p = U_{p_1} + U_{p_2} + U_{p_3} .$$

As is shown by an analysis of the concentration dependence of U_p (Table 1) of the PVC+PG system, the introduction of the first portions of the filler (0.1–0.5 vol.%) leads to an increase in the value of the potential energy of the interaction. Within the range of filler concentrations 0.1–10 vol.% PG the maximum value of U_p is observed at $\varphi = 1$ vol.%. With a change in the filler concentration from 10 to 20 vol.% PG a further increase in the value of U_p is observed.

An inspection of the dependence $U_p = f(T)$ for the systems PVC + 3 vol.% PG and PVC + 3 vol.% BZh (Table 2) shows that with an increase in T the value of U_p decreases. However, within the entire temperature range U_p for the system PVC + 3 vol.% PG is greater than the value of the potential energy of interaction of the structural elements of the system PVC + 3 vol.% BZh. In this case a more intense variation of the value of U_p with an increase in T is characteristic for the system PVC + 3 vol.% PG compared to PVC + 3 vol.% BZh.

The observed character of the concentration dependence of U_p for PVC systems makes it possible to conclude that the boundary layer also takes part in forming both the macroscopic and structural-mechanical properties of the composition.

Taking into account relationships (3)–(5) and assuming that the distribution function $f(x)$ (the probability of deviation of a structural element from the equilibrium position) varies according to a Boltzmann distribution [7]:

$$f(x) = A \exp(-U_p/kT) \simeq A \exp(-\beta x^2/2kT)\left(1 + \frac{qx^3}{3kT}\right), \tag{6}$$

we determine its mean displacement from the equilibrium position as

$$\bar{x} = \int_{-\infty}^{+\infty} x f(x)\, dx . \tag{7}$$

The constant A in the Boltzmann distribution is determined from the normalizing condition for the function $f(x)$: $\int_{-\infty}^{+\infty} f(x)dx = 1$, whence $A = \sqrt{\beta/2\pi kT}$. Then

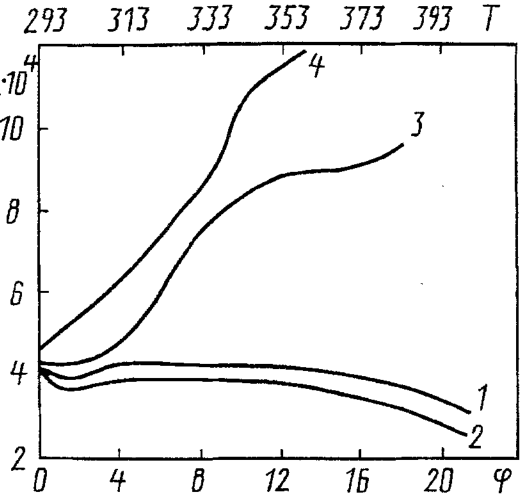
$$f(x) = \sqrt{\beta/2\pi kT}\, \exp(-\beta x^2/2kT)\left(1 + \frac{qx^3}{3kT}\right). \tag{8}$$

Substituting the quantity (8) into (7) we obtain

$$\bar{x} = \int_{-\infty}^{+\infty} x\sqrt{\beta/2\pi kT}\, \exp(-\beta x^2/2kT^2)\left(1 + \frac{qx^3}{3kT}\right) dx = \frac{qkT}{\beta^2}. \tag{9}$$

The quantity $\bar{x}$ makes it possible to determine the linear thermal expansion coefficient α_t of the system:

$$\alpha_t = \frac{\bar{x}}{dT} = \frac{qk}{d\beta^2}. \tag{10}$$



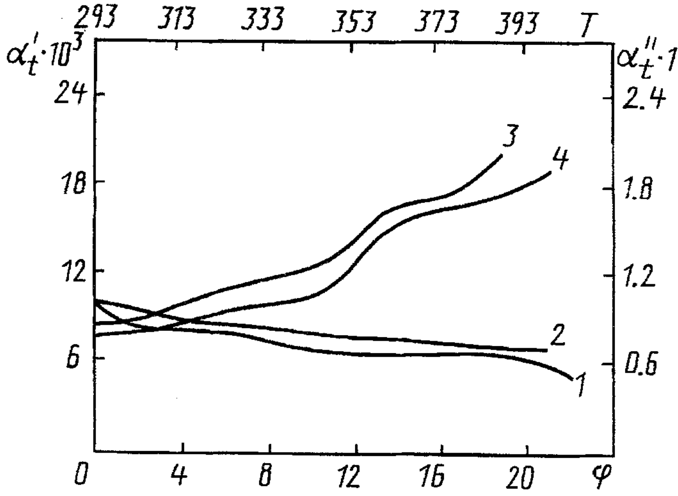


Fig. 2. Concentration (1 and 2) and temperature (3 and 4) dependences of $\Delta\beta_t$ of filled polymer systems: 1) theory; 2) experiment for the PVC+PG system; 3) PVC + 3 vol.% PG; 4) PVC + 3 vol.% BZh. $\Delta\beta_t$, K^{-1}.

Fig. 3. Concentration dependence (1 and 2) for the PVC+PG system and temperature dependence (3 and 4) for PVC + 3 vol.% PG: 1 and 3) α'_t; 2 and 4) α''_t. α'_t, α''_t, K^{-1}.

Taking into account that the temperature volume expansion coefficient is

$$\Delta\beta_t \simeq 3\alpha_t \simeq \frac{3qk}{d\beta^2}, \tag{11}$$

we calculate its value. As is shown by the results of calculations, the value of $\Delta\beta_t$ for the original PVC is $4.31 \cdot 10^{-4}$ K^{-1} and are close to the experimental value $4.20 \cdot 10^{-4}$ K^{-1} [8, 9].

An analysis of the concentration dependence of $\Delta\beta_t$ (Fig. 2) for the PVC+PG system shows that the minimum of this quantity is observed within the region $0 < \varphi \leq 3$ vol.% at $\varphi = 1$ vol.% PG. At 3 vol.% $< \varphi \leq 10$ vol.% PG $\Delta\beta_t$ is practically unchanged and only at $\varphi \geq 20$ vol.% PG is a decrease in it observed. As follows from data presented in Fig. 2, an increase in $\Delta\beta_t$ within the temperature range 293–403 K is observed for the systems PVC + 3 vol.% PG and PVC + 3 vol.% BZh. The dependence $\Delta\beta_t = f(T)$ shows that for the system PVC + 3 vol.% PG the temperature region of the transition from the glasslike state to the highlyelastic one lies within the interval 353–363 K, whereas for PVC + 3 vol.% BZh the corresponding interval is 348–358 K.

It is of interest to determine the linear thermal expansion coefficient along the direction perpendicular to the chain of the main valences. The values of α'_t (in the case of the H–Cl bond) and α''_t (the H–H bond) of PVC systems were determined according to the relationship

$$\alpha'_t = \frac{q'k}{d\kappa^2}. \tag{12}$$

As is shown by an analysis of Fig. 3, $\alpha_t < \alpha'_t < \alpha''_t$ for the PVC+PG system within the entire range of concentrations. Such a relationship between the values of the linear thermal expansion coefficient is evidence that the forces of the intermolecular interaction are weaker along the direction of the H–H bond compared to those acting along the direction of H–Cl.

An analysis of the concentration dependence of α'_t and α''_t of the PVC+PG system shows that at $\varphi \geq 10$ vol.% PG the forces of the intermolecular interaction increase. This is evidently connected with the fact that the possibility of interaction of a large number of side groups of PVC macromolecules with the filler surface arises.

The temperature dependence of α'_t and α''_t shows that within the temperature region 293–373 K an increase in their values is observed. It should be noted that within the region of the temperature-induced α-transition, as well as within the region of the highly elastic state, the temperature expansion coefficient $d\alpha_t'/dT$ ($d\alpha_t''/dT$) increasesd. This is evidence that upon transition from the glasslike state to the highly elastic one the forces of intermolecular interactions decrease along the transverse direction. In this case the mobility of the structural elements of the system increases. At the same time the introduction of the mineral PG leads to a substantial decrease in their mobility compared to the original PVC or systems with polymer fillers like BZh.

Taking into account the frequency shift for the structural elements of the polymer with an increase in temperature and its contribution to the anharmonic component of the spectrum of the system, we carry out a calculation of the value of the specific heat C_V according to [10]:

$$C_V = 3Nk + (A_3 - A_4)\,T\,, \tag{13}$$

where A_3 and A_4 are functions of Φ_3 and Φ_4, which are terms of the potential energy expansion.

It turned out that C_V of the PVC+PG system [11] can be extrapolated as a linear dependence within the temperature region 293–343 K. On this basis the values of (A_3-A_4) were determined. As is shown by the results of the calculations (Table 1), $(A_3-A_4) > 0$ within the entire range of the filler concentration and it depends on the concentration of the filler in the system. Thus for the original PVC the value of (A_3-A_4) is a maximum, whereas within the region of the filler concentrations 0.1– 0.5 vol.% PG it is practically unchanged and is 1.510 $\mathrm{J/(kg\cdot K^2)}$. The value of (A_3-A_4) reaches its minimum at $\varphi = 1-2$ vol.% PG. At $\varphi > 5$ vol.% PG an insignificant decrease in (A_3-A_4) is observed.

This character of the dependence of (A_3-A_4) on φ correlates well with the concentration dependence of $\Delta\beta_t$ for the PVC+PG system. This is evidence that upon thermal expansion of polymers, not only does Φ_3 affect the parameters of the system but Φ_4 as well. Since $(A_3-A_4) > 0$, the main contribution to both the thermal expansion and the heat capacity is evidently made by Φ_3, whereas Φ_4 affects the parameters of the system only in the case of the presence of external forces.

Thus, taking into account the anharmonic effects in filled polymer systems makes it possible to determine not only microscopic structural-mechanical parameters but also macroscopic parameters of polymers and polymer systems.

NOTATION

q (q'), force constants of the third order; F, force of interaction of the structural elements of the system; U_p, interaction energy of structural elements; β_t, temperature volume expansion coefficient; α_t (α_t', α_t''), linear thermal expansion coefficients; C_V, specific heat.

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