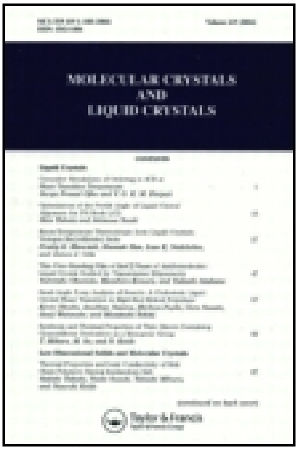

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K. Z. Gumargalieva [a] , I. G. Kalinina [a] , S. A. Semenov [a] & G. E. Zaikov [b]

[a] N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

[b] N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia

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Bio-Damages of Materials. Adhesion of Microorganisms on Materials Surface

K. Z. Gumargalieva[1], I. G. Kalinina[1], S. A. Semenov[1], and G. E. Zaikov[2]
[1]N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia
[2]N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia

Adhesion interaction of the most widely distributed species of microscopic fungi: Aspergillus niger*,* Trichoderma viride*,* Penicillium funiculosum*,* Aspergillus terreus *to surfaces of materials (polymers, metals) is studied. The force of adhesion interaction was measured by the method of centrifugal detachment. Based on the analysis of kinetic curves the macroscopic characteristics of adhesion microorganism–metal surface were obtained. We show on the example of Aspergillus niger that stochastic nature of adhesion of microorganisms cells is caused by heterogeneity of support surface, heterogeneity of conidium sizes, and their distribution by forces of adhesion obeys the Gauss law. We established that structure of cellular wall of microscopic fungi was changed in dependence on age, and change of force of adhesion interaction correlated with changes in cellular wall structure of microscopic fungi, and dominating role in strengthening of adhesion interaction was played by increase of albuminous components concentration in surface layer of cell.*

Keywords: adhesion; adhesion force; adhesion interaction; *Aspergillus niger*; *Aspergillus* terreus; microorganism; *Penicillium funiculosum*; polymer surfaces; *Trichoderma viride*

INTRODUCTION

Professor N. M. Emanuel's set problems in the field of applied works were characteristic by fundamental approach. In particular, at the beginning of eighties of the last century the questions of polymer

Address correspondence to G. E. Zaikov, N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygin Str., Moscow, Russia. E-mail: chembio@sky.chph.ras.ru

materials bio-damages traditionally related to micro-biological discipline were included by N. M. Emanuel into section of chemical destruction of polymer materials science. Actually, further investigations in this field showed that active destructing agents of materials under interaction with microorganisms were the products of their vital functions – metabolites representing famous chemical agents: water, salts, acids, alkali, ferments, toxins, i.e. finally bio-damage should proceed by laws of chemical destruction [1–10].

Investigation of result of bio-destruction is generally accepted, whereas it follows two stages: adhesion or microorganism connection to material surface with further growth of microorganism bio-mass as a result of substrate-support utilization. These two stages should predetermine further processes of material degradation.

At conditions of present-day ecologically fraught environment and fast adaptation of various microorganisms species to changing environment conditions from the one side, and accumulation of various waste of synthetic origin from the other side, the investigations in the field of development of both fast degradating materials for the cases of utilization necessity and stable materials for cases of protection from bio-destruction are necessary [11–12].

Studying of adhesion of microorganisms cells is of great interest now, but these investigations in many cases are "exotic" in relation to selection of microorganisms' species. In work [13] they studied selective adhesion to micaceous plates covered by polyethyleneimine, extremorphil cultures grown at high temperatures and low phosphorescent. By method of scanning electron microscopy they affirmed that adhesion of extremorphil to polyethylenimine covering was preferred in comparison with adhesion to polylysine. The main physical-chemical factors of material surface such as hydrophobicity, roughness, morphology of microorganisms cells are discussed in works [13–16]. These works and up to date state of the problem confirm the necessity of investigation of adhesion interaction nature on the interface material–cell's wall of microorganism with attempt of quantitative estimation of this process.

EXPERIMENTAL/MATERIALS & METHODS. RESULTS AND DISCUSSION

Adhesive cells of microorganisms act as aggressive bio-reagents as a result of evolving of exo-ferments or other low-molecular substances organizing so-called bio-film. That is why quantitative parameters of adhesion are determinative for rates of biofouling (biomass accumulation) and bio-destruction.

Interaction polymer surface–microorganism was determined by the value of adhesion force in dependence on contact time at various external conditions (temperature, moisture) to polymer materials of various degrees of hydrophilicity: polymethyl methacrylate, cellophane, polyethylene, acetylcellulose, epoxide resin and polyethylene terephthalate.

Conidiums of microscopic fungi *Aspergillus niger* were drifted on materials surface in doses from water suspension with definite titre by micro-batcher, then they were dried and aged at various thermo-moist conditions in the interval from 0 up to 24 hours. The value of conidiums *Aspergillus niger* adhesion force to surfaces of polymer materials was determined by method of centrifuge detachment [17]. Change of morphology, (form) and sizes of conidiums were studied by method of scanning electron microscopy "Tesla" BS300. Amount of flown off or residual conidiums on the surface of material as a result of action of centrifuge force (angle rate of rotor $\mathbf{w} = 15000$ revos for 15 minutes) was counted in Goryaev's chamber.

Change of amount of residual conidiums $\gamma = \mathbf{N}/\mathbf{N_o}$ *Aspergillus niger* after centrifugation in dependence on time of preliminary ageing at given thermo-moist conditions ($\mathbf{T} = 22°\text{C}$, $\boldsymbol{\varphi} = 30\%$) is presented in Figure 1. Adhesion interaction of system polymer material–microorganism has kinetic character. Each system polymer material–microorganism is characterized by time of end of adhesion forces formation between conidiums and surface (approaching the plateau by kinetic curve) which depends on external conditions.

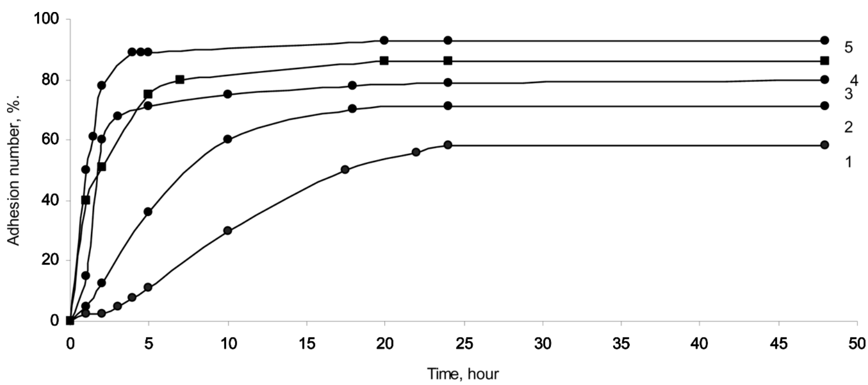

FIGURE 1 Kinetic curves of conidiums *A. niger* adhesion to various polymer materials at temperature 22°C and relative moisture 30%. **1** – polyethylene, **2** – epoxide resin, **3** – polymethyl methacrylate, **4** – acetyl cellulose, **5** – cellophane.

Presented in Figure 1 dependences are well described by Eq. (1):

$$\ln \gamma/\gamma_{\infty} = -\mathbf{K} \cdot \mathbf{t} \quad (1)$$

where γ, γ_{∞} – part of particles remained on the surface of polymer material after preliminary ageing during the time **t**, and irreversibly adhesive at given conditions accordingly, **K**-constant of rate of formation of adhesion forces between conidiums and material surface. Values of parameters determined from equation for investigated polymers and also the value of force influencing on one cell are presented in Table 1. At $\boldsymbol{\omega} = 15000\,\mathrm{min}^{-1}$ the force influencing on each conidium was equal to $\mathbf{F} = 1{,}2 \cdot 10^{-4}$ dyne/cell. As it is known [18] the value of force under adhesion corresponds to the value $\gamma = 50\%$. If we know $\mathbf{F_{50}}$, the time of kinetic curve approaching the plateau and exponential course of kinetic curves of adhesion we may determine the values of adhesion forces for each polymer at given thermo-moist conditions.

Thus, at fixed thermo-moist conditions each material may be characterized by proper set of values of **K** and **F**. By increase of adhesion of conidiums *A. niger* the investigated polymer materials are formed the following raw: polyethylene, epoxide resin, polymethyl methacrylate, cellophane, lavsan, acetyl cellulose.

As it was mentioned above, in experiments the polymer materials with various degree of hydrophilicity were used. It is obvious from Figure 1 and Table 1 that hydrophilic polymers have high values of adhesion force and constants of rates of their formation, whereas for hydrophobic polymer materials these values are significantly lower. Obviously, the values of **K** and **F** are determined by the ability of material to strong adhesion of microorganisms connected with material moister capacity.

For more detailed studying of process the influence of external exploitation factors on adhesion process was investigated. Kinetic curves of adhesion on polyethylene and cellophane at various temperatures of conidiums ageing on polymers surface are presented in

TABLE 1 Parameters of Adhesion of Conidiums *A. Niger* to Surface of Polymer Materials

Material	**k**, sec^{-1}	**F**, dyne/cell	γ_{∞}, %
Polyethylene	$1{,}66 \cdot 10^{-5}$	$3{,}3 \cdot 10^{-4}$	55
Epoxide resin	$2{,}20 \cdot 10^{-5}$	$6{,}6 \cdot 10^{-4}$	70
Polymethyl methacrylate	$1{,}0 \cdot 10^{-4}$	$1{,}1 \cdot 10^{-3}$	80
Cellophane	$1{,}0 \cdot 10^{-4}$	$1{,}6 \cdot 10^{-3}$	85
Acetyl cellulose	$1{,}3 \cdot 10^{-4}$	$2{,}5 \cdot 10^{-3}$	90

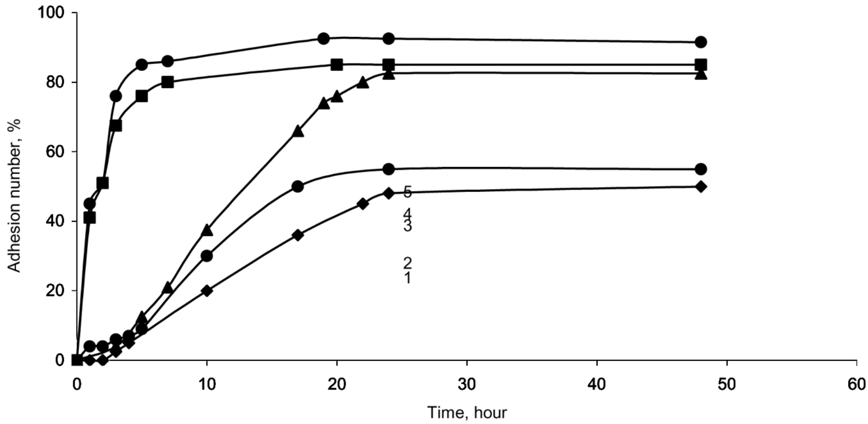

FIGURE 2 Kinetic curves of conidiums *A. niger* adhesion to polyethylene and cellophane at relative moisture 30% and various temperatures: **1** – polyethylene, **T** = 38°C; **2** – polyethylene, **T** = 22°C; **3** – polyethylene, **T** = 10°C; **4** – cellophane, **T** = 22°C; **5** – cellophane, **T** = 10°C.

Figure 2. It is obvious that with temperature rise adhesion of conidiums *Aspergillus niger* to polymer materials and rate of formation of adhesion bond are decreased, that is characteristic for phenomena namely of physical nature.

The values of characteristics of adhesion interaction for polyethylene and cellophane at various temperatures and relative moisture are presented in Table 2.

As it is obvious from Figure 2 and Table 2 the adhesion force (**F**) and constant of adhesion forces formation rate are observed at 98% relative moisture of air. Obviously, the conidiums of macroscopic fungi in air medium interact with surface of polymer material at the expense

TABLE 2 Adhesion Parameters of Interaction for Polyethylene and Cellophane at Various Thermo-Moist Conditions

		Polyethylene			Cellophane		
T, °C	**φ**, %	γ_∞, %	**k**, sec^{-1}	**F**, dyne/cell	γ_∞, %	**k**, sec^{-1}	**F**, dyne/cell
	0	70	$2{,}20 \cdot 10^{-5}$	$3{,}0 \cdot 10^{-4}$	–	–	–
10	30	85	$1{,}66 \cdot 10^{-5}$	$5{,}2 \cdot 10^{-4}$	90	$1{,}0 \cdot 10^{-4}$	$2{,}5 \cdot 10^{-3}$
	98	100	$9{,}70 \cdot 10^{-5}$	$1{,}9 \cdot 10^{-3}$	–	–	–
22	30	55	$1{,}66 \cdot 10^{-5}$	$3{,}3 \cdot 10^{-4}$	85	$1{,}0 \cdot 10^{-4}$	$1{,}6 \cdot 10^{-3}$
38	30	50	$1{,}66 \cdot 10^{-5}$	$1{,}3 \cdot 10^{-4}$	–	–	–

of both molecular forces and at the action of capillary forces of liquid condensed in gap between conidium and polymer surface under the action of forces of Coulomb interaction and other reasons. In the presence of moisture in air medium the condensation of vapor occurs between conidium and polymer surface. Capillary forces are the higher the higher the surface tension of liquid the vapor of which surround the region of interaction of conidiums with polymer surface and where moistening of polymer surface is better. Liquid interlayer between interacting objects (in given case between conidiums and polymer surface) excludes or to a great extent weaken the action of forces of electric nature. That is why results of experiments carried out with polyethylene at fixed temperature 10°C but at various air moistures which are illustrated in Figure 3 and Table 2 confirm physical character of adhesion interaction of system. For confirmation of assumption the adhesion interaction of *Aspergillus niger* on the surface of polyethylene at 22°C and relative moisture of air $\varphi = 30\%$ was studied during days on raster electron microscope. Increase of interaction time leads to the change of geometric forms of conidiums *Aspergillus niger* and increase of contact square almost by 100%. Probably, by this fact we may explain the kinetic character of conidiums adhesion to polymer surfaces that allows quantitative description of microorganisms adhesion process to various surfaces and its characterization by kinetic parameters.

The process of microorganisms adhesion is also determinative under biofouling of metals in water and air mediums [19–22]. In these

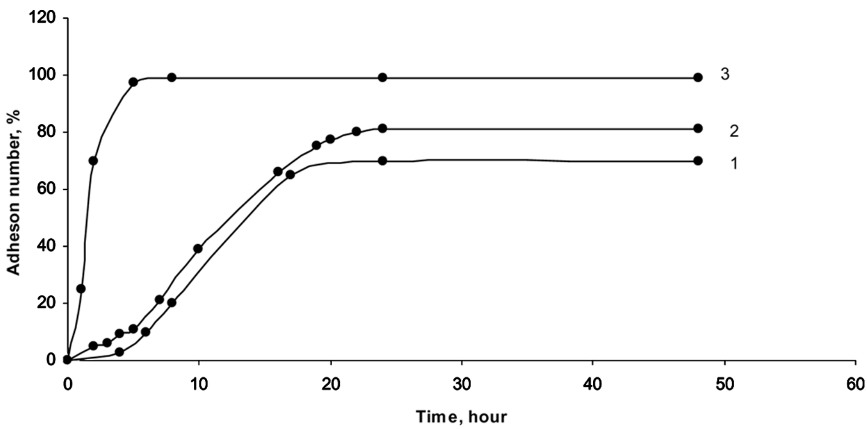

FIGURE 3 Kinetic curves of conidiums *A. niger* adhesion to polyethylene at 10°C and relative moisture of environment 0 (**1**), 30 (**2**), 100% (**3**).

experiments the conidiums of *Trichoderma viride* fungi were used which were met in water medium and possessed optimal sizes for quantitative microscopic analysis. They determined the force causing the detachment of 50% of conidiums from general amount of all presenting on metal surface cells from integral curves of distribution of conidiums by adhesion forces characterizing the dependence of part of detached particles on force of detachment.

The force of detachment of 50% of conidiums was calculated specially:

$$\mathbf{F_{50}} = \pi^3/675 \cdot \mathbf{R}(\mathbf{p_c} - \mathbf{p_{av}}) \cdot \omega^2 \cdot \mathbf{r}^3, \text{ dyne/cell}, \qquad (2)$$

where $\rho_{\mathbf{av}}$ – density of medium (water); $\rho_{\mathbf{c}}$ – density of conidiums equal to 1,15 g/cm^3, $\mathbf{R} = 4$ cm – the radius of centrifuge rotor, ω – number of revos, $\mathbf{r}$ – conidiums radius equal to $(3 \pm 0.3) \cdot 10^{-4}$ cm. The adhesion of conidiums to metal surface was characterized by two parameters γ_∞ and $\mathbf{F_{50}}$. The curves of conidiums *Trichoderma viride* adhesion to various metals are presented in Figure 4, the values of γ_∞ and $\mathbf{F_{50}}$ are presented in Table 3.

All the metals by adhesion parameters may be divided into two groups: the first is characterized by $\mathbf{F_{50}} \geq 10^{-4}$ dynes/cell; and the second by $\mathbf{F_{50}}$ from 10^{-5} up to 10^{-7} dyne/cell.

Prehistory of surface plays significant role, for example for nickel treated by cold plastic deformation $\gamma_\infty = 79 \pm 8\%$ and $\mathbf{F_{50}} = 2{,}0 \cdot 10^{-4}$ dyne/cell, and for nickel aged for 1 hour at temperature

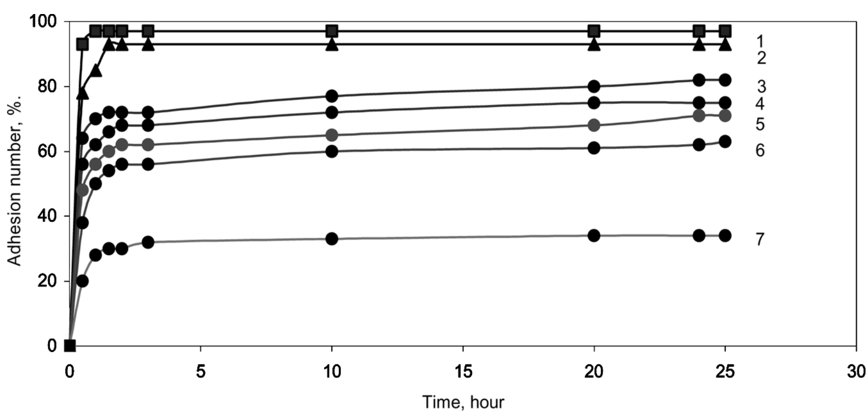

FIGURE 4 Curves of increase of conidiums *Tr. viride* adhesion to metals: **1** – zinc, **2** – copper, **3** – aluminum, **4** – nickel, **5** – titanium, **6** – tantalum, **7** – molybdenum.

TABLE 3 Adhesion Parameters of Conidiums *Trichoderma viride* at $\mathbf{T} = 22°C$ and $\boldsymbol{\omega} = 15000$ revos in Water Medium to Metals Treated in Solvent by **a** – boiling, **b** – at 22°C

		a		b	
No.	Metals	γ_∞, %	$\mathbf{F_{50}}$, %	γ_∞, %	$\mathbf{F_{50}}$, %
1	aluminum	95 ± 5	–	82 ± 5 (88B)	$3{,}0 \cdot 10^{-4}$
2	tungsten	0	$1{,}86 \cdot 10^{-7}$	0	$1{,}9 \cdot 10^{-7}$
3	gold	–	–	25 ± 5	$2{,}3 \cdot 10^{-5}$
4	copper	85 ± 3	$4{,}1 \cdot 10^{-4}$	93 ± 7	$5{,}8 \cdot 10^{-4}$
5	molybdenum	–	–	34 ± 5	$7{,}4 \cdot 10^{-5}$
6	nickel	62 ± 5	$1{,}67 \cdot 10^{-4}$	79 ± 8	$2{,}0 \cdot 10^{-4}$
7	platinum	–	–	53 ± 5	$2{,}2 \cdot 10^{-4}$
8	plumbum	96 ± 2	$7{,}00 \cdot 10^{-4}$	100 ± 1	$7{,}0 \cdot 10^{-4}$
9	silver	–	–	78 ± 5	$5{,}0 \cdot 10^{-4}$
10	tantalum	63 ± 8	$2{,}97 \cdot 10^{-4}$	65 ± 10	$2{,}5 \cdot 10^{-4}$
11	titanium	76 ± 5	$1{,}35 \cdot 10^{-4}$	71 ± 3	$9{,}0 \cdot 10^{-5}$
12	zinc	100	–	97 ± 3	$6{,}7 \cdot 10^{-4}$

700°C and pressure 10^{-4} mm of mercury $\gamma_\infty = 50 \pm 2\%$, and $\mathbf{F_{50}} = 8{,}2 \cdot 10^{-4}$ dyne/cell.

Minimum adhesion is observed on gold, tungsten and molybdenum, the maximum is on zinc, plumbum and copper. Aluminum and titanium take intermediate position.

In the whole the raw of limited number of adhesion is the following: plumbum, zinc, copper, aluminum, nickel, silver, titanium, tantalum, platinum, molybdenum, gold, tungsten; and by decrease of values of force of 50% detachment of conidiums: plumbum, zinc, copper, silver, aluminum, tantalum, platinum, nickel, titanium, molybdenum, gold, tungsten.

Thus, conidiums *Trichoderma viride* reveal low level of adhesion to metals which at experiment conditions are not oxidized and not form oxides at all, for example gold.

The results obtained testify that the main characteristic of adhesion – the force of adhesion is increased in time reaching equilibrium value and is determined by nature of material surface and type of microscopic fungi. The experimental fact of distribution of adhesion forces in dependence on applied stress was also noticed. This effect was studied earlier and probably was caused by both heterogeneity of surface of material and heterogeneity of conidiums by their sizes. The dependences of conidiums *Aspergillus niger* number remained on material surface after centrifugation (adhesion number γ) on angle rate of rotation for polyethylene and cellophane at temperature $\mathbf{T} = 22°C$

and moisture of environment $\varphi = 98\%$ are presented in Figure 5. From the data obtained we calculated forces of 50% detachment of conidiums $\mathbf{F_{50}}$ by formula (2). Results of experiments show that at time of conidiums ageing on polymer surface for 4 and 24 hours the adhesion force $\mathbf{F_a}$ (forces of 50% detachment of conidiums $\mathbf{F_{50}}$) is increased for polyethylene in 2 times, and for cellophane in 1, 5 times, and this fact obviously testifies to significant difference in constants of adhesion forces formation rates for the same system (Tables 1 and 2).

For more detailed investigation of dependences of adhesion number on number of revos $\gamma = \gamma\ (\boldsymbol{\omega})$ (in implicit form it is dependence of adhesion number on applied force $\gamma = \gamma\ (\mathbf{F})$ that represents the distribution by adhesion forces) the derivative of this function was determined for polyethylene $\dot{\gamma}\ (\mathbf{F}) = d\gamma/d\mathbf{F}\ (\mathbf{F})$ (Fig. 6). Dependence presented in Figure 6 is described by equation of the type corresponding to Gauss distribution:

$$\boldsymbol{\varphi}(\mathbf{x}) = \mathbf{A} \exp(-\boldsymbol{\alpha}\,\mathbf{x}^2) \text{ in coordinates } \boldsymbol{\varphi} = \boldsymbol{\varphi}(\mathbf{x}), \qquad (3)$$

where $\mathbf{A}$ and $\boldsymbol{\alpha}$ are constants.

Such distribution may be caused by both heterogeneity of conidiums by sizes and heterogeneity of polymer surface. With this aim the sizes of conidiums A. niger were determined on raster electron microscope "TESLA BS 300". Measured values of conidiums diameters on electron

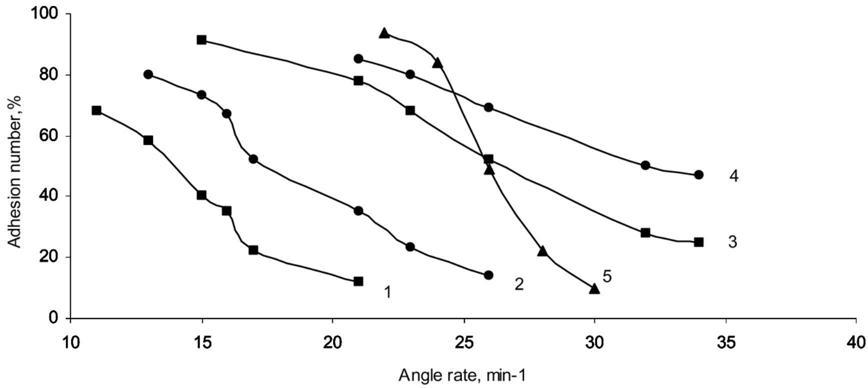

FIGURE 5 Distribution of adhesion number (γ) of conidiums *A. niger* in dependence on angle rate ($\boldsymbol{\omega}$) on polyethylene (1, 2) and cellophane (3, 4) at 22°C and $\boldsymbol{\varphi} = 98\%$. **1** and **3** – time of ageing is 4 hours; **2** and **4** – time of ageing is 24 hours; **5** – distribution of polystyrene particles in dependence on $\boldsymbol{\omega}$ in integral form at the same conditions of adhesion.

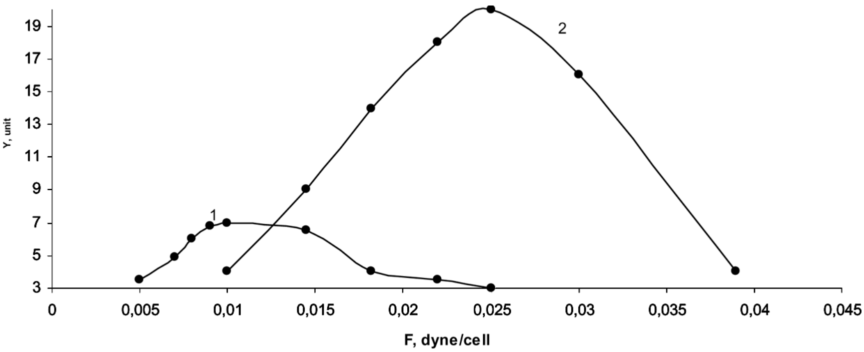

FIGURE 6 Distribution of conidiums *A. niger* by forces of adhesion on polyethylene in differential form. Time of ageing is 24 hours. **2** – distribution of polystyrene particles by adhesion forces in differential form. $\mathbf{T} = 22°C$, $\varphi = 98\%$.

micro-photographs demonstrate significant scattering by sizes (Fig. 7) that should influence on scattering of adhesion force values.

Let show that distribution of conidiums by sizes makes its contribution (i.e. is described by the same function) into distribution of adhesive conidiums by forces.

We present derivatives of adhesion number by radius and force: $\gamma(\mathbf{r}) = d\gamma/d\ \mathbf{r}(\mathbf{r})$; $\gamma\ (\mathbf{F}) = d\gamma/d\mathbf{F}\ (\mathbf{F})$.

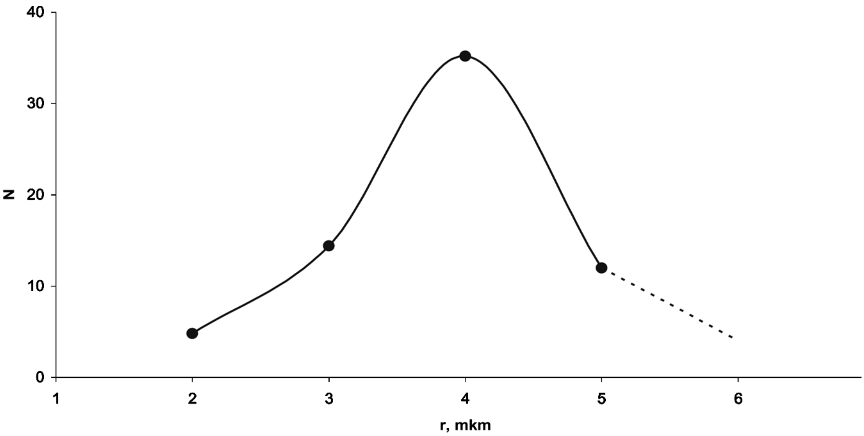

FIGURE 7 Distribution of conidiums *A. niger* by radiuses.

We should prove that from $\gamma = \gamma\ (\mathbf{r})$ it is consequent that $\gamma = \gamma\ (\mathbf{F})$. Let write the distribution by conidiums sizes in the following form:

$$d\gamma/d\mathbf{r} = (d\gamma/d\mathbf{F}) \quad (d\mathbf{F}/d\mathbf{r}) = \mathbf{K}\ d\gamma/d\mathbf{F} \tag{4}$$

For determination of value of $\mathbf{K}$ we present as $d\gamma/d\mathbf{r}$ from Eq. (2):

$$d\gamma/d\mathbf{r} = (3\ \mathbf{F}/\mathbf{r}) \quad d\gamma/d\mathbf{F};\ \mathbf{K} = 3\ \mathbf{F}/\mathbf{r} \tag{5}$$

It is consequent from experimental data (dependence $\mathbf{F} = \mathbf{F}(\mathbf{r})$ and $\gamma = \gamma\ (\mathbf{r})$) that for all values of radiuses ($\mathbf{r}$) of conidiums at functioning force of detachment from $\mathbf{F_1} = 5.5 \cdot 10^{-3}$ dynes per cell up to $\mathbf{F_2} = 2.3 \cdot 10^{-2}$ dynes per cell (Fig. 6) the values in right part of Eq. (5) will be $(3\ \mathbf{F}/\mathbf{r})\ d\gamma/d\mathbf{F} = 4.6 \pm 0.3$, and in left part of Eq. (5): $d\gamma/d\mathbf{r} = 4.7 \pm 0.3$.

In limits of experiment error these values are equal, i.e. distribution of conidiums by sizes is one of the reasons of real distribution by adhesion force. The heterogeneity of support should also contribute into distribution of particles by adhesion forces. For this we should have uniform by sizes particles.

With this aim we carried out experiment with spherical particles of polystyrene with diameter (**d**) 2,8 mcm of "SERVA" firm. We plot kinetic curves of adhesion and distribution of particles by adhesion force by obtained experimental values (Fig. 8).

The kinetic curves and curves of distribution of conidiums A. niger and polystyrene particles are similar, although there are some differences in parameters of adhesion interaction (Figs. 4 and 6).

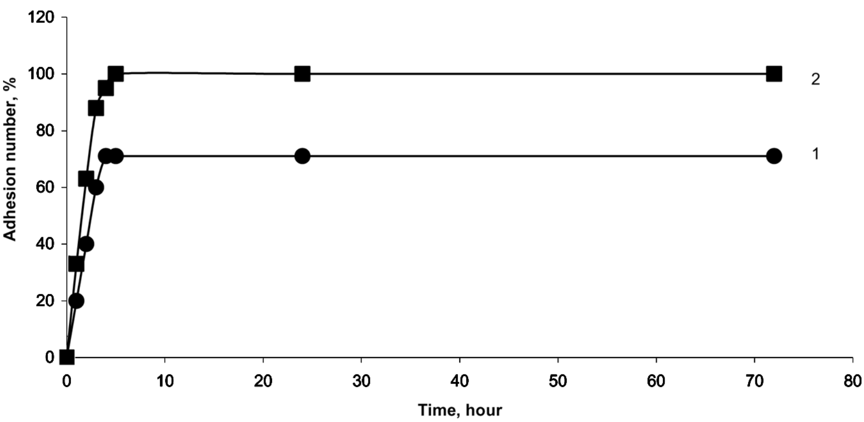

FIGURE 8 Kinetic curves of polystyrene particles adhesion to polyethylene (**1**) and cellophane (**2**) at $\mathbf{T} = 22°C$, $\varphi = 30\%$, $\omega = 15000\,\text{min}^{-1}$.

The constants of adhesion forces formation for polystyrene particles have high values in comparison with conidiums *A. niger*. Moreover, scattering of adhesion force values γ in the case of polystyrene particles is significantly lower.

Results of experiment give the basis to assume that adhesion interaction of system polystyrene particles–polymer is changed in time, distribution of particles by adhesion forces being described by Gauss equation. Consequently principle picture of polystyrene particles and conidiums *A. niger* adhesion to polymer surface is analogous and may be explained for polystyrene particles by the following:

1. increase of contact area of polystyrene particles with polymer surface causes the rise of adhesion force in time at the expense of deformation of surface itself;
2. capillary concentration of moisture in contact zone also promotes adhesion force;
3. energetic heterogeneity of the surface of polymer material causes distribution of polystyrene particles by adhesion forces.

Thus, adhesion of conidiums *A. niger* has stochastic nature caused by their heterogeneity by size and heterogeneity if polymer support, distribution of conidiums by adhesion forces obeys Gauss distribution. Quantitative characteristics of process of microscopic fungi interaction with solid polymer surfaces may serve as estimative criterion of processes of microdestruction of materials.

In fact, the adhesion process also should be determined by parameters of external wall of conidiums (structure of cell wall) and by their ability to evolve various organic substances (exo-ferments, organic acids, etc.) [9,10]. For establishment of correlation between adhesion properties of conidiums micro-destructors of polymer materials and structure of cell wall of cultures of various ages the samples obtained by the method of wash-out from surface of conidiums *Aspergillus niger*, *A. Terreus*, *Penicillium funiculosum*, *Trichoderma viride agar*, deposited on membrane filters "Synpor" (thickness of layer $\sim$0,01 mm) and dried in exiccator over $CaCl_2$ were studied by method of IR-spectroscopy with Fourier analysis.

Concentration of analyzed substances was estinated according to Lambet-Buger-Ber law with the help of the following equation:

$$\mathbf{C} = \mathbf{D}/\mathrm{l} - \mathbf{E}, \tag{6}$$

where **l** – the depth of beam penetration, **E** – extinction coefficient.

For comparative quantitative analysis of IR-spectra the absorption bands significantly changed in intensity in the course of growth process should be chosen. As such band have been selected: 1545–1550 cm^{-1} (amide 2)–deformational vibrations of NH-group, 1275–1280 cm^{-1}–stretching vibrations P=O of phospholipids, 831–835 cm^{-1} – deformational non-planar vibrations of CH-group of α-glycanes.

The values of optical densities and concentrations of analysed substances for four types of conidiums of microscopic fungi are presented in Table 4. In the case of some types of conidiums in the course of growth noticeable quantitative changes in structure of cell walls occur, and for other types significant changes were not observed.

As the example of IR-spectra of surface layer of conidiums Aspergillus niger of various development times are presented in Figure 9. The IR-spectra of 15- and 30-days conidiums are almost completely coincide, that is explained by known factor of metabolic processes decay and reaching of cell quiescent state already after 13–14 days. So, for conidiums of *Trichoderma viride* type the concentration of amides in the surface layer of cell is decreased from 45% (the age is 3 days) down to 26–28% to the moment of 15 days. Weak rise of concentration of phospholipids (from 42 up o 56%) and glycane (from 13 up to 18%) components is observed. Probably synthesis of these substances is continued for more than 3 days.

TABLE 4 Characteristics of IR-Spectra of Conidiums of Fungi of Various Ages

		Conidiums age, days					
		3		15		30	
Microscopic fungi	ν, cm^{-1}	D	C, %	D	C, %	D	C, %
Aspergillus niger	1550–1560	0,01	5	0,08	58	0,07	56
	1275–1278	0,84	71	0,20	34	0,20	34
	831–835	0,78	24	0,14	8	0,15	10
A. terreus	1550–1560	0,10	37	0,07	30	0,08	32
	1275–1278	0,54	47	0,56	54	0,55	50
	831–835	0,48	16	0,50	16	0,52	18
Penicillium funiculosum	1550–1560	0,05	5	0,01	1	0,02	2
	1275–1278	0,57	70	0,36	73	0,35	71
	831–835	0,57	25	0,39	26	0,40	27
Trichoderma viride	1550–1560	0,12	45	0,06	28	0,05	26
	1275–1278	0,48	42	0,38	54	0,39	56
	831–835	0,42	13	0,41	18	0,41	18

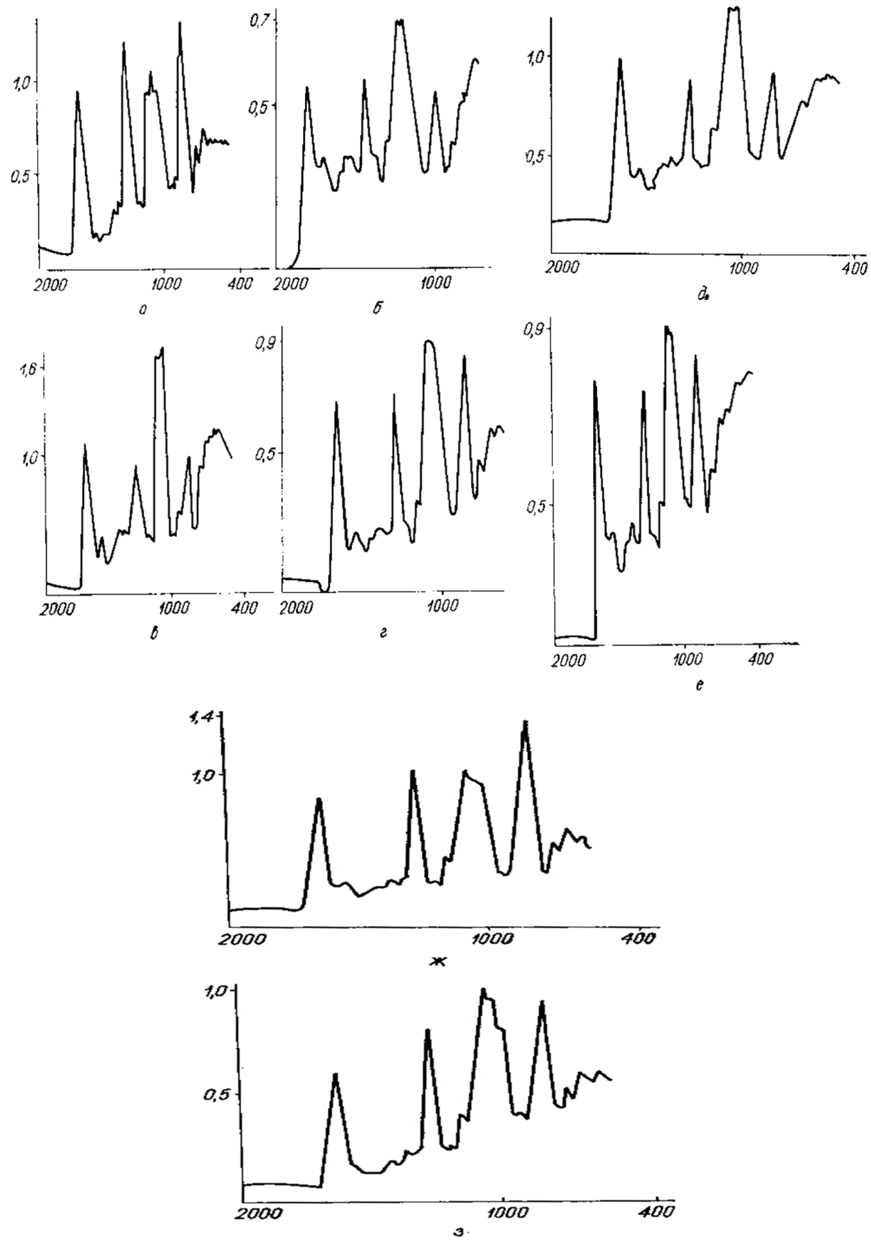

FIGURE 9 IR-spectra of the surface layer of conidiums: **a** – *A. niger*, 3 days; **b** – *A. niger*, 15 days, 30 days; **c** – *A. terreus*, 3 – days; **d** – *A. terreus*, 15 days, 30 days; **e** – *Tr. viride*, 3 days; **f** – *Tr. viride*, 15 days, 30 days; **j** – *P. funiculosum*, 3 days; **h** – *P. funiculosum*, 15 days, 30 days.

When considering IR-spectra of surface layer of conidiums *Penicillium funiculosum* and *A. terreus* it is obvious that there are no significant changes in their spectra. Comparable analysis of spectral characteristics of walls of 3, 15 and 30-days conidiums of these types of microscopic fungi shows that surface layers of these cells are not different from each other in chemical structure. Concentrations of amide, phospholipids and glycane compounds are practically not changed.

Analysis of spectra of surface layer of conidiums *A. niger* of various ages shows that at the stage of growth the concentration of albumin components is increased (from 5 up to 58%) and phospholipids (from 71 down to 34%) and α-gkycanes (from 24 down to 8%) concentrations are decreased. Probably, albumin synthesis in the surface layer of *A. niger* is intensively proceeds for 15 days. In particular this type of conidiums was selected for investigation of their properties of adhesion to polymer materials.

Integral distribution of conidiums *A. niger* of various ages by adhesion forces to polyethylene at temperature 22°C and relative moisture of environment 98% is presented in Figure 10. As it is obvious from the figure curves of 15 and 30 days conidiums are completely coincide. The force of adhesion of these conidiums is as follows: $\mathbf{F}_{50}^{15} = \mathbf{F}_{50}^{30} = (1.1 \pm 0.02)\ 10^{-2}$ dynes per cell, where $\mathbf{F}_{50}^{15}$ and $\mathbf{F}_{50}^{30}$ – the forces of 50% detachment ($\gamma = 50\%$) of 15- and 30-days conidiums correspondingly, that is in 3,4 times higher for adhesion force in the case of 3-days conidiums.

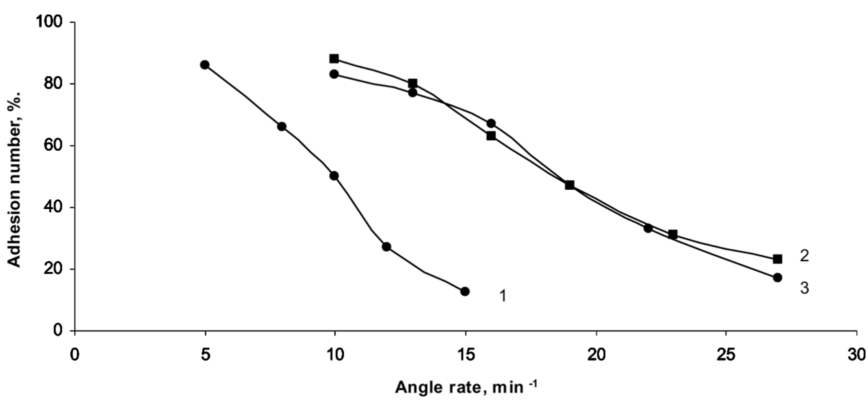

FIGURE 10 Distribution of adhesion number (γ) of conidiums *A. niger* in dependence on angle rate ($\boldsymbol{\omega}$) on polyethylene at $\mathbf{T} = 22°C$ and $\boldsymbol{\varphi} = 98\%$. The time of conidiums ageing on the surface of polyethylene is 24 hours. **1** – s-days conidiums, **2** – 15-days conidiums, **3** – 30-days conidiums.

For 3-days conidiums adhesion force is: $\mathbf{F}^{3}_{50} = (3{,}2 \pm 0{,}2) \cdot 10^{-3}$ dyne/cell.

When comparing data on adhesion of 15- and 30-days conidiums with IR-spectra of their surface layer we see that after 14–15 days of cultivation of fungi stabilization of al parameters, decay of metabolic processes and cell transition into quiescent state are observed.

For conidiums with small sizes (*A. terreus*, *P. funiculosum*) the concentrations of the main components of cell wall practically are not changed, whereas for conidiums with large sizes (*T. viride*, *A. niger*) such changes are observed (Table 4). Obviously, for conidiums of small sizes the surface layer of cell is formed for the time not exceeding 3 days. For conidiums of larger sizes (for example *A. niger*) the process of surface layer formation is not stopped by the moment of 3 days and continued for longer time. At the first moment of adhesion the intensive evolving of albumin macromolecules occur [11]. For the case of *A. niger* conidiums the part of albumin component is increased in the course of cell growth and their adhesive interaction is also increased.

CONCLUSION

Experimental material allows assuming that adhesion force of conidiums of microscopic fungi in the course of their growth is changed differently. It depends on change of albumin components concentration in the surface layer of cell having mosaic structure. In those cases when these changes are significant (predominantly for conidiums of large sizes) the increase of force of adhesion interaction with surfaces occurs and if there are no clear changes (predominantly for conidiums of small sizes) the adhesion force is not changed.

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