THE KINETICS OF ELECTRON-BEAM DISPERSION OF POLYMERS WHEN OBTAINING COATINGS

A. V. Rogachev and V. V. Kharitonov

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The kinetics of the variation in surface charge is considered, taking into account its destruction when acted upon by a beam of electrons. It is shown that the experimentally established features of dispersion kinetics can be explained by the presence of a surface charge.

When a beam of electrons acts on polymers, complex physical changes occur [1]. Under vacuum conditions, and for fairly high electron beam energies, destruction of the macromolecules is observed, as is a separation of fairly active volatile products, which can be adsorbed on the surface and undergo secondary polymerization [2]. This phenomenon has recently been used to obtain thin polymer coatings. When combined cooling occurs on the surface of the products of dispersion of different polymers and metal atoms, it is possible for chemical interaction to occur between them, which opens up new possibilities for synthesizing new materials, including composition materials [3]. When electrons interact with a surface, the latter becomes charged, due to penetration of electrons into the polymer and their retention in traps in the surface layer. The presence of a surface charge and its storage considerably complicates the technological methods of carrying out and controlling the polymer dispersion process. It is therefore of particular interest to investigate the features of electron-beam dispersion of polymers connected with the induction of electric charge.

The value of the electrostatic charge on the surface is determined by the electron flux density, the secondary electron emission coefficient, the conditions under which the volatile fragments are separated, and their ionization coefficient. Note that the secondary emission coefficient depends very much on the energy of the instant electrons. For fairly low values it usually has a value exceeding unity. It is well known, e.g., that when the surface of PTFE is irradiated with a beam of electrons, it becomes charged for an energy of the irradiated particles of ~1.5 keV [1]. For lower values of the electron energy, the secondary electron emission coefficient is greater than unity, and surface charging does not occur.

Taking these factors into account, and assuming that the electrical conductivity of the polymer is fairly low, the change of the surface charge density with time can be described by the following equation:

$$dQ = Idt - \alpha(U)Idt - \beta dm. \tag{1}$$

As already mentioned, the secondary electron emission coefficient depends on the accelerating voltage of the electrons, and in the linear approximation, which is justified in [1], it can be calculated from the relation

$$\alpha(U) = \alpha_0 - bU. \tag{2}$$

As in [1, 4], we will assume that the dispersion velocity is related to the power supplied to the evaporation zone

$$V = kUI. \tag{3}$$

Taking Eqs. (2) and (3) into account, Eq. (1) takes the form

$$dQ = [1 - \alpha_0 - U(\beta k - b)]Idt.$$

The appearance of a charge on the surface gives rise to an electric field, which slows down the incident electrons. The effective accelerating voltage is then

$$U = U_y - \frac{Q}{2\varepsilon_0}.$$

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Since $dQ = -2\varepsilon_0 dU$, we obtain

$$dU = \frac{1}{2\varepsilon_0} I\,[U(\beta k - b) + \alpha_0 - 1]\,dt.$$

After integration we have

$$\frac{1}{\beta k - b} \ln |U(\beta k - b) + \alpha_0 - 1| = \frac{1}{2\varepsilon_0} It + \ln C$$

or

$$U = \frac{1 - \alpha_0}{\beta k - b} + \frac{C}{\beta k - b} \exp\left(\frac{\beta k - b}{2\varepsilon_0} It\right).$$

The integration constant C is found from the initial condition $U(t = 0) = U_y$. We obtain

$$C = U_y(\beta k - b) + \alpha_0 - 1. \tag{4}$$

Taking (4) into account we have

$$U = \frac{1 - \alpha_0}{\beta k - b} + \left(U_y - \frac{1 - \alpha_0}{\beta k - b}\right) \exp\left(\frac{\beta k - b}{2\varepsilon_0} It\right). \tag{5}$$

It should be noted that the quantity $U_0 = (1 - \alpha_0)/(\beta k - b)$ is numerically equal to the accelerating voltage, for which no charge storage occurs on the surface of the polymer, i.e., $dQ/dt = 0$. We will introduce the charging time constant

$$\tau = \frac{2\varepsilon_0}{(b - \beta k)\, I}.$$

Then, Eq. (5) takes the form

$$U = U_0 + (U_y - U_0) \exp\left(-\frac{t}{\tau}\right). \tag{6}$$

Equation (6) is similar in form to the equation given in [1], which was established experimentally by investigating the charging of a surface without dispersion. Equation (6) defines the kinetics of the polymer dispersion. Analysis shows that for fairly large dispersion times $t \gg \tau$, the value of the accelerating voltage of the electron gun has no appreciable effect on the ratio of dispersion, and correspondingly on the overall yield of volatile products. Hence, to ensure that the dispersion process is economic and steady for such times, the accelerating voltage of the electron gun must be set to be close to U_0, and to ensure a high rate of dispersion it is necessary to use fairly intense electron fluxes. However, it must be taken into account that a change in the electron current density over a wide range affects the rate of dispersion in more than one way. This is due to the fact that when I is increased, the charging time constant is reduced, and charge is rapidly stored on the surface, which reduces the effective electron energy and hence the rate of dispersion.

Taking Eq. (6) into account, Eq. (3) takes the form

$$V = kI\left[U_0 + (U_y - U_0) \exp\left(-\frac{It}{c}\right)\right],$$

where

$$c = \tau I = \frac{2\varepsilon_0}{b - \beta k}.$$

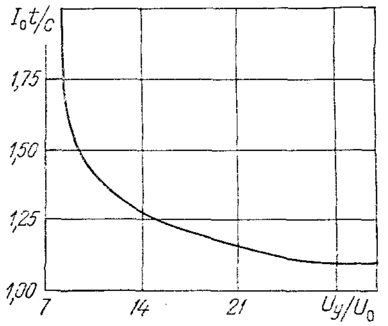

Fig. 1. Graph of I_0t/c as a function of the relative accelerating voltage U_y/U_0 of the electron gun.

Then

$$\frac{dV}{dI} = k\left[U_0 + \left(1 - \frac{It}{c}\right)(U_y - U_0)\exp\left(-\frac{It}{c}\right)\right]. \tag{7}$$

It follows from Eq. (7) that for any values of the accelerating voltage in the initial stages of dispersion ($It/c < 1$) $dV/dt > 0$, i.e., when the current density is increased for a fixed electron-gun accelerating voltage, an increase in the rate of dispersion is observed.

The maximum rate occurs under technological conditions for which the following relation is satisfied:

$$U_0 - \left(1 - \frac{I_0t}{c}\right)(U_y - U_0)\exp\left(-\frac{I_0t}{c}\right) = 0. \tag{8}$$

A graphical solution of Eq. (8) showed that depending on the accelerating voltage of the electron gun, the value of I_0t/c varies from 1 to 2 (see Fig. 1). The maximum rate of dispersion for fairly large values of U_y occurs when $I_0t/c \approx 1$. An accelerating voltage of $U_y = U_0(\exp 2 + 1)$ corresponds to a value of $I_0t/c = 2$. For lower values of U_y, the rate of dispersion increases monotonically as the electron current density increases.

Hence, the choice of the optimum polymer dispersion modes, particularly when the electron flux acts for only a short time, should be made taking into account all the technological parameters. The dispersion of the polymers due to the action of an electron beam which varies with time is of practical interest in this connection.

Note that the dependence of the rate of dispersion on the electron current density established above agrees with experimental measurements of the dispersion of PTFÉ under different conditions [4], which enables us to conclude that the surface charge has a decisive effect on the kinetics of electron-beam destruction of the surface.

NOTATION

Q, magnitude of the electric charge; I, electron current density; $\alpha(U)$, secondary electron emission coefficient; U, effective accelerating electron voltage; β, degree of ionization of the volatile dispersion products; $dm = Vdt$; V, rate of dispersion (flux density of the volatile products); k, reduced coefficient of electron energy conversion into the work required to break the chemical bonds; U_y, accelerating potential difference of the electron gun; ε_0, permittivity.

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