DIFFUSIONAL–RELAXATIONAL MODEL OF THE FORMATION OF POLYMER BOUNDARY LAYERS IN ADHESIONAL COMPOUNDS

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The variation in density of active centers is described by a diffusion equation of hyperbolic type, which is solved by numerical methods. The results of the calculation are compared with known experimental data.

As a result of studying the physicochemical processes occurring at the interface between polymers and inorganic materials and the properties of the resulting systems, numerous experimental data are obtained, and provide the basis for very different practical applications. Thus, it has been established that, in boundary layers, complex processes of structural rearrangement [1] and redistribution of the functional groups of macromolecules [2] occur in the formation of adhesional contact. The density and strength properties of the surface layers vary nonmonotonically over the thickness of the layer [3]. In accordance with the concepts of rheological adhesion theory proposed in [4] and experimentally confirmed in [5, 6], the failure of compounds is cohesional in character in most cases; rupture of the metal–polymer bond occurs over the weak section of the polymer boundary layer.

Theoretical investigations of interphase adhesional processes are generally acknowledged to be considerably remote from experimental research, and aim, as a rule, at the development of particular theories of adhesion. At the same time, as noted in [7], the conditions have been created for the construction of models allowing the adhesion of polymers to be described from common physicochemical principles.

In the present work, on the basis of the fundamental hypothesis of nonequilibrium thermodynamics and molecular-kinetic theory, analytic description of the behavior of polymer macromolecules in the boundary layers is attempted, taking account of the basic factors influencing their state.

Diffusion Equation of Active Centers

A polymer in adhesional contact with the substrate surface is regarded as a system of kinetic correlated formations in the potential field of the surface. The size of these kinetic elements and the degree of binding is determined by the physical state of the polymer, i.e., the level of mobility of particular sections of the macromolecules, depending on the energy ratio of thermal motion and molecular interaction. To describe the adhesional interaction, an active center is introduced: an arbitrary fragment of a macromolecule characterized by a higher energy of interaction with its surrounding kinetic elements. The nature of this center may be different [8, 9], and may even change in the course of motion. These concepts follow from the model of physical points developed in [2, 10], taking account of their dynamics. Analysis of the behavior of the active centers shows that the transfer of the centers is determined by their concentration and structure and the magnitude of the intermolecular field, and is discrete in character, in the general case. In connection with this, the finiteness of the velocity of motion is taken into account in describing the diffusion of the centers, by introducing the characteristic diffusional relaxational time of the active centers τ_r. On the basis of these concepts, the flux of active centers may be determined from Eq. (1), which follows from the Onsager relation [11]

$$j = -L\frac{\partial E}{\partial x} - D\frac{\partial n}{\partial x} - \tau_r\frac{\partial j}{\partial t}. \qquad (1)$$

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The first term in Eq. (1) describes the convective diffusion (or energodiffusion) due to the gradient in the integral interaction potential of the active center with adjacent micromolecules and the substrate surface. The second and third terms determine the transfer of centers under the action of the concentration gradient, taking account of the relaxational character of the motion.

To establish the form of the kinetic coefficient L, the characteristic features of the active-center behavior in an external potential field are considered. The motion of the active center under the action of the force $F = -\partial E/\partial x$ may be regarded as rotation around some point 0 at a distance ℓ from the center. Then the acceleration and maximum velocity of motion in the direction x normal to the substrate surface is determined from the relations

$$a_x = a_0 \frac{F}{m} \sin^2\alpha,$$

$$v_{\mathrm{max}} = \frac{a_0}{2\pi} \frac{\lambda\tau_r F}{ml} \sin^2\alpha.$$

The mean velocity $v_{\mathrm{av}} = v_{\mathrm{max}}/2$ after averaging over the angle α is

$$v_{\mathrm{av}} = -\frac{a_0}{8\pi} \frac{\lambda\tau_r}{ml} \frac{\partial E}{\partial x}.$$

Hence the flux of active centers on account of energodiffusion is

$$j_E = n v_{\mathrm{av}} = -\frac{a_0}{8\pi} \frac{\lambda\tau_r n}{ml} \frac{\partial E}{\partial x}. \tag{2}$$

As a result of comparing Eq. (2) with the first term of Eq. (1), it is found that

$$L = \frac{a_0}{8\pi} \frac{\lambda\tau_r n}{ml}. \tag{3}$$

The potential field in which the active center exists is represented as the superposition of two fields: the field of the substrate surface, described by a Born–Mayer exponential potential [12] and the field of active-center interaction $E_M(n)$. It may be shown that, regardless of the form of the pair-interaction function, the interaction potential of an individual center with the others surrounding it is $E_M = -\sigma n$. Hence, the resulting potential is determined by the expression

$$E = -\sigma n - E_0 \exp\left(-\frac{x}{R}\right). \tag{4}$$

Taking account of Eqs. (2)-(4), Eq. (1) may be brought to the form

$$\frac{\partial j}{\partial t} = -\frac{j}{\tau_r} - \frac{D}{\tau_r} \frac{\partial n}{\partial x} - \frac{\gamma n}{\tau_r} \left[-\sigma \frac{\partial n}{\partial x} + \frac{E_0}{R} \exp\left(-\frac{x}{R}\right) \right], \tag{5}$$

where $\gamma = L/n$.

After differentiating Eq. (5) with respect to the coordinate and taking account of the law of conservation of the number of active centers $\partial j/\partial x = -\partial n/\partial t$, the following diffusion equation of hyperbolic type is obtained

$$\tau_r \frac{\partial^2 n}{\partial t^2} - (D - \gamma n\sigma) \frac{\partial^2 n}{\partial x^2} + \frac{\partial n}{\partial t} + \gamma\sigma \left(\frac{\partial n}{\partial x}\right)^2 - \frac{E_0\gamma}{R} \exp\left(-\frac{x}{R}\right) \frac{\partial n}{\partial x} + \frac{E_0\gamma n}{R^2} \exp\left(-\frac{x}{R}\right) = 0. \tag{6}$$

Introducing the dimensionless quantities $\tau = t/\tau_r$, $X = x/R$, $N = n/n_0$, Eq. (6) takes the following dimensionless form after the appropriate transformations

$$\frac{\partial^2 N}{\partial \tau^2} - Q(1 - PN) \frac{\partial^2 N}{\partial X^2} + \frac{\partial N}{\partial \tau} + PQ \left(\frac{\partial N}{\partial X}\right)^2 - F \exp(-X) \frac{\partial N}{\partial X} + FN \exp(-X) = 0. \tag{7}$$

The dimensionless parameters appearing in Eq. (7) are as follows: $Q = D\tau_r/R^2$; $P = \gamma n_0 \sigma/D$; $F = E_0\gamma\tau_r/R^2$.

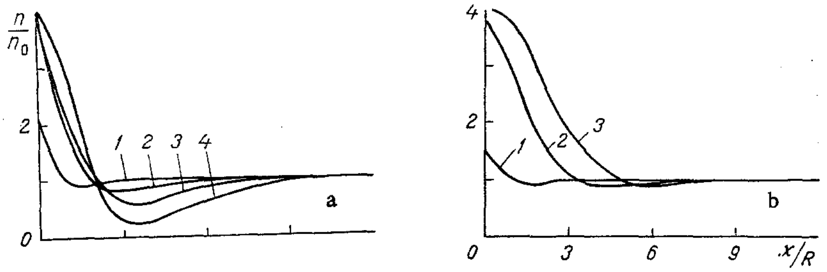

Fig. 1. Distribution of the density of active centers over the polymer thickness when Q = 0.1, P = 0.1, F = 3 (a) and Q = 1, P = 0.1, F = 2.5 (b) for various times: a) $\tau = 0.1$; 2) 1.7; 3) 3.3; 4) 6.5.

Initial and Boundary Conditions

The initial and boundary conditions are chosen in the following form

$$N(0, X) = 1; \quad \left.\frac{\partial N}{\partial \tau}\right|_{\substack{\tau=0 \\ X>0}} = 0;$$
$$N(\tau, \infty) = 1; \qquad N(\tau, 0) = \frac{n_1(\tau)}{n_0}. \tag{8}$$

The form of the function $n_1(t)$ is obtained as a result of analyzing the behavior of the active center at the surface, taking account of the microheterogeneity of its adsorptional properties. In the general case, adhesion of the center to the surface occurs when the section of the macromolecule which is able to take this center encounters a center of the substrate surface with a relatively higher potential. Then, on the basis of molecular-kinetic concepts

$$dn_1(t) = bW_a n_M dn_p. \tag{9}$$

Since the active centers forming adhesional bridges with the metal surface do not participate in further bond-generation processes, it follows that

$$dn_p = \frac{n_{0,p} - n_1(t)}{\tau_r}\,dt. \tag{10}$$

Finally, on the basis of Eqs. (9) and (10), the following differential equation is obtained

$$dn_1(t) = k\,\frac{n_{0,p} - n_1(t)}{\tau_r}\,dt, \tag{11}$$

where $k = bW^a n_M$.

The solution of Eq. (11) with the initial condition $n_1(0) = n_0$ is the expression

$$n_1(t) = n_{0,p} - (n_{0,p} - n_0)\exp\left(-\frac{kt}{\tau_r}\right). \tag{12}$$

Results and Discussion

The density of active centers in different layers of the polymer in the course of adhesional contact with the substrate surface is calculated by a grid-characteristic method, with the following parameter values: X = 0-100; τ = 0-10; F = 0.1-5; Q = 0.1-10; P = 0.1; $n_{0,n} = 4n_0$; k = 2. The boundary conditions used here are Eqs. (8) and (12). The limits of variation of X and τ are determined from physical considerations, and of the parameters F, Q, P on the basis of preliminary calculations in which the data obtained are susceptible to physically sound interpretation. The results of the calculations are shown in Figs. 1-4. It may be shown that, even in the initial stages of the formation of adhesional contact, redistribution of the density of active centers occurs close to the surface (Fig. 1). For all the cases considered, the formation of a region with minimum density and with the corresponding energy of molecular interaction at some distance from the surface is characteristic. The depth of the minimum and its coordinate depend on the relation between the parameters Q, F, P and varies in the course of adhesional-contact formation. It may be shown that, when

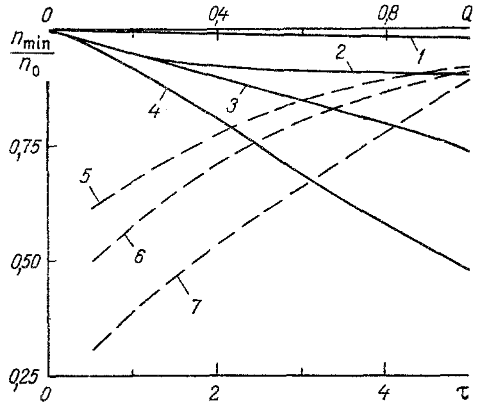

Fig. 2. Dependence of the minimum of the active-center density on the time τ (curves 1-4) and on Q (5-7) when P = 0.1 (1-7); F = 0.5 (1), F = 3 (2-7); Q = 1 (1, 2), 0.5 (3), 0.1 (4); τ = 3.5 (5), 4.5 (6), 6.3 (7).

Q = 1 and F < 3, $n_0 - n_{min}$ is small and varies only slightly with time (Fig. 2). Marked increase in depth of the minimum is observed at higher F (i.e., at contact with a more active substrate surface). The parameter Q, which characterizes the diffusional activity of the polymer, influences the value of n_{min} when Q < 1 (F = 3). When Q > 1, the depth of the minimum is relatively small at practically all stages of formation of adhesional contact (Fig. 2). However, at such values of Q, active displacement of the coordinate of the minimum into the volume of the polymer is established (Fig. 3). Analysis of the calculation results shows that, with variation in one of the parameters, correlated change in the characteristics of the distribution of active-center density is observed: decrease in depth of the minimum is accompanied by displacement to greater distance from the substrate surface. Increase in F here is equivalent in its effect to decrease in Q.

The following quantity may be used as the physical characteristic of the influence of the substrate surface on the state of the polymer

$$B_j = \frac{F}{QP} = \frac{E_0}{\sigma n_0}.$$

It may be established that, when P = 0.1, $n_0 - n_{min}$ sharply increases when B_j > 30-40 (Fig. 4). When B_j < 30, the appearance of a layer with a sufficiently low density of active centers is not observed in the polymer. Hence, B_j = 30 may be regarded as the quantitative criterion separating the surfaces into active and inactive categories.

Redistribution of the physical points (active centers) may be associated with change in structure of the polymer [1, 2] or its cohesional strength [5, 6]. In connection with this, it may be noted that the data obtained within the framework of the given diffusional–relaxational model is in complete agreement with the results of structural investigation of the boundary layers.

The region with a low density of macromolecules forming close to the substrate surface [2] may be identified with the region of the polymer having a minimum energy of molecular interaction.

The calculation results obtained allow specific form to be given to the well-known empirical concepts regarding the physicochemical features of failure of adhesional compounds. Under definite conditions of compound formation, when, in view of the incomplete adhesional contact and the specific properties of the polymer and the substrate material, the integral value of the phase-interaction energy is less than the cohesional energy of the polymer, and the failure of the compound is of adhesional type and is determined to a considerable extent by the kinetics of accumulation of the active centers adsorbed at the substrate surface. If no chemical changes (oxidation, structuring, destruction, etc.) occur in the boundary layers, however, the optimal temperature–time conditions of formation of metal–polymer compounds corresponds to the conditions in which the phase-interaction energy is equal to the cohesional energy, which is realized at a definite density of adhesional bonds at the surface, that is

$$n_1(t_{opt}, T_{opt}) = \text{const}.$$

Then, on the basis of Eq. (12), taking account of the exponential temperature dependence of τ_r [18], it follows that

$$t_{opt} = \frac{\tau_{f,0}}{k} \exp\left(\frac{U_r}{RT_{opt}}\right). \qquad (13)$$

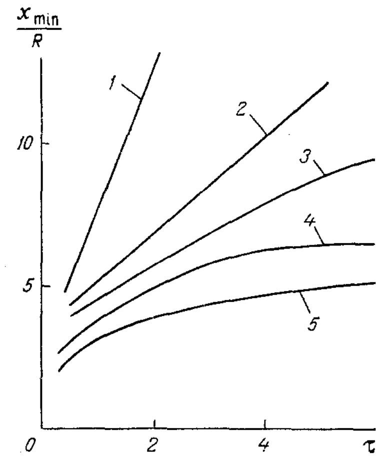

Fig. 3

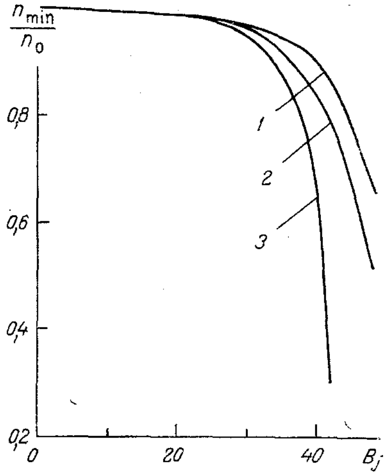

Fig. 4

Fig. 3. Dependence of the coordinate of a minimum of the active-center density on the time of bond formation (P = 0.1): 1) Q = 10, F = 1.5 (B_j = 1.5); 2) 1, 1 (10); 3) 1, 3 (30); 4) 0.5, 3 (60); 5) 0.1, 3 (300).

Fig. 4. Dependence of the depth of the minimum of active-center density on B_j at times of formation τ = 1.8 (1), 3.6 (2), 6.3 (3).

Equation (13), obtained in the given diffusional—relaxational model, coincides with the analogous relation established by a semiempirical method on the basis of analyzing the correlation of the diffusion and adhesion parameters [13]. The results of calculating the optimal parameters of compound formation using Eq. (13) are in sufficiently complete agreement with the experimental data on the adhesional strength of compounds of pentaplast with various metals [13, 14].

These features of the behavior of polymer macromolecules in boundary layers are also of interest in analyzing the cohesional failure of compounds. Since the rupture of macromolecules in equilibrium conditions occurs in the region with the minimum density of active centers, a polymer strongly adhesionally bound to the surface will always remain on the substrate surface after failure of the compound, as is evident from Fig. 1. This result may be regarded as the theoretical justification for the hypothesis of weak boundary layers [4]. Thus, the formation of a layer with relatively low cohesional strength may occur not only as a result of local or selective diffusion to the surface of the low-molecular compounds present in the polymer composition, as indicated in [4, 14], but also as a result of redistribution of active centers of the macromolecules in the field of the substrate surface and the associated change in the grid of physical points.

Note that the calculation results obtained under the assumption of a linear dependence of the strength of the compound on the density of active centers are confirmed by experimental data on the influence of the duration of contact formation and the nature of the polymer on the adhesion [5, 15].

NOTATION

j, flux density of active centers, $m^{-2}\cdot sec^{-1}$; L, kinetic coefficient of energodiffusion, $sec\cdot kg^{-1}\cdot m^{-3}$; E, integral interaction energy, J; D, diffusion coefficient, $m^2\cdot sec^{-1}$; n, density of active centers, m^{-3}; x, coordinate in the direction normal to the substrate surface, m; τ_r, relaxation time, sec; t, current time, sec; ℓ, instantaneous radius of rotation of the center; m, effective mass of segment, kg; α, angle between the radius of rotation and the x axis, rad; v_{max}, maximum velocity of motion of center, $m\cdot sec^{-1}$; v_{av}, mean velocity of motion of center, $m\cdot sec^{-1}$; j_E, density of convective flux of active centers, $m^{-2}\cdot sec^{-1}$; E_M, interaction energy of isolated active center with other centers, J; σ, specific energy of interaction of active centers, $J\cdot m^3$; E_0, characteristic interaction energy of active center with surface, J; R, characteristic length of variation in surface field, m; λ, free path length of active center, m; γ, specific kinetic coefficient of energodiffusion, referred to active-center density, $sec\cdot kg^{-1}$; n_0, initial density of active centers, m^{-3}; b, constant value, m^3; W_2, probability of impact of the potential active center of a macromolecule with the active center of a metal substrate; n_M, density of active centers of the metal substrate, m^{-3}; n_p, density of potential active centers, m^{-3}; $n_{0,p}$, maximum possible density of potential active centers, m^{-3}; t_{opt} and T_{opt}, time and temperature for compound formation corresponding to maximum adhesional strength, sec and K; $\tau_{r,0}$ constant, sec; U_r, effective activation energy of relaxational mobility of macromolecules, J·mole^{-1}.

LITERATURE CITED

1. Yu. M. Malinskii, Usp. Khim., 39, No. 8, 1511-1519 (1970).
2. Yu. S. Lipatov, Interphase Phenomena in Polymers [in Russian], Kiev (1980).
3. Yu. S. Lipatov, Physical Chemistry of Filled Polymers [in Russian], Moscow (1977).
4. Ya. O. Bikerman, Mekh. Polim., No. 3, 516-519 (1973).
5. N. I. Egorenkov and L. I. Kuzakov, Vysokomol. Soed., 23(A), No. 3, 633-669 (1981).
6. M. M. Kalnin' and Yu. Ya. Malers, Vysokomol. Soed., 27(A), No. 4, 793-799 (1985).
7. L. M. Prytykin and V. L. Vakula, in: Adhesional Compounds in Mechanical Engineering [in Russian], Riga (1983), pp. 3-6.
8. G. M. Bartenev, Structure and Relaxational Properties of Elastomers [in Russian], Moscow (1979).
9. G. V. Vinogradov and A. Ya. Malkin, Rheology of Polymers [in Russian], Moscow (1977).
10. I. P. Perepechko, Introduction to Polymer Physics [in Russian], Moscow (1978).
11. P. M. Kolesnikov, Methods of Transfer Theory in Nonlinear Media [in Russian], Minsk (1981).
12. M. Green (ed.), Surface Properties of Solids [Russian translation], Moscow (1972).
13. E. N. Sokolov and A. V. Rogachev, Vests. AN BSSR, Ser. Fiz.-Tekh. Nauk, No. 2, 53-58 (1982).
14. B. Ya. Deryagin, N. A. Krotova, and V. P. Smigla, Adhesion of Solids [in Russian], Moscow (1973).
15. V. L. Vakula and L. M. Pritykin, Physical Chemistry of Polymer Adhesion [in Russian], Moscow (1984).

HEAT TRANSFER BETWEEN A STATIONARY GRANULAR PACKING AND A DESCENDING FLOW OF DUSTY GAS

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The transfer of heat from a stationary granular bed (packing) to a gas—particle flow has been investigated experimentally. A correlation is obtained for calculating the heat-transfer coefficient in the system.

In our view, the use of gas suspensions in apparatus with a stationary granular packing is very promising for a number of processes accompanied by a strong heating effect (catalytic processes, fuel processing, waste-heat recovery, etc.). For these systems the published information concerning external heat transfer (from the packing to the gas suspension) is extremely sparse [1, 2].

The heat transfer experiments were carried out on an apparatus with an open gas—particle flow system. The advantages as compared with other systems (semiclosed and closed) are explained in detail in [3]. The principal element of the apparatus was a column of square cross section containing the packing, which was supported on wire grids attached to the column base. In all the experiments we used only monodisperse packing. In some cases this took the form of smooth steel balls, and in others the form of round porcelain granules with a slightly rough surface. As the particles added to the gas flow we used three narrow fractions of sand and electrical corundum 12 (GOST 3647-71) of polyfractional composition. The prin-

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