

INVESTIGATION OF THE VISCOELASTIC PROPERTIES OF METAL-PIGMENTED POLYVINYL CHLORIDE BY THE POTENTIALS OF THE INTER- AND INTRAMOLECULAR INTERACTIONS OCCURRING IN IT

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An algorithm for calculating the frequency spectrum of polyvinyl chloride pigmented with a metal has been developed on the basis of the Hamiltonian formalism. The dependence of the viscoelastic properties of this composite in the frequency range unattainable for low-molecular crystals on the inter- and intramolecular interactions occurring in it and the surface properties of the pigment was determined.

Metal-pigmented flexible-chain polymers are among the heterogeneous polymers, the energy-exchange processes occurring in which are not clearly understood [1, 2]. The most characteristic feature of these polymers is that practically all their components are diametrically different in physical properties. This poses a number of theoretical and practical problems [3], the solution of which calls for the development of new methods for determining the functional dependences between the micro- and macroproperties of a composite. Since amorphous polymers contain only fluctuating structural elements with finite lifetimes [4], which are difficult to investigate by direct methods, acoustic-spectroscopy methods appear to have the greatest promise for investigating these polymers [5]. However, in this case, the problem on the dependence of the viscoelastic properties of heterogeneous systems based on flexible-chain polymers on the inter- and intramolecular interactions occurring in them and the content of a microatomized metal with which they are pigmented remains unsolved. Because of this, the aim of the present work is to develop and analyze a physical model of a heterogeneous polymer system that would allow us to find quantitative relations between the macroscopic parameters of a polyvinyl chloride (PVC) composite and the characteristics of its molecular mobility.

Model. In accordance with the ergodic principles of statistical thermodynamics [6], to define structures formed in a heterogeneous polymer system, we will perform double averaging: over the space x, y, z and the time t , considering a PVC macromolecule as a separate subsystem [7]. In this case, when the system is subjected to the action of a mechanical force field with an ultrasonic frequency, all its structural elements and the corresponding-configuration conformation levels will manifest themselves as autonomous structural units. It should be noted that the supermolecular structure of polymers, through which their viscoplastic properties are transferred to the macroscopic level, represents a configuration of macromolecules, for the description of which there are no correct quantitative methods [8]. Therefore, in what follows the structure organization of the molecular system being investigated and its structural elements will be classified by one indication: geometric, thermodynamic, or kinetic characteristics. It should be noted that, in the PVC being considered in the condensed state, there can arise fluctuation structures (which can be discrete) with finite lifetimes [9]. It will be assumed that the total lifetime of separate relaxing structures is determined by the Boltzmann formula [10].

Based on the data of [1, 2], we will construct a two-component PVC system consisting of a pigment and a boundary layer at $\varphi \geq \varphi_{cr}$. Since the particles of the pigment are spherical in shape, it will be assumed that the centers of the spheres form a simple cubic lattice, the sites of which are imbedded into a polymer matrix in the state of a boundary layer. In accordance with [11], the behavior of such a system in a dynamic mechanical field is considered as a cooperative change in the conformational state of its elements. In this case, a PVC macromolecule will be represented as a condensed system of atoms interacting with each other due to the potential forces [7].

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The specific internal energy of the indicated system will be determined by summation of the potential energy of interaction of an atom with any other atom of the principal-valence chain of a PVC macromolecule and the potential interaction energy of an atom forming a pair with another atom as a result of the intermolecular interaction and due to the existence of active centers on the surface of a microatomized pigment. The sum obtained is multiplied by the number of atoms in the system. It is assumed that the lifetime of fluctuating structures representing atomic structure formations satisfy the condition $\tau \gg 0$, i.e., they do not break down and do not change substantially under the action of a periodic external force field.

As the potential of the intramolecular interatomic interaction we will use the interatomic Lennard–Jones potential $u_1(r)$ [12] representing the sum

$$u_1(r) = A \left[\left(\frac{l}{r} \right)^{m_1} - \left(\frac{l}{r} \right)^{m_2} \right] + BG \left(\frac{l}{r} \right)^{m_3}. \quad (1)$$

Since, in the PVC there occur dipole-dipole u_o , induction u_{in} , and dispersion u_{dis} interactions between the monomeric links and segments, the energy of their attraction $\left(-A \left(\frac{l}{r} \right)^{m_2} \right)$ is equal to [9]

$$-A \left(\frac{l}{r} \right)^{m_2} = u_o + u_{in} + u_{dis} = -\frac{1}{r^6} \left[\frac{2}{3} \frac{\mu_1^2 \mu_2^2}{kT} + \alpha_1 \mu_2^2 + \alpha_2 \mu_1^2 + \frac{3}{4} \frac{I_1 I_2 \alpha_1 \alpha_2}{I_1 + I_2} \right]. \quad (2)$$

The potential $A(l/r)^{m_1}$ in (1) defines the repulsion of electron clouds in the process of interaction of PVC atoms. The potential $BG(l/r)^{m_3}$ is a function of the temperature and defines the pressure exerted by the flux of carriers emitted by an atom and directed to the other atoms of the body. From (2) we obtain, in accordance with [12], that $m_1 = 12$, $m_2 = 6$, and $m_3 = 5$.

The force of interaction of an atom of the principal-valence chain of a PVC macromolecule with another atom of the macromolecule, which is offset by the distance r from the first-mentioned atom, is equal to

$$|\mathbf{F}_1(r)| = -\frac{\partial u_1(r)}{\partial r} = \frac{A}{l} \left[m_1 \left(\frac{l}{r} \right)^{m_1+1} - m_2 \left(\frac{l}{r} \right)^{m_2+1} \right] + \frac{BGm_3}{l} \left(\frac{l}{r} \right)^{m_3+1}. \quad (3)$$

Accordingly, the intermolecular interaction can be represented in the form of the Morse potential $u_2(r)$ [13]. The force of the intermacromolecular interaction ($\mathbf{F}_2(r)$) of an atom with another atom of the primary-macromolecule chain, which is offset by the distance r from the first-mentioned atom, is equal to

$$|\mathbf{F}_2(r)| = -\frac{\partial u_2(r)}{\partial r} = 2\alpha D \left\{ \exp[-2\alpha(r-a)] - \exp[-\alpha(r-a)] \right\}. \quad (4)$$

The force $|\mathbf{F}_2(r)|$ acting on the system is equal to the additional external pressure P exerted on this system. For determining the interrelation between $|\mathbf{F}_2(r)|$ and P , it will be assumed that the atoms of the polymer system are homogeneously distributed with a density n_i over the planes z_i ($i = 0, 1, \dots$) parallel to the outer boundary of the composite XOY for which $i = 0$. First, we will determine the resultant $|\mathbf{R}_{qi}|$ of the forces of interaction γ of an atom of a macromolecule with coordinates $x = 0, y = 0, z = z_g$ with atoms of other macromolecules, lying in the plane z_i . In the plane z_i we will separate an elementary area $2\pi y dy$ that includes $2\pi y dy n_i$ atoms. In this case, the resultant $|d\mathbf{R}_{qi}|$ will be equal to

$$d\mathbf{R}_{qi} = 2\pi y dy n_i \left[\mathbf{F}_1(z_{qi}) \frac{\mathbf{z}_{qi}}{z_{qi}} + \mathbf{F}_2(r_{qi}) \frac{\mathbf{r}_{qi}}{r_{qi}} \right], \quad (5)$$

where $r_{qi} = \sqrt{z_{qi}^2 + y^2}$; $|z_{qi}| = |z_q - z_i|$; $\bar{E}(l) = \frac{1}{n_i} \sum_{\beta=1}^{n_i} G_\beta$.

The quantity $|\mathbf{R}_{qi}|$ will be defined as

$$\mathbf{R}_{qi} = \int_0^\infty d\mathbf{R}_{qi} = 2\pi n_i \left\{ \left[A \left(\frac{l^{m_1}}{\xi^{m_1-1}} - \frac{l^{m_2}}{\xi^{m_2-1}} \right) + BG \frac{l^{m_3}}{\xi^{m_1-1}} \right] \frac{\mathbf{z}_{qi}}{\xi_{qi}} + D \left[2 \exp(-\alpha(r_{qi} - a)) - \exp(-2\alpha(r_{qi} - a)) \right] \frac{\mathbf{r}_{qi}}{r_{qi}} \right\}, \quad (6)$$

where $\xi_{qi} = |\mathbf{z}_{qi}|$, and \mathbf{R}_q is calculated by summation of \mathbf{R}_{qi} over all i :

$$\mathbf{R}_q = \sum_i^n \mathbf{R}_{qi}. \quad (7)$$

If the distance between the planes z_i is small, the force \mathbf{R}_q can be defined as

$$\mathbf{R}_q = \sum_{i_1}^n \mathbf{R}_{qi_1} + \sum_{i_2}^n \mathbf{R}_{qi_2} = \mathbf{R}_1 + \mathbf{R}_2, \quad (8)$$

where, in the first approximation [10],

$$|\mathbf{R}_1| = K_1 x_1. \quad (9)$$

The system of equations (5)–(6) was solved using the method of successive approximations [14]. The first approximation for the steps between the layers of atoms of the principle-valence chain of a PVC macromolecule along the z axis was selected arbitrarily. In a small iteration cycle, all steps, other than the steps $h_q = z_{q+1} - z_q$ ($q = 0, 1, \dots, i$), were constant. A deviation of the values of $|\mathbf{R}_{qi}|$ from a smoothly converging series was considered as an indication of an error in h_q ; in this case, a new step was selected on condition that $\Delta h = (h_{qi} - h_{qk}) \leq \delta$. The searching steps h_q selected for PVC systems were equal to the steps used for the initial PVC. This allowed us to perform a comparative analysis of the relative shifts of the relaxation spectra of heterogeneous polymer systems. It was established that, when $C(q) \geq 10$, the relative value of the step between the layers of atoms in the direction of the z axis is rapidly stabilized in both cases and remains practically unchanged independently of C . In our investigations, we increased the distance r from zero to the value corresponding to the ultimate strength of the system, i.e., it was assumed that $r \leq 1.245l$ in relation (3) and $r \leq 1.629l$ in relation (4) [15].

In addition to the inter- and intramolecular forces (8), surface (\mathbf{F}_{sur}) and mass (\mathbf{F}_{mass}) forces can act on a PVC macromolecule in the direction of the z axis [15]. In this case, the equilibrium equation for an arbitrary ensemble of atoms of the systems in the projection on the z axis in the Hamiltonian model [16], in which $r(t)$ is a coordinate, has the form

$$\mathbf{R}_q + \sum_n \mathbf{F}_{\text{sur}} + \sum_M \mathbf{F}_{\text{mass}} = M \frac{d^2 \xi}{dt^2}. \quad (10)$$

Let us consider, in accordance with [11], the behavior of an individual macromolecule, the ends of which are fixed due to the steric hindrances formed by the pigment particles and the roughness of their surface, i.e., $h_i = z_{i+1} - z_i = \text{const}$. It has been established that if a PVC macromolecule is in a medium with a temperature thermostat, an elastic force acts on its ends and, in doing so, binds them [17]. The ends of this macromolecule are held fixed because they are acted upon by the force $\mathbf{R}_1(r)$ equal to the elastic force in absolute value and opposite to it in direction. According to (10), we have

$$M \frac{d^2 \xi}{dt^2} + \frac{3kT}{nl^2} \xi = 0, \quad \sum_n \mathbf{F}_{\text{sur}} = \frac{3kT}{nl^2} \xi. \quad (11)$$

Solving (11), we obtain the eigenfrequency of vibrations of a segment of a PVC macromolecule:

$$\omega = \sqrt{\frac{3kT}{Mnl^2}}. \quad (12)$$

It is seen from relation (12) that the high-frequency maximum ω is due to the displacement of the chain segment equal in value to the segment responsible for the vitrification of the polymer [5]. For example, even in the PVC region with a temperature of (4.2–77) K, the mechanical losses caused by the intermolecular cooperative local motion of groups of molecules were maximum at a frequency of $6 \cdot 10^4$ Hz. It is significant that, in the case where a weak ultrasonic field of higher frequency acts on the system, the chains of macromolecules play the role of crosslinks; therefore, at $\omega \geq 10^5$ Hz the deformations of the composite are practically entirely reversible [10].

It has been established in [4] that 1–2% of the atoms of the surface of a microatomized metal pigment are coordinationally unsaturated and that these atoms represent active centers of interaction of the pigment with a polymer macromolecule. We will calculate the potential of the field formed by a system of such centers, assuming that the interaction occurs in the medium with a large value of ϵ [11]. For this purpose, we will select a coordination system with origin in the system of two ion-radicals and $r_i/r_k \ll 1$. In this case, the general expression for the interaction potential $\phi_k(r_k)$ will be as follows:

$$\phi_k(r_k) = \sum_i \frac{q_i}{4\pi\epsilon\epsilon_0 |r_k - r_i|} \quad (13)$$

It can be expanded into the series

$$\begin{aligned} \phi_k(r_k) = & \sum_i \frac{q_i}{4\pi\epsilon\epsilon_0 r_0} + \frac{1}{4\pi\epsilon\epsilon_0} \sum_i \sum_{\alpha} \frac{\partial}{\partial x_i^{\alpha}} \left(\frac{q_i}{|r_k - r_i|} \right) \Bigg|_{r_i \rightarrow 0} x_i^{\alpha} + \\ & + \frac{1}{8\pi\epsilon\epsilon_0} \sum_i \sum_{\alpha, \beta} \frac{\partial^2}{\partial x_i^{\alpha} \partial x_i^{\beta}} \left(\frac{q_i}{|r_k - r_i|} \right) \Bigg|_{r_i \rightarrow 0} x_i^{\alpha} x_i^{\beta} + \dots, \end{aligned} \quad (14)$$

where $(\alpha, \beta) = 1, 2, 3$. On condition that $\frac{\partial}{\partial x_i^{\alpha}} \left(\frac{q_i}{|r_k - r_i|} \right) \Bigg|_{r_i \rightarrow 0} = \frac{\partial}{\partial x_i^{\alpha}} \left(\frac{q_i}{|r_i - r_k|} \right) \Bigg|_{r_i \rightarrow 0}$, this expression is simplified and takes the form

$$\phi_k(r_k) = \phi^{(0)} + \phi^{(1)} + \phi^{(2)} + \dots \quad (15)$$

Here

$$\phi^{(0)}(r_k) = \sum_i \frac{q_i}{4\pi\epsilon\epsilon_0 r_k}, \quad (16)$$

$$\phi^{(1)}(r_k) = \frac{1}{4\pi\epsilon\epsilon_0} \sum_i q_i r_i \nabla \frac{1}{r_k}, \quad (17)$$

$$\phi^{(2)}(r_k) = \frac{1}{8\pi\epsilon\epsilon_0} \sum_{\alpha, \beta} \frac{\partial^2}{\partial x_i^{\alpha} \partial x_i^{\beta}} \left(\frac{1}{r_k} \right) \sum_i q_i x_i^{\alpha} x_i^{\beta}. \quad (18)$$

Since the net charge of the system is equal to zero, $\varphi^{(0)}(r_k) = 0$ and $\varphi^{(1)}(r_k) = 0$ can be represented in the form

$$\varphi^{(1)}(r_k) = \frac{\mathbf{P}_i \mathbf{r}_i}{4\pi\epsilon\epsilon_0 r^3}, \quad (19)$$

since $q_i \neq 0$ and $\mathbf{P}_i \neq 0$, $\varphi^{(2)}(r_k) = 0$ and $\varphi_k(r_k) = \varphi^{(1)}(r_k)$. Taking into account the isotropism of the heterogeneous polymer system, we will assume that the index k is the number of fluctuating structures that are formed around a particle of a microatomized pigment; these structures are distributed homogeneously in a sphere of radius $r_i \geq d$. In this case, summation in (17) $\mathbf{P}_i \mathbf{r}_i$ can be replaced by integration over the solid angle β

$$\varphi^{(1)}(r) = \sum_i \frac{\mathbf{P}_i \mathbf{r}_i}{4\pi\epsilon\epsilon_0 r^3} = k \int_{\beta} \frac{\mathbf{P}_i \mathbf{r}_i}{4\pi\epsilon\epsilon_0 r^3} d\beta. \quad (20)$$

Accordingly, the strength of the field induced as a result of the ion-radical interaction will be equal to

$$\mathbf{E} = -\nabla\varphi^{(1)} = \frac{3\mathbf{P}_i \mathbf{r}_i r_k}{4\pi\epsilon\epsilon_0 r^5} - \frac{\mathbf{P}_i}{4\pi\epsilon\epsilon_0 r^3}, \quad (21)$$

and the force of interaction of an active center of the pigment surface with a polymer macromolecule will be determined as

$$\mathbf{F}_k = q_i \mathbf{E}. \quad (22)$$

By analogy with (9), we obtain

$$|\mathbf{F}_k| = K_2 x_2. \quad (23)$$

If a polymer system is subjected to the action of an external controlling field $\sigma(t)$, causing shear deformation, expression (10) takes the form

$$M \frac{d^2 \xi}{dt^2} + \mathbf{R}_2 + \mathbf{R}_1 = \eta \sigma$$

or

$$M \frac{d^2 \xi}{dt^2} + B \frac{d\xi}{dt} + K\xi = \eta \sigma, \quad (24)$$

where $\left| B \frac{d\xi}{dt} \right| = |\mathbf{R}_2|$ and $|K\xi| = |\mathbf{R}_1|$; we assume that the boundary conditions for $\xi = \xi(x, y, z, \tau)$ have the form $\xi(x, y, 0, \tau) = \xi(x, y, z_{qi}, \tau)$ and solve (24) in the following way:

$$\xi = A \exp j\omega \left(\tau - \frac{z_{qi}}{v} \right), \quad \sigma = \sigma_0 \exp j\omega t.$$

Let us represent (24) as

$$\frac{d^2 \xi}{dt^2} + 2\beta \frac{d\xi}{dt} + \omega_k^2 \xi = a \sigma_0 \exp j\omega t, \quad (25)$$

from where

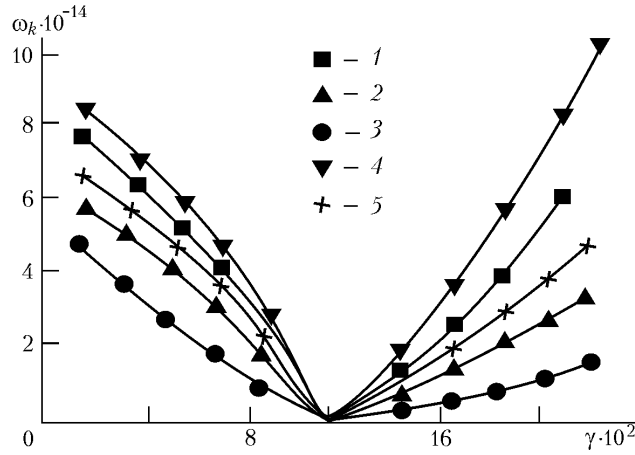


Fig. 1. Dependence of the value of ω_k on γ for the following bonds: 1) C-C; 2) H-H; 3) H-Cl; 4) H-W; 5) Cl-W.

$$\omega_k = \left\{ \frac{K}{2M} \pm \left[\left(\frac{K}{2M} \right)^2 - \frac{4K_1K_2}{M_1M_2} \sin^2 \frac{K_i a_i}{2} \right]^{1/2} \right\}^{1/2}, \quad (26)$$

where $2\beta = B/M$, $M^{-1} = M_1^{-1} + M_2^{-1}$, and $K = K_1 + K_2$. In the case where $K_i = 0$ and $\omega_i = 0$, we will obtain the first acoustic branch of the structures formed; the second acoustic branch begins with the boundary frequency $\omega_2 = (K/2M)^{1/2}$.

Experimental, Results, and Discussion. As an investigation object, we used a C-65 PVC obtained by suspension polymerization and purified by reprecipitation from a solution with $MM = 1.4 \cdot 10^5$ [4]. The polymer being investigated was pigmented with a powder of a microatomized tungsten (W) ($d = 12 \cdot 10^{-6}$ m), which was preliminary degreased with CCl_4 and dried at $T = 393$ K. The investigation samples were prepared by direct mixing of the pigment with the PVC in the T - P regime at $T = 403$ K and $P = 10.0$ MPa. The viscoelastic properties of the PVC system, subjected to the action of a field with a frequency of 0.4 MHz, were investigated by the pulsed method and the rotating-plate method under the shear-deformation conditions [4]. The density of the composite was determined in accordance with [18].

In the computational relations (3), (4), and (13), the energy of binding of atoms of the principal-valence chain of a polymer micromolecule was equal to $42 \cdot 10^{-21}$ N-m and the energy of the intermolecular interaction was equal to $3.5 \cdot 10^{-21}$ N-m at a distance between the atoms of a monomeric link of $1.54 \cdot 10^{-10}$ m (C-C), $1.08 \cdot 10^{-10}$ m (H-H), and $1.78 \cdot 10^{-10}$ m (H-Cl) [10]. Expression (26) was solved using (3) and (4) for a maximum possible shift of the structural elements of the polymer from their equilibrium position [15]. In this case, the relative mean-square shifts of these elements were respectively equal to (0.026–0.038) and (0.095–0.130).

Figure 1 shows the dependence of the frequency of vibrations of PVC elements on the degree of their displacement from the equilibrium position $\gamma = \frac{|r-l|}{l} = \left| \frac{r-a}{a} \right|$. It is seen from this figure that, at all the values of γ , the frequency spectrum of the C-C bond is harder than the frequency spectra of the H-H and H-Cl bonds. The frequencies of vibrations of structural elements of the macromolecules at the polymer-pigment interface exceeds the corresponding values of ω_k for the structural elements of the macromolecules found in the bulk of the polymer matrix.

Figure 2 shows the dependence of the quasielastic constants of the PVC structural elements interacting with the active centers of the tungsten surface W on the degree of their displacement γ and the distance from them to the active centers. It has been established (Fig. 2) that when the displacements of the indicated structural elements are equal to 0.001 and 0.01 and $r = r_0$, K is equal to $2.89 \cdot 10^5$ N/m and $2.54 \cdot 10^4$ N/m. In this case, at all values of N , K sharply decreases with increase in distance from the PVC structural element to the surface of the microatomized tungsten. Figure 3 shows the dependence of ω_k on r in the case where the PVC structural elements interact with the active centers of the surface of the microatomized tungsten w . When the value of γ varies in a discrete range ($\gamma = 0.001$,

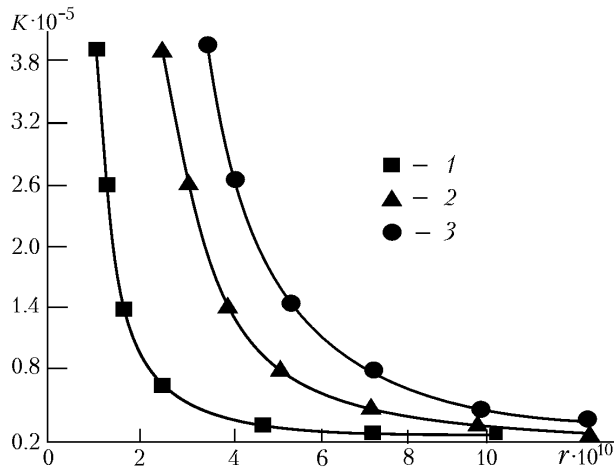


Fig. 2. Dependence of the value of K on r for PVC + W composite at $\gamma = 10^{-3}$ (1), 10^{-2} (2), and 0.245 (3) for $N = 20$.

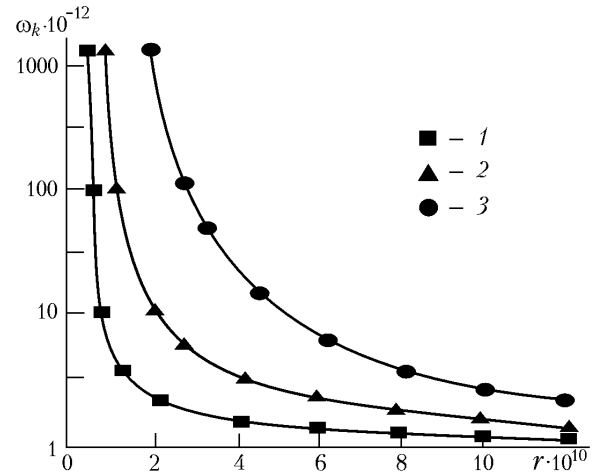


Fig. 3. Dependence of the value of ω_k on r for PVC + W composite at $\gamma = 10^{-3}$ (1), 10^{-2} (2), and 0.245 (3) for $N = 40$.

0.01) and the distance between the PVC structural elements is in equilibrium, the vibrational frequency of the atoms falls within the range $4.41 \cdot 10^{15} - 1.31 \cdot 10^{15}$ Hz. When the Cl-W interaction is realized and the displacements of the elements are equal to $0.100l$ and $0.245a$, the frequencies of their vibrations are decreased to, respectively, $2.39 \cdot 10^{14}$ Hz and $1.59 \cdot 10^{14}$ Hz. If, in accordance with [5], $2 \cdot 10^2$ monomeric links of a chain participate in a cooperative motion in a PVC containing $1.4 \cdot 10^{22}$ recurring identical units in a unit volume, complex vibrations of various types can arise in the range $1.2 \cdot 10^{12} - 7.1 \cdot 10^{13}$ Hz at r_i changing from $r_i \leq 1.245l$ to $r_i \leq 1.629l$ because, primarily, of the disruption of the weakest intermolecular bonds.

At the same time, it is seen from Eq. (26) that, in the case where $10^{-18} \leq B \leq 10^{-12}$ N·sec·m⁻² and $2 \cdot 10 \leq n \leq 10^2$, the dynamic PVC + W system can be purposefully controlled with the use of a low-power external periodic field that provides synchronization without disruption of the inter- and intramolecular bonds. This opens up possibilities to use heterogeneous polymer systems with $\varphi \geq \varphi_{cr}$ as dampers, generators and/or energy transformers.

The results obtained are in good agreement with the data of the IR-spectroscopy investigations carried out in [11]. The appearance of the optical bands at 930, 1335, 1428, and 1730 cm⁻¹ responsible for the $(2.79 - 5.19) \cdot 10^{13}$ Hz vibrations of the composite investigated at $T = 313$ K points to the fact that the PVC macromolecules are structurally ordered and execute stretching vibrations.

Thus, the frequency spectrum of the structural elements of heterogeneous polymer systems based on PVC, which is a typical representative of flexible-chain polymers, is determined not only by the type of the inter- and intramolecular interactions occurring in them, but also the type of the microatomized metal with which they are pigmented. At $\varphi \geq \varphi_{cr}$, a definite dynamic system with new properties different from the properties of low-molecular crystal lattices can be obtained. The results obtained can be used for engineering calculations of the structural-mechanical characteristics of a composite.

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NOTATION

A, D , energies of the intra- and intermolecular bonds respectively, J; a , distance, m; B, C , constants; d , diameter of a particle, m; E , strength, C·m⁻²; $G, E(l)$, energy and mean energy, J; $F_1(r), F_2(r)$, forces, N; F_{sur} and F_{mass} , surface and mass forces, N; I_1, I_2 , ionization potential, eV; $j = \sqrt{-1}$; h_q , step; Δh , distance; K, K_1, K_2 , quasielastic-force coefficients, N·m⁻¹; k , Boltzmann constant, J·K⁻¹; l , equilibrium distance between the atoms, m; M , mass of a segment, kg; MM , molecular mass; m_1, m_2, m_3 , coefficients; N , number of segments; n , number of monomeric links;

P , pressure, Pa; \mathbf{P}_i , electric moment, C·m; q_i , charge, C; \mathbf{R}_{qi} , force, N; \mathbf{R}_q , resultant force, N; r , distance between the atoms, m; r_k , distance from an active center of the surface, m; T , temperature, K; t , time, sec; $u_1(r)$, Lenard–Jones potential, N·m; $u_2(r)$, Morse potential, N·m; u_o , u_{in} , and u_d , energies of the orientation, induction, and dispersion interactions, J; v , velocity, m·sec⁻¹; XOY , coordinate system; x, y, z , coordinates, m; α , constant; α_1, α_2 , polarizability; β , solid angle; γ , relative displacement; δ , constant; ϵ , permittivity; ϵ_0 , dielectric constant, F·m⁻¹; η , cross section, m²; μ_1, μ_2 , dipole moment, C·m; ξ , displacement, m; σ , shear stress, N·m⁻²; τ , lifetime, sec; ϕ and ϕ_{cr} , content and critical content of a pigment, vol.%; $\phi_k(r_k)$, potential, V; ω , cyclic frequency, sec⁻¹. Subscripts: 0, initial value; 1, 2, ..., ordinal number; $i, k, q, g, \alpha, \beta$, indices characterizing the frequency; sur, surface, mass, mass; o, orientation; in, induction; dis, dispersion; cr, critical.

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