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Maxwellian relaxation and internal friction in the polyvinyl butyral-polyvinyl chloride system

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The Maxwellian relaxation and internal friction of a mixture of amorphous polymers: polyvinyl butyral (PVB) - polyvinyl chloride (PVC) are studied. It has been found that by changing the temperature (T) and content (φ) of the ingredients, it is possible to control the value of viscoelastic moduli, viscosity, damping force, and energy dissipation due to Maxwellian relaxation caused by the action of ultrasonic vibrations with a frequency (ω) of 0.4 MHz on the composite. The use of computational methods, models, and a phenomenological approach made it possible to differentiate the effects of relaxation and indicate the ways to optimally combine the desired properties of the components in the system.

Keywords: polymer, viscoelasticity, viscosity, relaxation.

Introduction

The evolution of the process of modifying polymers as promising materials in various fields of science and technology has shown that an economically viable and promising direction of high-volume production is the creation of composites based on existing systems [1]. The use of a mixture of two polymers that differ in their physical and chemical parameters makes it possible to obtain a composite with an improved set of properties that are not present in the respective ingredients. However, despite the fact that polymer-polymer systems are intensively studied theoretically and experimentally, unfortunately, it is still impossible to predict the set of properties of these promising materials [2]. This is especially true for PVC, which is of the most significant scientific and applied interest among high-tonnage polymers [3]. At the same time, it is noted that no active modifiers have yet been proposed for it that meet the needs of the industry [4]. It is characteristic that PVC is a convenient object of study, since changes in its supramolecular structure (SMS) under the influence of heterogeneous factors are possible within a wide range.

About 4500 types of materials and products are made on its basis [4]. Of considerable scientific interest is also PVB, a carbon-chain amorphous polymer [5], which is widely used as a matrix for the manufacture of heterogeneous polymer systems (HPS) for various purposes. Accordingly, the prediction, creation, and use of a mixture of PVB and PVC as two linear polymers is an urgent task of polymer physicochemistry.

Therefore, the aim of this work is to investigate the influence of viscoelasticity and damping effects on the Maxwellian relaxation and internal friction of a mixture of linear polymers (PVB and PVC) using the ultrasonic method and to indicate the ways of practical use of the newly developed system.
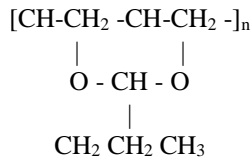
I. Experimental part. Objects and methods of research

A mixture of two linear polymers was studied: redeposited PVC-KSP-67-C-63 with MM = $1.4 \cdot 10^5$ and $T_g = 354$ K and PSH-DS-9439 (Labtech) with MM = $5.0 \cdot 10^4$, $T_g = 331$ K. The samples were prepared by

hot pressing at $T = 403$ K in the pressure-temperature mode at a pressure of 10 MPa. The acoustic properties of the system were studied at a frequency of $\omega = 0.4$ MHz by the pulse method in conjunction with the rotating plate method under longitudinal and shear deformation [6]. The calculation of the number of modes of ultrasonic vibrations of isotropic PVC and PVB as an amorphous mixture was based on the Clemens-Debay-Maison theory [7].

II. Model. General characteristics, basic concepts

PVC [CH$_2$ -CHCl]$_n$ is a typical representative of linear flexible-chain polymers, PVB is a carbocarbon-chain amorphous polymer of acetal of polyvinyl alcohol and butyric aldehyde

$$[CH-CH_2 -CH-CH_2 -]_n$$
$$| \qquad |$$
$$O - CH - O$$
$$|$$
$$CH_2 \; CH_2 \; CH_3$$

in the macromolecule contains (65÷ 78) % vinyl butyral, (32÷ 19) % vinyl alcohol, and (≤ 3 %) vinyl acetate chains. In these polymers, only fluctuating structural elements with a finite lifetime (τ_i) - microblocks (or supernets) - can exist [8]. In a wide temperature range, macromolecules can exhibit various forms of mobility [1]. As models, let us represent microblocks by point masses M_i (i = 1,2,3) in the form of atomic groups [5]. According to [1], they are united by inter- and intramolecular bonds through which the relaxation properties of the system encoded in the macromolecule configuration are transmitted to the macrolevel. At the same time, in accordance with the principle of temperature and time equivalence [1], it is possible to record both the elastic and viscous response of the polymer system to the action of ultrasonic vibrations.

Let us consider the relationship between the change in pressure Δ P and the volumetric strain Δ V/V_0 of a PVC+PVC composite under the action of an ultrasonic field of low intensity in the mode $\gamma(t) = e\gamma_0^{j\omega t}$. To do this, we use the phenomenological approach to determining the viscoelastic properties of the medium, as specified by Maxwell [7], which is based on the combination of viscous flow with elastic shear deformation. In this case, we identify the Maxwell's relaxation time τ_i with the settled life of the structural element. This will allow us to describe the mechanical properties of viscoelastic bodies by introducing the coefficients of viscosity (R_1, R_2) and viscoelastic compressibility (χ_1, χ_2). To determine the behavior of the PVB+PVC systems in the ultrasonic field, we use the method of electromechanical analogy [9]. Accordingly, we will determine the relationship between the electric voltage U and the amount of electricity q in the case of a circuit consisting of resistance R_1, capacitance C_1 connected to a circuit formed by a parallel connection of capacitance C_2 and active resistance R_2. On the equivalent Maxwell's substitution scheme, this corresponds to the moduli of all-round compression K_1, viscosity η_1 of PVC,

and shear G_2 and viscosity η_2 of HBM, $C_1 = K_1^{-1} = \chi_1$, $C_2 = G_2^{-1} = \chi_2$; $R_1 = \eta_1$, $R_2 = \eta_2$.

We calculate this circuit taking into account the presence of harmonic ultrasonic vibrations, which are the source (at $T \sim const$) of the external pressure P. The parallel connection $C R_{22}$ is equivalent to the complex resistance Z_2, where after the corresponding mathematical calculations we have:

$$\dot{Z}_2 = \frac{R_2(1-j\omega\tau_2)}{1+\omega^2\tau_2^2}, \qquad (1)$$

$j = \sqrt{-1}$; $\tau_2 = R_2 C_2$ is the Maxwellian relaxation time, which characterizes the mechanism of energy exchange processes in the HBC. The calculation of the values $\dot{Z}_3$ and $\dot{Z}_4$ as the complex resistances of the series connection of the capacitive resistance of capacitor C_1 and the resistance R_1 with Z_2 shows that

$$\dot{Z}_3 = \frac{1}{j\omega C_1} + \frac{R_2 - j\omega C_2 R_2^2}{1+\omega^2\tau_2^2}, \qquad (2)$$

and

$$\dot{Z}_4 = R_1 + \dot{Z}_3 = \frac{(R_1+R_2)+\omega^2 R_1\tau_2^2}{1+\omega^2\tau_2^2} - j\frac{1+\omega^2 R_2^2 C_2(C_1+C_2)}{\omega C_1(1+\omega^2\tau_2^2)}, \qquad (3)$$

The presence of the real (R_e) and imaginary (I_m) parts of the resistance value $\dot{Z}_4$ makes it possible to calculate internal friction as the dissipation of the energy of the deformation process of the PVB+PVC systems:

$$tg\,\delta = \frac{R_e(\dot{Z}_4)}{I_m(\dot{Z}_4)} = \frac{\eta'}{\eta''} = \frac{1+\omega^2 R_2^2 C_2(C_2+C_1)}{\omega C_1[(R_1+R_2)+\omega^2 R_1\tau_2^2]}, \qquad (4)$$

where

$$\dot{Z}_4 = \dot{\eta} = \eta' - j\eta'' - \qquad (5)$$

is the complex viscosity of the composite, and

$$\eta' = \frac{(R_1+R_2)+\omega^2 R_1\tau_2^2}{1+\omega^2\tau_2^2} - \qquad (6)$$

its valid part and

$$\eta'' = \frac{1+\omega^2 R_2^2 C_2(C_1+C_2)}{\omega C_1(1+\omega^2\tau_2^2)} - \qquad (7)$$

imaginary part. The complex viscosity is characterized by the ratio of the shear stress to the strain rate of the system [7]. Using Euler's transformation [1], we can represent relation (5) as

$$\dot{\eta} = |\acute{\eta}|e^{j(\delta-90^0)}, \qquad (8)$$

where $|\acute{\eta}| = \left(\eta^2 + \eta'^2\right)^{1/2}$. For a purely elastic body, $\delta = 0$, for liquids, $\delta = 90^0$, and in this case, $0 < \delta < 90^0$, i.e., the PVB+PVC system is a viscoelastic body [7].

Let us analyze the relation (4) for the case when $C_1 \ll C_2$ i $R_1 \gg R_2$. After appropriate mathematical transformations, we have that

$$tg\delta = \frac{1}{\omega\tau_1}, \qquad (9)$$

where $\tau_1 = R_1C_1$ is the Maxwellian relaxation time of PVC.

Relation (9) confirms the conclusion that the PVB+PVC system, when behaving mechanically in an ultrasonic field, is characterized by a superposition of elastic and viscous forces, i.e., it is a viscoelastic material [7]. According to Maxwell, the relaxation time of the system (τ_i) is defined as [7]:

$$\tau_i = \frac{viscosity}{shear\ modulus} = \frac{\eta}{G}. \qquad (10)$$

An examination of the relations (6) and (7) shows that they take the following form:

$$\eta' = \frac{(R_1+R_2)+\omega^2\tau_2^2R_1}{1+\omega^2\tau_2^2}, \qquad (11)$$

$$\eta'' = \frac{1+\omega^2\tau_2^2+\omega^2\tau_2\tau_{12}}{\omega C_1(1+\omega^2\tau_2^2)}, \qquad (12)$$

where $\tau_{12} = R_2C_1$ is the relaxation time due to the structural interaction of PVC with PVB in the system. Let us consider the boundary conditions for changes in R_i and C_i ($i=1,2$) for the case of dominance of the properties of PVB and/or PVC in the composite. Thus, in the case of $R R_1>_2$, equation (11) takes the form

$$\eta' = \eta_1 = R_1, \qquad (13)$$

Taking into account that the PVB+PVC system is a viscoelastic body and has a viscosity $\dot{\eta} = \dot{G}/j\omega$, we have: $C_2 \gg C_1$ (where $C_1 = 1/G_1$; $C_2 = 1/G_2$). Thus,

$$\eta'' = \eta_2 = \frac{1}{\omega C_1} = \frac{G_1''}{\omega}, \qquad (14)$$

that is, $\dot{\eta} = \eta_1 - j\eta_2$.

If the conditions $C_1 \gg C_2$ and $R_1 \gg R_2$ are met, reasoning similarly to (13), (14), we have

$$\eta' = \eta_2 = R_2 , \ \eta_2'' = \frac{1}{\omega C_2} = \frac{G_2''}{\omega} \qquad (15)$$

That is, depending on the dominance of the influence of PVB (2) or PVC (1) on the magnitude of the energy and entropy interaction in the PVB+PVC system, the viscoelastic properties of the composite can be changed in a wide range η, G, K at T, ω - const. At the same time, for PVB+PVC, the value of internal friction, according to Eq. (4), is equal to $tg\,\delta_{12} = \Psi(\tau_{21}^{-1})|_T$ where $tg\delta_1 < tg\delta_{12} < tg\delta_2$ at 293 K $\le T \le T_{g2} \le T_{g1}$, and T_{g1}, T_{g2} are the glass transition temperatures of PVC and PVB, respectively. Using the electrical analogy to mechanical models of viscoelastic bodies [9], we have that $q_1 = \sum_{i=5} q_i$ where q_1 is the amount of electricity that passes through R_l and corresponds to $q_2(R_2C_2)$; $q_3(C_1)$; $q_2 = q_4 + q_5$, in the case of the circuit R_2C_2,

$$\frac{dq_4}{dt}R_2 = \frac{q_5}{C_2};$$

and the voltage drop, $U(C_2)=U(R_2)$, is described as a homogeneous differential equation:

$$-\frac{d(q_2-q_4)}{dt}R_2 = \frac{q_2-q_4}{C_2}, \qquad (16)$$

whose solution at initial conditions $t = 0$ shows that

$$q_4 = q_2(1 - e^{-t/\tau_2}); \ q_5 = q_2e^{-t/\tau_2}. \qquad (17)$$

To determine the amount of electricity q_2 and q_3 as parts of the total amount q_1 passing through the area R_1, we use the corresponding integral-differential equations, solving which we obtain that

$$q_2 = q_1\left(\frac{t}{\tau_2}\right)e^{-C_1/C_2} ; \ q_3 = q_1\left(1 - \frac{t}{\tau_2}e^{-C_1/C_2}\right). \qquad (18)$$
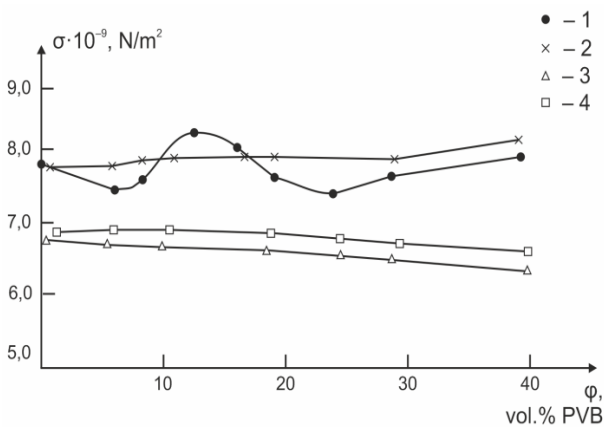
Thus, in the PVB+PVC system, during the period of action (T_0) of the ultrasonic field, redistribution of deformation processes occurs, which, according to the proposed model, are equivalent to the initial charge q_1, have a relaxation character, being a function of time (t). At $0 \le t \le T_0$, according to Kirchhoff's law, the full charge q_1 is preserved (relations 17, 18). This observation becomes essential when considering the issue of changes in the strain (ε_i) of a composite under the action of an ultrasonic field. Given that replacing the electrical model with a mechanical one allows us to use the relationship between the total pressure change Δp and the volumetric strain of the body described by the previous equations, we obtain an additional "relaxation" strain that is added to the volumetric and shear strains. That is, from equations (17), (18) it follows that

$$\varepsilon_2 = \varepsilon_1\left(\frac{t}{\tau_2}\right)e^{-C_1/C_2} ; \ \varepsilon_3 = \varepsilon_1\left(1 - \frac{t}{\tau_2}e^{-C_1/C_2}\right). \qquad (19)$$
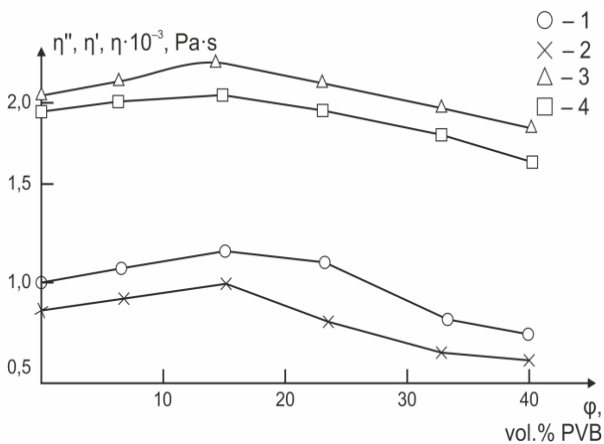
III. Results and discussion

The results presented in Fig. 1 show that as the content of PVB in PVC increases within $0 < \varphi < 40.0$ vol. %, the dependence of G varies nonlinearly, tending to decrease. In the process of changing the value of the modules in the region of 12.0 vol. % PVB, the maximum values of G are observed, and for composites containing 23.0 vol. %, its value (at $T = 319$ K) corresponds to the minimum. It should be noted that the value of the modulus at $\varphi = 12.0$ vol. This indicates that there is an energy and entropy relationship between the structure of PVC and PVB [10]. The studied PVB contains hydroxyl, acetate, butyral groups, and the macromolecule has dipoles C-H (79.60 %); O-H (10.40 %); C-O (10.0 %), the presence of which provides the value of the strength of their unit interaction with the structures of the PVC macromolecule [CH$_2$ CHCl], respectively, 5.56, 15.70, 20.80;/· 10^{-9}, H [11]. This is manifested in the characterization of changes in the value of G, K of the system. Fig. 2 shows the values of the shear viscosity η and the bulk viscosity η', which depend on the content of PVB in PVC. The concentration dependence η

$(\varphi)|_T$ is characterized by a maximum at $\varphi = 12$ vol. % and a minimum value in the region of 40.0 vol. %. It should be noted that in the range of $6.0 < \varphi < 12.0$ vol. %, the coefficient $(d\eta/d\varphi)|_T$ is 1.1 (Pa·s)/vol.%, and at $12.0 < \varphi < 40.0$ vol. % is negative and equals 0.9. The coefficient of change of η' with concentration is 0.8 (Pa·s)/vol.% for G $6.0 \div 12.0$ vol. % PVB and - 0.5 (Pa·s)/vol.% at a concentration of $12.0 \div 32.0$ vol. %. It should be noted that in the considered range of PVB content, the values of the dynamic shear strength of the system are lower than for the original PVC (η - PVC at $T = 300$ K is 289 Pa· s). However, at $0 \leq \varphi \leq 12.0$ vol. %, we have that the η of the system is greater than the η of the PVC. This nature of the dependence of η on $\varphi|_T$ indicates that the structure of the composite is not homogeneous, undergoing different amounts of deformation under the action of ultrasonic vibrations $\omega = 0.4$ MHz. Knowing the value of the bulk and shear viscosity, we estimate the dynamic (η'') viscosity of the PVB-PVB system as = 4/3 $+\eta'' \eta\eta'$ [7]. The analysis of the results obtained (Fig. 2) indicates the nonlinear nature of the dependence $\eta'' = f(\varphi)|_T$.
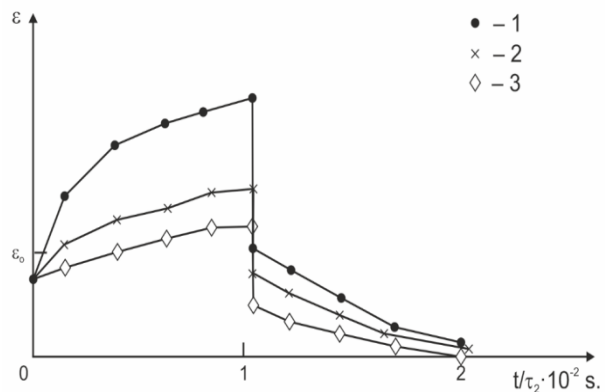
When considering the process of thermal activation of the system, it is also necessary to take into account the change in the effective length l of the kinetic units of the PVB+PVC structure that participate in the energy exchange processes of the composite. It is known [7] that when a segment of length l takes on a configuration with energy $E \geq E_0$ (where E_0 is the total thermal energy according to the Debye theory [9]), it creates an additional contribution to the value of internal friction, providing a change in the value of body deformation. Given that the probability of such a segment with a higher configurational energy satisfies the Boltzmann equation [1], an increase in temperature causes an increase in not only local but also segmental mobility of the composite structure elements. This is manifested in an increase in the strain of the system, which is (according to Equation 19) of a relaxation nature. Knowledge of the structure-sensitive characteristics (η, τ) of the composite allows us to determine the value of l as [12]

$$l = \left(\frac{4kT\tau}{\pi\eta}\right)^{1/3}, \qquad (20)$$

and determine its participation in the deformation process of the system as a function of T and φ. Based on the temperature changes of l, we present a quantitative relationship between the volume of the structure element V (where $V = Sl$, S is the cross-sectional area of the macromolecule, according to the Kirckwood-Reisman model [9] and the internal pressure P of the composite at $T < T_{g2}$ in the form of a linear relationship [10]

$$P = -K\varepsilon, \qquad (21)$$

where $\varepsilon = \Delta V/V$ is a relative insignificant change in the volume of the composite; K is the modulus of comprehensive compression of the system at a constant temperature. Under the influence of the pressure of the ultrasonic wave, a process of a kind of mechanical modulation of the internal pressure of the system occurs, which is manifested in a change in the strain value of the composite (Eq. 19), which is relaxation in nature (Fig. 3).

Fig.1. Concentration dependences of viscoelastic modulus of PVB+PVC sestems: at T=319 K, 1 – σ-experiment; 2 – calculation; at T=325 K; 3 – σ-experiment; 4 – σ- calculation.

Fig. 2. Concentration dependence of the dynamic viscosity of PVB+PVC systems: at T=310 K, 1 – η-experiment; 2 – η′-experiment; 3 – η″-experiment; 4 – μ''-calculation.

Fig. 3. Dependence of strain ε_i on the time of action of the ultrasonic field (pressure is applied at t = 0 and released again at $0 \leq t \leq \tau_0$) on the PVB+PVC system: at T=300 K, 1 – 1- ε_4; 2 – 2- ε_2; 3 – 3- ε_3.

In this case, the strain value ε_1 corresponds to the change in charge q_1 with time (at $\omega = 0.4$ MHz) and contains an elastic component $\varepsilon_0 = (1/K)P_0 e^{j\omega t}$, which occurs when the ultrasonic vibration source is turned on. Subsequently, at $t = T_0/4$ ($T_0 = 2/\pi\omega$), when the voltage P is removed, it turns into a viscoelastic one, relaxing according to the law of the form (19). Since the relaxation time of $\tau_1 \tau_2 \tau_{21}$ depends not only on R, C, but according to Arenius' law [9], also on temperature, this is manifested in a change in the value of the viscoelastic parameters (K, G, ε, tg δ) of the composite (Figs. 1, 2, 3).

Maxwellian relaxation and internal friction in the process of volumetric, longitudinal, shear deformation. Deformation processes are relaxation in nature, due not only to the intrinsic relaxation time τ_1 (PVC) and τ_2 (PVB), but also to the effective relaxation time τ_{21} of the composite elements. Due to this, an additional relaxation modulus of volumetric compression arises, and the initial, purely elastic deformation of ultrasonic vibrations degenerates into a viscoelastic one. This makes it possible to predict the conditions for creating a composite, the complex of its viscoelastic properties, and the operating conditions in external temperature and dynamic mechanical fields.

Conclusions

The studies have shown that the newly developed systems based on a mixture of amorphous polymers PVB and PVC, which differ sharply in glass transition temperatures, have a set of viscoelastic properties that can be controlled in a targeted manner. It has been established that under the action of an ultrasonic field, using the phenomenological approach and the method of electromechanical analogy, the system exhibits

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Максвеллівська релаксація і внутрішнє тертя в системі полівінілбутираль-полівінілхлорид

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Досліджено максвеллівську релаксацію та внутрішнє тертя суміші аморфних полімерів: полівінілбутираль (ПВБ) – полівінілхлорид (ПВХ). Встановлено, що змінюючи температуру (T) та вміст (φ) інгредієнтів можна регулювати величину в'язкопружних модулів, в'язкості, демпфруючої сили, дисипації енергії за рахунок максвеллівської релаксації, обумовленої дією на композит ультразвукових коливань частотою (ω) 0,4 МГц. Використання обчислювальних методів, моделей та феноменологічний підхід дозволив диференціювати ефекти релаксації і вказати шляхи оптимального поєднання в системі бажаних властивостей компонентів.

Ключові слова: полімер, в'язкопружність, в'язкість, релаксація.