

RELATIONSHIP BETWEEN THE ENERGY SUPPLY  
PARAMETERS AND THE PHYSICOCHEMICAL  
CHARACTERISTICS OF POLYMER COMPOSITIONS  
DURING DRYING AND THERMAL PROCESSING

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UDC 667.645;621.396.6

The effect of the type of energy supply on the formation of temperature and concentration fields in the thermal processing of polymer compositions is considered.

The thermal processing of filled polymer compositions used as coatings is a complex physicochemical process which generally involves the removal of solvents, a transition of the material from one physical state to another, and chemical transformations connected with the formation of a polymer binding structure. At present the thermal processing of such systems is usually considered by using the approximate idea that the mean temperature of the material under quasi-stationary heating conditions uniquely determines its physicochemical state. This assumption may not be entirely justified since it ignores the fact that the main features of the energy supply (thermal radiation, convection, conduction, and combined) have a considerable effect on the development of the temperature fields in processed polymer compositions, and consequently, the concentration fields, by which, in this case, we mean the degree of uniformity of the hardening of the system in the volume. In the final analysis this leads to the formation of a polymer coating with different qualitative characteristics.

It is assumed that the use of the main energy supply and the development of a certain temperature field in the polymer are ways of influencing the formation of the polymer coating. Investigations of the hardening of a series of characteristic filled polymer systems which we have carried out showed that the mechanism by which the processes occur in them are different for different types of energy supply.

Figure 1 shows kinetic curves of the change in the content of the epoxy groups in a model system based on ÉD-20 epoxy resin, hardened with maleic anhydride using thermal radiation (supplied by a KG220/1000 short-wave infrared generator), and using conductive energy supply, other conditions being equal. The epoxy group content in the composition at different stages of polymerization was determined by potentiometer titration [1]. As can be seen from Fig. 1 the curves are different, as can clearly be seen by comparing the curves of the rate of exhaustion of the epoxy group (curves 4). For conductive hardening of the composition there is an initial rapid increase in the fraction of reacted epoxy group  $\alpha$ , and then a smoother behavior of the  $\alpha(\tau)$  curves (Fig. 1b). During the process  $d\alpha/d\tau$  decreases. For thermal-radiation hardening of the polymer systems the  $\alpha(\tau)$  curves have an S-shaped form: the process first occurs at a velocity  $v_m$ , which increases exponentially, there is then a rising part on the  $\alpha(\tau)$  curve at a constant velocity which exceeds the initial velocity  $v_{ok}$  in conductive hardening, the velocity of the process then decreases, and the change in  $v_m$  then occurs smoothly (Fig. 1a). The slow development of the hardening first observed (the induction period) for radiant energy supply compared with conductive energy supply can be explained as follows. In conductive energy supply the hardening begins from the substrate, where, before temperature polymerization starts, due to adsorption interaction between the polymer and the substrate there are submolecular structures which play the role of ready polymerization centers [2]. For thermal radiation energy supply, due to the particular features of the formation of the temperature field as a result of the permeability of the system to infrared radiation, new polymerization centers are formed in the inner layers of the coating having a maximum temperature. The formation of a coating proceeds mainly from a certain internal layer to the external layers. In other words, at the beginning of the thermal radiation processing process a kind of "readjustment" occurs having submolecular structures over the whole volume of the polymer. Due to steric effects the velocity of the process at this stage is slowed down compared

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A. V. Lykov Institute of Heat and Mass Transfer, Academy of Sciences of the B. SSR, Minsk. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 39, No. 1, pp. 26-33, July, 1980. Original article submitted June 5, 1979.

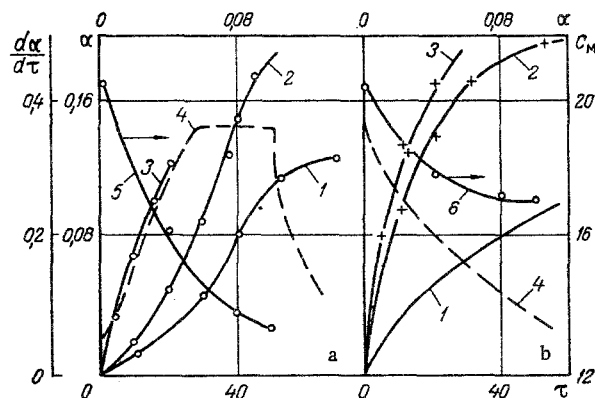


Fig. 1. Kinetic curves of the content variation  $\alpha(\tau)$  (1-3), the rate of disappearance  $d\alpha/d\tau = f(\alpha)$  (4) of the epoxy groups in a model composition with thermal radiation (a) and conductive (b) energy supply, and curves of the disappearance of the methylol groups  $C_M$  in thermal radiation (5) and convective (6) hardening; 1,4)  $t = 60^\circ\text{C}$ ; 2)  $75^\circ\text{C}$ ; 3)  $90^\circ\text{C}$ ;  $C_M$ , %;  $\tau$ , min.

with conductive hardening. Then, due to the volume nature of the absorption of the infrared radiation, a large number of polymerization centers (nuclei) is formed in the system, and the velocity of the process increases and exceeds  $v_{ok}$ . When a system based on FR-300 phenol-formaldehyde resin hardens, which occurs by means of a polycondensation mechanism with interaction between the methylol groups and atoms of hydrogen of the phenol rings, it was also found that, under exactly the same conditions, the rate at which the methylol groups are exhausted in convective energy supply is much less than in thermal radiation supply (Fig. 1, curves 5 and 6).

Hence, the above data confirms the effect of infrared radiation on the intensity and mechanism of the hardening processes in polymer systems.

It was stated in [3] that intense infrared radiation at certain frequencies excites vibrational energy of the appropriate groups of atoms in the molecule, thereby producing a chemically nonequilibrium system of molecules. In this case the rate constant of the chemical reaction depends on the population of the quantum levels of the internal (vibrational in our case) degrees of freedom of the molecules and is not related explicitly to the temperature of the hardened systems. The estimate of the infrared radiation power given in [4] using the example of a two-level system, by means of which one can determine the population of the vibrational level exceeding the population of thermodynamic equilibrium, confirms the possibility of the above-mentioned effect of the acceleration of the process. However, it is shown theoretically in [5] that it is difficult to achieve selective heating.

It is therefore advisable to carry out a more detailed consideration of the features of the process by which temperature and mass-content fields are formed in thermal-radiation energy supply. It is difficult to obtain experimentally the temperature and concentration distribution in a layer of polymer coating, particularly in the early stages, when the polymer is in the liquid state, in view of its limited thickness. Hence, we attempted to study the development of the temperature and concentration fields in the coating in the case of thermal radiation energy supply theoretically using a physical-mathematical model of the process [6]. We assumed that the mechanism by which the coating is formed consists solely in polymerization of the bonding system, and the external conditions of energy supply are determined by the parameters of thermal radiation-convective heat exchange. In this case the heat and mass transfer processes in the coating layer can be described by the following set of differential equations:

$$\frac{\partial \Theta}{\partial Fo} = \frac{\partial^2 \Theta}{\partial \xi^2} + Ki_p Pd (1-u)^n \exp \left[ -\frac{1}{P\Theta + P_0} \right] + Ki_l Bu \exp(-Bu\xi), \quad (1)$$

$$\frac{\partial u}{\partial Fo} = Lu \frac{\partial^2 u}{\partial \xi^2} + Pd(1-u)^n \exp \left( -\frac{1}{P\Theta + P_0} \right) \quad (2)$$

with the initial conditions

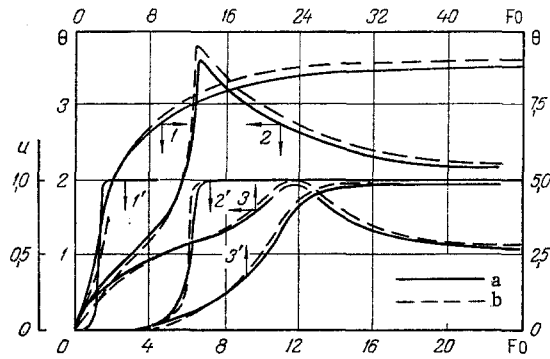


Fig. 2. Effect of the criterion  $K_i l$  on the kinetic curves  $\Theta(\xi, Fo)$  (1-3) and  $u(\xi, Fo)$  (1'-3'): 1, 1')  $K_i l = 1$ ; 2, 2') 0.14; 3, 3') 0.01; a)  $\xi = 0$ ; b)  $\xi = 1$ .

$$\Theta(\xi, 0) = 0, \quad (3)$$

$$u(\xi, 0) = 0 \quad (4)$$

and the boundary conditions

$$\frac{\partial \Theta(0, Fo)}{\partial \xi} = Bi [\Theta(0, Fo) - 1], \quad (5)$$

$$\frac{\partial \Theta(1, Fo)}{\partial \xi} = 0, \quad (6)$$

$$\frac{\partial u(0, Fo)}{\partial \xi} = \frac{\partial u(1, Fo)}{\partial \xi} = 0. \quad (7)$$

Here the first term on the right side of Eq. (1) describes conductive heat transfer in the system, while the second represents the presence of an internal heat source due to chemical transitions, characterized in this case by the value of the factor  $K_0$  in front of the exponential, and the effective activation energy  $E$ . The third term in Eq. (1) takes into account the internal heat source due to the permeability of the system, with a radiation attenuation factor of  $\beta$ . Equation (2) describes the concentration distribution (the degree of excess) in the volume of the system due to the chemical reaction complicated by diffusion processes. We used a nonlinear method [7] to solve Eqs. (1)-(7) numerically. The thermal characteristics of the coatings (the thermal conductivity  $\lambda$ , the thermal diffusivity  $\sigma$ , and the heat capacity  $c$ ) and the kinetic constants of the hardening of the polymer systems (the activation energy  $E$ , the heat of reaction  $Q$ , and the factor  $K_0$  in front of the exponential) were taken from [8, 9].

Figures 2 and 3 shows the effect of the external heat-exchange criteria  $K_i l$  and  $Bi$  on the heating curves of irradiated ( $\xi = 0$ ) and thermally insulated ( $\xi = 1$ ) surfaces, and also on the kinetics of the chemical transition on the surfaces. As can be seen from Fig. 2, as  $K_i l$  increases, other conditions being equal, the temperature in the quasi-stationary state  $\Theta_{st}$  increases, the time taken to emerge from the quasi-stationary mode  $Fo_{st}$  decreases, the temperature drop over the thickness of the coating increases, and the time taken for the chemical transitions to occur in the system decreases. In addition, the thermal effect of the reaction is different depending on the value of  $K_i l$ . For  $K_i l = 0.01-0.14$ , when the amount of radiant heat dissipated in the system is comparable with the amount of heat dissipated in chemical transitions in the polymer matrix, the curves of  $\Theta(\xi, Fo)$  have pronounced extrema, while the value of the maximum temperature  $\Theta_{max}$  is determined by the value of  $K_i l_p$ . For large values of  $K_i l$  ( $K_i l > 1$ ), other conditions being equal, the curves of  $\Theta(1, Fo)$  and  $\Theta(0, Fo)$  have an asymptotic form.

The effect of the  $Bi$  criterion of the kinetic curves  $\Theta(1, Fo)$  and  $u(\xi, Fo)$  is the opposite of the effect of  $K_i l$ . When  $Bi$  is increased by an order of magnitude from 0.2 to 2 (Fig. 3) the temperature of the system after reaching its quasi-stationary state  $\Theta_{st}$  falls sharply, and approaches in absolute value the temperature of the medium  $\Theta_{st} \approx 1$ . In this case the temperature field in the system is established rapidly, and the radiant flux is, in effect, "blown away" and does not have any appreciable effect on the formation of the temperature field. Due to the low level of the temperature of the coating in this case the chemical processes in the system are characterized by low intensity and do not continue to the end. When the radiant heat exchange predominates ( $Bi$  small) the heating of the system is characterized by high values of  $\Theta_{st}$  and pronounced nonstationary conditions. When

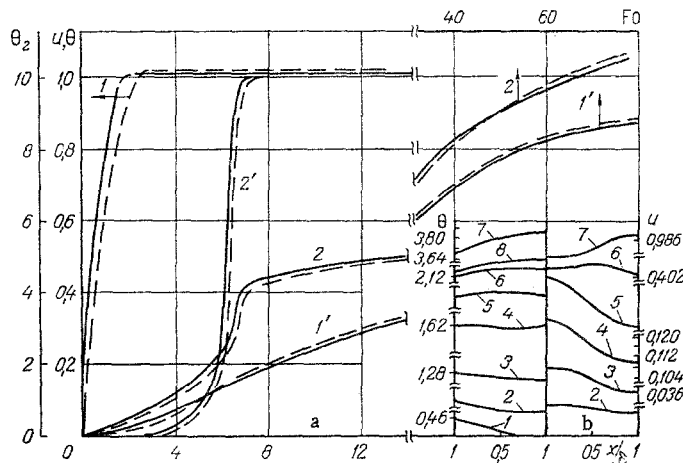


Fig. 3. Effect of the criterion  $Bi$  on the kinetic curves  $\Theta(\xi, Fo)$  (1, 2) and  $u(\xi, Fo)$  (1', 2'), a: 1, 1')  $Bi = 2$ ; 2, 2') 0.02; a)  $\xi = 0$ ; b)  $\xi = 1$ ; the dimensionless temperature field  $\Theta(\xi, Fo)$  and the dimensionless concentration field  $u(\xi, Fo)$ , b: 1)  $Fo = 1$ ; 2) 3; 3) 4; 4) 5; 5) 6; 6) 6; 7) 7; 8) 24.

the criteria  $Ki_l$  and  $Bi$  increase simultaneously the system is characterized by the rapidity with which the heat and mass transfer processes occur and by considerable temperature drops over the thickness.

Figure 3b shows characteristic curves of the evolution of the temperature and concentration fields in a polymer system for combined radiant-convective energy supply. As can be seen from Fig. 3, when the system is heated to the temperature of the medium ( $\Theta = 1$ ) the maximum temperature is observed on the free surface of the layer. Here chemical transitions begin, the intensity of which decreases as the distance from the surface of the coating increases. When the surface temperature reaches the temperature of the medium, due to the permeability of the composition to infrared radiation, equalization of the temperature field occurs, and then the temperature difference over the thickness changes, the temperature on the free surface of the layer becomes less than inside. The concentration field changes similarly. In this case there is then a lag in its development compared with the temperature field. The heat dissipated in the chemical transition causes some deformation of the temperature field, which can be seen particularly clearly from Fig. 4a, in which we show the kinetic dependence of the temperature drop on the surfaces of the coating  $\Delta\Theta = \Theta(0, Fo) - \Theta(1, Fo)$  for different values of  $Ki_l$  and  $Bi$ . The presence in the coating layer of an internal source of heat, due to the chemical transitions in the polymer matrix, also explains the form of curves 1-5 in the region of the external points.

Analysis of curves 1, 4, and 5 shown in Fig. 4a shows that when  $Ki_l$  increases from 0.01 to 1 the drop  $\Delta\Theta$  increases in proportion with emergence into the steady state. The increase in the convective component of the heat transfer  $Bi$  from 0.02 to 2 (curves 1-3), other conditions being equal, facilitates equalization of the temperature field over the thickness of the coating with simultaneous reduction in the temperature level.

Hence, analysis of the effect of the criteria  $Ki_l$  and  $Bi$  on the heat and mass transfer processes shows that by changing the ratio between the value of the radiant and convective fluxes, one can not only affect the temperature levels of the process but also control the formation of the temperature field in the coating, and consequently, the concentration field also. Experiments carried out on model systems with a thickness of  $\delta = 4$  mm, which enabled a layer analysis to be carried out in the final stages of the hardening, when the hard body of the polymer is formed, showed that the qualitative characteristics of the coating are extremely sensitive to the particular features of the temperature distribution over the thickness. The characteristics of the coating were determined by an analysis of layer sections ( $\delta_l \approx 0.25$  mm) from specimens of the materials being investigated. At this stage of the process of coating formation the most significant features are the degrees of hardening  $N$  of the polymer binding, determined by the extraction method, and the value of the equilibrium swelling  $k$  in pairs of solvents [10].

As can be seen from Fig. 4b, for convective energy supply the greatest degree of hardening of a polymer system based on epoxy resin (EKM compound) [11] is observed at the boundary layers, and in the case of thermal radiation energy supply the maximum hardening is characteristic for a certain internal layer and is due to the permeability of the system. Analysis of the equilibrium-swelling curves, which are one of the characteristics

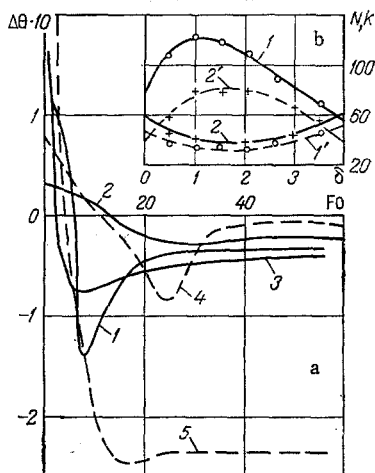


Fig. 4. Effect of the criteria Bi (1-3) and  $K_{iL}$  (4, 5) on the temperature drop  $\Delta\Theta(Fo)$  a [1] Bi = 0.2; 2) 0.02; 3) 2.0; 1-3)  $K_{iL} = 0.14$ , 4)  $K_{iL} = 0.01$ ; 5) 1.0; 4, 5) Bi = 0.2] and the change in the value of the equilibrium swelling  $k(\delta)$  (1, 2) and the degree of hardening  $N(\delta)$  (1', 2') in the polymer composition for convective (1, 1') and thermal radiation (2, 2') energy supply b; k, n, %;  $\delta$ , mm.

of the structure of cellular polymers, also shows that over the thickness of the layer the formation of the structure due to the action of radiant energy takes place from a certain internal layer, determined by the permeability of the composition to infrared radiation, to the external boundaries of the coating in the direction of the flow of heat. Investigation of the submolecular structure of the composition by electron microscopy confirmed that it is difficult for convective and radiation energy. For convective energy supply there is a nonuniform structure with large formations. An excess of radiant energy supply is accompanied by a more uniform structure consisting of globules whose dimensions on the whole do not exceed 0.02-0.03  $\mu\text{m}$  [6].

An integral estimate of the state of the coating of PÉK compound, carried out using a thermomechanical method [12], confirms that radiant energy supply in this case enables one to obtain a material with a higher vitrification temperature  $T_c$ , and a higher destruction temperature  $T_d$ , with a much lower value of high-elastic deformation  $\epsilon$ .

The specific features of the formation of the temperature field in a polymer coating in the case of radiation energy supply can be explained by the increase in the adhesion contact in the polymer-metal system, observed in [13], and the high hermetic sealing properties of crystallizing pentone polymer. In this case the volume nature of the absorption of infrared radiation in the coating layer leads to effective destruction of the submolecular formations which exist in the melt, and facilitates the formation of a finely divided polymer structure characterized by high values of the density, degree of crystallinity, and small swelling in solvent.

Hence, the above data show that the particular features of the formation of temperature fields in polymer coatings for different forms of energy are due to the specific difference in the concentration field, and have a considerable effect on the formation of the structural and physicochemical characteristics of the material. For radiation energy supply the conditions are produced in which finer polymers and more uniform structures are obtained, giving high quality coatings. This must be taken into account when developing the technology for the thermal processing of polymer materials.

#### NOTATION

$T_0$ ,  $T$ , initial and current temperature of the coating;  $T_m$ , temperature of the air;  $\Theta = (T - T_0)/(T_m - T_0)$  dimensionless temperature of the coating;  $a$ , thermal diffusivity;  $A$ , absorption power of the coating;  $D$ , diffusion coefficient;  $\lambda$ , thermal conductivity;  $c$ , thermal capacity;  $\gamma$ , density;  $\alpha_k$ , convective heat transfer coefficient;  $i$ , number of moles of reacting groups per unit volume of polymer;  $K_0$ , factor in front of the exponential;  $R$ , gas constant;  $u$ , concentration;  $Q$ , thermal effect of the reaction;  $q_n$ , density of the incident radiant flux;  $\xi = x/\delta$ , dimensionless coordinate over the thickness of the coating;  $K_{iL} = Aq_n\delta/\lambda(T_m - T_0)$ , Kirpichev criterion characterizing the thermal effect of the reaction;  $K_{iP} = Qi/c\gamma(T_m - T_0)$ , analog of the Predvoditelev criterion, characterizing the rate of occurrence of a chemical excess in the system;  $Bu = \beta\delta$ , Bouguer criterion;  $Lu = D/a$ , Lykov number,  $Fo = a\tau/\delta^2$ , Fourier number;  $P_0 = RT_0/E$ ;  $P = R(T_m - T_0)/E$ ;  $Bi = \alpha_k\delta/\lambda$ , Biot number.

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APPROXIMATION OF TRANSFER PROPERTIES AND  
THE SOUND SPEED OF WATER BY A DEPENDENCE  
OF THE TAIT ISOTHERM EQUATION TYPE

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UDC 532.2.022 + 532.13 +  
534.22:519.245.001.5

The heat conduction and speed of sound of water are described with great accuracy by dependences of the Tait isotherm equation type on the basis of available literature data.

The possibility of approximating the heat conduction and viscosity coefficients and the speed of sound of water by dependences of the Tait isotherm equation type [1]\*

$$v = v_s' \left[ 1 - A \ln \frac{p + B}{p_s + B} \right]. \quad (1)$$

is examined in this paper.

To find the empirical coefficients of the heat conduction equation

$$\lambda = \lambda_s' \left[ 1 - A_\lambda \ln \frac{p + B_\lambda}{p_s + B_\lambda} \right] \quad (2)$$

we write it for two states and then obtain by dividing one by the other

\*We have replaced the parameters  $p_0, v_0$  in the Tait equations by the parameters  $p_s, v_s$  of a saturated liquid.