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ON THE CRITICAL INDICES OF THE POLARIZATION PROCESS IN POLYVINYL ALCOHOL FILMS

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The polarization of polyvinyl alcohol films has been investigated. It has been established that it is a consequence of the breakdown of the cluster of intermolecular hydrogen bonds in the polyvinyl alcohol–water system. The critical indices of the breakdown process from the viewpoint of the phase, percolation, and fractal approximations have been found.

One of the basic scientific and practical problems in the physics of polymers is the problem of finding an effective method of mathematical description of macroscopic properties of a large group of materials, including polymers proper and composites based on them. In the last 15–20 years, the scaling, percolation, and fractal approaches have been used for solving such problems [1–4].

The scaling hypothesis is applicable to inhomogeneous systems with fluctuations of the order parameter (density, concentration, mass, etc.). It makes it possible to establish universal relations between the system's characteristics in the field of critical phenomena and find equations of state with the help of which one can calculate the necessary parameters with a comparatively small volume of experimental material.

The effects described by the percolation theory also belong to the class of critical phenomena and have their own set of critical indices. These percolation critical indices are related to the critical indices of phase transitions and the dimension of the corresponding fractal by a number of relations that permit determining by two found indices all of the others [1].

For polymers, the presence of a wide range of temperatures in which softening occurs should obviously lead to some specific features of the vitrification–softening phase transition characteristic of them. This process is classified with phase transitions of the second kind, but there is still no unified opinion on the possibility of critical phenomena in it [2]. The application of the percolation approach to the analysis of this phase transition is of interest.

The aim of the present work is to determine the critical indices of the polarization process as a process of breakdown of the percolation hydrogen-bond net in polyvinyl alcohol films (PVA). Unlike other alcohols, PVA forms stable associates of macromolecules upon cooling of its aqueous solution. Upon drying at room temperature of the solution poured on glass, an elastic film is formed. The water left in it forms with the PVA molecules intermolecular hydrogen bonds, and the degree of hydration thereby is 3–4 H_2O molecules per OH-group of the monomer [5]. If this system is kept for a long time, phase transformations (polymerization, crystallization) occur in it and H_2O molecules (or their complexes) are shifted to the film surface. The rate of these processes increases with increasing drying temperature.

In [6], a relation between the extent and ordering of the hydrogen-bond net and the dielectric constant ε in solid polyamides was found. It may be expected that in PVA films the processes of measurement of the temperature dependence $\varepsilon(T)$ in a weak low-frequency electric field will be accompanied by a disruption of the hydrogen bonds. In this case, a critical point — a percolation threshold, near which the temperature dependences of the dielectric constant $\varepsilon(T)$ and the order parameter $g(T)$ are representable in the form of power functions with critical indices — should exist. In using the probability method, this should be power functions $\varepsilon(x)$ and $g(x)$, where x is the probability of disruption of the hydrogen bonds.

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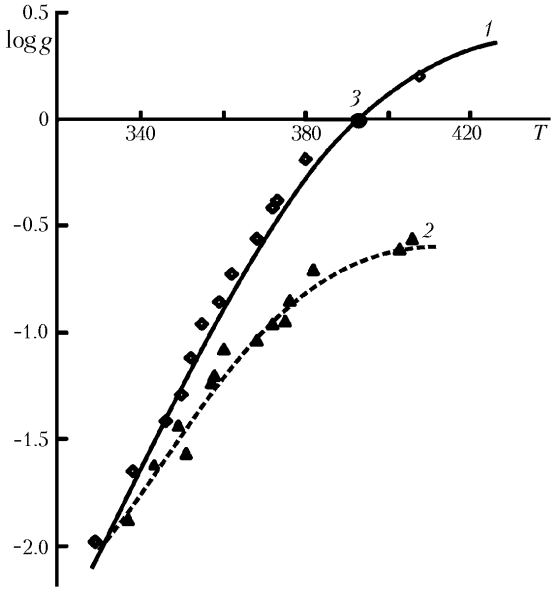

Fig. 1. Temperature dependence of the Kirkwood factor at frequencies of: 1) 100; 2) 1000 Hz (at point 3, $g = 1$). T, K.

Materials and Measuring Technique. To obtain films, the PVA powder was dissolved in distilled water heated to 353–373 K, poured into alcohol-washed Petri dishes, and dried at 288–293 K for four days. The films were separated from the substrate and placed in a measuring cell between two copper electrodes. The capacity of the flat capacitor obtained and the dielectric loss tangent were measured by means of an E7-11 alternating current bridge at frequencies of 100 and 1000 Hz. We used a standard three-electrode measuring cell with a guard ring. The samples were heated to a temperature of 400–420 K at a rate of 1–1.5 deg/min. The value of ε was calculated by the flat capacitor formula. Approximation of the experimental points was carried out by means of a computer program of mathematical analysis. The film thickness (~100 μm) was measured by a micrometer. The use of teflon spacers has made it possible to show that in these films a large portion of the losses (quantity tan ε) is determined by the through conductivity. Therefore, in the present paper only the dependences $\varepsilon(T)$ and $g(T)$ are discussed.

Features of the Vitrification–Softening Phase Transition. Our previous investigations [7] have shown that the values of ε at frequencies of 100 and 1000 Hz (ε_{100} and ε_{1000}) increased from 5–7 at 290 K to ε_{100} = 600–800 and ε_{1000} = 70–90 at 400–420 K. Upon cooling, ε_{100} and ε_{1000} took their previous values, and after repeated measurements on the same samples they increased slightly, to values one-to-two orders lower. In the 290–410 K range, the experimental dependences $\varepsilon(T)$ are given by a relation of the form $\varepsilon_{100} \propto \exp(-U_a/kT)$, and in the coordinates ln $\varepsilon_{100}(1000/T)$ they are approximated by straight lines by whose slope the activation energy is calculated: upon the first heating $U_a \approx 60$ and upon the second one 25 kJ/mole. As is known [6], the energy of single hydrogen bonds is 10–30 kJ/mole. Therefore, the U_a values obtained for PVA are close to the energy of disruption of double and single hydrogen bonds.

To explain the results obtained, it should be noted that in polar materials with "rigid" dipoles the polarization value is usually determined from the Debye formula for the dipole orientation:

$$P = \frac{N\overline{\mu}^2 E}{3kT}. \tag{1}$$

According to (1), the values of P, as well as of ε, should decrease with increasing T, which is usually observed experimentally for many polar materials, with a few exceptions: ethers of benzoic acid and dichlorethane. It was found by different methods [8] that in these substances the dipoles of adjacent OH groups are oriented in antiparallel due to the hydrogen bonds so that their dipole moments are compensated. Such hydrogen bridges are rather sta-

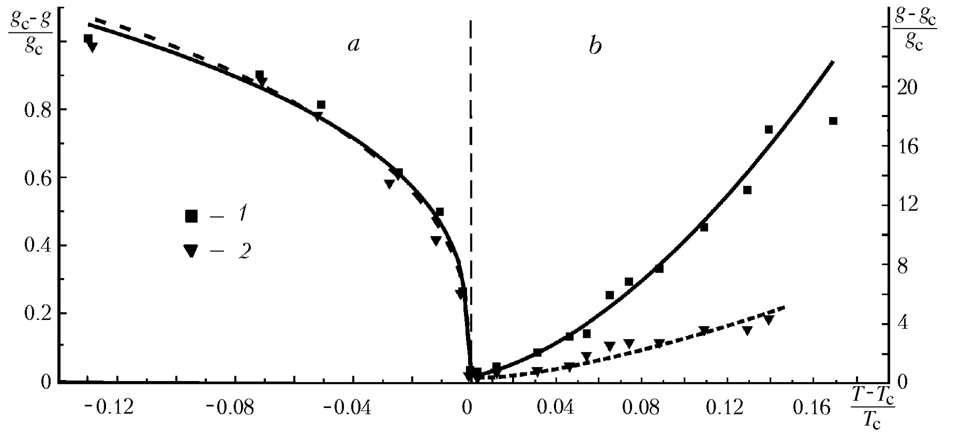

Fig. 2. Temperature dependence of the reduced Kirkwood factor $\frac{g_c - g}{g_c}$ (a) and $\frac{g - g_c}{g_c}$ (b) in the vicinity of the critical point at frequencies of: 1) 100; 2) 1000 Hz.

ble, but with increasing T they decay and the portion of polar groups increases so that the polarization caused by the decay exceeds the contribution of its orientation component. Evidently, in PVA films a similar situation takes place.

The experimental dependence $\varepsilon(T)$ permits calculating the temperature dependence $g(T)$ of the orientation Kirkwood factor $g = 1 + z \langle \cos \theta \rangle$ taking into account the orientation of adjacent dipoles. In the case of antiparallel orientation, the condition $0 < g < 1$ should be fulfilled, in the case of arbitrary orientation $g = 1$, and for parallel orientation $g >> 1$.

Figure 1 shows the dependences $g(T)$ calculated by the Kirkwood–Frelich equation [7] for frequencies of 100 and 1000 Hz upon the first heating of the films. As is seen from Fig. 1, at low temperatures $g << 1$, which is characteristic of the antiparallel orientation $\bar{\mu}$ of adjacent OH-groups. And the values of g_{100} and g_{1000} thereby almost coincide, since the disruption of the hydrogen bonds is only due to the rotational motion of the OH-groups about the axis of macromolecules. With increasing T the difference between the values of g_{100} and g_{1000} increasingly widens, since the disruption of the hydrogen bonds is due to the mobility of larger segments. At T = 393 K, g_{100} = 1, and at this point all hydrogen bonds are broken and the antiparallel orientation $\bar{\mu}$ is arbitrary. The further increase in $g_{100} > 1$ is caused by the appearance of some collective orientation $\bar{\mu}$, which manages to follow only a lower frequency of the electric field (100 Hz).

It should be noted that the structural model of the investigated films is the closest to the theoretical models of two- and three-dimensional grids (Onsager, Ising) [1, 9]. In these models, the role of the order parameter is played by the medium dipole moment in the grid node, and for PVA films — by the factor g. Near the point of the phase transition of the second kind, the following relations of the form

$$\frac{g - g_c}{g_c} \propto \left(\frac{T - T_c}{T_c} \right)^{\beta}, \quad T < T_c \text{ and } g \equiv 0, \quad T > T_c \tag{2}$$

should hold for it. However, because of the above spreading of the vitrification–softening phase transition, it may be suggested that for some temperature ranges the dependences

$$\frac{g - g_c}{g_c} \propto \left(\frac{T - T_c}{T_c} \right)^{\beta}, \quad T < T_c \text{ and } \frac{g_c - g}{g_c} \propto \left(\frac{T_c - T}{T_c} \right)^{\gamma}, \quad T_c < T < T_c' \tag{3}$$

take place. This is also evidenced by the absence of a sharp jump of ε in the dependence $\varepsilon(T)$. The extension of the phase transitions in materials of the type of ferroelectrics is explained by the special properties of the structure and (or) composition fluctuations, and, primarily, by the dissimilarity of their dimensions [10, 11]. If the fluctuations are homogeneous, then the phase transition should be clear; otherwise its extension is observed. However, the detailed nature of spread phase transitions has, up to now, been little studied. In the case of polymers, it may be suggested that the increase in $\varepsilon(T)$ at $T < T_c$ is largely determined by the rotation of hydroxyl groups about the axis of macromolecules, and at $T > T_c$ — by the mobility of segments in the crystalline and amorphous regions. These are the same factors that also determine the frequency dependence of ε.

The recalculation of $g(T)$ in accordance with (3) and the analysis performed have shown that extreme points can be approximated by power functions with exponents having values of β_{100} and $\beta_{1000} \approx 0.33$–$0.36$ at $T < T_c$ and $\gamma_{100} = 1.48$ and $\gamma_{1000} = 1.1$ at $T > T_c$. The graphs of these functions are given in Fig. 2. It should be noted that in the vitrification region the values of β are close to the values in the three-dimensional Ising model, $\beta = 0.381$ [10]. In the softening region such a coincidence is absent.

Percolation and Fractal Approaches. Proceeding from the features of the structure and composition, in PVA films a three-dimensional percolation net of hydrogen bonds should exist. Each node of this percolation net contains two OH-groups: one from the PVA macromolecule and the other from the H_2O molecule. They are oriented in anti-parallel ($\varepsilon = 0$) and form two hydrogen bonds. Prior to heating, the degree of hydration of each of such nodes is 3–4 H_2O molecules on average. Upon heating in a weak electric field, a disruption, of hydrogen bonds followed by a bound water loss occurs.

In the percolation theory of growth and disruption, the following problems are distinguished: problems of lattice bonds and nodes, continual problems, and problems on random nodes [12, 13]. The probability that a bond is in one of the states intact or broken is denoted as x. For the problem of bonds it is assumed that the state of one bond is independent of the states of the others. For the problem of nodes the bonds are blocked and the nodes decay with a probability of $1 - x$. The percolation threshold x_c for the problem of bonds on any lattice does not exceed the threshold for the problem of nodes on the same lattice.

Since the x-ray degree of crystallinity of the investigated films $C = 0.5$–0.6, which points to the presence of not only crystalline but also amorphous regions and, moreover, the IR spectra of these films contain absorption bands characteristic of the isotactic (850 cm^{-1}) and syndiotactic (916 cm^{-1}) conformations, the model can be used on random nodes. Two nodes in the problem of random nodes are considered to be linked if the distance between them does not exceed some fixed value. The effects described by this problem belong to the critical phenomena taking place at phase transitions.

We are investigating the probability of damage of a node — the disruption of two hydrogen bonds and the threshold x_c at which a continuous grid of damaged nodes (infinite cluster) is formed. As $x = 0$, we take the point $T = 304$ K, for which $\ln \varepsilon = 0$ and all hydrogen bonds are intact. As $x = 1$, we take the point $T = 386$ K, for which $g = 1$ and all hydrogen bonds are broken (see Fig. 1). In this case, the dependence $\varepsilon(x)$ in the vicinity of the critical point should be determined by the scaling relation

$$\frac{\varepsilon_c - \varepsilon}{\varepsilon_c} \propto \left(\frac{x_c - x}{x_c}\right)^{-q}, \quad x < x_c \quad \text{and} \quad \frac{\varepsilon - \varepsilon_c}{\varepsilon_c} \propto \left(\frac{x - x_c}{x_c}\right)^{t}, \quad x > x_c, \tag{4}$$

where t and q are critical indices of the percolation theory.

For the problem of random nodes in three-dimensional systems, the relation $x_c = 2.7/w$, where w is the mean coordination number in the random grid of nodes, has been obtained. For isotactic PVA with a "plane zigzag" molecular chain, $w = 6$ ($x = 0.45$), and for syndicotactic PVA with a "spiral" molecular chain, $w \le 4$ ($x_c = 0.675$).

As a result of the analysis of the function $\varepsilon(x)$ in accordance with (4), the critical indices of the process of destruction of the percolation cluster in the PVA films have been obtained: $x_c = 0.6$, $t = 1.41$, and $q = 1.10$. According to current notions, the percolation cluster in the vicinity of the x_c point is fractal with a fractal dimension d_f, which is related to the critical indices of the percolation theory by the relation [1]

$$d_f = d - \frac{t}{\nu}, \tag{5}$$

where $d = 3$. The correlation radius is found by the formula

$$R = \left(\frac{x - x_c}{x_c} \right)^{\nu} . \tag{6}$$

Here the critical index of the correlation radius is

$$\nu = \frac{q + 2t}{d} . \tag{7}$$

As a result, we obtain: $d_f = 1.92$, $\nu = 1.31$.

In the case of three-dimensional systems, the value of $d_f < 2$ is characteristic of the special form of fractals, the model of whose formation appears in the literature under the name DLA (diffusion-limited aggregation). This is one of the modifications of the Witten–Sander (WS) model [14], in which the dimension d_f is almost independent of the type of lattice but strongly depends on the trajectory of the walk of the clusters or particles forming a fractal. For the Brownian diffusion at $d = 3$ and the cluster–cluster association, $d_f = 1.77$. The value obtained by us is close to this value.

The results presented make it possible to draw the following physicochemical picture of destruction of the fractal cluster in the system investigated by us. As the temperature increases, first the "defective" nodes with the least activated energy (weakened hydrogen bonds, favorable steric conditions for the rotation of OH-groups and displacement of freed H_2O molecules to the film surface, etc.), which are situated at different sites of the film, are destroyed. The regions of destroyed nodes grow and form a multitude of small clusters. Subsequently, aggregation of such clusters and an increase in their sizes occur. At $x = x_c$, a continuous three-dimensional net (infinite cluster) is formed from them. If, in the film, there was no second three-dimensional net of stronger chemical bonds, at this instant the film would break down into many pieces, inside which the bonds are still intact. A further increase in ε occurs due to the orientation of the dipoles of free OH-group by the electric field.

Upon cooling after the first heating, hydrogen bonds are formed again, but this time between PVA molecules without the participation of water.

Thus, in the present paper, for qualitative description of disordered systems in the region of the diffuse vitrification–softening phase transition, the scaling theory of percolation clusters has been used. We have obtained the values of the critical indices: order parameter, percolation critical indices, correlation radius, and fractal dimension of the percolation cluster of hydrogen bonds in the PVA films.

On the basis of the results obtained, we propose a physicochemical model of polarization of PVA films as a process of destruction of the percolation cluster formed by hydrogen bonds. The question of universal critical indices and of classes of materials for which they are applicable requires additional studies.

NOTATION

C, degree of crystallinity; d, topological dimension; d_f, fractal dimension; E, electric-field strength, V/m; g, Kirkwood orientation factor; g_{100} and g_{1000}, Kirkwood factor at frequencies of 100 and 1000 Hz; g_c, Kirkwood factor at a critical point; k, Boltzmann constant, J/K; N, concentration of polar groups, mole/l; P, polarization; q, t, critical percolation indices; R, correlation radius; T, temperature, K; T_c, temperature at a critical point, K; $T_c' > T_c$, temperature characterizing the phase transition diffusion for polymers, K; U_a, activation energy of the polarization process, J/mole; w, mean coordination number; x, probability (of node damage) of the percolation theory; x_c, probability at a critical point; z, number of closest dipoles; β, γ, critical indices in the vicinity of the point of the phase transition of the second kind; β_{100}, β_{1000}, γ_{100}, γ_{1000}, critical indices at frequencies of 100 and 1000 Hz; tan δ, dielectric loss tangent; ε, dielectric constant; ε_{100}, ε_{1000}, dielectric constant at frequencies of 100 and 1000 Hz; ε_c, dielectric constant at a critical point; θ, angle between dipoles; $\overline{\mu}$, dipole moment of a group; ν, critical index of the correlation radius. Subscripts: a, activation; c, critical; f, fractal.

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