INFLUENCE OF β^--RADIATION ON ACOUSTIC PROPERTIES OF POLYVINYLCHLORIDE-BASED HETEROGENEOUS SYSTEMS

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Experimental results concerning the β^--irradiation (up to a dose of 1.5 Gy) influence on the acoustic properties of filled, and filled and plasticized polyvinylchloride (PVC) are reported. The magnitudes of Young's modulus E of PVC systems and the dissipative energy loss by an ultrasonic field with a frequency of 0.4 MHz in them have been shown to depend on the absorbed β^--dose and the temperature T, as well as on the type and the content of components in the system. Various relaxation states of the system were found to demonstrate a reduction of the ultrasonic logarithmic decrement with the radiation dose growth. At 290 K $\leq T \leq$ 400 K, the shear, μ, and Young's moduli of original PVC turned out the most sensitive to the influence of β^--irradiation, while the introduction of fillers and plasticizers into the composite reduced the effect of its irradiation. The influence of β^--rays on acoustic properties of PVC systems is maximal for absorbed doses within the interval $0.45 \div 1.5$ Gy and gives rise to the increase of the moduli by $30 \div 40\%$. The experimental results have been analyzed by introducing the structural parameter of a composite; as such, the relative width of the peak in the temperature dependence of energy dissipation in the constant ultrasonic deformation mode has been selected.

1. Introduction

The contemporary nuclear and space techniques need in materials with improved acoustic properties and enhanced radiation resistance [1]. The most promising among them are polymers and polymer-based composites [2]. An improvement of polystyrene (PS) and polymethylmethacrylate (PMMA) properties by subjecting those substances to irradiation allowed one to extend the scope of their application [3]. Unlike radiation-induced damages in solids [2], radiation-induced effects in polymers are considered in the physics and the chemistry of those substances as those improving their properties [4], which is associated with the formation of additional covalent bonds in polymers [5]. However, irradiation of polymers is often followed by a deterioration of their operational characteristics [6]. Such an ambiguity of the influence of irradiation on polymeric materials complicates their practical use [7]. It especially concerns the action of low-exposure doses ($D \leq 2 \div 3$ Gy) on viscoelastic properties of composites obtained on the basis of large-tonnage amorphous polymers, where PVC plays a key role [8]. Therefore, the purpose of our research was to experimentally study the influence of β^--irradiation (within the expose dose interval $0 < D \leq 1.5$ Gy) on the E and μ values and the dissipation energy loss Δ at longitudinal and shear deformations in PVC systems. The researches were carried on in the temperature range 290 K $\leq T \leq$ 400 K and making use of 0.4-MHz ultrasonic vibrations.

2. Experimental Technique

The study of acoustic characteristics in PVC systems is related to the measurements of the propagation velocities of longitudinal, υ_l, and transverse, υ_t, ultrasonic waves, as well as the corresponding decay factors α_l and α_t [4]. These parameters were determined with the use of an experimental ultrasonic installation operating at a frequency of 0.4 MHz. Its work is based on the method of transmitting pulse signal together with the rotating plate method [3].

The magnitudes of v_l and v_t were calculated by the formulas [3]

$$v_l = \frac{v_p d}{d \pm \Delta\tau_l v_p}, \tag{1}$$

$$v_t = \frac{v_p d}{\sqrt{d^2 + (\Delta\tau_t v_p)^2 - 2d\Delta\tau_t v_p \cos\alpha}}, \tag{2}$$

where d is the specimen thickness, v_p the velocity of ultrasonic wave propagation in an immersion liquid (silicone oil PFMS-4) at a temperature of the experiment, $\Delta\tau_{l,t}$ the duration of the ultrasonic signal transmission through a studied specimen (they were measured by a time-interval counter), and α the rotation angle of the specimen (the Brewster angle).

The parameters α_l and α_t were determined by the relations

$$\alpha_{l,t} = \frac{1}{d} \ln \frac{\mathrm{A}_0}{\mathrm{A}_{l,t}}, \tag{3}$$

where A_0 is the amplitude of an ultrasonic wave in the immersion liquid, and $\mathrm{A}_{l,t}$ are the amplitudes of longitudinal (l) and transverse (t) ultrasonic waves after their transmission through the specimen.

Knowing the propagation velocities v_l and v_t and the decay factors α_l and α_t, the real (μ', E') and imaginary (μ'', E'') parts of elastic moduli are determined as follows:

$$\mu' = \frac{\rho v_t^2 \left(1 - \frac{\alpha_t^2 v_t^2}{\omega^2}\right)}{\left(1 + \frac{\alpha_t^2 v_t^2}{\omega^2}\right)^2}, \tag{4}$$

$$\mu'' = \frac{\frac{2\alpha_t v_t}{\omega} \rho v_t^2}{\left(1 + \frac{\alpha_t^2 v_t^2}{\omega^2}\right)^2}, \tag{5}$$

$$E' = k' + \frac{4}{3}\mu' = \rho v_l^2 \frac{1 - \left(\frac{\alpha_l v_l}{\omega}\right)^2}{\left[1 + \left(\frac{\alpha_l v_l}{\omega}\right)^2\right]^2}, \tag{6}$$

$$E'' = k'' + \frac{4}{3}\mu'' = \rho v_l^2 \frac{2\frac{\alpha_l v_l}{\omega}}{\left[1 + \left(\frac{\alpha_l v_l}{\omega}\right)^2\right]^2}, \tag{7}$$

$$E(\mu) = \left[E'(\mu')^2 + E''(\mu'')^2\right]^{1/2}. \tag{8}$$

The phase angles δ_i and the logarithmic decrements Δ_i are found from the relations

$$\mathrm{tg}\,\delta_l = E''/E'; \quad \mathrm{tg}\,\delta_t = \mu''/\mu', \tag{9}$$

$$\Delta_i = \frac{\pi}{2}\,\mathrm{tg}\,\delta_i, \tag{10}$$

where $i = l, t$.

The measurement errors are: $\Delta v_l/v_l = 0.5\%$, $\Delta v_t/v_t = 1.5\%$, and $\Delta\alpha_{l,t}/\alpha_{l,t} = 8\%$.

The object of our researches was PVC S-6359-M with a molecular weight of 1.4×10^5. As fillers, we used superfine powders of kaolin (K) from the Prosyanivs'ke deposit (the average particle dimension was $2 \div 3$ μm) and bentonite (B) from the Pyzhevs'ke one (the average particle dimension was $0.2 \div 0.4$ μm) [4]. Dibutyl phthalate (DBP) and dioctyl phthalate (DOP) were used as plasticizers. Specimens were prepared in the T–p regime at $T = 393$ K and $p = 10.0$ MPa. As a source of β^-- irradiation, we used ${}_{91}\mathrm{Pa}^{234}$, ${}_{38}\mathrm{Sr}^{90}$, and BF 90SS-5m [4], as well as samples of a radioactive solution of K^{42} (TU-1050). The value of D was determined by the Flammersfeld relation [7].

Before experimental researches, the specimens were annealed for 24 h at $T = T_g - 10$ K, where T_g is the vitrification temperature; afterwards, they were cooled down to 293 K at a rate of 3 K/min. For subsequent comparative studies, specimens with identical – to within accuracy of 2% – moduli E and μ and identical – to within accuracy of 10% – decrements Δ_l and Δ_t were selected. The both specimens were considered identical by their initial viscoelastic properties. One of them was used to study the temperature dependences of the parameters E, μ, Δ_l, and Δ_t in the ranges 293 K $\leq T \leq T_g$ and $T \geq T_g$, and at $\omega = 0.4$ MHz. The other specimen, before being studied similarly to the former, was subjected to β^--irradiation to an exposure dose of $(0 \div 1.5)$ Gy. Then, the specimens of the second group, before carrying out the researches of their viscoelastic properties, had been held at rest for two months until the induced secondary radiation activity disappeared. The subsequent study of viscoelastic characteristics of irradiated specimens was fulfilled similarly to that of non-irradiated ones. The difference between the obtained two sets of results was considered as a consequence of the influence of β^--irradiation on the complex of properties of heterogeneous polymer systems (HPSs).

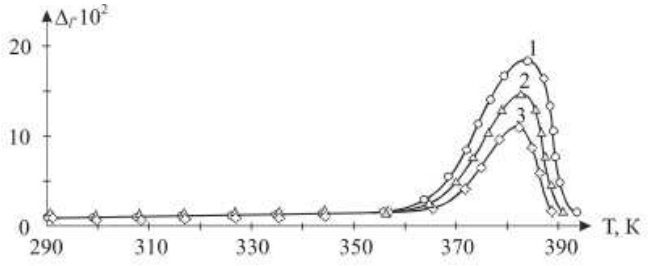

Fig. 1. Temperature dependences of the decrement Δ_l for PVC (*1*), PVC + 1*D* (*2*), and PVC + 6*D* (*3*) systems. $D = 0.25$ Gy

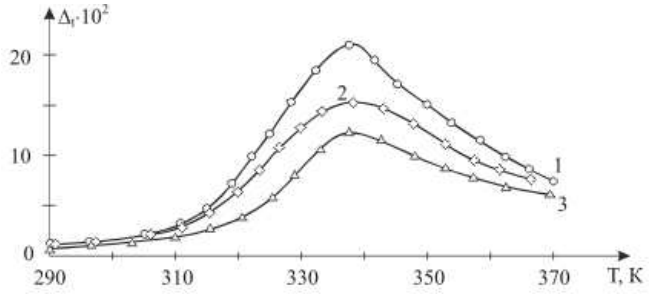

Fig. 2. Temperature dependences of the decrement Δ_t for PVC + 4B + 10DOP (*1*), PVC + 4B + 10DOP + 1*D* (*2*), and PVC + 4B + 10DOP + 6*D* (*3*) systems. $D = 0.25$ Gy

3. Experimental Results and Their Discussion

The results of our experiments concerning the temperature dependences of the parameters Δ_l and Δ_t are presented in Figs. 1 and 2, respectively. The figures testify that irradiation of annealed specimens brought about a reduction of the decrement. However, the character of the dependences $\Delta_{l,t}(T)$ remained identical for all PVC systems.

In Fig. 3, the temperature dependences of the relative increments of $\Delta_{l,t}$-values in irradiated specimens with respect to the $\Delta_{l,t}$-increments in annealed but not irradiated ones are depicted. We assume that the radiation absorption Δ_R is defined as $\Delta_R = \Delta_0 - \Delta_\beta$, where Δ_0 and Δ_β are the logarithmic decrements in specimens not subjected and subjected, respectively, to a certain dose of β^--irradiation. The character of this dependence is preserved for all HPSs. The growth of the temperature above T_g makes the dependence to be leveled off.

Figure 4 demonstrates the temperature dependences of the relative variation of Young's modulus for the annealed specimens, irradiated and not irradiated beforehand. The ratio $\frac{E_1 - E_2}{E_1} = \frac{\Delta E}{E_1}$, where E_1 and E_2 are Young's moduli of the annealed and irradiated specimen and the annealed and not irradiated one,

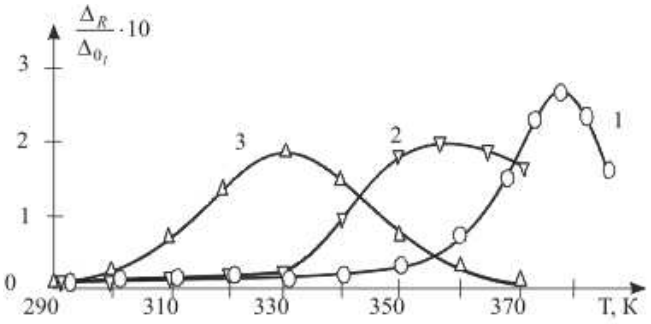

Fig. 3. Temperature dependences of the relative variation of the logarithmic decrement for PVC(l) (*1*), PVC(l) + 5%DBP (*2*), and PVC(l) + 4B+12%DOP (*3*) systems. $D = 0.42$ Gy

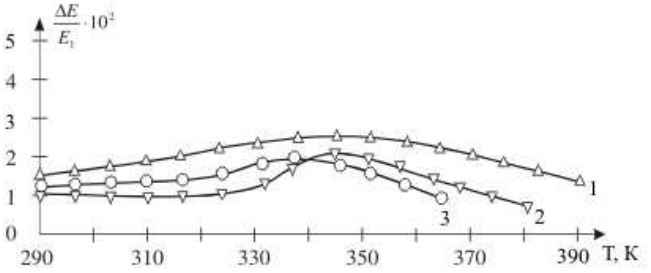

Fig. 4. Temperature dependences of the relative variation of Young's modulus for PVC + 15PB (*1*), PVC (*2*), and PVC + 8PK + 12DBP (*3*) systems. $D = 1.25$ Gy

respectively, was chosen as a modulus variation criterion. It is characteristic that, provided plasticizing and filling agents have been introduced into the systems under investigation, all the latter reveal a less intensive but typical dependence of the modulus variation with temperature at $T \geq 303$ K. The exposure dose of β^--irradiation $D \leq 0.12$ Gy does not change the values of Young's and shear moduli substantially at $T \leq 303$ K. However, if 0.12 Gy $< D <$ 0.35 Gy, the maximal relative change of the logarithmic decrement diminishes by 3.8%. If the dose D grows further to 1.5 Gy, the amplitude of decrement variation decreases (Figs. 1 to 3) and that of modulus variation increases (Fig. 4). In particular, expose doses of β^--irradiation from the interval 0.45 Gy $< D <$ 1.5 Gy have the largest effect on the E- and μ-values in filled and plasticized, and plasticized systems (Fig. 4), increasing their magnitudes by 30–40%. The temperature dependences of the modulus and decrement variations reveal relaxation maxima, the amplitude and position of which depend on the type and the content of ingredients, as well as the exposure dose (in the latter case, irradiation was carried out at $T = 303$ K) (Figs. 1 to 4).

To analyze our experimental data (Figs. 1 to 4), we introduced a numerical criterion—the relative width of peaks in the $\Delta_i = f(T)_{i=l,t}$-dependences at the $\frac{1}{\sqrt{2}}$-level in the constant ultrasonic deformation mode. The curves of dependences $\Delta_i = f(T)$ show that their shape remains constant; however, the peak width intensively changes for filled and plasticized systems. For instance, in the case of PVC + 4B + 10DOP systems, the width of the peak in the $\Delta_l(T)$-dependence diminishes by a factor of 1.7, as D changes from 0.25 to 1.5 Gy. The decrement value in the Δ_i-maximum enables us to assert [3] that the number of segments, which are contained in a unit volume of HPS and participate in the deformation process, diminishes; so does the number of monomer links between anchoring sites. In accordance to that, a reduction of mobile structural elements makes the maximum of dissipative energy loss 1.7 times lower (Figs. 1 and 2).

Let us use the model of a fixed linear polymer macromolecule [10] in order to evaluate the influence of the β^--irradiation dose on the effective relaxation time τ of structural elements in PVC [9]:

$$\frac{\tau_\beta}{\tau_i} \cong \frac{\mathrm{tg}\delta_i}{\mathrm{tg}\,\delta_\beta} = \frac{\Delta_i}{\Delta_\beta}, \tag{11}$$

where the subscripts i and β denote non-irradiated and irradiated specimens, respectively. Since $\tan\delta_i/\tan\delta_\beta = \Delta_i/\Delta_\beta > 1$, this is equivalent to the growth of the polymer network stiffness [3]. The increase of T gives rise to the initiation of a quasisynchronous motion of microblocks with the resonance frequency [5]

$$\omega_0^2 = \frac{2E\,(\mu)}{\rho L_i^2(1-\nu)}, \tag{12}$$

where ρ is the density, L_i is the total length of kinetic structural elements, and

$$\nu = \frac{2-(\upsilon_l/\upsilon_t)^2}{2\left[1-(\upsilon_l/\upsilon_t)^2\right]}$$

is Poisson's ratio.

Our calculations for PVC in the temperature interval 290 K $\leq T \leq T_g$ give that, in the case of macromolecular mobility of the local type, the value of ω_0 falls into the range $(1.6 \div 3.0) \times 10^{13}$ s^{-1}. However, the atoms of lateral groups condensed in PVC—both fixed and non-fixed under the action of β^--irradiation— and the main valency chain together with a segment mobility at $T \geq T_g$ give their contribution to the energy dissipation and the modulus change. The growth of T is accompanied by nonlinear variations of characteristics concerned (Figs. 1 to 4). Such a behavior is associated with the fact that, owing to an increase of the thermal energy in the system, the destruction of anchoring sites in macromolecules becomes more intensive than the growth of the macromolecule energy per unit length under the action of β^--irradiation.

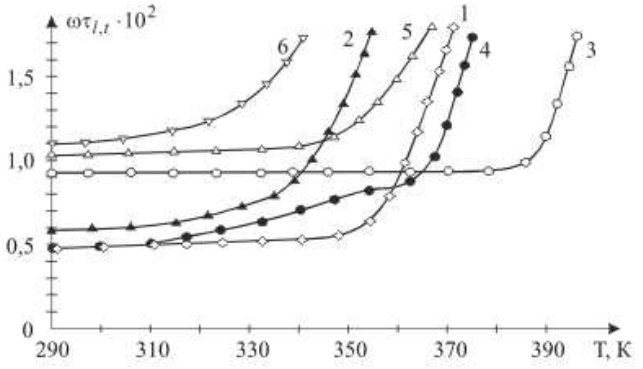

Fig. 5. Temperature dependence of $\omega\tau_i$ for the following systems: *1* – PVC (l); *2* – PVC + 6 DBP (l); *3* – PVC + 15B (l); *4* – PVC + 8K + 3 DOP (l); *5* – PVC + 8B (t); *6* – PVC + 15K + 12 DBP (t) ($D = 0.50$ Gy)

In the case of plasticized systems (at $\varphi \geq 6.0\%$DOP, DBP), the intensity of the anchoring chain destruction in a macromolecule grows, first of all, due to the elimination of weak intermolecular bonds [4].

Supposing that [9]

$$\frac{\Delta E(\mu)}{E_1(\mu_1)} = \frac{\Delta_i}{\omega\tau_i}, \tag{13}$$

we used our experimental data on $\Delta E(\mu)/E_1(\mu_1)$ and Δ_i (Figs. 1 to 4) to study the temperature dependence of the quantity $\omega\tau_i$, which belongs to key characteristics of the relaxation spectrum of the systems under consideration [10] and which can be purposely controlled by β^--irradiation and by varying the type and the content of components (Fig. 5).

4. Conclusions

The experimental research of the influence of β^--irradiation (the exposure dose $D \leq 1.5$ Gy) on acoustic properties of PVC, which is filled with bentonite and kaolin and which contains a DBP (DOP) plasticizer, has been carried out in the temperature range 290 K $\leq T \leq$ 390 K. The parameters E, μ, Δ_l, and Δ_t were demonstrated to change nonlinearly with the

exposure dose growth at an ultrasonic field frequency of 0.4 MHz. In particular, the values of E and μ do not change in the range $D \leq 0.12$ Gy ($T = 303$ K), but increase if D grows further. The maximal relative variations of elastic moduli are observed in the dose range 0.45 Gy $< D <$ 1.5 Gy. In this case, the logarithmic decrement for the ultrasonic wave energy damping simultaneously diminishes by 3.8%. We have also analyzed our experimental results in the framework of the model of a fixed linear polymer macromolecule, where all microblock chains undergo the same deformation under the action of ultrasonic vibrations, and there is no chain separation from fixed sites.

1. N. Bohr, *The Penetration of Atomic Particles Through Matter* (I Kommission Hos E. Munksgaard, Kobenhavn, 1948).
2. S.A. Pozdnev, Zh. Eksp. Teor. Fiz. **126**, 1051 (2004).
3. *Physical Acoustics, Vol. 2B: Properties of Polymers and Nonlinear Acoustics,* edited by W.P. Mason (Academic Press, New York, 1965).
4. B.B. Kolupaev, Inzh.-Fiz. Zh. **80**, 186 (2007).
5. A.A. Koptelov, Prib. Tekhn. Eksp. **3**, 157 (2003).
6. A.L. Fradkov, Usp. Fiz. Nauk **175**, 113 (2005).
7. E.V. Malinovskii, A.M. Rogalya, and Yu.A. Kunitskii, FKVS **12**, 94 (2007).
8. T.V. Kovenya, Mezhdunar. Novosti Mira Plast. **4**, 39 (2007).
9. V.V. Klepko, B.B. Kolupaev, and E.V. Lebedev, J. Polymer Sci. B **49**, 18 (2007).
10. G.M. Bartenev and S.Ya. Frenkel, *Polymer Physics* (Khimiya, Leningrad, 1990) (in Russian).

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ВПЛИВ β^--ВИПРОМІНЮВАННЯ НА АКУСТИЧНІ ВЛАСТИВОСТІ ГЕТЕРОГЕННИХ СИСТЕМ НА ОСНОВІ ПОЛІВІНІЛХЛОРИДУ

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Р е з ю м е

Наведено результати експериментальних досліджень впливу β^--променів поглинутої дози (0÷1,5) Гр на акустичні властивості наповненого, наповненого та пластифікованого полівінілхлориду (ПВХ). Показано, що величина модулів пружності ПВХ-систем та дисипативних втрат енергії ультразвукового поля частотою 0,4 МГц залежить від поглинутої дози β^--випромінювання, температури, типу та вмісту інгредієнтів. Встановлено, що для різних релаксаційних станів системи величина декременту затухання зменшується в міру збільшення дози опромінення. При 290 K $\leq$ T $\leq$ 400 K найбільш інтенсивно впливають β^--промені на модулі пружності (Юнга (E) та зсуву (μ)) вихідного ПВХ, а введення наповнювачів та пластифікатора зменшує ефект опромінення композита. Максимальна дія β^--променів на величину акустичних характеристик ПВХ-систем спостерігається для поглинутих доз (0,45–1,5) Гр, збільшуючи числове значення модулів на (30–40)%. Аналіз отриманих експериментальних результатів пояснено на основі структурного параметра композита, кількісною мірою якого вибрано відносну ширину кривої максимуму температурної залежності дисипації енергії в режимі постійної ультразвукової деформації.