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# Stabilization of Polymers from the Influence of Biological Media. Kinetic Method of Biocide Efficiency Estimation

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*In this article the contributors show the value of application of kinetic methods for the estimation of biocide activity. Authors have developed methods of quantitative estimation of biocide efficiency independent of their solubility in water. It is found that inhibited kinetics of microscopic fungal growth on nutriment with biocides is described by a logistic equation. They suggest parameters for the characterization of biocide efficiency.*

**Keywords** Biocides; biodegradation; kinetic; methods of investigation; polymers; stabilization

## Preface

It was found in an investigation of the connection between aging and the biodeterioration processes that:

1. Metabolites of *Aspergillus niger* microscopic fungus may physically influence the material. This process may proceed during short exposure times, when the concentration of organic acids is low and their diffusion in the material is practically absent.
2. In the case of microorganism influence on a polymer, chemical reactions follow a random law and lead to the decrease of important properties. Degradation products formed during aging facilitate the growth of microorganisms.
3. The kinetics of microorganism growth on polymers with different degrees of aging is described by the same functional dependence, i.e., the macrokinetic regularities of polymer overgrowth do not depend on aging.

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## Introduction

Biocides are used to protect polymers from the influence of microorganisms. Numerous investigations have focused upon the efficiency of the application of chemical stabilizers for various classes of polymers [1–5]. On the whole, the investigation of the biocidal action of substances is semiquantitative, and their selection empirical [6,7]. Moreover, existing methods of estimation of microorganism growth on polymeric surfaces do not allow us to estimate the influence of biocides on different stages of their growth. As bio-overgrowth of the materials increases with time, kinetic methods of investigation may be suitable for determination of the inhibiting cation of biocides.

The application of a kinetic method requires the selection of a microorganism growth parameter, which allows easy determination of changes with time.

## Materials and Methods

The development of microorganisms was estimated from the growth of the biomass of the colony. Biomass was determined by weighting the dry mass, which was obtained by filtration on a Millipore system and drying at 105°C to constant weight.

The following widely applied biocides were selected for investigation: merthiolate (sodium salt of ethylmercurithiosalicylic acid), nyctedin (1,6-diguanidinohexanedihydrochloride), oxydiphenyl (ODP) and copper sulfate. Industrial products were used with no additional purification. Mould fungi selected as bioagents were *Aspergillus flavus*, *Aspergillus niger*, *Aspergillus terreus*, *Trichoderma viride*, *Penicillium chrysogenum*, *Penicillium funiculosum*, *Paecilomyces varioti*.

Preliminary evaluation of these strains showed that *Aspergillus niger* modelled the action of other species in its influence on polymeric substrates. For this reason this microscopic fungus was used in most experiments; moreover, it is often found on the materials during use and storage of polymer-based articles and materials.

It is known that a general equation describing the development of biological systems of this type, is [8]:

$$\varphi(t) = \frac{1}{m} \cdot \frac{dm}{dt}, \quad (1)$$

where  $\varphi(t)$  is the specific rate of the microorganism growth, and  $m$  is the biomass amount at time  $t$ . The general solution of this equation is:

$$m = m_0 \exp \left[ \int \varphi(t) dt \right], \quad (2)$$

where  $m_0$  is the value of germinating spore biomass (initial amount of the biomass).

This equation may be applied for practical purposes, if the form of  $\varphi(t)$  is known.

One of possible solutions of Eq. (1) is the so-called logistic function, presented as [9]:

$$\varphi(t) = \frac{b}{1 + \exp^{\frac{a}{b}t}} \quad (3)$$

and

$$m = \frac{m_{\infty}}{1 + a \exp(-bt)}, \quad (4)$$

where **a** and **b** are parameters and  $m_{\infty}$  is the maximum amount of biomass reached during microorganism growth.

This function satisfactorily describes the growth of biomass of *Aspergillus niger* on Chapect-Dox nutriment (Fig. 1) before the biomass decrease starts.

Analysis of Eqs. (3) and (4) allows us to make a supposition about the probable physical significance of parameters **a** and **b**. Thus, at **t** approaching zero

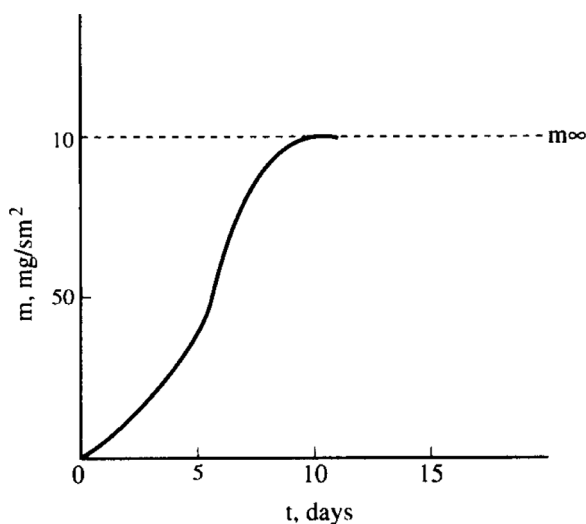
$$\varphi_0 = \frac{b}{2}$$

and

$$a = \frac{m_{\infty} - m_0}{m_0},$$

i.e., the parameter **b** characterizes the specific rate of fungus growth on the nutriment and quantitatively equals 1/2 of the maximum possible growth rate. The parameter **a** characterizes the possibility for a spore to form biomass under the conditions of incubation. At any given time **t**, the higher the amount of biomass, the higher is **b**, i.e., **b** is the rate constant of the microorganism development.

A study of *Aspergillus niger* development in various conditions of cultivation showed that the value of parameters **a** and **b** does not depend on initial concentration of spores introduced into the nutriment. Moreover, the value of parameter **b** does not depend on nutriment volume (Table 1).



**Figure 1.** Typical curve for the growth of *Aspergillus niger* on a Chapect-Dox nutriment.

**Table 1.** Values of **a** and **b** parameters for the growth of *Aspergillus niger* in various conditions of cultivation (liquid Chapeck-Dox medium, nutriment volume equals 50 ml)

	$m_{\infty}$ , mg/cm <sup>2</sup>	$m_0 \cdot 10^2$ , mg/cm <sup>2</sup>	<b>a</b>	$b \cdot 10^2$ , h <sup>-1</sup>
Concentration of spores, ml <sup>-1</sup>				
10 <sup>6</sup>	10.2 ± 0.3	3.2 ± 0.2	316 ± 26	3.7 ± 0.3
10 <sup>4</sup>	9.5 ± 0.2	3.0 ± 0.2	316 ± 28	3.7 ± 0.3
10 <sup>2</sup>	5.2 ± 0.2	1.6 ± 0.2	316 ± 26	3.7 ± 0.3
Nutriment volume, ml				
50	10.2 ± 0.4	3.2 ± 0.2	316 ± 26	3.7 ± 0.3
20	3.8 ± 0.3	3.4 ± 0.2	115 ± 15	3.8 ± 0.2
10	2.5 ± 0.2	3.3 ± 0.3	75 ± 10	3.7 ± 0.3
5	1.8 ± 0.2	3.5 ± 0.3	51 ± 5	3.8 ± 0.2

These data show that the specific rate of fungus growth is defined by the nature of the nutriment only. This allows the possibility of applying the logistic function equation to the study of kinetics of microorganism growth rate in the presence of biocides and the estimation of the efficiency of their action, i.e., in conditions of inhibited growth of biomass.

### Water-Soluble Biocides

Figure 2 shows the kinetic curves of biomass growth of *Aspergillus niger*, applied to liquid Chapeck-Dox nutriment containing various concentrations of common biocides-merthiolate and nyctedin. The lag-phase (the time after inoculation until the moment of biomass observation) clearly increases with biocide concentration. The change of slope with increasing biocide concentration shows that, even at concentrations lower than the limiting concentration (at which microorganism growth is absent), nyctedin and merthiolate decelerate fungus growth.

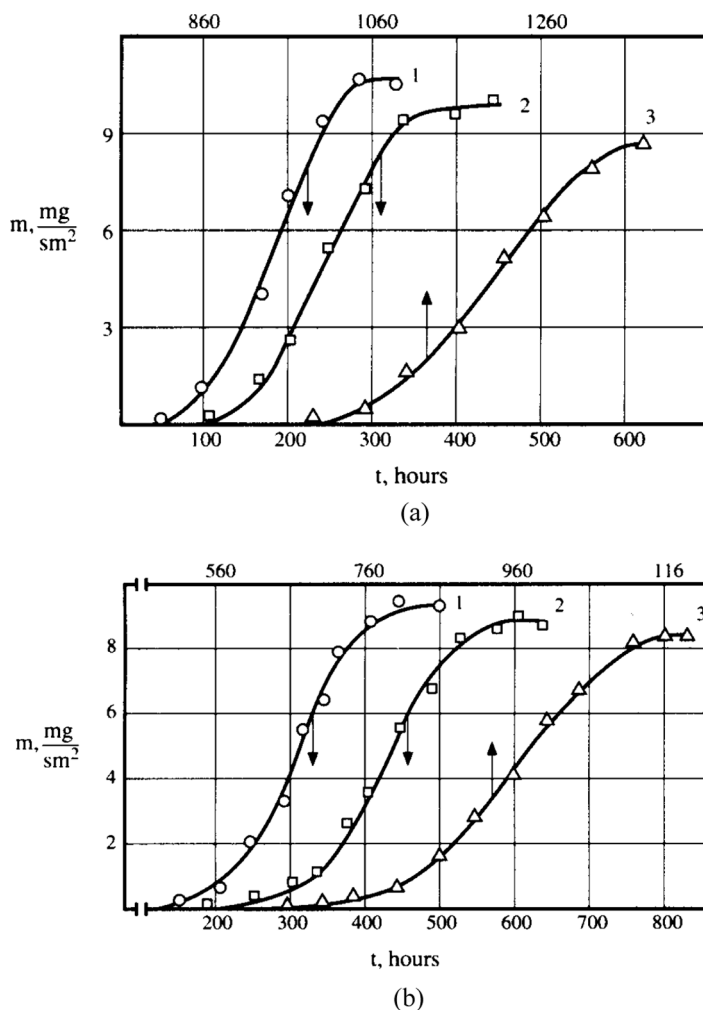
All curves are described by a logistic function equation of the following form:

$$m = \frac{m_{\infty}}{1 + a \exp(-b\tau)}, \quad (5)$$

where  $\tau = t - L$  and  $L$  is the lag-phase duration (induction period).

The value of **b** changes with increasing biocide concentration; however, in every experiment at constant biocide concentration the specific rate of the growth, calculated according to Eq. (3), changes very little (approximately 2%) over an extended duration.

Thus, it may be concluded that the specific rate, at least during the initial stage of the microorganism growth, does not depend on consumption of components of the nutriment and accumulation of metabolism products (decelerating biomass growth) and is defined by the presence of biocide only. It is therefore possible to use a single-factor equation for a non-competitive fermentation reaction for the



**Figure 2.** (a) Kinetic curves of the biomass growth of *Aspergillus niger* on liquid nutrient Chapect-Dox in the presence of biocides. Merthiolate: (1) 0; (2) 0.1 mg/l; (3) 0.5 mg/l; (b) Kinetic curves of the biomass growth of *Aspergillus niger* on liquid nutrient Chapect-Dox in the presence of biocides. Nyctedine: (1) 30 mg/l; (2) 50 mg/l; (3) 90 mg/l.

analysis of biocide influence [10]:

$$\varphi_u = \frac{\varphi_0 K_c}{K_c + C_u}, \quad (6)$$

where  $\varphi_u = \frac{b}{2}$  is the maximum possible specific rate of micromycete growth in the presence of biocide;  $\varphi_0$  is the maximum possible specific rate of the micromycete growth on the nutrient without biocide;  $C_u$  is the biocide concentration in the nutrient; and  $K_c$  is a constant, quantitatively equal to the concentration of biocide, at which

$$\varphi_u = \frac{1}{2} \varphi_0.$$

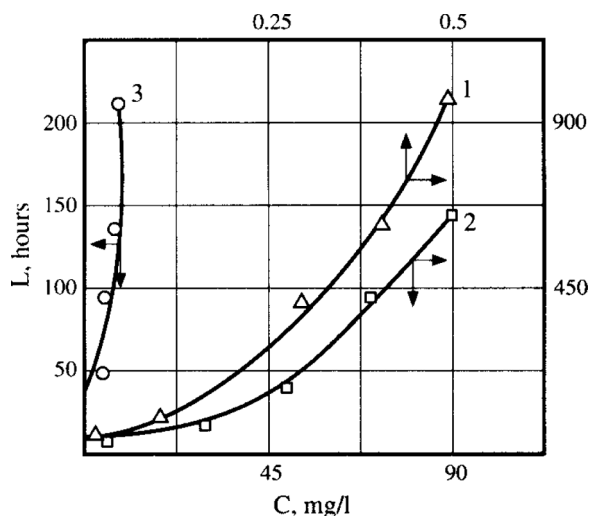


Figure 3. Lag-phase versus biocide concentration: (1) merthiolate; (2) nyctedine.

Eq. (6) can be solved according for  $K_c$ , giving:

$$K_c = \frac{\varphi_u C_u}{\varphi_0 + \varphi_u}.$$

For each investigated biocide  $K_c$  is practically independent of concentration in the range of experimental accuracy. Thus, it can be concluded that  $K_c$  is a constant that characterizes the activity of the biocide towards the particular microorganism.

Thus,  $K_c$  estimation may be applied to the quantitative estimation of biocidal activity of various substances. Calculations showed that for merthiolate  $K_c$  is 0.78 mg/l, and for nyctedin it is 79.5 mg/l. In practice, merthiolate is used in concentrations no lower than 1 mg/l, and nyctedin in concentrations not lower than 1 g/l.

The dependence of lag-phase duration on biocide concentration (Fig. 3) is described by the exponential equation:

$$L = L_0 \cdot e^{K_1 C_u}, \quad (7)$$

where  $K_1$  is a constant.

Consequently,  $K_1$  may also be used for comparative estimation of biocide efficiency. The data presented show that the application of the kinetic method for the study of water-soluble biocides allows us to use  $K_c$  and  $K_1$  values for their characterization.

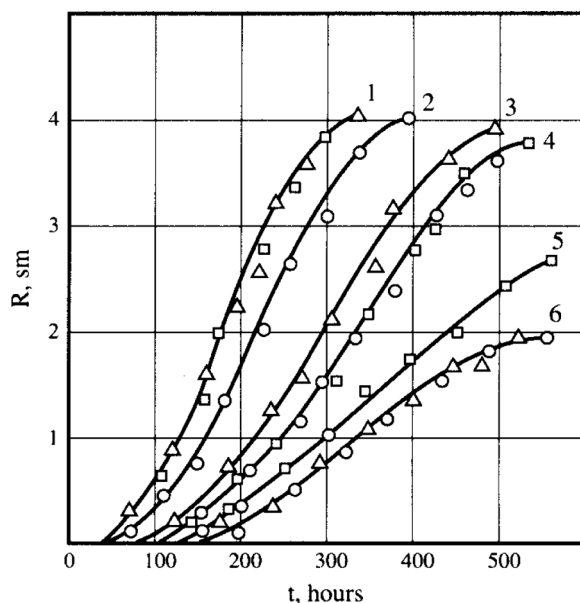
### Water-Insoluble Biocides

From the points of view of physical chemistry, technology and economy, water-insoluble biocides are more suitable for practical use. The use of agar nutrients for the estimation of the efficiency of these biocides may lead to errors in the results. Thus, in the estimation of the biocidal activity of a water-insoluble polymer

stabilizer, ionol, a change of its concentration does not lead to a corresponding change of the kinetic curves of microorganism growth (Fig. 4) estimated by the change of colony radius. This is connected with an inhomogeneous distribution of ionol in the nutriment volume (Fig. 5).

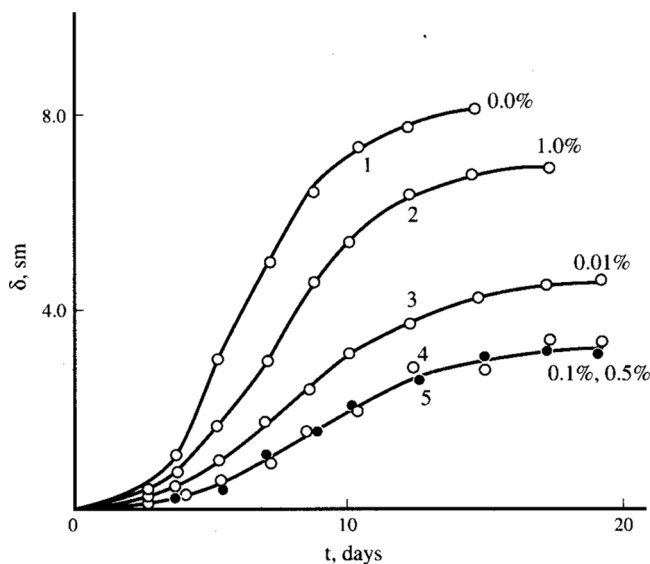
Ionol extraction (using alcohol) of layers from the agar medium, with spectrophotometric determination of its concentration, showed that ionol is distributed in the nutriment (inhomogeneously) and concentrates close to the agar – air interface (Fig. 6). In this case the ionol concentration in the surface layer is nearly constant, with no dependence on ionol amount introduced. Such a complicated distribution in the volume of the medium is observed for other water-insoluble substances. Thus, the application of agar nutriment for the study of water-insoluble substances by their introduction into the nutriment volume leads to mistaken conclusions.

The necessity for testing of water-insoluble substances demands the development of special methods. As the application of agar medium leads to contradictory results, it is necessary to select a support which must provide continuous access of nutrition substances to microorganisms growing on its surface. As the growth of fungus occurs in the volume of the medium as well as on the surface, the support must provide easy and full removal of biomass from it, if possible, in order to increase experimental accuracy. The above-mentioned demands are fulfilled by a hydrogel, three-dimensional hydroxyethylmethacrylate (poly-HEMA) possessing a porous structure, which is usually used as a biomedical polymer [11]. In this case the pore size and cross-link density are easily controlled during synthesis. Hydrogels produced for medical purposes are easily sterilized and biomass is easily removed from the surface because adhesion is weak. This allows multiple use of a hydrogel support for biocide testing.



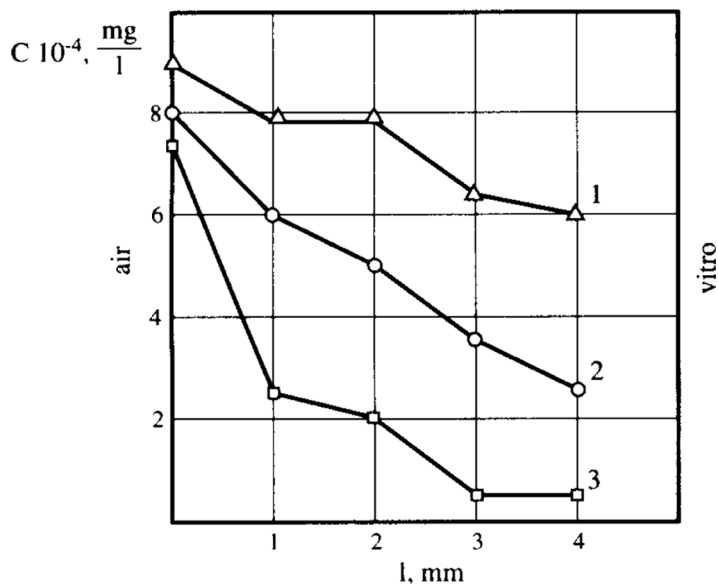
**Figure 4.** Inhibition of the colony growth of different microscopic fungi, *Aspergillus niger* (1, 2), *Trichoderme viride* (3, 4), and *Penicillium cyclopium* (5, 6), on the agar nutriment of Chapec-Dox in the presence of the stabilizer biocide ionol:  $\square$  – 2.5 mg/l;  $\circ$  –  $5 \times 10^4$  mg/l;  $\Delta$  –  $7.5 \times 10^4$  mg/l.





**Figure 5.** Kinetic curves of a three-dimensional colony of *Aspergillus niger* on the agar nutrient with ionol at different concentrations: (1) 0%, (2) 1%; (3) 0.01%; (4) 0.1%; and (5) 0.5%.

Testing is performed according to the following method: the biocide is dissolved in a suitable solvent and is precipitated on a glass support and covered by a hydrogel plate. In this case the biocide becomes attached to the hydrogel surface. The hydrogel plate is then turned upside down and is placed into a Petri dish (or any other vessel) containing liquid nutrient, allowing the lower surface of the plate to contact



**Figure 6.** Distribution of ionol in agar nutrient in volume containing ionol: (1)  $7.5 \times 10^4$  mg/l; (2)  $5.0 \times 10^4$  mg/l; and (3)  $2.5 \times 10^4$  mg/l.

the medium. As a consequence of the highly porous structure of the material, the medium is absorbed and feeds the surface to which the biocide is applied. This provides continuous access of nutrition

\* Hydrogel poly-hydroxymethylmethacrylate.

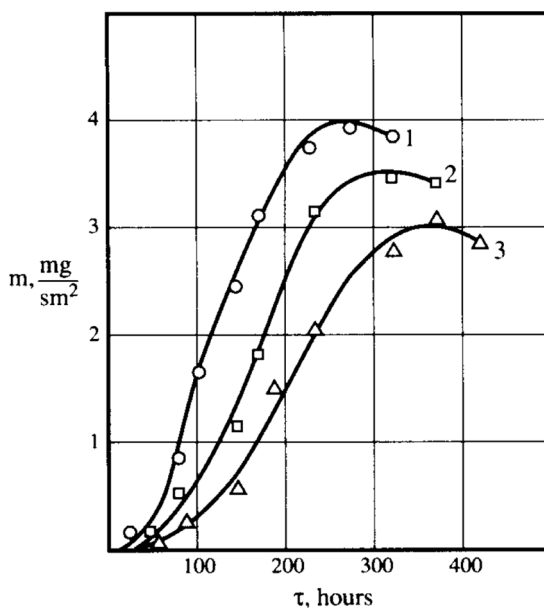
substances to the growing microorganisms. Biomass removal from the support is performed by washing off in distilled water.

Hydrogel is also applicable for testing water-soluble biocides. In this case the biocide in the required concentration is introduced into the liquid nutriment in contact with the support.

The above-mentioned kinetic regularities are found for the growth of microorganisms on a hydrogel surface. Even in this case microscopic fungus growth is described by a logistic function. Figure 7 shows the kinetic curves of *Aspergillus niger* growth on a hydrogel support in contact with a medium containing different concentrations of  $\text{CuSO}_4$ . It is seen that the lag-phase increases with the concentration and the curve slope changes.

Analysis of the results for the kinetics of growth of *Aspergillus niger* on liquid nutriment containing  $\text{CuSO}_4$  on a hydrogel support (Table 2) shows that values of specific rate of growth and lag-phase duration do not depend on the applied method. The parameter  $a$  and the final biomass  $m_\infty$  change. This is connected with the fact that fungus growth occurs in the case of hydrogel support, on the surface only. Consequently, parameters  $a$  and  $m_\infty$  cannot be applied for characterization of biocides.

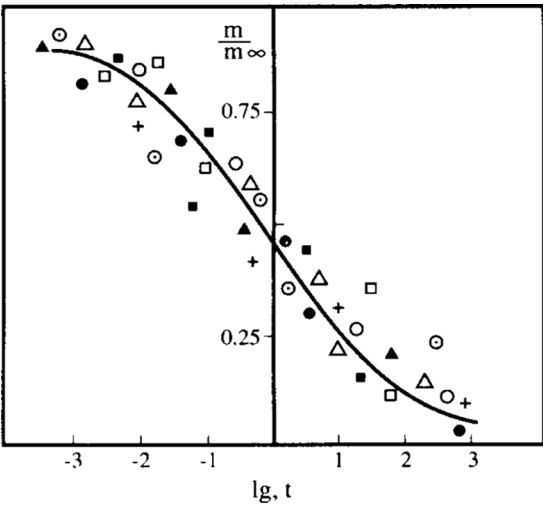
According to the suggested methods, a range of substances was investigated, both water- soluble and insoluble. Among these substances were known fungicides



**Figure 7.** Kinetic curves of *Aspergillus niger* biomass accumulation on the surface of hydrogel support (from poly-HEMA) depending on the  $\text{CuSO}_4$  concentrations: (1) 1000 mg/l; (2) 2000 mg/l; and (3) 2500 mg/l.

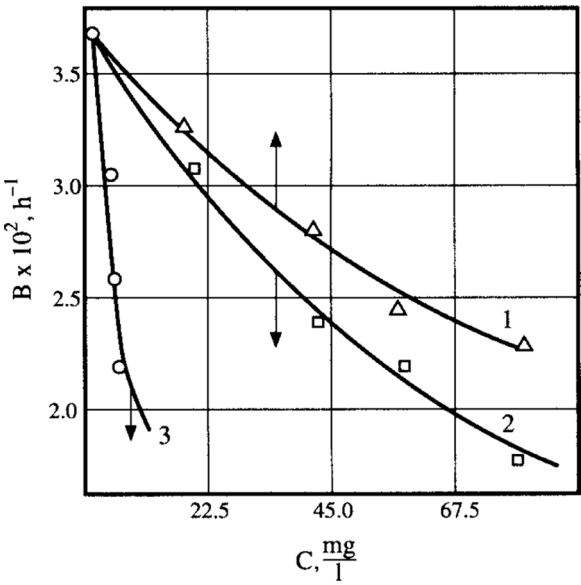
**Table 2.** Parameters for biomass accumulation in the presence of CuSO<sub>4</sub>

CuSO <sub>4</sub> , mg/l	Condition of cultivation									
	Chapek-Dox liquid medium					Poly(HEMA)* plate on Chapek-Dox				
	$m_0 \cdot 10^2$ , mg/cm <sup>2</sup>	<b>m</b> , mg/cm <sup>2</sup>	<b>a</b>	$b \cdot 10^2$ , h <sup>-1</sup>	<b>L</b> , h	$m_0 \cdot 10^2$ , mg/cm <sup>2</sup>	<b>m</b> , mg/cm <sup>2</sup>	<b>a</b>	$b \cdot 10^2$ , h <sup>-1</sup>	<b>L</b> , h
1000	3.6	4.08	111	2.4	48	3.5	100	111	2.4	48
1500	3.3	4.00	122	2.1	72	3.5	80	122	2.1	72
2000	3.7	3.75	104	1.9	120	3.7	90	102	1.9	126
2500	3.7	3.54	93	1.6	168	3.5	80	93	1.6	168

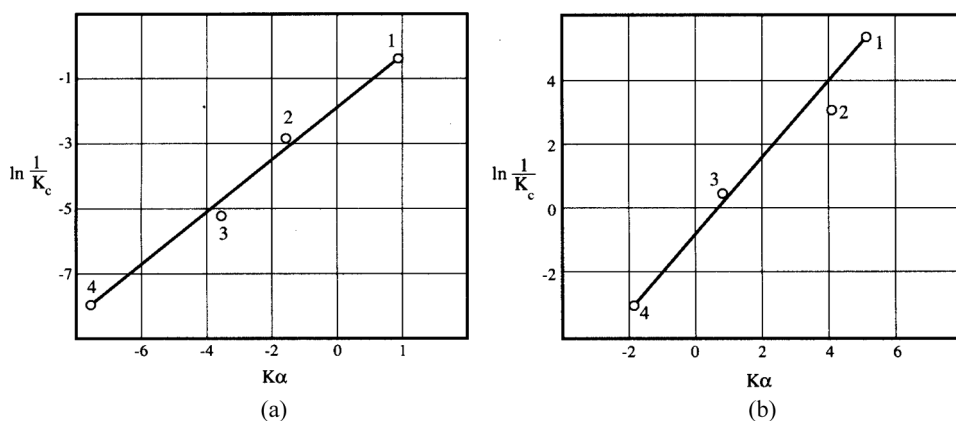


**Figure 8.** Generalized kinetic curve of *Aspergillus niger* biomass inhibited growth in the presence of different biocides:  $\odot$  – merthiolate;  $\blacktriangle$  – nyctedine;  $\Delta$  – alkyl benzyl dimethyl-ammonium chloride;  $\blacksquare$  –  $\text{CuSO}_4$ ;  $\square$  – oxydiphenyl-phenol;  $\bullet$  – *N*-paratolylmaleimide;  $+$  – ionol;  $\circ$  – phlamale(bis(0-1-chlortribrom-isopropyl)-trichlor-2-brompropylphosphonate).

and substances acting as stabilizers of polymers, antioxidants, corrosion inhibitors, etc. It was found that kinetic curves in every case are described by a logistic function. The kinetics of *Aspergillus niger* growth in the presence of biocides may be presented by a generalized curve (Fig. 8) for all investigated substances. Consequently, the



**Figure 9.** Parameter  $b$  versus concentration for different biocides: (1) merthiolate; (2) nyctedine, and (3) alkylbenzyl dimethyl-ammonium chloride.



**Figure 10.** Constant  $K_c$  versus  $K\alpha$  for (a) water-soluble biocides: (1) merthiolate, (2) alkylbenzyltrimethylammonium chloride, and (3) nyctedme; and for (b) water-insoluble biocides: (1) oxydiphenylphenol, (2) *N*-paratolyl-amaleimide, (3) phlamale, and (4) ionol.

general microkinetic regularities are independent of the mechanisms of biocidal action of the investigated substances.

The dependence of lag-phase duration and the parameter  $b$  of Eq. (5) on concentration of biocide are the same for both water-insoluble and water-soluble substances and may be described by Eqs. (6) and (7). Thus, even in this case the parameters  $K_c$  and  $K_1$  are characteristics of biocide efficiency.

Concentration dependencies of  $b$  and the lag-phase duration may be presented by generalized curves (Fig. 9) for all investigated substances. This proves the supposition about the independence of microkinetic regularities of inhibited growth of microscopic fungi on the cellular mechanism of biocide action. Consequently, there must be some limiting stage of the interaction process of biocide with microorganisms that is common to all investigated substances. It appears that this stage is the penetration of the biocide through the cell membrane. In this case the ability of a substance to penetrate into the cell will be one of the most important properties defining its efficiency as a biocide.

It was found that the parameters  $K_c$  and  $K_1$  are clearly connected with each other and with biocide efficiency (Fig. 10) for all investigated substances. It is seen, that values of  $K_c$  and  $K_1$  constants, depicted in corresponding coordinates, are on a single straight line. This regularity may be applied for practical purposes, such as the prediction of biocidal activity of substances and preliminary estimation of the concentration in the polymer, required for safe protection from bio-overgrowth and biodeterioration.

### The Influence of Aging on Bioresistance of Polymeric Materials

The composition and structure of a polymeric material is known to change during aging under the influence of various external factors. These changes may facilitate the growth of microorganisms on polymers and their biodeterioration. In this case during chemical degradation even bioresistant polymers become accessible for the growth of a microorganism colony. In general, this may be connected with assimilation of components of the polymer and its aging products by microorganisms,

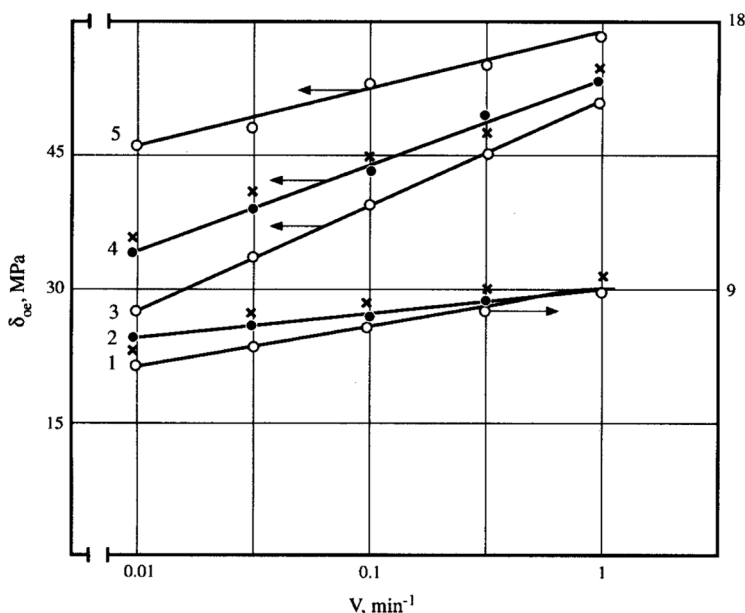
or with the influence of metabolites developed in the bioagent. These features of the influence of microorganisms on polymers are not yet clear.

The influence of metabolites on polymers in many cases is similar to the influence of other aggressive media and may cause degradation cross-linking, polymer-analogous transformations, plasticization, etc. [11].

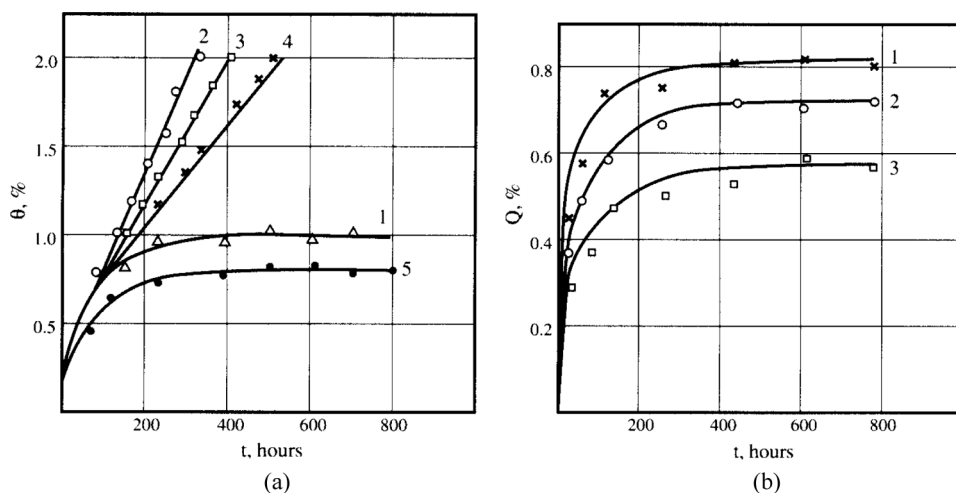
We have shown during studies of the influence of metabolites on the mechanical properties of polymethylmetacrylate (PMMA), that a change of mechanical properties is observed even on short-duration contacts of PMMA with a metabolite solution (less than 1 min before stretch begins). It is seen from Figure 11 that in PMMA stretching in a solution of metabolites from the culture liquid (on which *Aspergillus niger* was grown) the efficiency of medium action increases with a decrease of stretching rate. In this case the dependence of medium action efficiency on stretching rate has the same character, as in the case where alcohol solution is the medium [12].

The investigation of the change in pH of the culture liquid and its spectrophotometric analysis showed that the development of colonies of *Aspergillus niger* is accompanied by accumulation of organic acids. Diffusion of acids into PMMA follows the general form of electrolytic diffusion from water into polymers (Fig. 12). For organic acids with high volatility (acetic, propionic, butanoic), the dependence of the amount of absorbed solution on its concentration is described by a curve with a minimum. For non volatile acids – citric, succinic, malic – the amount of absorbed medium decreases as the solution concentration increases. At low concentrations of acids, their absorption by PMMA is lower than 1%.

A study of the mechanism of acid influence, participating in metabolite composition [13], showed that the change of PMMA mechanical properties is connected, in general, with the influence of monobasic acids (Fig. 13) of high volatility. The

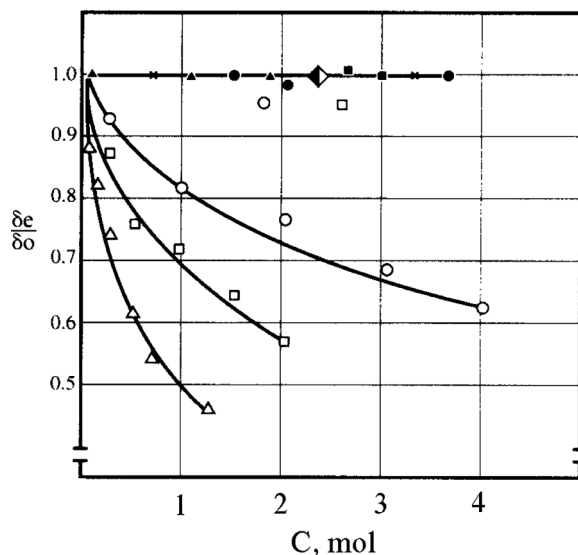


**Figure 11.** Elasticity of PMMA  $\alpha_{oe}$ , versus the rate of deformation ( $\gamma$ ) in the media: (1) PE-cultivation nutrient; (2) PE-water (●), Chapeck-Dox (x); (3) cultivation nutrient after growth of colonies of *Aspergillus niger*; (4) water (●) and Chapeck-Dox nutrient (x); (5) air.



**Figure 12.** PMMA sorption of water (1) and acid solutions of different concentrations. (a) (2) 2 m oil; (3) 2 m propionic, (4) 5 m acetic; (5) 2 m acetic. (b) (2) 1 m wine; (3) 2 m citric acids.

influence of monobasic acids on the mechanical properties of PMMA follows the known rule of Duclo-Traube [14]. According to this rule an increase of the size of an organic compound by one  $-\text{CH}_2-$  unit increases its surface activity in solution by three times. Conversely, the concentration at which the properties of the articles change decreases by three times. In a number of papers it was shown that the validity of this rule confirms an absorption mechanism of polymer strength decrease [15]. Thus, it was found that the change of mechanical properties of the polymer may



**Figure 13.** Reduced elasticity of PMMA samples on elongation in acid solutions and water versus acid concentration: (o) acetic, ( $\square$ ) propionic, ( $\square$ ) butyric oil, ( $\Delta$ ) wine, ( $\blacksquare$ ) citric, ( $\blacktriangle$ ) oxalate, (x) amber and ( $\blacklozenge$ ) fumaric. Rate of elongation:  $0.01 \text{ min}^{-1}$ .

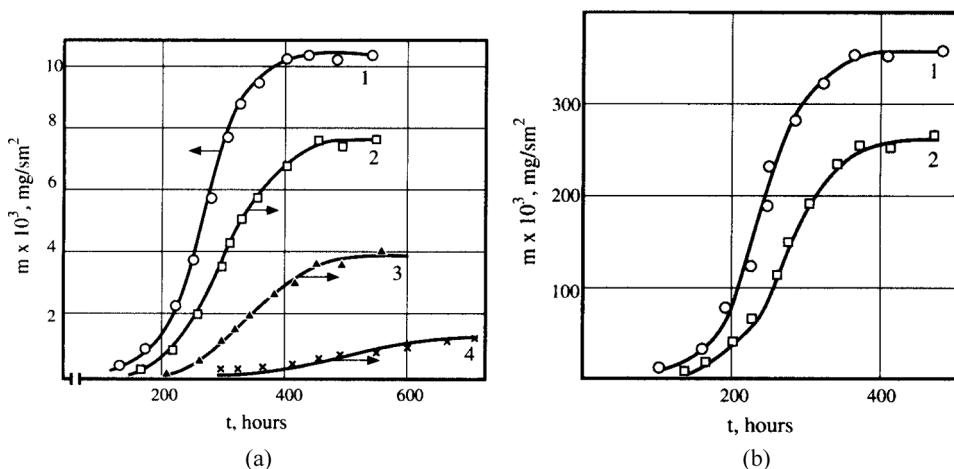
be the result of a physical influence (not connected with the chemical structure of macromolecules) as well as the chemical influence of microorganism metabolites. The energy of the formation of new surface decreases abruptly, and the development of cracks in stressed materials is simplified as a result of adsorption of organic acids contained in the metabolite, i.e., their physical aging. Taking into account that the formation of cracks (or microcracks) during aging of polymeric materials is a normal phenomenon, it can be concluded that the physical effect of microorganism metabolites growing on the surface of polymers may lead to catastrophic cracking under stress.

The above-mentioned kinetic approach was used for the study of the kinetics of growth of *Aspergillus niger* on materials aged in artificial conditions. We selected materials most often influenced by microorganisms during storage and use: fabric insulation for wires, and tarpaulins based on the natural polymers flax and cotton. The selected materials may be seen as models, owing to their high rate of aging.

The aging regimes used imitated the most severe conditions of use: for wire insulation made from PVC, heat and water influence; for tarpaulins, heat, water and UV radiation. Samples with different aging times were inoculated by a suspension of *Aspergillus niger* spores. Kinetics of the development of microscopic fungus was estimated by biomass growth, which was washed off samples of materials by distilled water onto a darcon filter, and then dried to constant weight at 105°C.

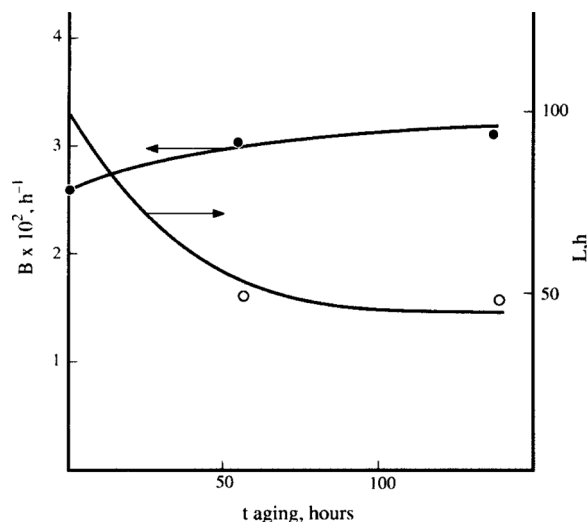
Kinetic curves of *Aspergillus niger* biomass growth on PVC wire insulation and on tarpaulin are shown in Figure 14. It is seen that overgrowth kinetics changes significantly with increased aging. Overgrowth on aged samples proceeds more rapidly.

Figure 15 shows the change of parameter **b** and the lag-phase duration (**L**). It is seen that the lag-phase decreases with aging, and the specific rate of the growth, characterized by the parameter **b**, increases. It may be supposed that this is connected with accumulation of aging products in the material, which may be used by microorganisms as nutrition substances. For natural fibers aged for 60 and 150 h, the lag-phase duration is similar. This may suggest that the processes of adaptation



**Figure 14.** Kinetic curves of *Aspergillus niger* biomass accumulation on the materials: (a) three types of acetic cellulose, (2) PMMA, (3) PVC wire insulation, (4) PE; (b) two types of tarpaulin textile (1) linen, (2) cotton.

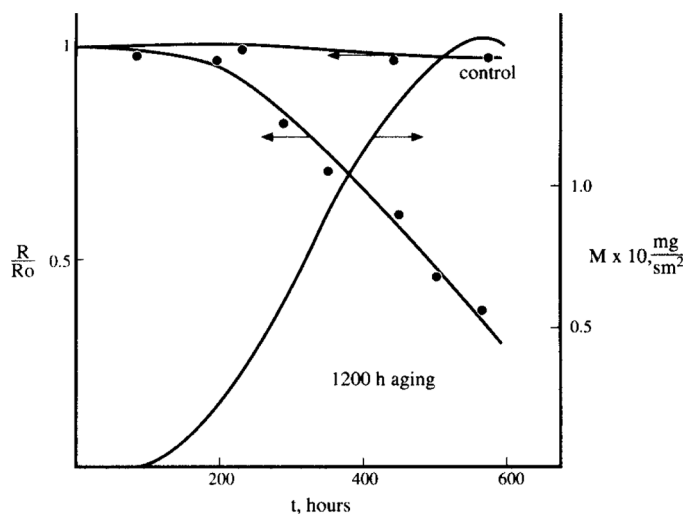




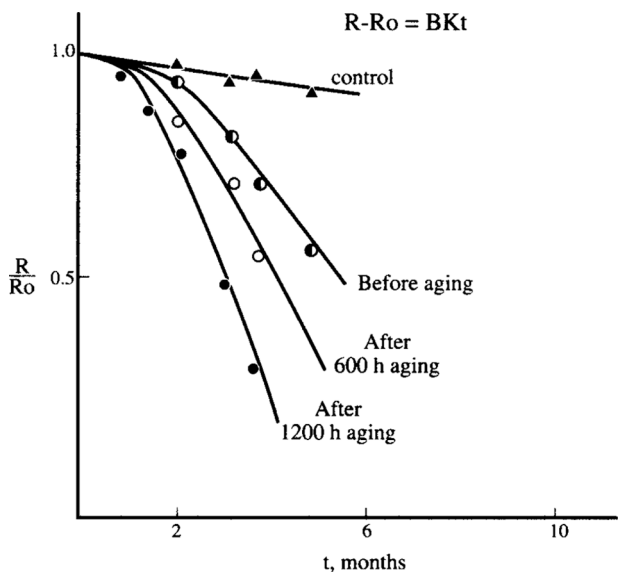
**Figure 15.** Relationship of constants  $b$  and  $L$  for PVC samples from wire insulation after aging for different times.

of microorganisms to the material are practically complete in fibers at relatively small times of aging.

The growth of *Aspergillus niger* on the investigated materials leads also to a change of their useful properties. Figure 16 compares amounts of biomass and electrical resistance of wires. In the case of testing without removal of microorganisms from the sample surface, the decrease of resistance correlates with the amount of biomass on the wires. If biomass is first removed from the wire insulation, the resistance is restored to the control value. This phenomenon is observed at small times of influence of microorganisms. If this time is increased up to several months, then, as is



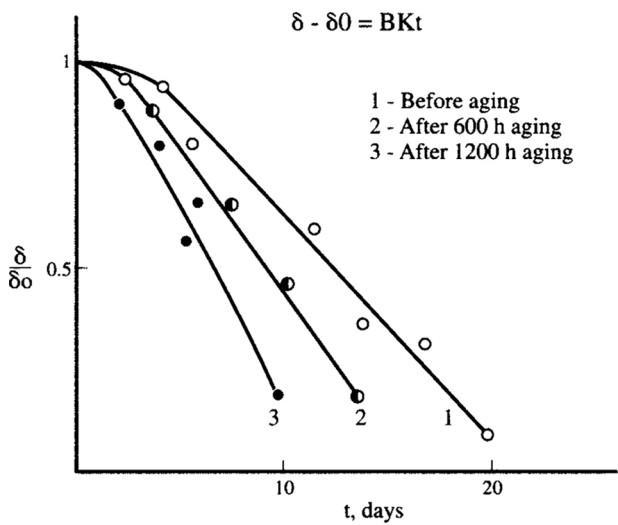
**Figure 16.** Relative electric resistance and biomass accumulation versus time on samples of PVC wire insulation after aging for 1200 h.



**Figure 17.** Decrease of relative resistance of PVC wire insulation versus aging time ( $R_0$  is the resistance after biomass removal).

seen from Figure 17, the value of the resistance decreases even after biomass removal. In this case an increase of aging time leads to a more significant decrease of the resistance. All graphical dependencies presented in Figure 17 have a linear part, described by the equation:

$$R = R_0 - BKt, \tag{8}$$



**Figure 18.** Breaking strength for filaments of tarpaulin versus time of action of *Aspergillus niger* biomass (1) without preliminary aging and after aging in ambient use conditions for (2) 600 h and (3) 1200 h ( $\alpha_0$  is the strength after aging).

where  $R_0$  is the initial value of electrical resistance;  $R$  is the value at time  $t$  and  $B$  and  $K$  are constants.

In such a view the time dependence of property change is connected with a degradation process proceeding statistically under the influence of aggressive media (causing decomposition of macromolecules with the formation of active radicals) [11]. In this case the rates of the chemical reaction and diffusion of the aggressive medium into the material are comparable. It can be assumed that under the influence of metabolites of *Aspergillus niger*, polar groups are formed that affect the wire insulation. Accumulation of these groups is the main cause of the decrease of insulation resistance.

Similar aging influences on bioresistance were also obtained for tarpaulins (Fig. 18). Thus, the change of break strength of fibers is larger for aged samples. The presence of linear parts on curves, described by an equation of the form of Eq. (8), allows us to propose that the change of strength characteristics is controlled by a statistically occurring degradation reaction. Thus, for the materials investigated, the processes of aging and biodeterioration act symbiotically, reinforcing each other [16].

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