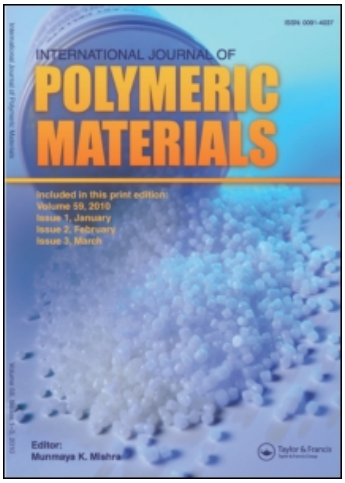

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Characteristics of Plasticized PVC Biodegradation

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The influence of microscopic fungus Aspergillus niger on the diffusion desorption of the plasticizer (dialkylphthalate) in PVC were studied. It was shown that desorption of dialkylphthalate is accelerated by bio-overgrowth of plasticized PVC samples. Thus, the transfer of the plasticizer is controlled by its diffusion.

Keywords: Plasticized PVC; biodegradation; dialkylphthalate; fungi; aspergillus niger

RESULTS AND DISCUSSION

Problems of biodegradation were not discussed or considered in the works devoted to the study of plasticized PVC-plasticates aged under model or climate conditions or during long-term exploitation of 15–30 years [1, 2]. This is partly caused by the fact that desorption of corrosion inhibitors, as well as increased temperature regimes are not suitable conditions for growing of microorganisms. But aging of PVC-plasticate-made articles made of plasticized PVC under real conditions of their exploitation is often bound to the processes of diffusional desorption of plasticizing additives from the material [3, 4].

The desorption of phthalate plasticizer accumulated by microorganisms, widely used in PVC may lead, to biodegradation of the plasticized PVC material.

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In this connection, we have studied the features of microscopic fungus effects on diffusion desorption of the plasticizer (dialkylphthalate) from plasticized PVC of I-40-13 type (GOST 5960-72).

Microscopic fungus Aspergillus niger, obtained from polyvinylchloride insulation of wires exploited in the regions of tropical climate, was used as a bioagent.

Cultivation of the microscopic fungus on plasticized PVC was performed under optimal conditions for growing of the microorganism ($T = 29°C$, $\varphi = 100\%$) during 12 months.

Quantitative estimation of dialkylphthalate (DAP) concentration in the wire isolation was conducted with the help of UV-specrophotometric analysis. DAP concentration in the samples was calculated by intensity of the absorption bend $\lambda = 230$ nm, characteristic for that substance.

It was shown [5–7] that regularities of the change of plasticizing additive concentration in plasticate is determined by the ratio of diffusion and desorption rates. For most of system containing a migrating low-molecular component one of the following two variants of the process take place. If the rate of desorption from the surface is lower than that of low-molecular component transfer in the material volume, the total rate of the process is defined by the intensity of additive desorption into the environment (so-called desorptional sphere of the proceeding process).

Thus, if desorption of the component proceeds much faster than its diffusion in the material, the total rate of the process and consequently the amount of migrated low-molecular additive will be limited by diffusion (diffusional sphere).

Diffusional desorption of low-molecular components from polymer materials at the process proceeding in various spheres were calculated from the expressions [5, 7]:

In diffusional domain

$$\frac{m_t}{m_0} = \frac{8}{\pi}\exp\left(\frac{\pi^2}{4}\cdot\frac{D}{l^2}\cdot t\right) \tag{1}$$

In the desorption domain

$$\frac{m_t}{m_0} = \exp\left(-\frac{W}{S\cdot l}\cdot t\right), \tag{2}$$

where m_0 and m_t are initial and current concentrations of low-molecular component in the polymer material at the moment of time t, respectively; W is the desorption rate of components form the material surface; D is the diffusion coefficient in the material; S is the solubility of the component in the material; I is the half thickness of the material film.

Eqs. (1) and (2) may be generalized as follows:

$$\frac{m_t}{m_0} = \exp(-kt), \tag{3}$$

where k in the effective rate constant of low-molecular component transfer from the material.

Based on Eq. (3) and the values of plasticizer concentration in the plasticized item, obtained by UV-spectrometric analysis, one can calculate the effective rate constants of DAP transfer in the samples studied, k. Obtaining these constants, diffusion coefficients (D) and desorption rates (W) for dialkylphthalate from the test samples of PVC-plasticate and those treated by bio-overgrowing are easily calculated. The parameters k, D and W, obtained with the help of our experimental data, are shown in the Table I.

Comparison of these values with corresponding sorption-diffusional parameters, determined by other (independent) techniques, allows us to make a valid conclusion about the type of the plasticizer transfer.

D_p and W_p were calculated using the literature values of physico-chemical and sorption-diffusional characteristics of DAP and PVC-plasticate [5, 7].

TABLE I Sorption-diffusional parameters for the PVC-plasticate – dialkylphthalate system

Parameter	*Experimental k, D, W*		*Calculated D_p, W_p*
	Micromycete influence	*Influence of* $T = 30°C$ $\varphi = 100\%$	*Influence of* $T = 30°C$
Effective rate constant, k, s^{-1}	$1.0 \cdot 10^{-8}$	$1.6 \cdot 10^{-9}$	–
Diffusion coefficient, D, cm^2/s	$0.64 \cdot 10^{-10}$	$0.82 \cdot 10^{-11}$	$1.1 \cdot 10^{-10}$
Desorption rate, W, $g/cm^2 \cdot s$	$1.5 \cdot 10^{-10}$	$2.4 \cdot 10^{-11}$	$4.3 \cdot 10^{-11}$

Note: Calculation of the diffusion coefficient by the Eq. (1) accepts DAP solubility in PVC-plasticate as $0.3\ g/cm^3$.

The rate of dialkylphthalate desorption from the insulation surface was calculated by the Herz equation:

$$W_p = \frac{P_T}{(2\pi MkT)^{1/2}}, \tag{4}$$

where P_T is the pressure of plasticizer vapours at temperature T; M is the molecular mass of DAP (390 g/mol).

The pressure of DAP vapours at 30°C, P_{30}, was calculated by interpolation dependences obtained from the Clausius-Clapeyron equation:

$$\lg P_T = -\frac{A}{T} + B, \tag{5}$$

where A and B are constants.

To determine constants A, B and P_{30} the system of two equations of the (5) type for 293 and 333 K was solved.

Plasticizer vapour pressures at current temperatures are shown in special literature and are $1.3 \cdot 10^{-4}$ and $4.0 \cdot 10^{-3}$ dyn/cm^2, respectively. Calculations have shown that the pressure of DAP vapours at 30°C is $3.4 \cdot 10^{-4}$ dyn/cm^2. The desorption rate (W_p), obtained from Eq. (4), is shown in Table I.

The coefficient of dialkylphthalate diffusion from plasticized PVC (D_p) at 30°C were calculated with the help of the data from the work [7], which show the coefficient D values for DAP in plasticized insulation at various temperatures. Applying an equation of the Arrhenius type, the effective activation energy was calculated and found to be 58.4 kJ/mol. Then, based on the expression mentioned, D_p at 30°C shown in tables was obtained.

The analysis of the data from this table shows close values of W and W_p for test samples. The agreement between diffusion coefficients D and D_p was less than satisfactory. Consequently, the plasticizer loss at complex temperature-humidity influence on PVC-insulation (T = 30°C and φ = 100%) is mainly determined by its desorption from the material surface. This conclusion correlates with the data reported by Bezveliev [4].

Satisfactory coincidence of D and values is observed at microscopic fungus influence on the plasticized PVC. In this case, the values of W and W_p are different at least by an order of magnitude.

Thus, the analysis performed shows that transfer of the plasticizer under influence of a microscopic factor on the PVC-plasticate is limited by diffusion of plasticizing additive in the material volume.

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