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EFFECT OF INCREASED COMPACTING PRESSURES ON THE PHYSICOMECHANICAL CHARACTERISTICS OF METAL-FILLED POLYVINYL CHLORIDE

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Based on the principles of linear thermodynamics, molecular physics, and spatial organization of amorphous polymers, the energy of formation of microdefects and the increments in their volumes as functions of the compacting pressure and the content of the filler of polyvinyl chloride systems are calculated.

Among promising methods of modifying the physicomechanical properties of polymers is their doping with highly disperse additions and directional control of the technological processes of producing composite materials [1]. Here the question of studying the effect of the T–p compaction mode on their properties remains virtually open [2, 3].

As the subject of inquiry, we selected industrial polyvinyl chloride (PVC) of the S-65 grade with a molecular weight of $1.4 \cdot 10^5$ that was produced by suspension polymerization and was purified by reprecipitation from soluton. Cyclohexane of "KhCh" grade ($T_{\text{boil}} = 425.5$ K, $n_D^{290\text{K}} = 0.9466$) was chosen as the solvent. For more intense dissolution of PVC in cyclohexane, a prepared 3% solution was heated on a water bath with a reflux cooler at a temperature of 310 K. PVC was reprecipitated from the obtained solution with methanol ($T_{\text{boil}} = 335$ K, $n_D^{290\text{K}} = 0.7925$). The precipitated polymer was washed repeatedly on a filter with methanol and dried in air and then in vacuum at a temperature of 320 K to a constant weight in 10 h. The reprecipitated PVC was a homogeneous powder of white color that was subsequently used for producing composites. As the filler, a highly disperse iron (Fe) powder that was reduced with hydrogen was selected, with a predominant particle size of 15 μm.

The specimens were prepared in the T–p mode, which differs from the p–T mode [4] in that the polyvinyl chloride was placed in a mold, which was heated to a temperature of 460 K, and only afterward was a required pressure of 10, 60, 120, 200, and 300 MPa applied, maintaining the temperature mode for another 7 min. Spontaneous cooling during formation of blocks was effected at the corresponding pressure up to $T < T_{\text{gl}}$. The glass transition temperature (T_{gl} of the original PVC was 354 K, and the yield temperature (T_{y}) was 456 K.

The density (ρ) of the PVC systems was studied using the method of hydrostatic weighing [5], and the hardness (H_{V}) was studied, using the Vickers method, on a PMT-3 microhardness meter with loading for a time of 2 min [6]. With a confidence coefficient of 0.95, the mean relative measurement error for ρ and H_{V}, respectively, was 0.2 and 1.3%.

Table 1 presents experimental data on the physicomechanical properties of the PVC systems.

It follows from the data presented that the density of the original polymer increases with the pressure over the entire range considered. However, the density of the PVC compositions increases only at pressures up to 200 MPa. A further increase in it leads to a decrease in the density adequate for the filling (see Table 1).

The rise in the density of the PVC systems in the range of 10–200 MPa is caused by "healing" of defects of the material, i.e., a reduction in its free volume [7]. The subsequent decrease in the density of the PVC compositions for $p > 200$ MPa is linked with mechanodestructive phenomena, since, at the metal–polymer–metal interface in the composition, large mechanical stresses and, correspondingly, high temperatures may

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TABLE 1. Density and Hardness of the PVC Systems as Functions of the Compacting Pressure and the Coefficient of Filling

Material	p, MPa									
	10	60	120	200	300	10	60	120	200	300
	ρ, kg/m^3					$H_V \cdot 10^{-6}$, N/m^2				
PVC	1366	1385	1419	1428	1449	150	143	158	140	147
PVC + 5 wt.% Fe	1380	1401	1410	1426	1420	147	141	154	139	144
PVC + 15 wt.% Fe	1504	1524	1549	1568	1550	154	155	159	150	151
PVC + 25 wt.% Fe	1686	1746	1764	1778	1756	155	157	161	155	174

develop [6, 7]. Here, the energy of the thermal motion of the kinetic elements of the PVC structure can be higher than the energy of their chemical bond, which causes a decrease in the molecular weight of the macromolecules and, ultimately, a change in the properties of the polymer system [1-3].

The change in the density gradient of the PVC systems ($\Delta\rho/\Delta p$) with the compacting pressure within 10–200 MPa has an extremum character ($33 \cdot 10^{-3}$, $24 \cdot 10^{-3}$, $34 \cdot 10^{-3}$, and $47 \cdot 10^{-3}$ sec^2/m^2), with a minimum for the system that contains 5 wt.% Fe. This system offers the greatest resistance to straining.

The minimum of the coefficient $\Delta\rho/\Delta p$ in the pressure range of 10–200 MPa for the PVC + 5 wt.% Fe system is associated with the most complete realization of adhesion-adsorption bonds at the interface in the low-filling region [6], with induction of the directive action of the filler on the polymer far into the depth of the binder as a result of the intermolecular interaction, and with a decrease in the internal pressure of the system [2-4, 8].

In the dependence of the hardness on the compacting pressure in the pressure range of 60–120 MPa, a tendency toward an increase in H_V is observed. A rise in the hardness is also noted in the pressure range of 200–300 MPa. This is caused by the fact that within the limits of pressures $p \leq 120$ MPa, structural ordering takes place in the volume of the polymer matrix. With a subsequent rise in the compacting pressure (200–300 MPa), structural ordering of the PVC is realized at the polymer–highly disperse filler interface [6].

In the region of pressures of 60 and 200 MPa, H_V decreases due to redistribution of the free volume of defects by smaller increments [7] and formation of microdefects in the block structure at a higher level of compacting pressures [8]. The relative rise in the hardness of the PVC systems at $p \simeq 120$ MPa results from maximum molecular ordering of the binder at pressures of 120–130 MPa [9].

The change in the density of the compositions with increase in the filler content in the PVC system proceeds in an extremum manner with a minimum of ρ for the PVC + 5 wt.% Fe system in the pressure range $p \geq 120$ MPa. Here, the minimum of H_V is noted over the entire pressure range considered (see Table 1).

The minima of ρ and H_V result from the most complete realization of the energy interaction between the components, the formation of relatively large boundary structures, a decrease in the elasticity of the macrochains in them, and the loosening action of the filler [6, 8, 10].

The absence of a linear correlation between ρ and H_V in the property–pressure dependence is linked with the fact that H_V is determined primarily by the structure of the surface layers and the density is determined by the structure of the entire volume of the polymer system.

Using the thermodynamic approach to the description of the state of polymer systems and the theory of free volume and molecular processes of microindentation [11], we determine the energy of formation of microvoids and their dimensions for the given PVC systems. To this end, we employ the equation of state of Spencer and Gilmore in the two-parameter form [12]

$$\left(p+\frac{a}{V^2}\right)(V-b)=RT. \tag{1}$$

Since a/V in a first approximation is equivalent to the energy (E) of formation of microvoids [11] and b is estimated by four volumes of all molecules (V_d), Eq. (1) for $p \ll \pi$ assumes the form

$$1 - \frac{RT}{E} = 4\frac{V_d}{V}. \tag{2}$$

With allowance for the fact that the coefficient of packing of macromolecules in amorphous polymers (K) is [13]

$$K = \frac{N_A \Sigma \Delta V_{ip} \rho}{\mu_p}, \tag{3}$$

where V_{ip} are the increments in the volumes of the atoms and atomic groups that enter into a structural link of the polymer, we obtain a relation for determining E as the energy barrier that is overcome by the fluctuations of the atoms and atomic groups in the thermal motion:

$$E = \frac{RT\mu_p}{\mu_p - 4N_A \Sigma \Delta V_{ip} \rho}. \tag{4}$$

Taking into account that the local strain of the composition upon microidentation eliminates microvoids, from this standpoint the microhardness is determined as the work needed to close unit free volume. Disregarding the strain of the polymer volume, since the microhardness is measured in short-duration tests and characterizes, mainly in the first stage, the strain resistance, it is represented in the form of the maximum internal pressure [11]:

$$H_V \approx \pi = \frac{E}{V_h}. \tag{5}$$

Then, with account for expressions (4) and (5), the volume of the microvoids per mole of the substance is determined as

$$V_h = \frac{RT\mu_p}{(\mu_p - 4N_A \Sigma \Delta V_{ip} \rho) H_V}. \tag{6}$$

In the case of a composition, it is necessary to make corrections for the molecular weight and the volume of the number of structural elements of the filler that are statistically bound up with the PVC macromolecules.

Proceeding from the law of additivity of the quantity of a substance and expressing the mass of the components in terms of their mass factions and the composition mass, we find that

$$\mu_c = \frac{\mu_p \mu_f}{\mu_f (1 - \varphi_f) + \mu_p \varphi_f}. \tag{7}$$

Knowing the number of structural elements of the polymer and the filler in the system, we determine the volume of the number of structural elements of the filler per binder link:

$$V_f = \frac{\mu_p \varphi_f \Sigma \Delta V_{if}}{(1 - \varphi_f) \mu_f}, \tag{8}$$

and their total volume

$$V_{tot} = \frac{\mu_p \varphi_f \Sigma \Delta V_{if}}{(1 - \varphi_f) \mu_f} + \Sigma \Delta V_{ip}, \tag{9}$$

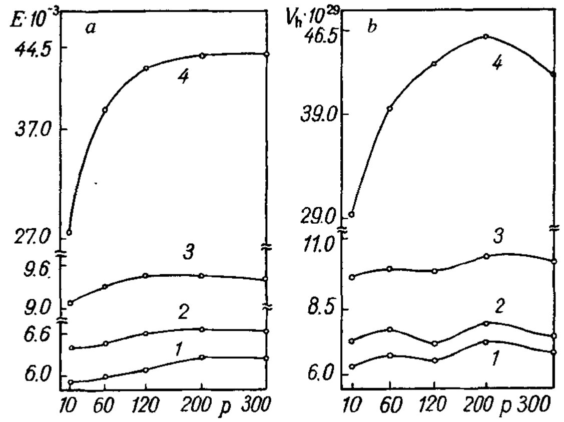

Fig. 1. Energy of formation of microvoids (a) and averaged microvoid volume (b) as functions of the compacting pressure in the T–p mode: 1) PVC; 2) PVC + 5 wt.% Fe; 3) PVC + 15 wt.% Fe; 4) PVC + 25 wt.% Fe. E, J/mole; V_h, m^3; p, MPa.

where ΔV_{if} are the increments in the volumes of the atoms that enter into a structural cell of the filler. Then, relation (4) for the PVC compositions has the form

$$E=\frac{RT\left(\dfrac{\mu_p\mu_f}{\mu_f(1-\varphi_f)+\mu_p\varphi_f}\right)}{\dfrac{\mu_p\mu_f}{\mu_f(1-\varphi_f)+\mu_p\varphi_f}-4N_A\left(\dfrac{\mu_p\varphi_f\Sigma\Delta V_{if}}{(1-\varphi_f)\mu_f}+\Sigma\Delta V_{ip}\right)p}. \tag{10}$$

The increments in the volumes of the atomic group of a structural link of the PVC ($\Sigma\Delta V_{ip}$) and a filler atom Fe (ΔV_{if}) were calculated following Melvin and Hughes [14].

The evaluation of E and V_h was carried out at a temperature close to the glass transition temperature of polyvinyl chloride $T_{gl} > T = 350$ K, where the fraction of the geometric free volume is practically invariable.

Figure 1a shows the energy of formation of microvoids as a function of the compacting pressure and the filler concentration.

For all the systems, a rise in E is observed in the pressure range of 10–200 MPa. With increase in the filler concentration, the coefficient $\Delta E/\Delta p$ increases most intensely within the limits of fillings $\varphi > 15$ wt.% Fe and pressures 10–120 MPa. In the pressure range of 200–300 MPa an insignificant rise in E is observed for the original polymer. In the case of the filled PVC, a subsequent pressure buildup gives rise to a "plateau" region on the E–p dependence. Saturation of E is virtually completed in the pressure region up to 120 MPa.

A rise in the energy of formation of microvoids of the PVC systems in the pressure range of 10–120 MPa is caused by "healing" of structural defects, a decrease in the fraction of the free volume, molecular ordering of the structure, and an increase in the number of intermolecular bonds [9, 10]. The change in $\Delta E/\Delta p$ within the limits of $10 \le p = 120$ MPa with increase in the Fe content in the PVC is related to a rise in the number of active centers of interaction between the system components. The passage to a "plateau" in the function $E = f(p)$ for the compositions is due to the effect of increased external and internal force fields on the mobility of the structural elements of the PVC and their energy interaction.

Figure 1b shows the dimensions of the microvoids that result from the fluctuations of the thermal motion of the structural subsystems of the PVC. Their size varies not only with rise in the compacting pressure but also with increase in the coefficient of filling of the compositions. The change in V_h in the pressure range of 10–60 MPa is caused by redistribution of the free volume of the defects by smaller increments [7]. The decrease in V_h in the region of pressures of 120 MPa for the original PVC and the low-filled compositions ($\varphi \le 15$ wt.% Fe) is due to the maximum molecular ordering in the binder volume [9]. The monotonic increase in V_h in the pressure range of 10–200 MPa for a higher filling ($\varphi \geq 25$ wt.% Fe) is caused by the predominance of the loosening action of the filler over the structural changes of the PVC under the action of the compacting pressures. The decrease in V_h in the region of pressures of 300 MPa for all the systems is related to segmental depression, i.e., a decrease in the degree of high elasticity of the macrochains [2-4].

A comparison of the microvoid volumes with the increments in the volumes of the structural elements of the PVC and the compositions V_{tot} ($0.978 \cdot 10^{-29}$, $1.018 \cdot 10^{-29}$, $1.145 \cdot 10^{-29}$, and $1.654 \cdot 10^{-29}$ m^3) shows that, within the limits of the pressures and coefficients of filling considered, a dissimilar number of structural elements (6.39–7.63, 7.02–7.57, 8.59–9.08, and 18.60–29.92) participate in the fluctuations of the thermal motion, which is indicative of "unfreezing" of the segmental mobility of the PVC systems to a different degree.

Thus, the physicomechanical properties of the metal-filled PVC can be directionally controlled by both a highly disperse metal filler and the external force field of the T–p mode.

NOTATION

E, effective activation energy of formation of microvoids; V_h, averaged microvoid volume; V, molar volume; φ_f, mass fraction of the filler in the polymer; p, compacting pressure; π, constant of internal pressure; μ_p, molecular weight of a structural link of the polymer; μ_f, molecular (atomic) weight of the structural subsystem of the filler; a, van der Waals force constant in the equation of internal pressure; b, volume inaccessible to molecules; N_A, Avogadro's number.

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