

Physical and Chemical Aspects of Long-Term Biodeterioration of Some Polymers and Composites

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ABSTRACT: A biodeterioration study was performed on synthetic polymeric materials including homogenous film made from poly(tetrafluorine ethylene), copolymer film made from tetrafluorine ethylene and perfluoromethyl vinyl ether, vulcanized rubber containing natural caoutchouc, and vulcanized rubber, the main component of which was synthetic butadiene nitrile caoutchouc. The materials were exposed for 12 years to the open air, in mycological containers, and in a cellar in maritime climate conditions: air humidity 72%–90% and seasonal average temperature of 17°C in summer and –2.5°C in winter. The studies of optical and electron microscopy revealed that microorganisms were able to develop not only on the surface of the materials but also to penetrate inside into deeper layers. The fungi that produced the most intensive deterioration in the fluorine polymers and vulcanized rubbers belonged to the *Alternaria*, *Aspergillus*, *Aureobasidium*, *Cladosporium*, *Penicillium*, *Oidiodendron* and *Trichoderma* genera. The fungi *Aspergillus fumigatus*, *A. niger*, *Aureobasidium pullulans*, and *Trichoderma viride* produced the most intensive deterioration in the fluorine films, whereas *Alternaria tenuissima*, *Cladosporium herbarum*, *C. sphaerospermum*, and fungi of the *Oidiodendron* genus were widespread on vulcanized rubbers. Fungi of the *Aspergillus* and *Penicillium* genera prevailed on both fluorine films and rubbers exposed in a cellar. Infrared spectroscopy indicated that the structures of poly(tetrafluorine ethylene) and the copolymer of tetrafluorine ethylene and perfluoromethyl vinyl ether did not change after the 12-year exposure; only insignificant changes in surface morphology were observed by optical microscopy. Vulcanized rubber made both from natural and from synthetic caoutchouc exposed for the same length of time showed rather evident changes in appearance and structure. X-ray graphical analysis revealed that new crystallization of the caoutchouc and a possible change in chemical composition of the fillers had occurred.

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Keywords: biodeterioration, polymeric materials; fungi; X-ray analysis, IR spectra

INTRODUCTION

Large amounts of synthetic polymeric materials of various formulations are produced and used in various spheres of

human activity; when finally discarded, they enter the environment as pollutants. From polymeric materials, derivatives of low molecular mass (residuals, plasticizers, solvents, and products of destruction) can migrate out of the materials. So, the toxicological properties of every polymeric material can be characterized by the peculiarities of its leaching components and of derivatives formed under the influence of the environment.

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Destruction of discarded or exploited polymeric materials can occur rather differently in different conditions. Climatic conditions of a geographical zone, microbial diversity under those conditions, and anthropological factors influence the processes of the destruction of materials (Fleming, 1991; Lugauskas et al., 1997). Many materials used in technical application are made from synthetic polymers, which are usually resistant to environmental factors, and when they are discarded into the environment, they become pollutants that degrade very slowly or remain persistent for many years. Such materials include vulcanized rubbers made from natural and different synthetic caoutchoucs, polyurethanes, phenol plastics, polyethylene, polyamides, terephthalates, fluorine plastics, and silicon organic plastics (Williams, 1982; Gu et al., 1994, 1996; Lugauskas et al., 1997).

The participation of microorganisms, especially fungi, in deterioration and degradative processes has been shown in several studies (Moriyama et al., 1993; Mitchel et al., 1996; Wilimzing and Bock, 1996; Gu et al., 1997; Little et al., 2001). Nevertheless, there has been insufficient evaluation of the effect of microorganisms and the metabolites they produce on polymeric materials. Microorganisms and their metabolic products together with environmental pollutants significantly influence the occurrence of structural changes in materials. Homogenous materials made from large molecular components usually are more resistant to microbial deterioration, whereas the resistance of multicomponent materials decreases when the main component has a low molecular mass, and additives such as plasticizers are included (Williams, 1986; Webb et al., 1999).

Microbiological destruction of polymeric materials is determined by variety of factors. The surface structure of a material is very important for the first contact between a microorganism and the material (Whitney, 1993; Verran et al., 2000). Important criteria of material susceptibility are surface tension, wettability, and being moisture proof (Czchowski and Rapp, 1990; Shneider et al., 1992; Jaskelevičius et al., 2002). How intense further development of a microorganism is depends greatly on the chemical composition of the material (Costerton et al., 1991).

The susceptibility of hydrophobic polymer materials to microorganisms becomes evident when they are affected by other factors. During exploitation, polymeric materials can be affected by various aggressive environmental factors including acid rain, ozone, moisture, ultraviolet rays, solar radiation, and various chemical substances. Under such conditions, the physical and chemical properties of materials change, their resistance to mechanical factors weakens, and surface polarity and wettability increase. This leads to the formation of microcracks, in which microorganisms begin to develop, and destruction processes intensify. Thus, biological damage to materials may significantly affect their physical integrity (Gu, 1998).

Investigation of the resistance or susceptibility of materials of a particular composition to attack by microorganisms is important as a part of an assessment not only of the suitability of those materials for a particular application, but also their ability to degrade after being discarded (Mayer and Kaplan, 1994; Whitney, 1996).

The objectives of the current work were to investigate possible microbial influence on the deterioration processes of polymeric materials under different conditions, to identify the micromycetes most actively causing deterioration of the materials, and to assess the peculiarities of deterioration of the materials.

MATERIALS AND METHODS

Materials

In this study four polymeric materials exposed under natural conditions for 12 years were analyzed: a homogenous film made from poly(tetrafluorine ethylene), a film made from tetrafluorine ethylene and perfluoromethyl vinyl ether, a vulcanized rubber, the main component of which was natural caoutchouc, and a vulcanized rubber whose main component was synthetic butadiene nitrile caoutchouc.

Exposure Conditions

A Mycological station was established in Neringa (Juodkrantė, Lithuania) on the Curonian Spit, a narrow peninsula separating the Curonian Lagoon from the Baltic Sea. The station was 500 m from the coast of the Curonian Lagoon and covered with three-layer vegetation.

Long-term exposure of materials was carried out in accordance with the standard GOST 9.906-83 (1984). The materials were exposed to three variant conditions:

1. In the open air where the materials were affected by all climatic factors of a maritime climate: high air humidity (72%–90%), temperature (average in winter -2.5°C , in summer 17°C), and direct solar radiation and precipitation. Samples of materials were held on support racks, positioned at 30° to the horizontal.
2. In mycological containers ($1.0 \times 0.75 \times 0.55$ m) with sloping roofs and four slatted sides having slits to permit an exchange of ambient air. The containers were positioned 0.2 m above the ground. Materials were free-hanging in the containers and protected from direct solar rays and precipitation; however, relative air humidity, temperature, and natural ventilation were not regulated.
3. In a damp, unheated cellar in which relative humidity (80%–97%) and temperature (6°C – 16°C) were not regulated and altered very little during different seasons in a year. The materials were free-hanging on the support racks.

Evaluation of Fungal Deterioration of Materials

During exposure, each material was inspected visually to evaluate fungal growth. Samples of the polymeric materials were examined using scanning electron microscopy (JEOL JES-5600) when contamination on the material surface was detected.

Fungi were isolated from the polymeric materials by direct isolation or by washing of a sample with sterile water. Plastic coupons (5.0 × 5.0 cm) were placed into 250-mL flasks containing 100 mL of sterile distilled H₂O. The flasks were shaken, and dilution series were prepared from each flask. The obtained microbial suspensions were plated on Malt agar (Difco), and grown fungi were isolated in pure cultures. Fungal strains were identified on the basis of their morphological properties. Fungi from the materials were isolated 3 times a year, which showed the species found most often (spreading frequency >30% on tested samples of a particular material).

Investigation of Structural Changes in Polymeric Materials

We investigated the polymeric materials with an Intel QX microscope in reflected light with 60× and 200× magnifications (dimensions of the *X* axis of the pictures were 3000 and 1000 μm, respectively). The fractal dimensionality of the obtained scenes was evaluated using the Image J program (version 1.29). An increase in fractal dimensionality was interpreted as a complicated scene of different elements on the surfaces of the materials. The appearance of a high number of elements on the surfaces showed high biodeterioration of a material and appearance of corrosion centers.

The infrared spectroscopy method allowed the assessment of chemical changes on the surfaces of the polymeric films as a result of the influence of different agents. To study the influence of long-term exposure on the materials, IR spectra of fluorinated films were recorded with a Specord 75IR spectrometer operating in the range of 4000–400 cm⁻¹ in transmittance mode. IR spectra of vulcanized rubber samples were not obtained because this method is unacceptable to use with them.

Wide-angle X-ray diffraction (WAXD) patterns were recorded on a diffractometer DRON 3.0 (Sankt Peterburg, Russia). A nickel-filtered Cu-Kα X-ray beam (wavelength = 0.15418 nm) was used as the source. Diffraction intensity was measured in the 2θ range of 10–50° at a scanning speed of 1° min⁻¹. The power of the source was tuned to 30 kV/30 mA.

RESULTS AND DISCUSSION

Growth of Microorganisms on Polymeric Materials

Fluorine polymers are known as highly resistant materials and, discarded, are hardly degradable (Hendricks and Lau,

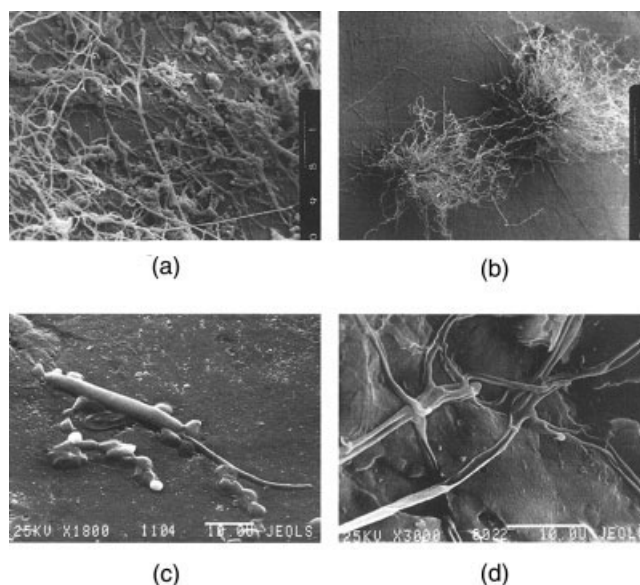


Fig. 1. Development of fungi on polymeric materials and their induced deterioration: (a) film made from poly(tetrafluoroethylene) in the eighth year of exposure to the open air (magnification ×500), (b) film made from tetrafluoroethylene and perfluoromethyl vinyl ether in the fourth year of exposure in a mycological container (×550), (c) vulcanized rubber containing natural caoutchouc in the second year of exposure to the open air (×1800), and (d) vulcanized rubber containing synthetic butadiene nitrile caoutchouc in the 7th year of exposure to the open air (×3000).

1996; Smith and Babb, 1996; Goodwin and Mercer, 1997; Lee et al., 1999; Kim et al., 2003). Their main negative influence on the environment is that they accumulate as pollutants. Nevertheless, it should be mentioned that their monomeric components can exert a toxic effect, as shown by the cytotoxic effect that tetrafluoroethylene and fluorinated vinyl ethers have been found to have on warm-blooded animals (Knöfler and Neupert, 1985; Keller et al., 2000; Altuntas et al., 2003).

Our investigation showed that the influence of environmental factors on materials made from fluorine polymers resulted in their having reduced transparency, the presence of spots, and pollutants settled on the surface. The films, especially those exposed to the open air, were covered by dust of inorganic and organic origins, and this enhanced the establishment and development of fungi, as the pollutants could have served as a nutrition source. On the surface of the poly(tetrafluoroethylene) film, an area hardly available for microbial nutrition, contamination by micromycetes occurred, too. Gradually the film was covered by fungal hypha with spore-bearing structures. Figure 1(a) shows deterioration of the material by a fungal consortium in the eighth year of exposure to open air.

Samples of a copolymer made from tetrafluoroethylene and perfluoromethyl vinyl ether also were contaminated by fungi. In the fourth year of exposure clearly formed small

colonies could be detected [Fig. 1(b)], and, later, spread hypha with spores or even a dense mycelium were observed on samples exposed to all variants. It is more likely that fungi developed on the surface of these films because of outside deposits on the materials. Previously, it was reported that the use by microorganisms of other environmental carbon sources may enable them to attack plastics more vigorously (Whitney, 1996).

Fungi isolated from these films belonged to various genera and species. On the surface of the poly(tetrafluorine ethylene) film exposed to the open air, fungi of the *Aspergillus*, *Aureobasidium*, *Trichoderma*, *Cladosporium*, *Penicillium*, and *Scytalidium* genera prevailed (Table I). From the film kept in a mycological container, fungi of the *Penicillium* genus were most frequently isolated, with fungi of the *Alternaria* and *Mucor* genera also distributed. *Aureobasidium pullulans* and *Trichoderma viride*, which were found on the samples in the open air, also were detected under these exposure conditions. The film exposed in a cellar had been deteriorated mostly by fungi of the *Penicillium*, *Aspergillus*, and *Oidiodendron* genera. The copolymer of tetrafluorine ethylene and perfluoromethyl vinyl ether exposed to the open air was contaminated mostly by fungi of the same genera as the poly(tetrafluorine ethylene) film, but the species composition varied. In addition, *Alternaria alternata*, *Acremonium strictum*, and *Mucor racemosus* were among the dominant species. The material kept in a mycological container was contaminated mostly by the same fungal species that prevailed on the material in the open air. Fungi of the *Aspergillus* and *Penicillium* genera clearly dominated on the surface of the film exposed in a cellar, as well as on the poly(tetrafluorine ethylene) film.

From a toxicological point of view, vulcanized rubbers that occur in nature cause problems, as leaching of various ingredients of these materials take place (Bowman, 1994; Handreck, 1996). The toxicological impact of compounds of the disulfide class, including thiuram, which was used as a vulcanization accelerator in these rubbers, has been reported in many studies. Thiuram disulfides (TDs) can have cytotoxic effects, causing mammalian cell necrosis and apoptosis (Nobel et al., 1995; Cereser et al., 2001). TDs also inhibit enzymes (caspases, aldehyl dehydrogenase, dopamine β hydroxylase, and cytochrome P-450 2E1 (Vallari and Pietruszko, 1982; Serio et al., 1984; Nobel et al., 1997; Kharasch et al., 1999). It was reported that TDs cause an irreversible mitochondrial injury as a result of the induction of the mitochondrial permeability transition (Chavez et al., 1989; Jay, 1991; Balakirev and Zimmer, 2001). In addition, tetramethyl thiuram disulfide has been found to have a mutagenic effect (Korhonen et al., 1983; Rannung and Rannung, 1984). Toxic effects by some other components of the tested rubbers—dibutylphthalate, paraffin-based oils, and naphtenic oils—as well as teratogenic effects of these oils also have been reported (Korhonen et al., 1983).

Our investigation showed that microorganisms colonized both natural and synthetic-based butadiene nitrile caoutchouc rubber. During exploitation and storage, both types of rubber were affected by light, ozone, chemical, physical, and mechanical factors, and this led to loss of primary material properties and changed structure and surface integrity (Lugauskas et al., 1997). After such changes, man-made materials become more suitable for contamination and development of microorganisms. Fungal propagules establish more easily on rough or microcrack-containing surfaces. Figure 1(c) shows the initial fungal growth on the material containing natural caoutchouc in the second year of exposure. Fungi were able to use nutrition debris that had accumulated on the surface or the material's components, allowing them to develop and spread widely onto surfaces and to penetrate deeper into the material [Fig. 1(d)]. Rubber is not an easily available substrate; therefore, not every microorganism that settles on a material can develop and grow. Microorganisms form communities, whose members often have different functions. One member of a community of microorganisms may inactivate a biocide in the plastic formulation, whereas others might degrade one or more components of a material (Little et al., 2001).

On the surface of both types of rubber exposed to the open air, fungi of the *Cladosporium*, *Oidiodendron*, and *Trichoderma* genera prevailed (Table I). Greater diversity of the dominating fungal species was detected on the material containing natural caoutchouc than on the synthetic rubber. The rubber samples kept in mycological containers were mostly deteriorated by fungi of the *Cladosporium* genus: *C. cladosporioides*, *C. herbarum*, and *C. sphaerospermum*. Other dominating fungi were of various genera and differed between the materials. The materials kept in a cellar were contaminated mostly by fungi of the *Aspergillus* and *Penicillium* genera.

The biodegradability of rubber greatly depends on the availability of its components to microorganisms. It was found that the main component of rubber most susceptible to microorganisms is natural caoutchouc, which can be completely utilized as a source of carbon and energy (Gu, 2003). Meanwhile, synthetic caoutchoucs have different degrees of susceptibility; one type that is rather susceptible is butadiene nitrile caoutchouc (Williams, 1982; Mahlis and Fediukin, 1989; Lugauskas et al., 1997). Such composite materials also contain additives, which can support biodegradation processes. Material based on synthetic caoutchouc contains the plasticizers stearine and dibutyl sebacinate ester, which can serve as nutritive sources for microorganisms (Nieder et al., 1990; Williams, 1996; Lugauskas et al., 1997).

Particular additives, such as thiuram disulfide, possess biocide properties and are expected to reduce the rate of degradation (Cole, 1990; Gillat, 1991; Hayase et al., 1991; Borgmann-Strahsen and Bessems, 1994). Nevertheless, the protection provided by a biocide may be transient, as it can

TABLE I. Dominant fungal species on fluorine films and vulcanized rubbers exposed in the open air, in mycological containers, and in a cellar

Materials	Dominant Fungal Species on Polymeric Materials Exposed to Different Conditions		
	In the Open Air	In Mycological Containers	In a Cellar
Poly(tetra fluorine ethylene) film	<i>Aspergillus fumigatus</i> Fresen. <i>Aureobasidium pullulans</i> (de Bary) G. Arnaud <i>Cladosporium cladosporioides</i> (Fresen.) G. A. de Vries <i>Oidiodendron echinulatum</i> G. L. Baron <i>P. brevicompactum</i> Dierckx <i>Penicillium cyaneum</i> (Bainier et Sartory) Biourge <i>Scytalidium lignicola</i> Pesante <i>Trichoderma viride</i> Pers.	<i>Alternaria alternata</i> (Fr.) Keissl. <i>Aspergillus niger</i> Tiegh. <i>Aureobasidium pullulans</i> (de Bary) G. Arnaud <i>Mucor strictus</i> Penicillium <i>cyaneum</i> (Bainier et Sartory) Biourge <i>P. funiculosum</i> Thom <i>P. implicatum</i> Biourge <i>P. meleagrimum</i> Biourge <i>P. nalgiovensis</i> Laxa <i>Trichoderma viride</i> Pers.	<i>Aspergillus fumigatus</i> Fresen. <i>A. niger</i> Tiegh. <i>Oidiodendron echinulatum</i> G. L. Baron <i>O. tenuissimum</i> (Peck) S. Hughes <i>Penicillium capsulatum</i> Raper et Fennell <i>Penicillium corylophilum</i> Dierckx <i>P. decumbens</i> Thom <i>P. implicatum</i> Biourge <i>P. lanosoviride</i> Thom <i>P. nalgiovense</i> Laxa <i>P. oxalicum</i> Currie et Thom
Tetra fluorine ethylene and perfluor methyl vinyl ether film	<i>Alternaria alternata</i> (Fr.) Keissl. <i>Aspergillus niger</i> Tiegh. <i>A. fumigatus</i> Fresen. <i>Acremonium strictum</i> W. Gams <i>Aureobasidium pullulans</i> (de Bary) G. Arnaud <i>Cladosporium herbarum</i> (Pers.) Link ex Gray <i>Mucor racemosus</i> Fresen. <i>Penicillium nalgiovense</i> Laxa <i>Trichoderma viride</i> Pers.	<i>Alternaria alternata</i> (Fr.) Keissl. <i>Acremonium murorum</i> (Corda) W. Gams <i>Aspergillus fumigatus</i> Fresen. <i>A. niger</i> Tiegh. <i>Acremonium strictum</i> W. Gams <i>Aureobasidium pullulans</i> (de Bary) G. Arnaud <i>Cladosporium herbarum</i> (Pers.) Link ex Gray <i>Geotrichum candidum</i> Link <i>Mucor racemosus</i> Fresen. <i>Penicillium capsulatum</i> Raper et Fennell	<i>Acremonium strictum</i> W. Gams <i>Aspergillus niger</i> Tiegh. <i>A. versicolor</i> (Vuill.) Tirab. <i>A. nidulans</i> (Eidam) G. Winter <i>Penicillium corylophilum</i> Dierckx <i>P. chrysogenum</i> Thom <i>P. decumbens</i> Thom <i>P. funiculosum</i> Thom <i>P. ochrochloron</i> Biourge <i>P. tardum</i> Thom
Natural rubber	<i>Aureobasidium pullulans</i> (de Bary) G. Arnaud <i>Chaetomium globosum</i> Kunze <i>Cladosporium sphaerospermum</i> Penz. <i>Mortierella alpina</i> Peyronel <i>Oidiodendron tenuissimum</i> (Peck) S. Hughes <i>O. echinulatum</i> G. L. Baron <i>Trichoderma viride</i> Pers. <i>Verticillium album</i> (Preuss) Pidopl.	<i>Aspergillus nidulans</i> (Eidam) G. Winter <i>A. niger</i> Tiegh. <i>Cladosporium herbarum</i> (Pers.) Link ex Gray <i>C. cladosporioides</i> (Fresen.) G. A. de Vries <i>C. sphaerospermum</i> Penz. <i>P. funiculosum</i> Thom <i>P. notatum</i> Westling <i>Verticillium album</i> (Preuss) Pidopl.	<i>Alternaria alternata</i> (Fr.) Keissl. <i>A. tenuissima</i> (Kunze ex Pers.) Wiltshire <i>A. niger</i> Tiegh. <i>A. nidulans</i> (Eidam) G. Winter <i>Cladosporium sphaerospermum</i> Penz. <i>Oidiodendron echinulatum</i> G. L. Baron <i>P. chrysogenum</i> Thom <i>P. decumbens</i> Thom <i>P. funiculosum</i> Thom <i>P. ochrochloron</i> Biourge
Synthetic butadiene nitrile rubber	<i>Alternaria tenuissima</i> (Kunze ex Pers.) Wiltshire <i>Cladosporium herbarum</i> (Pers.) Link ex Gray <i>Oidiodendron griseum</i> Robak <i>Oidiodendron rhodogenum</i> Robak <i>Trichoderma koningii</i> Oudem.	<i>Acremonium strictum</i> W. Gams <i>Alternaria tenuissima</i> (Kunze ex Pers.) Wiltshire <i>Aspergillus niger</i> Tiegh. <i>Cladosporium herbarum</i> (Pers.) Link ex Gray <i>C. cladosporioides</i> (Fresen.) G. A. de Vries <i>C. sphaerospermum</i> Penz. <i>Geotrichum candidum</i> Link <i>Oidiodendron rhodogenum</i> Robak	<i>A. niger</i> Tiegh. <i>A. oryzae</i> (Ahlb.) Cohn <i>Paecilomyces sulfurellus</i> (Sacc.) Samson et W. Gams <i>Phialophora melinii</i> (Nannf.) Conant <i>Penicillium capsulatum</i> Raper et Fennell <i>P. chermesinum</i> Biourge <i>P. funiculosum</i> Thom <i>Ulocladium atrum</i> Preuss

leach out into the environment and thus weaken a material's protection and render it susceptible to biodegradation (Whitney, 1996).

Fungi, able to grow on barely available substrata, can excrete aggressive metabolites. They may cause deterioration through organic acid production. Micromycetes are known to produce acetic, oxalic, glucuronic, carboxylic, and other acids (Torre et al., 1993; Sunessot et al., 1995; Dutton and Evans, 1996; Little et al., 2001). Acid participation in degradation has also been reported toward glass, masonry, concrete, metals, and other materials (Videla, 1986; Kaiser et al., 1996; Weissmann and Drewello, 1996; Wilimzing and Bock, 1996; Lugauskas et al., 1997). Microbial enzymes also play a very important role in the direct degradation of a material's components (Webb, 2000).

Studies on Material Structure after Exposure to Different Environmental Conditions

Optical Microscopy

The microbiological deterioration of a material from long-term exposure under different conditions begins on the surface of the material. An investigation of the morphology of material surfaces provides initial information for a comparison of the instability of materials exposed to different conditions.

In analysis of the surface of the poly(tetrafluorine ethylene) film, the greatest surface deterioration was observed in samples that had been kept in a mycological container [Fig. 2(c)], whereas the surfaces of the samples that had been in the open air and cellar conditions were practically unaffected. The fractal dimensionality factors did not differ much from the control (standard): $D_{S(\text{standard})} = 0.92$, $D_{OA(\text{open air})} = 1.16$, and $D_{C(\text{cellar})} = 1.26$. The highest surface deterioration occurred in the film kept in the mycological container [$D_{MC(\text{mycological container})} = 1.71$], which can be explained by the good development of fungi on the surface [Fig. 1(a)]. A very important morphological characteristic of a surface is its roughness. As examples of this criterion, the profiles of the material are presented in Figure 3. The roughness of the surface of the film increased from $0.75\ \mu\text{m}$ (the standard sample) to 1, 1.25, and $2.5\ \mu\text{m}$ after exposure to the open air, in a mycological container, and in a cellar, respectively.

The copolymer of tetrafluorine ethylene and perfluoromethyl vinyl ether was most corrugated under the condition of open air ($D_{OA} = 1.16$), whereas when in a cellar or in a mycological container, the fractal dimensionality factors were nearly equal to the standard ($D_S = 1.10$).

The surface of the vulcanized rubber containing natural caoutchouc suffered heavy changes: $D_{OA} = 1.44$. Figure 4 shows rough cracks and sparse hollows. The size of areas surrounded by cracks was about $500\ \mu\text{m}$. Meanwhile, the surface of the material kept in a mycological container

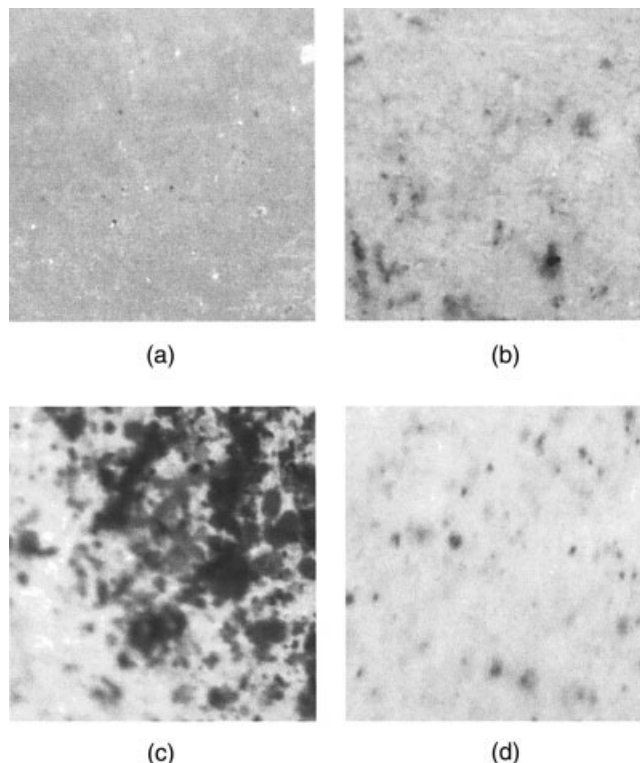


Fig. 2. Surfaces of poly(tetrafluorine ethylene) samples: (a) standard (control), (b) after exposure for 12 years in the open air, (c) after exposure for 12 years in a mycological container, and (d) after exposure for 12 years in a cellar (magnification $\times 200$).

showed almost no change. Slightly unexpected results were obtained for the material exposed in a cellar ($D_C = 0.9982$) compared with the standard sample ($D_S = 1.29$). Possibly, this is connected with smoothing of the surface by microbial growth, resulting in a thick uniform covering. Cracks were also seen on this surface; however, they were short and very different from those observed on the material exposed to the open air. Cracks of the rubber resulting most likely from aging were the most obvious signs of destruction of this polymeric material. However, for the samples kept in a mycological container and cellar, the filling of cracks probably masked this process.

The vulcanized rubber, the main component of which was synthetic butadiene nitrile caoutchouc, was more damaged under cellar conditions and in a mycological container ($D_C = 1.53$ and $D_{MC} = 1.34$) than in the open air ($D_{OA} = 1.11$; Fig. 5). Erosion areas, cracks, and even granules of components can be seen on the surfaces of samples. Absence of cracks in the material exposed to the open air could possibly be a result of the high plasticity of the synthetic rubber, as velocity of evaporation of plasticizers usually is lower than in a natural rubber. Nevertheless, on the surface of the material that was in the open air conditions, scales of the material's exfoliation could be observed. The reduction

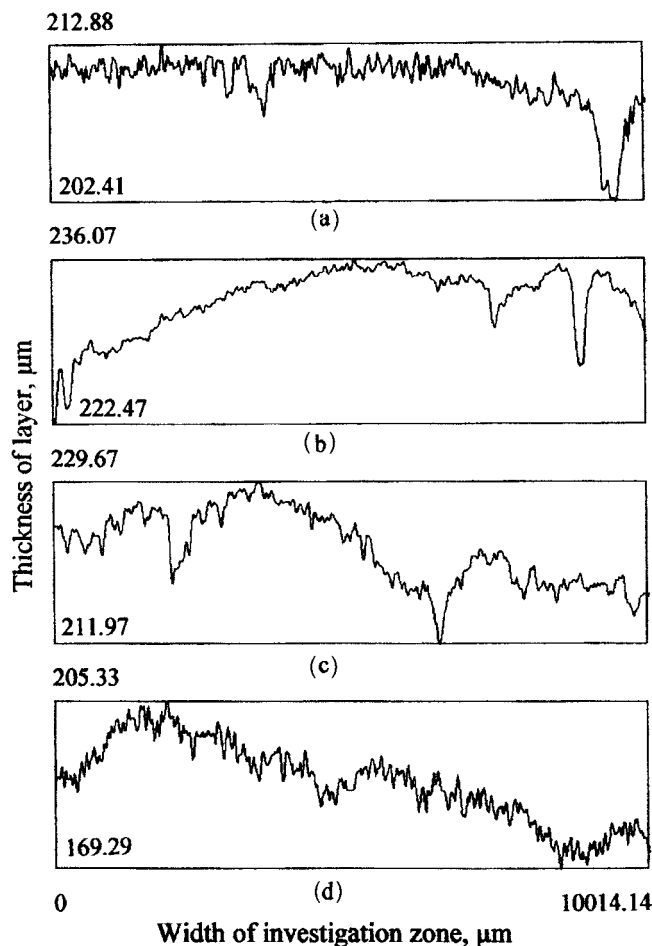


Fig. 3. Profiles of surfaces of poly(tetrafluorine ethylene) film samples: (a) standard (control), (b) after exposure for 12 years in the open air, (c) after exposure for 12 years in a mycological container, and (d) after exposure for 12 years in a cellar.

of fractal dimensionality in comparison with the standard ($D_S = 1.23$) can be explained by the decreased amount of cut-in filler and the uncompensated large increase in the number of scales on the surface of the rubber exposed to the open air. A large destroyed surface could be observed visually. To sum up, the natural rubber changed most when exposed to the open air, and synthetic butadiene nitrile rubber changed most in the mycological container and cellar conditions.

Characteristics of Films of Tetrafluorine Ethylene Polymer and Its Copolymer with Perfluoromethyl Vinyl Ether

IR spectra of the poly(tetrafluorine ethylene) showed the structure had stability. Thus, it can be concluded that this film was resistant to environmental influence (Fig. 6), despite the insignificant changes in the surface (Fig. 3). The main bands of valency fluctuations of links of C—C and

C=CF₂ macromolecular chains remained stable in the samples exposed to all variants and coincided with the standard. IR spectra of the copolymer did not show any essential changes in comparison with the standard.

X-Ray Analysis

The poly(tetrafluorine ethylene) sample had a narrow peak and, consequently, small crystalline polymeric films [Fig. 7(a)]. The X-ray spectra did not show changes, no matter what the exposure conditions were; thus, structured changes in volume did not occur. The sample of the film made from tetrafluoroethylene with perfluoromethyl vinyl ether had a broader peak of dissipation and, consequently, was more amorphous and had fewer polycrystals [Fig. 7(b)]. This can be related to the presence of copolymer fractions. Also, the X-ray spectra of the sample of this material showed practically no changes; only a smoothed shoulder on angle 16.0° could be seen in the samples kept in a mycological container and in a cellar, possibly from amorphization of the external layers of the polymeric film. To sum up, the polymeric films showed practically no structural changes in volume, no matter what the exposure conditions, and in the copolymer the amount of the amorphous phase possibly increased in

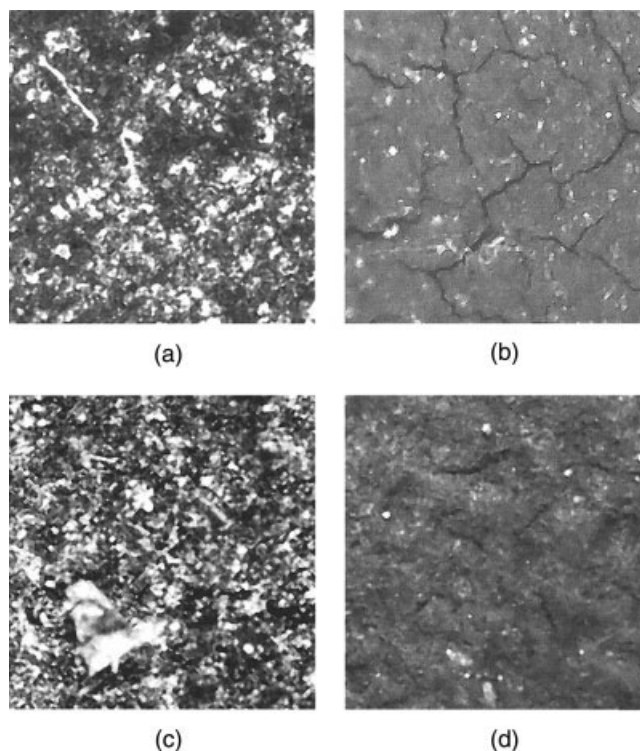


Fig. 4. Surfaces of samples of rubber containing natural caoutchouc: (a) standard (control), (b) after exposure for 12 years in the open air, (c) after exposure for 12 years in a mycological container, and (d) after exposure for 12 years in a cellar (magnification $\times 60$).

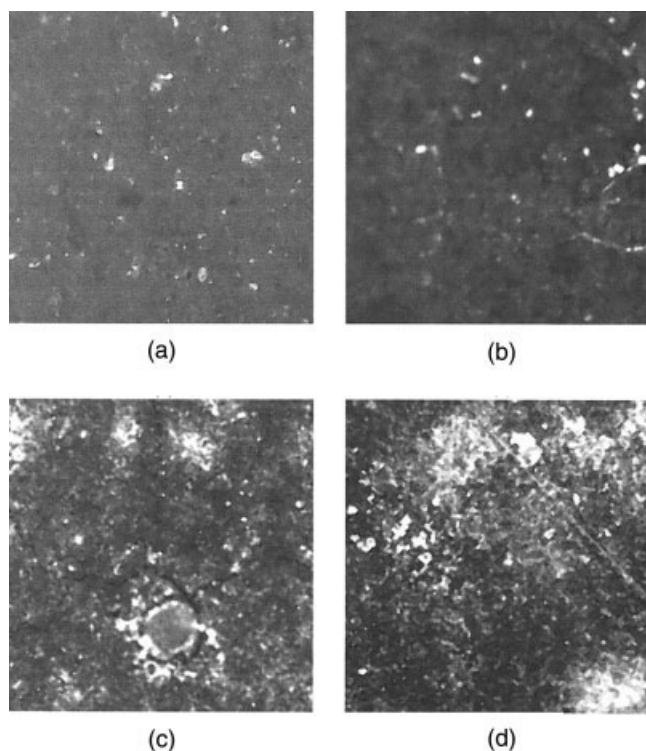


Fig. 5. Surfaces of samples of rubber containing the main component, synthetic butadiene nitrile caoutchouc: (a) standard (control), (b) after exposure for 12 years in the open air, (c) after exposure for 12 years in a mycological container, and (d) after exposure for 12 years in a cellar (magnification $\times 60$).

the samples exposed in a mycological container and in a cellar.

The X-ray spectra of vulcanized rubbers are shown in Figure 8. The X-ray spectrum of the standard sample of natural rubber is very similar to the spectra of the samples kept in a mycological container and in a cellar, except for the intensity variation of separate reflexes [Fig. 8(a)]. For

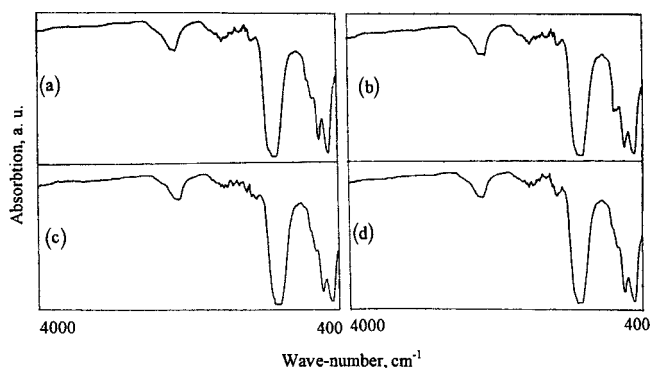


Fig. 6. IR spectra of poly(tetrafluorine ethylene) film samples: (a) standard (control), (b) after exposure for 12 years in the open air, (c) after exposure for 12 years in a mycological container, and (d) after exposure for 12 years in a cellar.

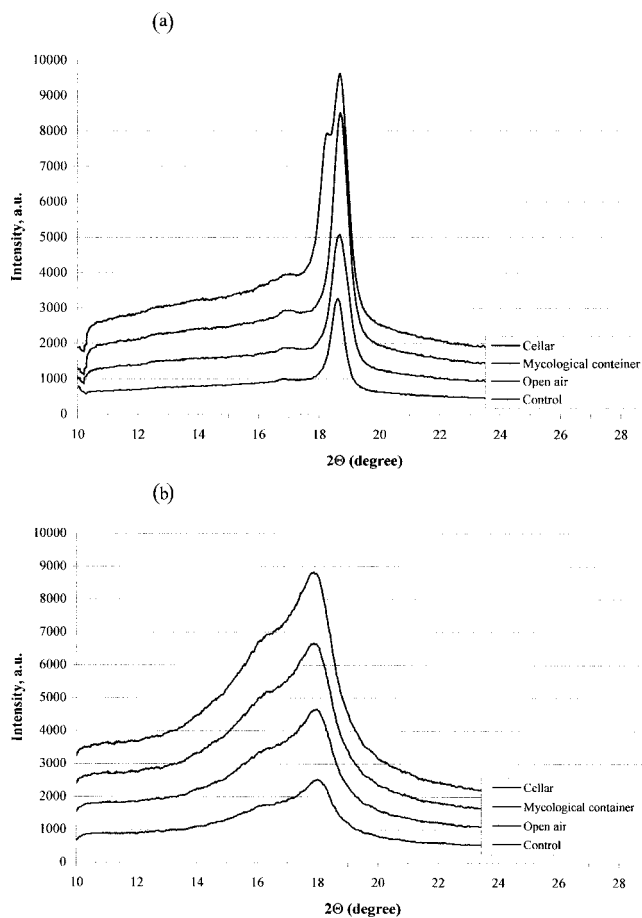


Fig. 7. X-ray spectra of films made from (a) poly(tetrafluorine ethylene) and (b) tetrafluorine ethylene and perfluoromethyl vinyl ether, exposed to different conditions.

this material, exposure to the open air characteristically made a rather large number of additional peaks appear. This possibly could correspond to changes in the chemical composition of the fillers.

The nature of the structural changes in the synthetic rubber differed significantly from the changes in the natural rubber. The X-ray spectrum of the standard sample is similar only with the spectrum of the sample exposed in a cellar [Fig. 8(b)]. For the samples kept in the open air and a mycological container, the essential changes in the structure occurred with the formation of new crystalline structures, as a broad reflex in the range of 2θ 15° – 27° (open-air exposure) or as its shaping with peaks 2θ 19° and a reflex of 20° – 27° 2θ (exposure in a mycological container) [Fig. 8(b)]. It is likely that new crystallization of butadiene nitrile rubber with changes in microblocks of the material occurred and that the chemical composition of the fillers changed.

The results show that the investigated materials were affected by microorganisms and other environmental factors. The fluorinated films showed high resistance. Even after long-term exposure their chemical structure did not show changes, despite finding that fungi had colonized

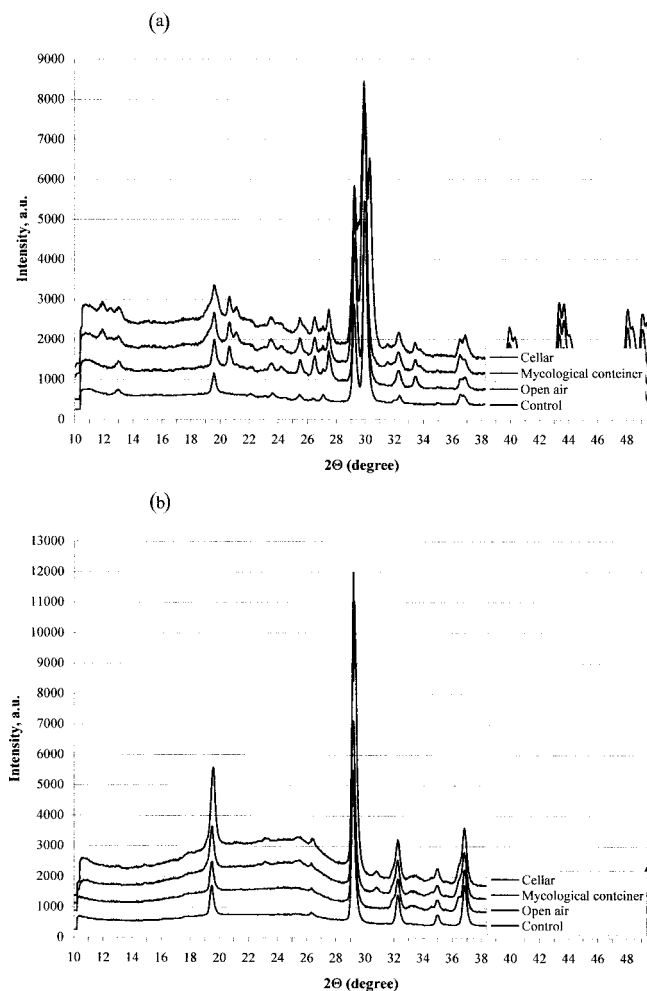


Fig. 8. X-ray spectra of (a) rubber containing natural caoutchouc and (b) rubber containing synthetic butadiene nitrile caoutchouc, exposed to different conditions.

these materials and that there were some differences in fractal dimensionality and an increase in surface roughness. Colonization of films by microorganisms does not necessarily mean that degradation of the plastic matrix is occurring (Whitney, 1996), as microorganisms can function as a result of settled pollutants. Analysis of the rubber samples showed changes in the structure of the material, which confirmed that the multicomponent vulcanized rubbers were more susceptible to deterioration caused by microorganisms and other environmental factors.

CONCLUSIONS

1. It was established by optical and electron microscopy that microorganisms caused deterioration of the surface of the polymeric material and were able to penetrate inside into deeper layers, accelerating the decrease in the physical integrity of the materials.
2. Fungi caused the most deterioration in fluorine polymers and vulcanized rubbers from the *Alternaria*, *Aspergillus*, *Aureobasidium*, *Cladosporium*, *Mucor*, *Penicillium*, *Oidiodendron* and *Trichoderma* genera. Fungi *Aspergillus fumigatus*, *A. niger*, *Aureobasidium pullulans* and *Trichoderma viride* caused the most intensive deterioration in fluorine films, whereas *Alternaria tenuissima*, *Cladosporium herbarum*, *C. sphaerospermum*, and fungi of the *Oidiodendron* genus were most widespread on vulcanized rubbers. Fungi of the *Aspergillus* and *Penicillium* genera prevailed on both fluorine films and rubbers exposed in a cellar.
3. Studies of the structures of the materials using infrared spectroscopy showed that material made from poly(tetrafluorine ethylene) and the copolymer made from tetrafluorine ethylene and perfluoromethyl vinyl ether were resistant to the influence of environmental factors and microorganisms. After 12 years of exposure under different conditions, the structure of these materials did not change, despite little changes occurring in their surface morphology. Degradation of such materials in a natural environment seems to be problematic; thus, specific means are needed for their utilization.
4. Vulcanized rubber made both from natural and from synthetic butadiene nitrile caoutchouc with the same length of exposure showed rather evident changes in appearance and structure. X-ray graphical analysis confirmed that changes occurred in rubber under the influence of microorganisms and other environmental factors because of new crystallization of caoutchouc and a possible change in the chemical composition of the fillers.

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