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Influence of Biological Factors in Aging of Polymeric Materials Under Natural Environmental Conditions

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Two copolymers were investigated for long-term influence of environmental factors. The polymers were exposed in the open air, in a special containers kept in the open air and in damp cellar. Microbiological evaluation of the exposed materials showed that these copolymers were contaminated by micromycetes. Scaning electron microscopy allowed to observe abundant fungal growth with well developed hypha, spore producing structures and formed colonies. As these polymers are hardly available for fungi, their development was possibly determined by outer nutritional and energy sources – pollutants settled on the materials. The heaviest contamination of the materials was noticed in cellar conditions where constant high humidity prevailed. IR spectroscopy of the materials showed that tetrafluorine ethylene and hexafluorine propylene copolymer kept in the open air and containers did not undergo structural changes. Meanwhile, IR spectrum of the sample exposed in cellar, showed high changes in structure. The results allow to conclude that microorganisms could have an effect on materials deterioration and destruction processes.Structural changes of the copolymer of tetrafluorine ethylene and vinylidene fluoride were observed after exposure of its samples in the open air, where all environmental factors influenced, and in the cellar, where combined effect of humidity and microorganisms took place.

Kyewords: polymers, microbial contamination, fungi, IR spectra, polymer structure.

1. INTRODUCTION

Polymeric materials are used in various fields of human activities. The physical state of these materials and durability of their exploitation depend greatly on their exploitation conditions. In the natural environment materials are affected not only by physical but also by biological factors, i.e. microorganisms [1 – 3].

Many factors influence the rate of ageing and degradation: temperature, light, moisture, the properties of the polymeric substrate – wetability, surface smoothness, chemical bonds and molecular weight, etc. [4]. Microorganisms can accelerate change of appearance of the materials, structural changes and limit their use in many fields. Micromycetes are one of the most aggressive microorganism groups able to deteriorate materials of various compositions [5 – 8].

Polymeric materials usually consist of one or several polymers, and additionally of fillers, pigments and dyes, softeners and plasticizers, stabilizators and antioxidants, hardeners, and lubricants etc. Many of materials of technical application are made from synthetic polymers, which are usually resistant to environmental factors. Those polymers are polyurethanes, fluorine plastics, phenol plastics, polyethylene, terephtalates, and silicon organic plastics, etc. [2, 9]. Nevertheless, these materials also suffer from environmental factors, including microorganisms, and can undergo changes in their appearance and structure.

The aim of the investigation was to evaluate the resistance of materials to microorganisms under different exposure conditions, to find out micromycetes deteriorating these polymers and to determine structural changes of the materials after long-term exposure to environmental factors.

2. EXPERIMENTAL

2.1. Exposure conditions

The Mycological station was arranged in Neringa (Juodkrantė, Lithuania) on the Curonian Spit. The station was located 500 m from the cost of the Curonian Lagoon and covered with three-layer vegetation.

The long-term exposure of materials was carried out in accordance with the standard GOST 9.906-83 [10]. The materials were exposed in three different ways:

1. In the open air where the materials were affected by all climatic factors of maritime climate (high air humidity (72 – 90 %), temperature (average in winter – –2.5 °C, summer – +17 °C), direct solar radiation and precipitation). Samples of materials were held on support racks, positioned at 30° to the horizontal;

2. In mycological containers of dimensions of 1.0×0.75× ×0.55 m, with sloping roofs and four sides having slits to permit an exchange of ambient air. The containers were positioned 0.2 m above ground. Materials were free hanging in the containers. The materials were protected from direct solar rays and precipitation, but relative air humidity, temperature and natural ventilation were not regulated;

3. In a damp, non-heated cellar, where relative humidity (80 – 97 %) and temperature (6 – 16 °C) were not regulated and altered very little during all the seasons of the year. The materials were free hanging on the support racks.

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The investigation in the Mycological station has been carried on a variety of polymers of different formulations. This work shows results of investigation on fluorine plastics – a copolymer tetrafluorine ethylene and hexa-fluorine propylene and a copolymer of tetrafluorine ethylene and vinilidene fluoride, which were exposed over 10 years.

2.2. Evaluation of fungal deterioration of materials

During the exposure, each material was inspected visually to evaluate fungal growth. Samples of the polymeric materials were also examined using scanning electron microscopy (JEOL JES–5600).

Fungi were isolated from the polymeric materials on malt agar by direct isolation or by washing of a sample with sterile water. Fungi were identified according their morphological properties.

2.3. Investigation of structural changes of polymeric materials using IR spectroscopy

The method of infrared spectroscopy allows to assess the chemical change on surfaces of polymeric materials occurring due to influence of different factors. To determine the influence of long-term exposure in natural conditions on materials, IR spectra were conducted on spectrometer Specord 75IR within the range of 4000-400 cm^{-1} in transmittance mode.

3. RESULTS AND DISCUSSION

The results of our investigation showed that synthetic fluorine polymeric materials of various formulations were contaminated and deteriorated by microorganisms, depending on exposure conditions and materials properties.

3.1. Development of micromycetes on materials

Microbiological investigation revealed that surface of the materials tested was contaminated by microscopic fungi. Fungal propagules on the materials were present under all exposure conditions, meanwhile, the highest contamination was observed on the materials exposed in cellar. Taking into account the fact that temperature fluctuations in the cellar were minimised and high humidity prevailed, conditions for development of fungi were favourable. Our investigation shows that the most intensive contamination and biodedeterioration was caused by species of fungi of these genera: *Aspergillus, Penicillium, Acremonium, Alternaria, Arthrinium, Cladosporium, Chaetomium, Humicola, Aureobasidium, Ulocladium, Olpitrichum, Fusarium, Phoma* and *Trichoderma.* Particularly high contamination on the polymer surfaces was noticed by *Aspergillus* and *Penicillium* fungi. Fungi belonging to *Dematiaceae* family prevailed on the materials exposed in the open air.

Not only spores settled on the materials were found, but moreover, all stages of fungal development were noticed: abundant growing hypha (Fig. 1 a, 2 a), formation of colonies (1 b) and spore-producing and bearing structures (Fig. 1 c, 2 b).

Growth of microorganisms on synthetic materials is possible when a nutritive source is available. Some polymeric materials serve for microbial nutritional and energy requirements. Materials containing plasticizers, softeners, fillers, lubricants, and other additives could be more easily used for utilisation by microorganisms [11 – 13]. The investigated materials do not contain such components, so nutritional and energy sources for microorganisms were, most likely, pollution and deposits on the surface of materials.

Possibility to use an environmental carbon source enable microorganisms to attack a polymer more successfully [14]. During the long-term exposure, the materials surface was covered by dust, pollen and various organic debris and this could have served as nutritional source for fungi.

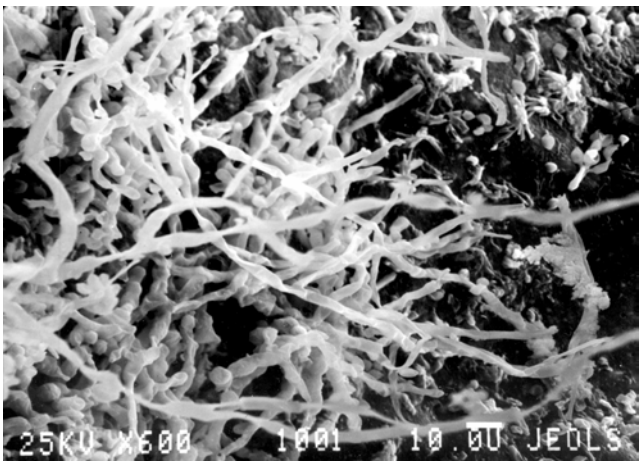
Materials surface smoothness is important for attachment of fungal spores. Fungi contaminate more easily materials with a rough or damaged surface [15]. The material consisting of tetrafluorine ethylene and vinylidene fluoride is composed of fibres, and this also helped for establishing of microorganisms. Fig. 2 c shows adhesed fungal spores on polymer fibres. Moreover, materials containing threads or fibres can serve as capillaries for distribution of moisture and chemical elements within material and contribute to fungal penetration into the material [2].

Susceptibility of such polymeric materials to microorganisms become more evident when they are affected by atmospheric factors. The polymers during their exposure were affected by humidity, solar radiation, ozone, acidic rains, and wind, etc. Constantly influenced by such factors, materials surface and deeper layers can undergo mechanical, physical and chemical changes. This can result in occurrence of microcracks, in which microorganisms can establish [9]. Influence of environmental factors on fluorine polymers, resulted in occurrence of spots, reduced transparency of the film and settled pollutants.

3.2. Analysis of IR spectra of the materials after the exposure

Using infrared spectroscopy, some changes in the polymer structure occurred during long-term exposure were noticed. The first material, film – copolymer consisting of tetrafluorine ethylene and hexafluorine propylene. Polytetrafluorine ethylene $(–CF_2–CF_2–)_n$ pos-sesses rather a simple structure and, thus, not complicated IR spectrum showing several intensive main oscillation bands. Meanwhile, the structure of the copolymer is more complicated, and consequently its spectrum reflects interaction of molecular chains, and valence and deformative oscillations of macromolecules of both polymers. Spectra of copolymers reflect a composition of a copolymer and distribution of comonomer blocks in the copolymer. Thus, interpretation of copolymer spectra basing only on the sum of spectra of its heterogeneousness is improper. Ratio of component amounts also influences copolymer crystallisation and an orderliness degree of chains.

After the long-time exposition in the open air and in a container, spectra of this copolymer did not showed



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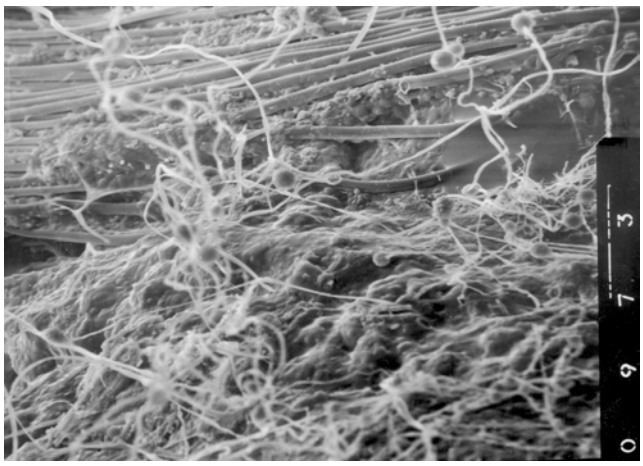

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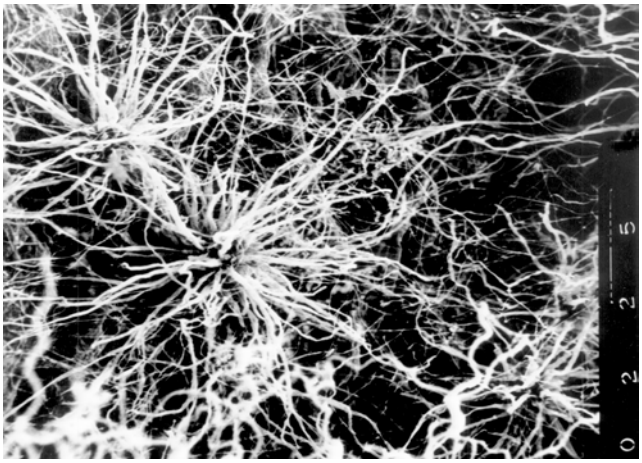

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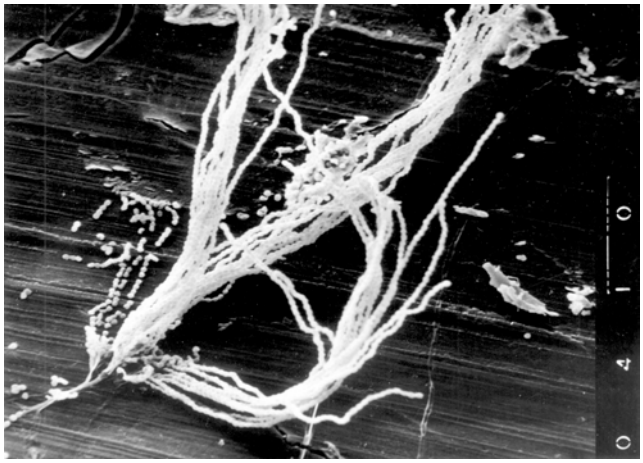

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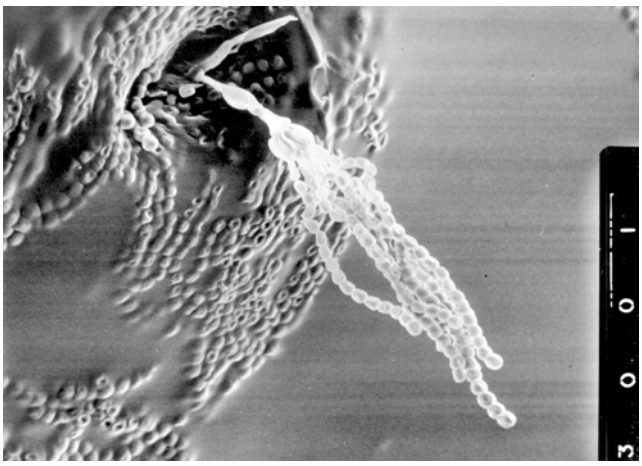

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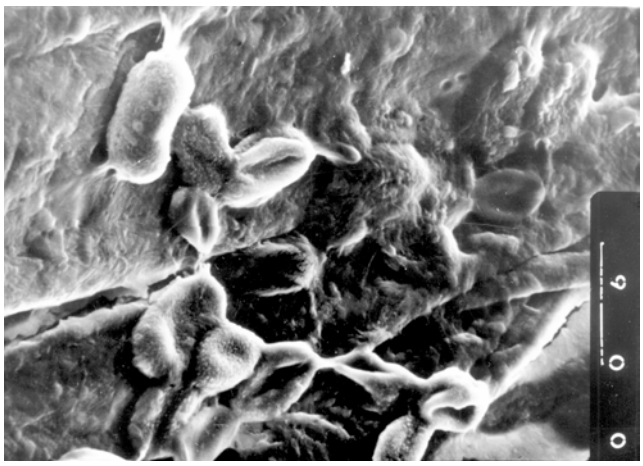

c

Fig. 1. Growth of fungi on the film made of tetrafluorine ethylene and hexafluorine propylene. The photos show well developed hypha (a, ×600), formation of new fungal colonies (b, × 200) and spore-bearing structures (c, ×600)

Fig. 2. Growth of fungi on the copolymer of tetrafluorine ethylene and vinylidene fluoride: abundantly growing hypha, (a, ×300), spore-bearing structures, (b, ×300) and attached spores to material fibres, (c, ×3000)

changes in comparison with the control sample. Nevertheless, a spectrum of the sample kept in the cellar shows deep changes. There are two new evident peaks at 3450 and 2950 cm^{-1} wave number. The 3450 cm^{-1} band is attributed to OH group valence oscillations (Fig. 3). The occurrence of this group could have been conditioned by absorbed moisture in the polymer. Under the open air and container conditions, humidity was not so constant as it was in the damp cellar, and OH oscillations in spectra of samples from these expositions were not detected.

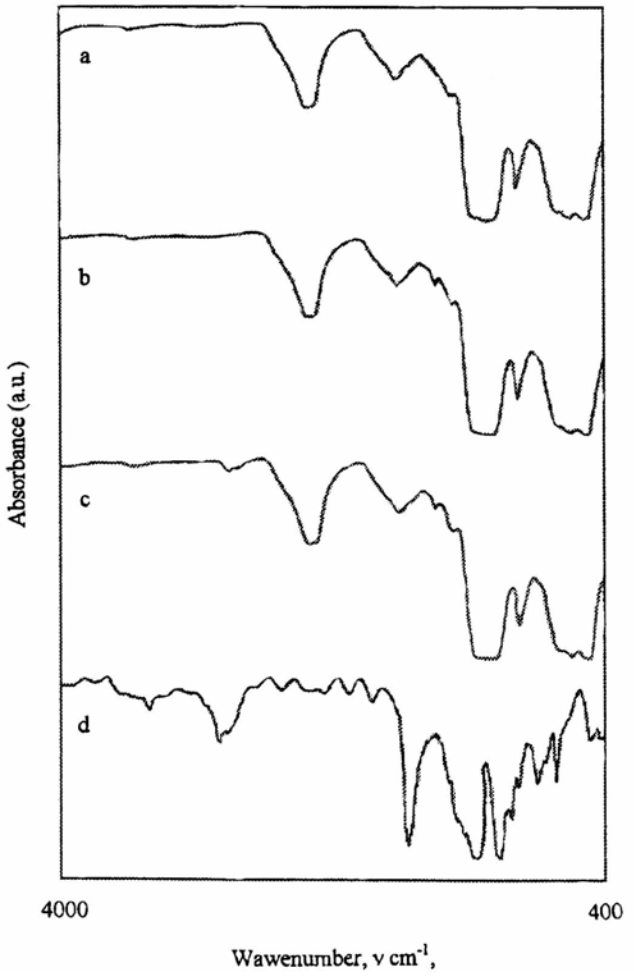

Fig. 3. IR spectra of the film made of tetrafluorine ethylene and hexafluorine propylene: a is the control sample and samples after exposure: b is in the open air, c is in a container, d is in cellar

The band 2950 cm^{-1}, showing CH_3 valence oscillations, can occur due to replacement of F atoms with hydrogen in CF_3 group. The band 2350 cm^{-1} dissappeared, indicating valence oscillations of CC bond.

More evident changes are observed in the region of shorter waves. Broad CF_2 oscillations bands (625, 638, 676, 1150, 1210, 1379 and 1792 cm^{-1}) and some small ones disappeared, and new CF_2 dominant bands 855, 980, 997 and 1070 cm^{-1} occurred. The first three bands should be attributed to polyhexafluorine propylene, as polytetrafluorine ethylene does not absorb waves at 900 – 1000 cm^{-1} region and does not have oscillation bands at this zone. Only bands of 516, 729, 1242 and 1379 cm^{-1} remain, which correspond to CF_2 and CC valence oscillations. The reason of disappearance of 2390 (CC), 1792 (CF_2) and 1450 (CF_2, CC) cm^{-1} bands in the spectrum of the sample kept in cellar could be explained by the nature of these bands: they are combinative bands, which occur due to interaction of valence oscillations of some molecular groups. It should be mentioned that not only constant humidity but also fungal metabolites secreted by fungi, which developed well under cell conditions on the polymer, could have influenced frequency of valence oscillations of broken groups and macromolecules. Due to interactions of such groups, oscillation frequency of combinative bands also changes.

Humidity causing OH valence oscillations can not affect structural changes of chemically resistant polyterafluorine ethylene and polyvinylidene fluoride copolymer. Since the influence of atmosphere and other aggressive factors is eliminated in cellar, the main structural changes observed in the spectrum are possible due to microbial action. Bands 850 and 778 cm^{-1} indicate that an amorphous phase has occurred which could have been caused only by intense chemical influence.

The fact that biological damage to materials may significantly affect its physical integrity was reported also by other authors [16]. Since fungi can utilise surface contaminants and products of their own metabolism, they release aggressive metabolites such as organic acids and grow deeper into the material, resulting in enlargement of the damaged area and thus enhancing its degradation. The copolymer consisting of tetrafluorine ethylene andvinylidene fluoride suffered mostly in open air conditions (Fig. 4).

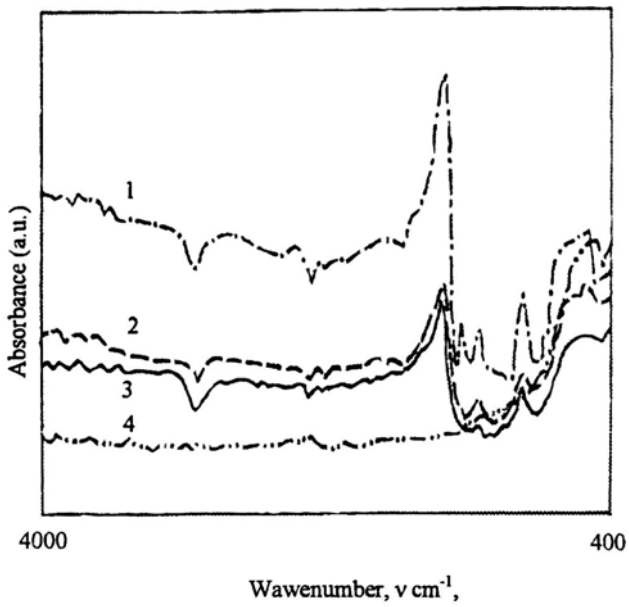

Fig. 4. IR spectra of the copolymer made of tetrafluorine ethylene and vinylidene fluoride: 3 is the control sample and samples after exposure: 1 is in cellar, 2 is in a container, 4 is in the open air

The spectrum of the sample shows that the band 420 cm^{-1} remains, which can be attributed to valence oscillations of CO group. As this band is not so evident in other spectra of this material, it could be supposed that the tetrafluorine ethylene and vinylidene fluoride copolymer was affected by aggressive environmental factors, which

caused oxidative processes in the upper layer of the material and the band of CO group occurred. The spectrum of the sample exposed in cellar also differs from the spectrum of the control sample and this indicates that the materials underwent significant change. The bands 1379 (CF), 1280 (CF_2), 1148 (CH_2), 1148 (CH_2). 535 (CF) and the combinative band 932 cm^{-1} (CF_2) became evident. These changes could have resulted from complex humidity and microbial action.

Thus, the results obtained allow to suppose that biocorrosion caused by microorganisms took place, and this phenomenon should be evaluated during exploitation and long-term storing of polymeric materials and their products.

4. CONCLUSIONS

The investigation of resistance of the fluorine polymers to environmental factors showed that the tested materials were attacked by micromycetes *Aspergillus, Penicillium, Acremonium, Alternaria, Arthrinium, Cladosporium, Chaetomium, Humicola, Aureobasidium, Ulocladium, Olpitrichum, Fusarium, Phoma,* and *Trichoderma.* Fungi were able to grow on the materials and develop reproductive structures. The most favorite conditions for fungal growth were in cellar.

IR spectroscopy of the tetrafluorine ethylene and hexafluorine propylene: copolymer revealed that structural changes occurred in the polymer after long- term exposure in cellar conditions. These changes could be related to the fungal development and their aggressive metabolic products. Structural changes of tetrafluorine ethylene and vinylidene fluoride propylene copolymer also took place. The most evident changes were noticed in samples kept in the open air, where all environmental factors influenced, and in cellar, where high humidity and microbiological action took place.

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