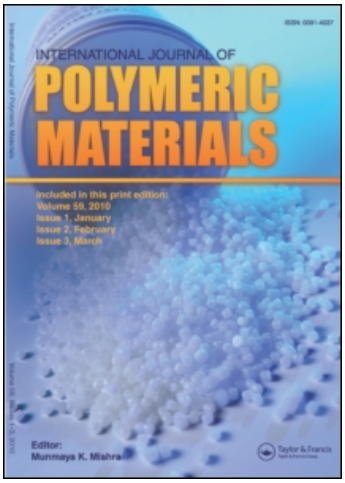

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Biodeterioration of Polymeric Materials: Generalized Kinetic Data

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Biodeterioration of Polymeric Materials: Generalized Kinetic Data

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The process of biodegradation of polymers was investigated. This process involves the adhesion of microorganisms cells with further growth of biomass producing aggressive media. Macrokinetic parameters of adhesion, biomass accumulation and biodegradation were obtained. The possibility of describing the biodegradation process by generalized kinetic relationships is presented.

KEY WORDS Biodegradation, biodeterioration, kinetic relationships, mechanisms, polymers.

INTRODUCTION

In 1970s–80s academician N. M. Emanuel promoted the idea of estimating the macroscopic processes proceeding during the time with the help of generalized kinetic curves, requiring a large amount of experimental material. And it does not matter if this process is tumor cells growth or aging of polymeric materials under the influence of the surroundings. Such an approach has first been developed by N. M. Emanuel for a quantitative description of the growth of tumor cells.[1]

Biodamaging of polymeric materials proceeds at their contact with living organisms and leads to the change of their performance characteristics.[2,3] In a general case the following processes participate in biodamaging:

—adsorption of microorganisms or substances, existing in tissues of the living organism, on the material surface;
—decomposition of the material as a result of specific influences of living organisms (polymeric material is as feeding source) or under the influence of metabolic products.

During the first process the chemical structure of the polymer does not change, the material plays the role of the support, for the adhesion and the growth of colonies of microorganisms (bioovergrowth) or the formation of collagen-like capsule at the application of the material as implant. The adhesion of microorganisms is the initial stage of bioovergrowing of materials, predetermining all further aspects of bioovergrowing and biodamaging of polymeric materials. In the stage of bioovergrowing the determination of biomass amount on the surface of polymeric

material is very important, because it influences the "surface" performance characteristics (optical, adhesive, etc.) of the material.

The second process leads directly to the aging of polymeric material under the influence of chemically active substances. In this phase, the "volumetric" performance characteristics (mechanical, dielectric, etc.) are affected.

The present paper covers the application of the method of generalized kinetic curves to estimate; i) the growth of microscopic fungi on the surface of polymeric material, ii) the biodegradation caused by biological medium of an organism or by the products of vital activities of growing microorganisms (metabolites), and iii) the adhesion of microorganisms on the surface polymers.

1. Kinetics of the Biomass Growth. Methods and Results

The growth and development of microscopic fungi directly on solid surfaces of polymers is usually estimated by means of a five-level GOST* method scale. This requires difficult determination of biomass in amounts of $\mu g/cm^2$ during the initial stages of growth.

To obtain the kinetic parameters of biomass accumulation we applied sensitive radio isotopic method.[4,5] The polymeric plates, contaminated by suspension of microscopic fungi of 10^6 cells/ml in water or Chapeck-Dox nourishing medium were exposed to tritium water vapours. In this case, the tritium accumulation in biomass proceeds in relation to the growth of their biomass, which consists on the average of 85% of water.[6,7] The amount of biomass was determined according to the difference between the contaminated and control samples for each polymer. The intensity of irradiation was measured by means of a liquid scintillation counter "Mark-388."

The growth of microorganisms was estimated from the change of dry biomass amount per unit of the sample surface.

Figure 1 presents the kinetic curves of biomass accumulation on the surface of polymers of different classes. All the investigated polymers possess similar character of the mass change, which is described satisfactorily by the exponential equation of the following form:

$$m/m_\infty = 1 - \exp(-kt) \tag{1}$$

where m = current biomass; m_∞ = equilibrium biomass; k = efficient constant of biomass growth.

Table I presents the values of m_∞, initial rate of biomass growth v_{init} and k_{eff} for two types of spore suspensions (in water and in nourishing medium of Chapeck-Dox), determined from the logarithmic form of the expression (2). The values of K_{eff} and v_{init} for suspensions in the nourishing medium is twice as high as in the water, while K_{eff} values are similar for both media. The high bioovergrowing rate of cells on the cellulose surface in comparison with other polymer surfaces is interactive. It is related to polymer hydrophilicity. In fact, the values of K_{eff} and

*GOST—standards USSR (former).

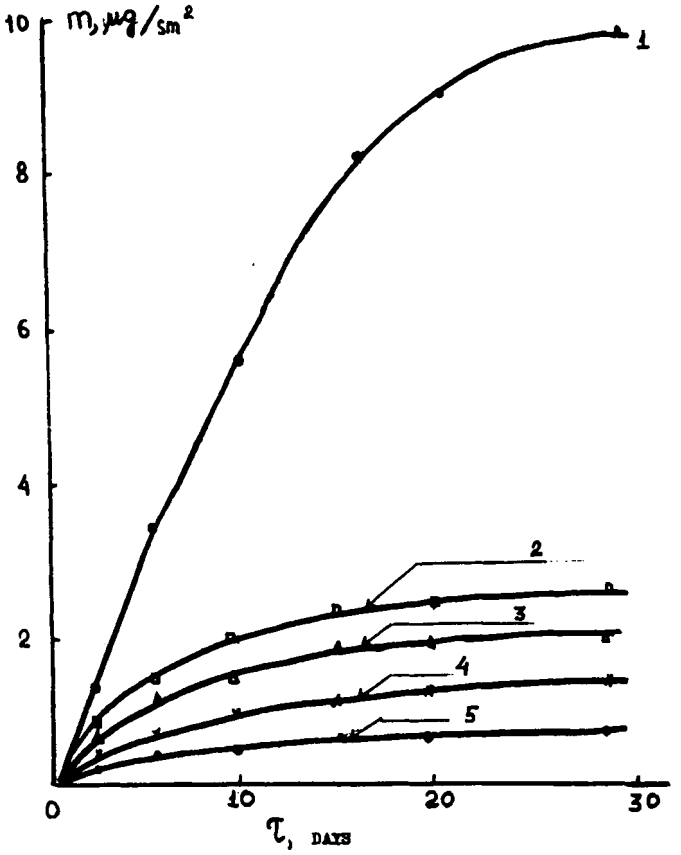

FIGURE 1 Kinetic curves of biomass accumulation of the microscopic funges on the polymer surfaces: 1—cellulose, 2—polymethylmethacrylate; 3—polyethylenetherephtalate; 4—polyethylene; 5—polytetrafluorine-ethylene.

TABLE I

Values of the initial rate of biomass accumulation v_{init} and boundary value m_∞ of biomass on the surface of various polymeric materials

No.	Investigated material	Treatment by mixture of spores in Chapeck-Dox medium			Treatment by mixture of spores in water		
		m_∞, μg/cm²	v_{init}, μg/cm²·day	K_{eff}, $\cdot 10^6$ s^{-1}	m_∞, μg/cm²	v_{init}, μg/cm²·day	K_{eff}, 10^6 s^{-1}
1.	Cellophane	10.5 ± 1	0.60 ± 0.05	1.0	5.80 ± 0.60	0.40 ± 0.080	1.5
2.	Polyethylene-terephtalate	2.4 ± 0.15	0.16 ± 0.02	1.2	0.27 ± 0.02	0.027 ± 0.003	0.9
3.	Polyethylene	1.5 ± 0.20	0.27 ± 0.02	0.9	0.27 ± 0.02	0.01 ± 0.001	1.3
4.	Polytetrafluor-ethylene	1.1 ± 0.1	0.04 ± 0.001	0.7	0.17 ± 0.02	0.01 ± 0.001	0.8
5.	Polymethyl-metacrylate				0.91 ± 0.50		
6.	Polyimide				0.05 ± 0.01		

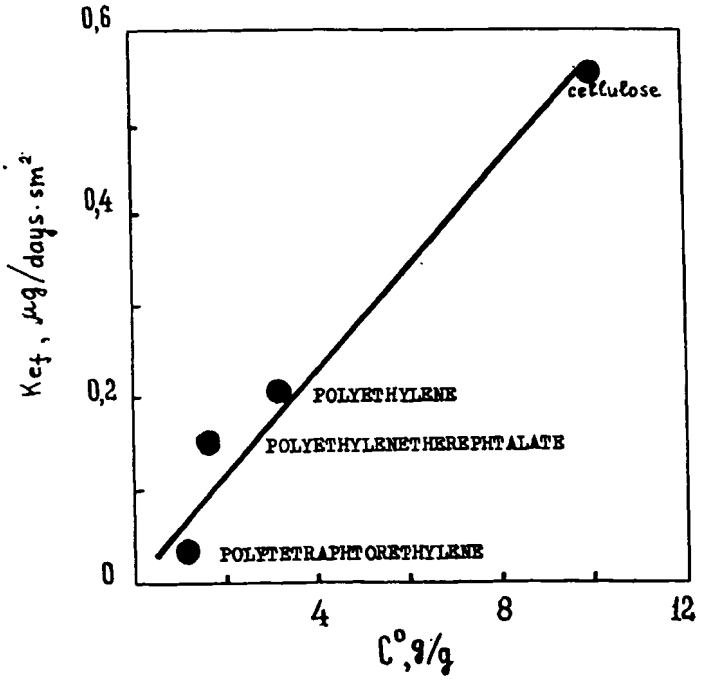

FIGURE 2 The dependence of rate constants of biomass overgrowth on water sorption by polymer.

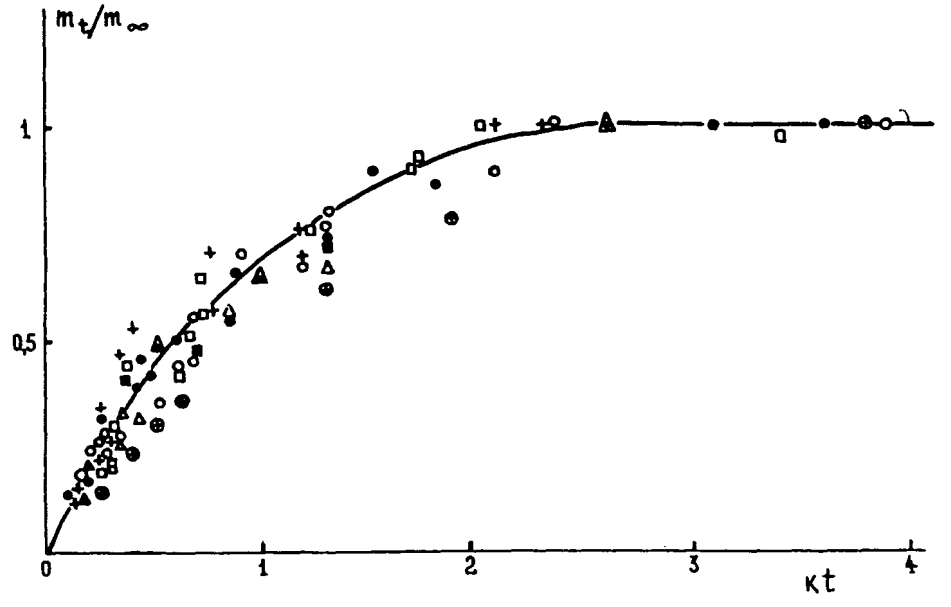

FIGURE 3 Generalized kinetic curve of the biomass overgrowth (fingi Aspergillus niger) on the polymer surface (T = 30°C, humidity 90%) from water suspension: ●—polyethylene (1), ○—polymethylmethacrylate (2), ⊕—polyethylenetherephtalate (3), □—cellulose (4), ■—polytetrafluorineethylene; from nutrient Chapek Dox suspension: + (1); △ (2), ▲ (3).

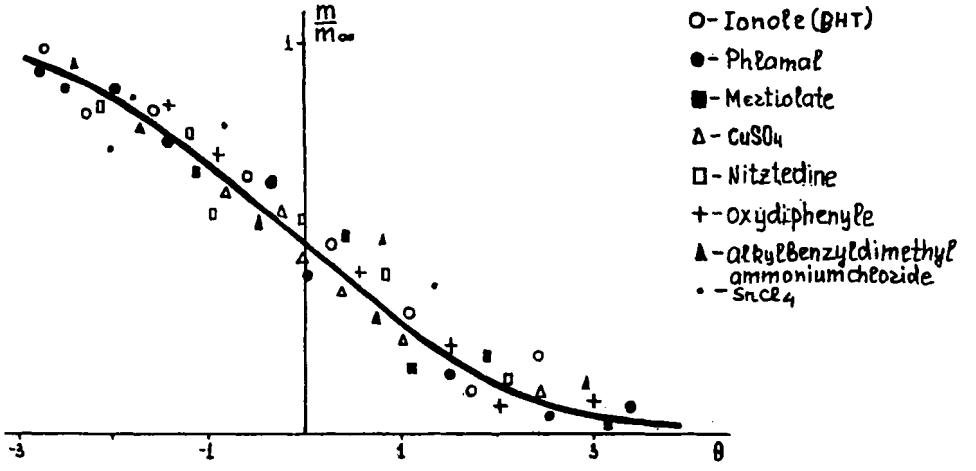

FIGURE 4 Generalized kinetic curve of inhibated biomass overgrowth in different biocides presence.

m_∞ are higher, the higher is solubility of water in the polymer (Figure 2). This allows us to predict the growth of biomass for polymers with known parameters of water solubility.

Figure 3 presents generalized kinetic curve in $m/m_\infty - kt$ coordinates, from which it follows that all the values of biomass correlate well with the curve in nondimensional coordinates independently from the nature of polymers, nourishing medium and type of microorganisms.

The obtained relationships hold also for the inhibited biomass growth in presence of biostabilizers, called biocides.[8]

Generalized kinetic curve of inhibited growth of biomass of Aspergillus niger microscopic fungus in presence of different biocides is presented on the Figure 4, where the amount of relative biomass is described by the following empyric equation:

$$m/m_\infty = \frac{1}{1 + e^{\theta}} \tag{2}$$

where $\theta = \ln a - \ln b$, a and b = constants characterizing biocide affinity.

2. Biodegradation

As it was pointed out, the degradation processes proceed simultaneously with the accumulation of biomass or at prolonged contact with biological medium of the organism.

To estimate the progress of bioaging of polymers, the changes in mechanical properties, for example stress at break (σ) are most often used. Polymers usually follow a linear correlationship between σ and the reciprocal of the number average degree of polymerization ($\bar{P}_n$)

$$\sigma = n - \frac{B}{\bar{P}_0}. \tag{3}$$

The following simple correlation may be obtained, connecting σ with implantation time for polymeric implantants, for which the degradation process proceeds according to the chance law:

$$\sigma/\sigma_0 = 1 - \frac{k}{\sigma_0} t. \tag{4}$$

Denoting the time of complete loss of the strength

$$\tau = \sigma_0/k \tag{5}$$

we obtain

$$\sigma/\sigma_0 = 1 - t/\tau. \tag{6}$$

Figure 5 presents generalized curve in coordinates of the equation (6) for bioaging of a series of biomedical polymers of the subskin cellular tissue of rabbits.[9,10] Thus, the value of k determined for the initial part of kinetic curves can be used to estimate the time of complete loss of implant strength in living organism according to the correlation (5).

Figure 6 presents the relative change of breaking stress of elementary fibers of tarpaulin fabric on incubation a suspension of Aspergillus niger fungus spores (C_0 = 10^6 spores/ml). Note that the breaking stress changes according to the linear law as a result of degradation from fiber surface:

$$\sigma/\sigma_0 = 1 - \frac{K_{\text{eff(surf)}} l}{l_0 \rho} \tag{7}$$

where ρ = density, l = film thickness or fiber diameter.

The effective decomposition of hydrolyzable bonds constants are the ones controlling the biodegradation of all polymers in the living organism medium. We have shown before, that polyethylene terephtalate degradates only in acidic medium of organism, for example at inflammation processes possessing rate constant of $1.3 \cdot 10^{-6}$ s^{-1} from the surface.[10] Polycaproamide degrades according to the mixed type of decomposition (from the surface and in the volume) with the rate constants of $0.15 \cdot 10^{-8}$ s^{-1} and 10^{-10} s^{-1}, respectively.

Finally, every polymer must be characterized by the list of efficient rate constants of degradation, as it is shown in the Table II. These data were obtained by authors of the present article.

3. Kinetics of Adhesion of Microorganisms

The biodegradation resulting from the interaction of microorganisms with polymeric surface—support, starts with adhesion. The adhered cells act as aggressive bioagents, producing metabolites or other low-molecular substances. Therefore, the

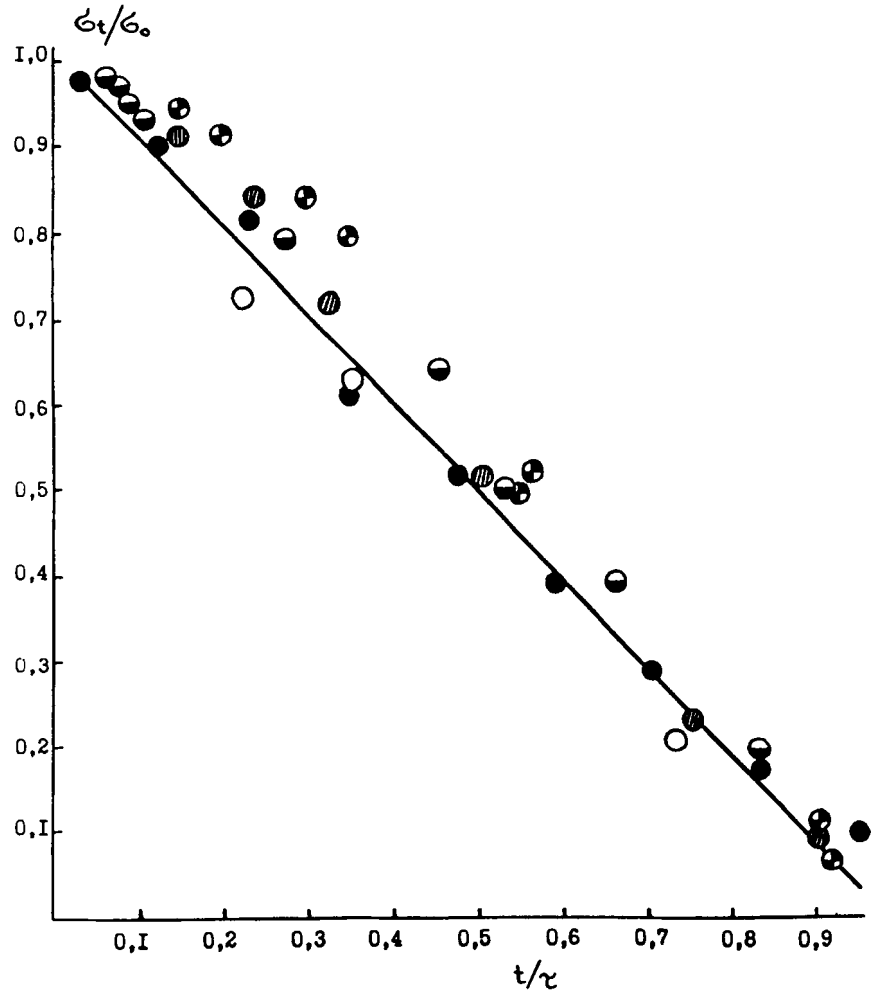

FIGURE 5 Relative change of the filament fiber strength of the sutures by implantation in subcutaneous tissue of rabbits versus relative tinel aging: ●—polyethylene; ◒—polyglycolide; ●—polyglactin, ◉—polyamide ○—polypropylene.

quantitative parameters of adhesion control the parameters of subsequent stages—bioovergrowing (biomass accumulation) and biodegradation.[11-13]

Adhesion strength (F_{adh}), determined by the method of centrifugal detachment, may serve as macroscopic parameter, for a quantitative estimation. To estimate F_{adh}, a suspension of microorganisms cells (10^6 spore/ml) was applied to the surface of a polymeric film, incubated for a definite period of time at different temperatures (T°C) and humidity (φ, %). After that, the films were attached to metal plates and centrifuged with forces, acting perpendicular to the surface. The number of cells (γ), detached from the surface into the volume of centrifugal glass with distilled water at particular field intensity, was determined by means of an optical microscope. The adhesion was estimated from the force of spores detachment from the polymeric surface:

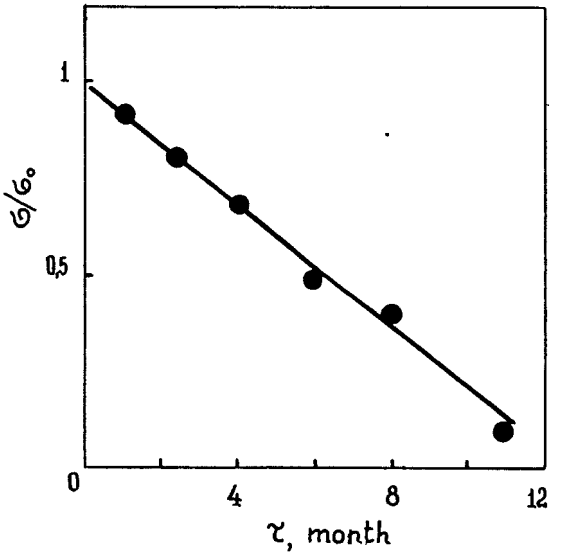

FIGURE 6 Relative change of the filament fiber strength of cellulose (tarpanlin fabric) versus time aging at incubation in the Aspergillus niger spore suspension (C_0 = 10^6 cell/ml).

TABLE II

Values of efficient rate constants of degradation under the influence of different media of organism on biomedical polymers

No.	Polymer	K_{acid}, s^{-1}	K_{salt}, s^{-1}	K_{H_2O}, s^{-1}	K_{enzyme}, s^{-1}
1.	Polycaproamide	—	$0.15 \cdot 10^{-8}$	10^{10}	—
2.	Polyglycolide	—	$1.30 \cdot 10^{-4}$	$0.8 \cdot 10^{-3}$	$5.00 \cdot 10^{-4}$
3.	Polyglactin	—	$5.00 \cdot 10^{-4}$	$0.9 \cdot 10^{-3}$	$0.13 \cdot 10^{-4}$
4.	PETP	$1.3 \cdot 10^{-6}$	—	—	—
5.	Polyethylene	—	—	—	$1.2 \cdot 10^{-9 \div 11}$
6.	Cellulose	—	—	—	$0.5 \cdot 10^{-6}$

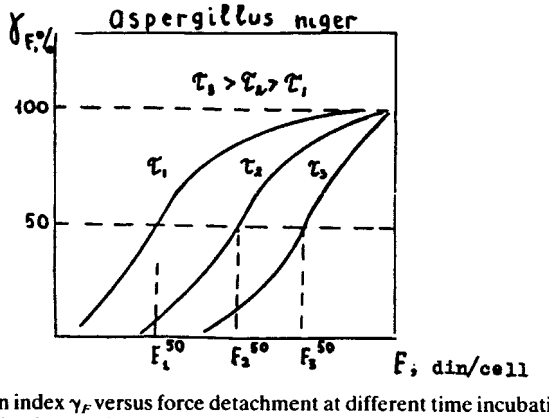

FIGURE 7 Adhesion index γ_F versus force detachment at different time incubation t of the Aspergillus niger spores on the polyethylene film.

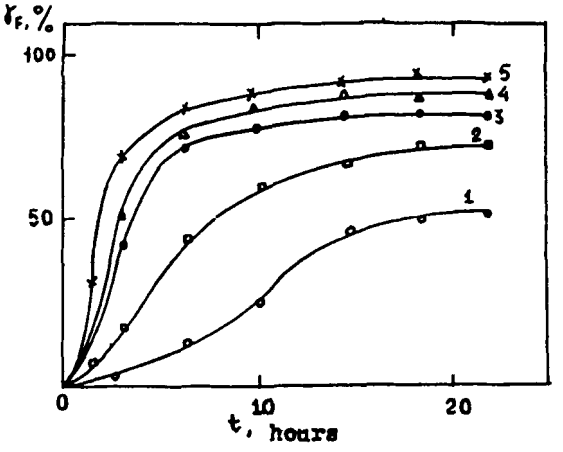

FIGURE 8 Kinetic curves of the Aspergillus niger spores adhesion on the polymer surface at T = 22°C, φ = 98%: 1—polyethylene, 2—epoxypolymer, 3—polymethylmethacrylate, 4—acetylcellulose, 5—cellylase.

TABLE III

Parameters of adhesion of Aspergillus niger conidia to the surface of different polymeric materials

No.	Material	k, hour^{-1}	F^{50}, dyn/cell	γ_∞, %
1.	Polyethylene	0.06	$3.3 \cdot 10^{-4}$	55
2.	Epoxy resin	0.08	$6.6 \cdot 10^{-4}$	70
3.	Polymethyl metacrylate	0.36	$1.0 \cdot 10^{-3}$	80
4.	Cellophane	0.36	$1.6 \cdot 10^{-3}$	85
5.	Acetyl cellulose	0.41	$2.5 \cdot 10^{-3}$	90

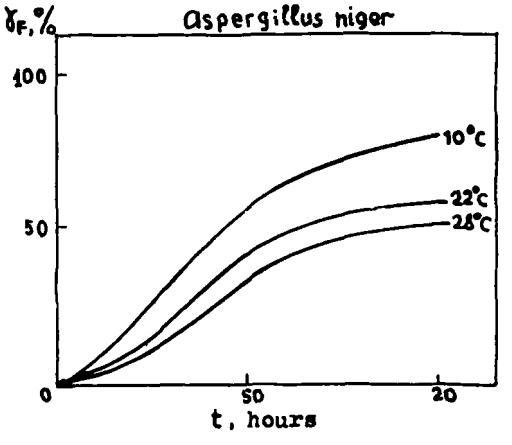

FIGURE 9 Kinetic curves of Aspergillus niger adhesion on the polyethylene surface at φ = 30% and different temperatures.

TABLE IV

Adhesive parameters of interaction for polyethylene and cellophane at different temperatures and relative humidity φ = 30%

	Polyethylene			Cellophane		
T, °C	γ_∞, %	K, hour^{-1}	F^{50}, dyn/cell	γ_∞, %	K, hour^{-1}	F^{50}, dyn/cell
10	85	0.06	$5.2 \cdot 10^{-4}$	90	0.36	$2.6 \cdot 10^{-3}$
22	55	0.06	$3.3 \cdot 10^{-4}$	85	0.36	$1.6 \cdot 10^{-3}$
38	50	0.06	$1.3 \cdot 10^{-4}$	—	—	—

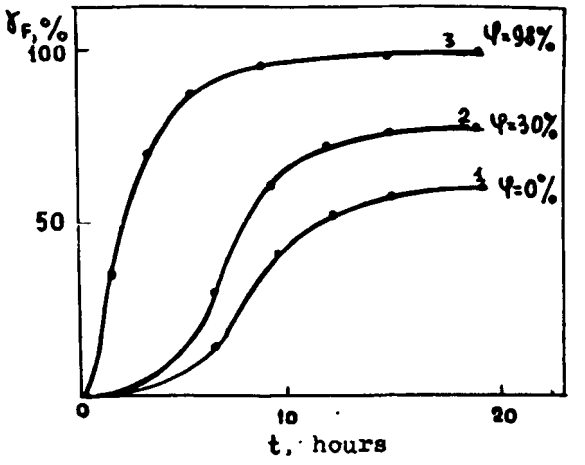

FIGURE 10 Kinetic curves of the Aspergillus niger spores adhesion on the polyethylene surface at T = 22°C and different humidities.

TABLE V

Adhesive parameters of conidia for polyethylene at different air humidity and constant temperature T = 10°C

φ, %	K, hour^{-1}	γ_∞, %	F^{50}, dyn/cell
0	0.08	70	$3.0 \cdot 10^{-4}$
30	0.66	85	$5.2 \cdot 10^{-4}$
100	0.56	100	$1.9 \cdot 10^{-3}$

$$F = \frac{1}{675} \cdot \pi^3 r^3 \omega^3 R(\rho_{cell} - \rho_l) \tag{8}$$

where r = radius of spores, ω = angular velocity of rotation, R = distance to rotor axis, ρ_{cell} = density of spores (cells), ρ_l = density of liquid, in which detachment was performed.

Typical kinetic curves of γ_F dependence on time of exposure of microorganisms spores to the surface are presented in the Figure 7. S-like curves of adhesion are characterized by two parameters: γ_∞ = the equilibrium value of the adhesion under

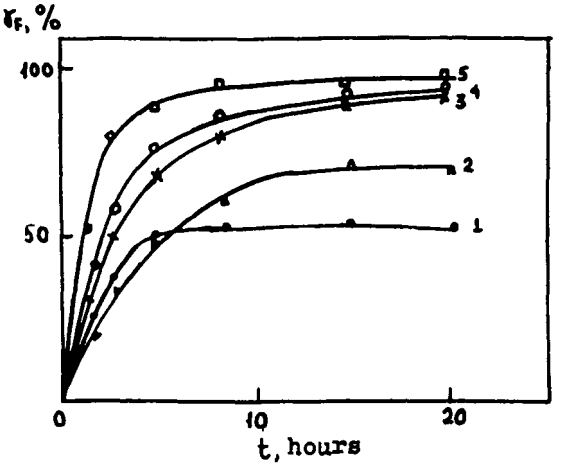

FIGURE 11 Kinetic curves adhesion of different fungis to polyethylene surface. 1—Aspergillus niger, 2—Penicillium cyclopium, 3—Paec. varioti, 4—Penicillium hrisogenium, 5—Aspergillus terreus.

TABLE VI

Adhesive parameters of microscopic fungi to the surface of polyethylene at φ = 98%, T = 22°C

Fungus type	γ_∞, %	K, hour^{-1}	r^*, μm	F^{50}, dyn/cell
Aspergillus niger	80	0.23	5.0 ± 0.5	$0.26 \cdot 10^{-1}$
Aspergillus terreus	94	1.96	1.0 ± 0.05	$0.31 \cdot 10^{-3}$
Paec. varioti	98	0.30	5.5 ± 0.7	$0.76 \cdot 10^{-1}$
Pinicillium chrysog.	94	0.40	1.5 ± 0.06	$0.45 \cdot 10^{-3}$
Pinicillium cyclopium	55	0.50	2.6 ± 0.4	$0.10 \cdot 10^{-1}$

*r = radius of spores for different types of fungi.

specific conditions and the rate constant of formation of adhesion intensities K_{eff}, determined from the expression describing the experimental curves:

$$\ln(\gamma/\gamma_\infty) = -k_{adh}t. \tag{9}$$

The influence of the material nature on adhesion of spores is shown on the Figure 8, where kinetic curves of adhesion in definite conditions (temperature and humidity) for different polymers are presented. The adhesion equilibrium plateau is reached in about 24 hrs. Table III shows the calculated values of adhesion parameters of *Aspergillus niger* conidia on various polymeric substrates.

The polymers are ranked according to conidia adhesion from hydrophobic polyethylene to hydrophilic cellulose.

Figure 9 presents the dependence of the adhesion index of Aspergillus niger spores at constant humidity and different temperatures. Table IV presents the values of parameters calculated from these kinetic curves for two extreme substances based on water solubility—polyethylene and cellophane.

As it is seen from the Figure 9, the temperature dependence is not expressed clearly for each polymer, which is confirmed by the constancy of the value of rate

TABLE VII

Parameters of biodamaging ability of polymers

Material	Adhesion parameters			Growth	Degradation			
	K_{eff}^{adh}, s^{-1}	F, dyn/cell	γ_x, %	m_x, $\mu g/cm^2$	K_{acid}^{eff}, s^{-1}	K_{salt}^{eff}, s^{-1}	K_{H_2O}, s^{-1}	K_{enzyme}, s^{-1}
Polyethylene (PELD)	$1.6 \cdot 10^{-5}$	$3.3 \cdot 10^{-4}$	55 ± 5	1.5 ± 0.2	—	—	—	$1.2 \cdot 10^{-9}$
Epoxypolymer	$2.2 \cdot 10^{-5}$	$6.6 \cdot 10^{-4}$	70 ± 5	4.5 ± 0.7	—	—	—	$1.7 \cdot 10^{-7}$
Polymethyl metacrylate	$2.1 \cdot 10^{-5}$	$1.1 \cdot 10^{-3}$	80 ± 5	3.8 ± 0.7	Have not been studied			
Polyethylene terephtalate	$1.1 \cdot 10^{-4}$	$2.5 \cdot 10^{-3}$	90 ± 5	2.4 ± 0.5	$1.3 \cdot 10^{-6}$	—	—	—
Cellulose	$1.0 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$	85 ± 5	10.5 ± 1.0	—	—	—	$0.5 \cdot 10^{-6}$
Polyamide	$1.7 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$	82 ± 5	3.9 ± 0.5	—	$0.2 \cdot 10^{-8}$	10^{-10}	—

K_{eff}^{adh} = constant of adhesion of Aspergillus niger microscopic fungus conidia; F = adhesion intensity of a single cell to polymer surface; γ_x = extreme adhesion index; m_x = biomass per surface unit; K_{acid}^{eff} = rate constant of degradation by mass in acidic medium; K_{salt}^{eff} = rate constant of degradation by mass under the influence of phosphate ions; K_{enzyme}^{eff} = rate constant of degradation under the influence of enzyme.

constant of adhesion intensities formation. Moreover, the adhesion intensity increases with the decrease of temperature.

Figure 10 presents kinetic curves of adhesion of Aspergillus niger spores to the surface of polyethylene at constant temperature and different values of humidity of exposition medium.

It follows from the calculated values of constants presented in the Table V, that at relatively small differences in γ_{∞} very large changes of K can be observed.

The values of adhesion parameters were calculated from kinetic curves of adhesion of conidia of different microscopic fungi spores, which were presented on the Figure 11.

The final task of the investigation of quantitative characteristics of bioovergrowth adhesion is determination of macroscopic kinetic parameters of biodamaging potential of polymers.

The biostability of material may be predicted with the help of experimentally obtained values of microscopic kinetic parameters of the interaction of microorganisms cells (spores conidia) with the polymeric surface. In general case, the biostability (B) is defined by the adhesion intensity, the amount of biomass and effective rate constants of degradation of accessible bonds:

$$B \sim \frac{1}{F_{\text{adh}}} \cdot \frac{1}{\Delta m_{\infty}} \cdot \frac{1}{K_{\text{eff}}^{\text{adh}}}.$$

For example, the values of biostability for cellophane determined from this expression (humidity $\varphi = 98\%$) was found to be equal to $0.5 \cdot 10^6$ s·cm^2/dyn·μg, and for polyethylene (five orders of magnitude higher): $0.4 \cdot 10^{11}$ s·cm^2/dyn·μg.

Thus it was shown that the investigation of kinetic regularities of microscopic processes, such as adhesion, bioovergrowth, biodegradation, allows us to analyze the mechanism of complex processes of biostability and biodecomposition of polymeric materials, and predict their performance in use.

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