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Biodegradation of Pre-Aged Modified Polyethylene Films

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1. Introduction

Synthetic polymers, which are ubiquitous in modern industrial society, contribute to improving comfort and quality of our life. Currently more than 260 million tonnes of plastics are being produced each year (O'Brine & Thompson, 2010). Among them polyolefins constitute the majority of consumed thermoplastics. Polyolefin materials, such as low-density polyethylene (LDPE), due to the exceptional mechanical and thermal properties, ease of fabrication and low cost, find diverse applications in many fields. Polyethylenes represent 64% of materials used for various applications such as containers, bottles, tubing, plastic bags, greenhouses, mulching films, which are usually discarded after only brief use (Peacock, 2000). These mostly one-trip applications lead to a large quantity of plastic waste accumulating, at the rate of 25 million tons per year (Meenakshi et al., 2002) in landfill and in natural habitats (Thompson et al., 2009). Thus, plastics - the most visible form of trash - have become ubiquitous in our environment, leading to long-term environment, economic and waste management problems (Koutny et al., 2006). Since plastic waste are often soiled by biological substances, physical recycling of these materials turned out impractical and generally undesirable (El-Naggar & Farag, 2010). Incineration of plastics, in turn, has various environmental and social constraints. It seems that the use of plastics, which can re-enter the biological life cycle through biodegradation will be the best choice (Sivan, 2011; Soni et al., 2009).

The term "biodegradation" indicates the predominance of biological activity in this phenomenon. Until recently, biodegradation was perceived as a decomposition of substances solely by the action of microorganisms. At present, when the complexity of biodegradation of many substances, especially polymeric materials, is better understood, a new definition of this process divide it into several steps and the process can stop at each stage (Lucas et al., 2008). During the first, extracellular step, which is called biodeterioration, the action of microorganisms in combination with other decomposer organisms or/and abiotic factors fragment polymeric materials into small fractions. To go across the plasmic membrane these small fractions of materials must be depolymerised to low molecular weight products. Due to the mixed action of abiotic factors and microbial communities, which secrete enzymes and free radicals, long polymeric chains are cleaved and small

oligomers are generated. After being transported into the cytoplasm the small molecules integrate the metabolism pathways. This so called assimilation is the essential step to produce microbial energy, biomass and primary and secondary metabolites. As mineralisation takes place CO_2 , N_2 , CH_4 , H_2O and different salts from completely oxidised metabolites are released in the extracellular environment (Lucas et al., 2008).

According to the new definition, biodegradation of plastics results from combination of biotic and abiotic factors which act synergistically to decompose organic matter. Such interaction of environmental factors is not only beneficial but, in some cases, required to degrade particularly stable compounds.

It is also noteworthy that a frequent source of misunderstanding concerning the term 'biodegradability of polymer' between the polymer scientists and microbiologists originates from the fact that for polymer scientists, degradation means the loss of physical properties, whereas microbiologists are interested in the complete mineralisation of the material (Koutny et al., 2006).

Polyethylene, like many conventional plastics, is resistant to degradation. Its recalcitrance to degradation is traced back to physical and chemical properties that limit chemical reactivity in general (Koutny et al., 2006). In addition, stabilizers contained in industrial polyethylene prevent degradation during processing and usage (Reddy et al., 2008).

Ohtake et al., estimated that it takes about 300 years to degrade LDPE films with thickness of $60\mu\text{m}$ (Ohtake et al., 1998). However, according to many published reports this estimation implies unrealistic constant rate of LDPE biodegradation. Conventional supposition assumes, that it takes rather thousands than hundreds years for the LDPE to be completely degraded (Kyrikou & Briassoulis, 2007). Formerly, some authors claimed that the poor biodegradability of synthetic substances is a consequence of their short time of presence the environment, so that the enzymes capable of degrading e.g. plastics are not available (Müeller, 2006). However, the research on the microbial metabolism of xenobiotics showed that the evolution of specificity of oxidoreductases secreted by microorganisms is relatively fast (Koutny et al., 2006; Wojcieszynska et al., 2011). These enzymes involved in the transformation of the molecular edifices increase the polarity of the molecule (Lucas et al., 2008). Nowadays, it also seems that even hydrophobic nature of polyethylene resulted from carbon-only backbone is not a hindrance during biodegradation, since fungi, due to their ability to form hydrophobic proteins, can easily attach to the polymer surface (Sahebnaazar et al., 2010). Contrary to previously described features of polyethylene, the high molecular weight itself represents a serious problem because, as a molecule of this size cannot cross a cell wall and a cytoplasmic membrane, it is inaccessible to intracellular metabolic pathways (Koutny et al., 2006). It is therefore necessary to reduce its molecular weight drastically by some predegradation method prior to biological attack. It has been shown that linear paraffin molecules having a molecular weight below 500, or n-alkanes up to C_{44} , can be utilized as a carbon source by microorganisms (Jakubowicz et al., 2006).

Many sources clearly indicate that biodegradation of LDPE could be accelerated by polymer pretreatments, such as photo-oxidation, thermo-oxidation and chemical-oxidation (Sahebnaazar et al., 2010).

Photo-oxidative degradation is the process of decomposition of the material by the action of light. It is well known that radiation in the wavelength region of 290–400 nm, which have

sufficient energy to cleave C-C bond (Mark et al., 1986) is not absorbed by pure LDPE. Its photo-oxidation can only be induced by some impurities (Briassoulis et al., 2004).

Thermo-oxidative degradation is an exposition of polymer to high temperatures. The sensitivity of polyolefins towards thermal oxidation is largely due to the presence of impurities, hydroperoxides and carbonyl groups (Briassoulis et al., 2004).

Though both types of abiotic oxidation produce functional macromolecules susceptible to random cleavage with the formation of low molecular weight oxygenated products containing carbonyl residues (Chiellini et al., 2007), the main difference between photo- and thermal oxidation is that photochemical reactions occur only on the surface of the polymer sample, whereas thermal reactions occur throughout the bulk (Briassoulis et al., 2004).

Hydrolysis is another way by which polymers can undergo degradation (Sahebnaazar et al., 2010). However, mechanism of the process strongly depend on polymer structure. Some polymer materials are hydrolysed via both bulk degradation and surface erosion, others hydrolyse through only one of the mechanisms.

Initial abiotic oxidation and/or hydrolysis of polyethylene is an important stage as it determines the rate of the further biodegradation process. At a second stage of environmental degradation polymer with increased bioavailability and biodegradability should be consumed by microorganisms in soil or during composting (Abrusci et al., 2011).

Another of the possible ways to accelerate biodegradation rate of polyethylene in the environment is copolymerisation, blending or grafting with functional polymers and compounds (Corti et al., 2010; Huang et al., 2005).

Few additives having hydrophilic groups make plastic less hydrophobic and susceptible for photo-, chemical and microbial degradation. The most desirable effect of this approach is microbial assimilation of the filler, serving as initial point of microbial attack, resulted in the increase of the surface area of the synthetic bulk material rendering it more susceptible not only to biotic but also abiotic oxidation (Chiellini et al., 2003; Singh & Sharma, 2008). As a result the remaining inert components should disintegrate and disappear (Chandra & Rustgi, 1998).

Among biodegradable plastics which can serve as degradable fillers are products of microbial fermentation (e.g., polyesters), modified natural products (e.g., starch, cellulose) and plastics based on chemical synthesis (e.g. polylactic acid, polycaprolactone) (El-Naggar & Farag, 2010). Despite advantages, such as good biodegradability, the commercial production of these polymers is 2.5–10 times more expensive than conventional polymers. Moreover, their physical or chemical properties often restrict their use (Ojeda et al., 2009). Therefore combination of their biodegradability with the excellent properties of conventional materials, such as low-priced LDPE, seems to be a promising alternative (Rosa et al., 2007).

Poly(butylene succinate) (PBS) is, next to poly(butylene succinate-co-butylene adipate) (PBSA) and poly(ethylene succinate) (PESu), a member of group of biodegradable aliphatic polyesters trademarked 'Bionolle' invented by Showa Denko (Japan) in 1990, and produced through a polycondensation reaction of glycols with aliphatic dicarboxylic acids and their derivatives (Tserki et al., 2006a). Among these three polyesters, PBS is the only one which is available commercially. However some studies revealed that the biodegradation of PBS is much slower than that of PBSA (H-S. Kim et al., 2006).

So a few years ago, we started testing the biodegradability PBSA. We are the only team which, in order to accelerate the biodegradation of synthetic polymers, applied modification of LDPE with poly(butylene succinate-co-butylene adipate) (PBSA). Since then we are investigating mechanisms of biodegradation of LDPE/PBSA compositions under different environmental conditions.

It is well known, that even though the mechanism of oxidation of LDPE is more or less understood, the knowledge of the behaviour of this polymer in blends with other materials is not sufficient. It was confirmed that the lack of additivity of component properties in blends is a main reason for difficulties in predicting their life-time (Oldak & Kaczmarek, 2005).

The purpose of this study was to examine the synergistic or antagonistic effects on the oxidation, hydrolysis and biodegradation of a commercial PELD films filled with PBSA copolyester. Investigations were conducted by first exposing polymeric films to the abiotic oxidation (action of photo- and/or thermal degradation), followed by abiotic hydrolysis under mild conditions, and subsequently to microbial biodegradation.

Several techniques were employed to elucidate the chemical and physical polymers structure. Changes in chemical structure of polymeric films caused by various types of degradation were interpreted on the basis of IR spectra analysis. The scanning electron microscope (SEM) was used to examine these polymers morphologically (surface topography); the excellent resolution provided by the SEM makes it one of the best tools for this purpose.

2. Experimentals

2.1 Film preparation

Low-density polyethylene (LDPE, type "FGNX23-D022", MFR of 2,2g/10min) was purchased from POLICHEM in Kędzierzyn-Koźle. Bionolle® (type #3001, MFR of 1,5g/10min.) was obtained from Showa Denko (Europe) GmbH. The LDPE and Bionolle® were homogenised in a Co-Knetter Buss high-speed mixer at 170°C. The homogenised material was further processed on a PLV 151 type Plasti-Corder extruder for the production of thin films. The compositions 85/15, 70/30, 40/60 LDPE/ Bionolle® were prepared with ratio of 33 rpm and 220, 230, 230, and 235°C set temperatures. Polyethylene film without any additives 100/0 was used as a control material. The films were extruded at the Institute for Engineering Polymer Materials and Dies in Gliwice (Poland). Each film was cut into 40 mm x 40 mm squares.

2.2 Abiotic treatment

2.2.1 Hydrolytic aging

Hydrolysis of films was carried out in phosphate buffer (pH 7.4) with sodium azide to prevent growth of microorganisms for 84 days.

2.2.2 Oxidative aging

The photo- and/or thermal degradation of polymers was achieved by placing the samples in an adapted oven for 16 days. Every 24 hours, the location of the samples was changed in a

clockwise direction. After four days, when a complete change of the position of samples within the chamber took place, they were inverted.

2.2.2.1 Photodegradation procedure

Films were positioned 15 cm from the lamp then UV-irradiated using a low-pressure mercury vapor lamp generating energy between 280 nm and 370 nm (TUV 6W, Philips, Holland) in air atmosphere at room temperature.

2.2.2.2 Thermodegradation procedure

The samples were subjected to dark heated exposure at 50°C in air atmosphere.

2.2.2.3 Photothermodegradation procedure

Photothermal degradation of polymers proceeded with simultaneous action of UV radiation and temperature under the same conditions as described for the individual processes.

2.3 Biodegradation experiments

2.3.1 Strains of fungi

Filamentous fungi *Aspergillus niger*, *Aspergillus terreus*, *Aureobasidium pullulans*, *Paecilomyces varioti*, *Penicillium funiculosum*, *Penicillium ochrochloron*, *Scopulariopsis brevicaulis*, *Trichoderma viride* and their mixture were employed for the biodegradation. *Aspergillus niger* and *Penicillium funiculosum* were isolated from dump in Sosnowiec and their identification was carried out by Institute for Ecology of Industrial Areas in Katowice, Poland. The others were purchased from Institute of Fermentation Technology and Microbiology in Łódź, Poland.

Fungi were maintained in test tubes containing Czapek-Doxa medium (NaNO₃, 2g; KH₂PO₄, 0,7g; K₂HPO₄, 0,3g; KCl, 0,5g; MgSO₄×7H₂O, 0,5g; FeSO₄×7H₂O, 0,01g; sucrose, 30g; Bacto Agar (Difco), 20g; distilled water, 1000ml; pH 6.0). Cultures were incubated at 28°C. After completion of sporulation, spores of fungi were separated from hyphae by centrifugation at 4000 rpm and resuspended in SDS solution. The spore suspension at a concentration of 10⁶ spores ml⁻¹ were either used for biodegradation tests or transferred to glycerol solution (50% v/v) before storage at -20°C.

2.3.2 Biodegradation procedure

Squares of each film (5 replicate samples) unexposed and pre-exposed to abiotic oxidation or/and hydrolysis were sterilised in 70% ethyl alcohol, rinsed with sterile distilled water and aseptically placed in Petri dishes containing modified sucrose-free Czapek-Doxa medium. Each film was covered with 0,1 ml spore suspension. Biodegradation was carried out at 28°C and relative humidity of > 90% for 84 days. Loss of water during incubation was supplemented with sterile distilled water.

After the incubation period, polymer samples were delicately removed from the soils and sterilised by immersion in 1% mercuric chloride for 5 minutes, rinsed in water and dried in a desiccator until a constant weight was obtained.

2.4 Assessment of degradation

Sample weight loss was determined gravimetrically on an analytical balance (Mettler Toledo, AB 240-S).

The tensile strength (R_m) and elongation at brake (ϵ_r) tests were carried out in accordance with EN ISO 527-3: 1995; EN ISO 527-1: 1996; EN ISO 527-2: 1996. Tests were performed on a tensile tester (INSTRON 4466). Results of mechanical strength evaluation were averaged over 5 replicate specimen.

Infrared spectra of the films were recorded on an FTS 40A spectrophotometer (BIO-RAD) over a range of 3700-700 cm^{-1} at a resolution of 2 cm^{-1} and over 32 scans. Samples were dissolved in a mixture of decahydronaphthalene and dimethylformamide at 70°C and analysed as thin films on the NaCl cell surfaces after evaporation of the solvent. Carbonyl index (CI) and terminal double bond index, were used as a parameters to monitor the degree of degradation of films. Carbonyl index is the ratio between the absorbance of the carbonyl peak (1712 cm^{-1}) and the absorbance of the CH_2 groups at 1465 cm^{-1} . Terminal double bond index is the ratio between the absorbance of the terminal double-bond peak (908 cm^{-1}) and the absorbance of the CH_2 groups at 1465 cm^{-1} (Gilan (Orr) et al., 2004).

The pieces of control and treated polyethylene films were cut with a sharp blade to obtain a small cube (5 mm). The cube samples were mounted on an aluminium stubs with double-sided adhesive carbon tape, and sputter-coated in Pelco SC-6 sputter coater (25 mA and 0,8 hPa) for 30 seconds with a thin film of gold to improve the electrically conducting properties of the sample surface. After sputtering the samples were imaged by the Tesla BS 340 scanning electron microscope (SEM) in a high-vacuum mode operating at 20 kV with secondary electron detector (ESD), and working distance (WD) of 10 mm. Collected images were compared with those recorded for the original untreated samples.

3. Results and discussion

The term degradation with respect to decomposition of polymeric materials has not been explicitly specified. The main problem is to determine the susceptibility of the polymer material to degradation in the environment and the length of time during which process will last. Several methods can be used to estimate polymer deterioration. Frequently used methods rely on gravimetric, spectroscopic and microscopic techniques, mostly in combination with each other (Sudhakar et al., 2008).

A simple and quick way to measure the degradation of polymers is by determining the weight variations. However, this measurement itself cannot be a reliable indicative of material degradability, since both an increase in weight and a weight loss of polymer sample, not directly related to the breakdown of polymer chain, may occur. A good example is an increase in weight due to accumulation of microorganism, whereas loss of weight can be due to the vanishing of volatile and soluble impurities (Lucas et al., 2008).

Deterioration of polymers can be also evaluated by change in their rheological properties. Contrary to the weight measurement, these properties directly depend on molecular weight of polymers, their crystallinity and the presence of branches and crosslinkings effects (Briassoulis et al., 2004).

Among others, Fourier transform infrared (FTIR) spectroscopy is most widely used in determining the structural changes in macromolecules. Since it is known that degradation of polymers can proceed *via* both hydrolysis and oxidation, with this tool it is possible to estimate the extend of modification of polymer main chain due to the action of abiotic or biotic factors. It is assumed, that the mechanism of polymer degradation can be determined by measuring the levels of ketone carbonyl, ester carbonyl and internal double bond absorbance peaks (Gilan (Orr) et al., 2004; Jakubowicz et al., 2006; Sudhakar et al., 2008).

Scanning electron microscopy (SEM) is a useful imaging approach for the visualization of different polymers, because it provides a consistent picture of the polymer morphology as a non-uniform structure characterised by variable thickness and variable polymer density. This technique allows to illustrate the surface topography of polymers with high resolution. Due to its high lateral resolution, its great depth of focus and its facility for x-ray microanalysis (SEM/EDX), SEM is often used in material science – including polymer sciences to elucidate the microscopic structure of polymers. In SEM, the surface of non-conductive samples must be coated with a thin layer of gold or platinum. Sometimes, a surface pretreatment (ion sputtering or chemical etching) is carried out to reveal structural details. Moreover, brittle fracture of samples (in liquid nitrogen in cryo-SEM) can give information about the internal morphology of bulk specimens. SEM micrographs indicate that polymers are characterised by different surface features and heterogenous local density of chemical components. They also show surface defects such as cracks, etching residues, differential swelling, depressions and perforations.

Currently, a number of different SEM techniques and sample preparation methods have been employed for study of polymers structure, including ultra-high resolution field emission SEM (UHR FE-SEM), scanning transmission SEM (STEM), low-vacuum SEM (LVSEM/cryo SEM) and environmental SEM (ESEM). In LVSEM mode, the delicate polymer samples are observed in frozen state, whereas in an ESEM mode the specimens can contain liquids. SEM equipped with an energy dispersive X-ray spectrometry profiling (SEM/EDX) is widely used to characterize the variation of chemical composition of polymers interface. STEM is used to analyze lamellar arrangements in polymers, their dimensions and crystallography. Especially the recent development of ultra-high resolution field emission scanning electron microscopy has opened new opportunities in polymer study at the molecular scale. These SEM techniques provide complementary data to transmission electron microscopy (TEM) and scanning probe microscopy (SPM).

In polymer studies the following applications of SEM have been made: study of surface microstructure of polymer films, fibres and powders (amorphous and crystalline); investigation of liquid crystals; control of the polymerization process; study of the structure of copolymers, polymer blends and networks (investigation of miscibility and adhesion of components); observation of structural defects and sample roughness; changes in the structure of polymers during stretching and upon loading (formation of crazes and cracks; fracture surface morphology; chemical agent transport processes through membranes (porosity of membranes) and after biotic (microbiological) treatment (Bonhomme et al., 2003; Borghei et al., 2010; González et al., 2006; Guise et al., 2011; Šašek et al., 2006; Vezie et al., 1995).

3.1 Biodegradation

The percentage weight loss of LDPE and LDPE/Bionolle® compositions after biodegradation with different filamentous fungi is shown in Table 1 (Łabużek et al., 2006a; Nowak et al., 2010).

Filamentous fungi	LDPE/Bionolle® film compositions			
	100/0	85/15	70/30	40/60
	Weight loss, %			
<i>Aspergillus niger</i>	0,12	0,16	1,29	24,0
<i>Aspergillus terreus</i>	0,08	0,08	0,17	0,35
<i>Aureobasidium pullulans</i>	0,04	0,05	0,28	0,25
<i>Paecilomyces varioti</i>	0,07	0,06	0,22	0,29
<i>Penicillium funiculosum</i>	0,15	0,22	1,24	60,0
<i>Penicillium ochrochloron</i>	0,06	0,04	0,29	0,27
<i>Scopulariopsis brevicaulis</i>	0,06	0,10	0,47	1,17
<i>Trichoderma viride</i>	0,02	0,04	0,18	0,34
Mixed fungal population	0,11	0,15	1,22	58,0

Table 1. Weight loss of films after biodegradation

It was found that pure LDPE and the blends 85/15 and 70/30 showed little loss of mass, which probably reflected the inertness of LDPE towards biological degradation. Unfortunately, even 30% Bionolle® wasn't enough to observe sufficient weight loss of film. Probably, the polyethylene matrix prevented microbes from accessing the polyester in the depth of the film. Similar relationships were observed for the polyolefins modified with 6-15% starch content, where only the surface of the material was susceptible to biodegradation (Nakamura et al., 2005). In a separate study, Rosa et al. found that the pure LDPE and the blends 25PHB/75LDPE and 50PHB/50LDPE showed little or no loss of mass during aging in simulated soil (Rosa et al., 2007). Also Lee et al. discovered that polystyrene (PS) in the P(3HB-co-3HV)/PS (95/5 by wt%) blend acts as a retardant of enzymatic attack to the surface of the blend film (Lee et al., 2003).

This phenomenon is likely due to the high-molecular weight hydrophobic chains of the synthetic polymer preventing enzymes from accessing the biodegradable polymers contained within the material (Nowak et al., 2011).

Among polymeric compositions, film containing 60% Bionolle® had the most obvious reduction in weight. Film lost 24%, 60% and 58% of its initial mass after incubation with *Aspergillus niger*, *Penicillium funiculosum* and mixed population of fungi, respectively. Other fungi caused slight film weight loss ranging from 0,25% to 1,17%. Taken together with our previous studies, the present findings show, that only fungi which were able to decompose Bionolle® (80-100% for 90 days), were also able to degrade 40/60 composition (Nowak et al., 2010).

Mechanical properties of the investigated films before degradation are shown in Table 2.

LDPE/Bionolle® film compositions	Mechanical properties	
	Rm, MPa	εr, %
100/0	16,40	516,0
85/15	14,02	518,4
70/30	10,80	336,8
40/60	20,50	485,0

Table 2. Mechanical properties of control films

The changes in tensile strength and elongation at break of films after biodegradation with selected fungi are shown in Figure 1. It has been reported that the changes in tensile strength and elongation loss are excellent indicators of degradation (Reddy et al., 2008).

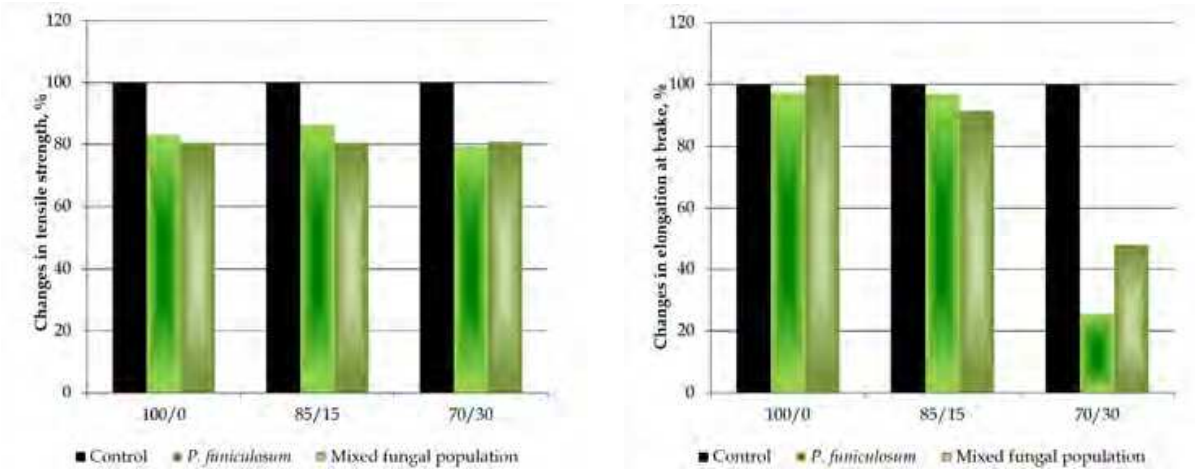


Fig. 1. Mechanical properties of films after biodegradation

Although little weight loss of polyethylene was observed after 84 days of biodegradation, a marked reduction in tensile strength imply that both *Penicillium funiculosum* and mixed fungi population excrete enzymes able to cleave macromolecules of LDPE. Slight increase in the elongation at break in samples incubated with mixed population of fungi, could be tentatively attributed to a sort of plasticisation effect exerted by low molecular weight fractions produced in the first stage of the biodegradation of the polymer matrix (Chiellini et al., 2003). After 84 days of biodegradation, the tensile strength of film containing 30% Bionolle® decreased by about 20%. At this time, elongation at break changed by about 74% and 52% after incubation with *Penicillium funiculosum* and mixed fungi population, respectively. Far-advanced decomposition of 40/60 blend, prevented determination of its mechanical properties.

Data obtained from FTIR spectra (spectra are presented elsewhere (Łabużek et al.) of examined films showed an increase in carbonyl and double bond indices, except for LDPE (decrease in carbonyl index by 57%), incubated with mixed population of fungi (Łabużek et al., 2006a). Increase in the internal double bond index is in accordance with the biodegradation mechanism suggested by Albertsson et al. who reported on the formation of terminal double bonds as a result of exposure to biotic environment (Albertsson et al., 1987). This can be attributed to biotic dehydrogenation (Chiellini et al., 2003). However, in contrast

with study of Albertsson et al., we found an increase in the amount of carbonyl residues (up to 525%) in LDPE after 84 days of incubation with *Penicillium funiculosum* (Albertsson et al., 1987). Carbonyl residues have been reported as major products formed in the presence oxidoreductases (Sudhakar et al., 2008).

Important aspect during the biodegradation of a material is the sustained growth of microorganisms during the entire process (Abrusci et al., 2011). The changes on the surface of polymers as a result of biodegradation are no less important (Nowak et al., 2011).

Figure 2 shows the micrographs of control films.

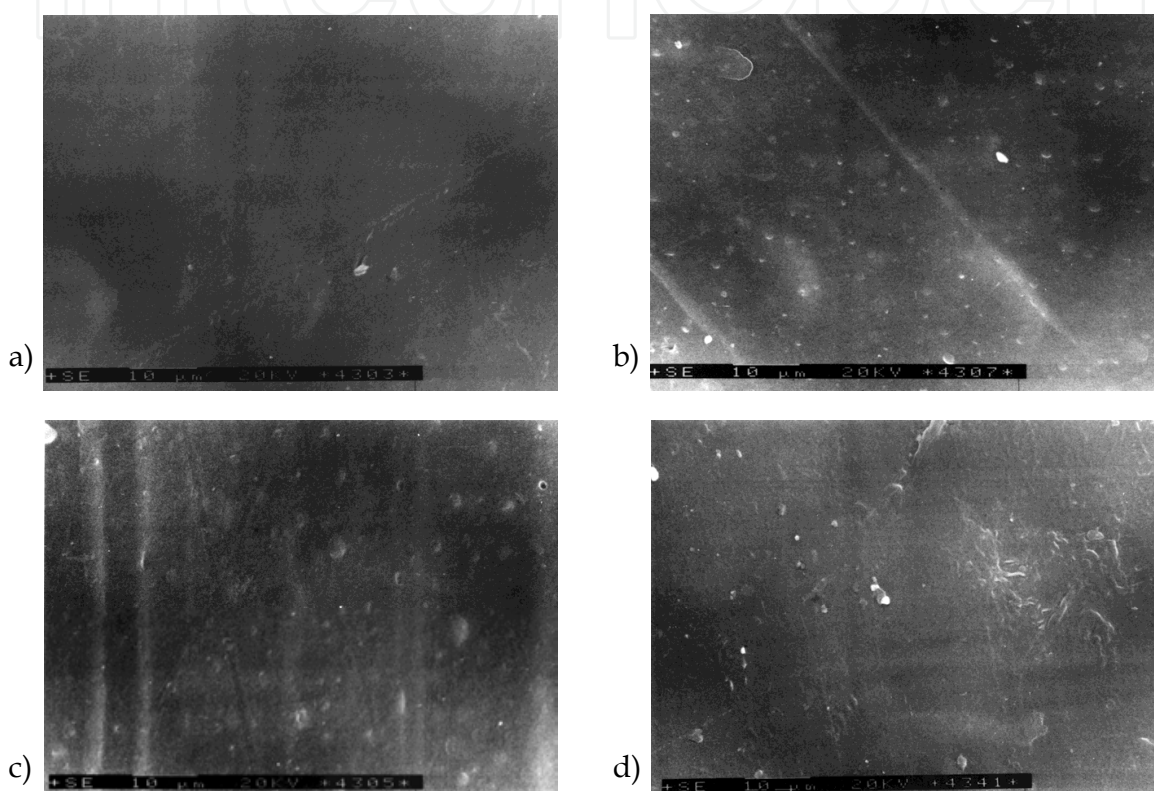


Fig. 2. SEM micrographs showing surface of control films a) LDPE b) composition 85/15 c) composition 70/30 d) composition 40/60

The photomicrograph shows that the surface of non-degraded material is smooth, without cracks and holes.

Neat polymer samples after biodegradation with filamentous fungi are presented in Figures 3-6.

Paecilomyces varioti (Figure 3c) and *Penicillium funiculosum* (Figure 3d) expanded their colonies over the entire surface of neat LDPE. Apart from hyphae and conidiophores, samples were covered with characteristic spores. *Aspergillus niger* (Figure 3a), *Aspergillus terreus*, *Aureobasidium pullulans* (Figure 3b), *Penicillium ochrochloron*, *Scopulariopsis brevicaulis*, *Trichoderma viride* and mixed fungal population grew less rapidly and primarily on the edges of the sample. Considerable change in mechanical properties (Figure 1) and FTIR spectrum of LDPE proved that growth of fungi cannot be considered only as a result of the surface moistness (Sahebazar et al., 2010). Moreover, knowing that the biodegradation

experiments were conducted in minimal solid medium, it is obvious that solid surface of LDPE, at least for some fungi, served as the source of carbon and energy.

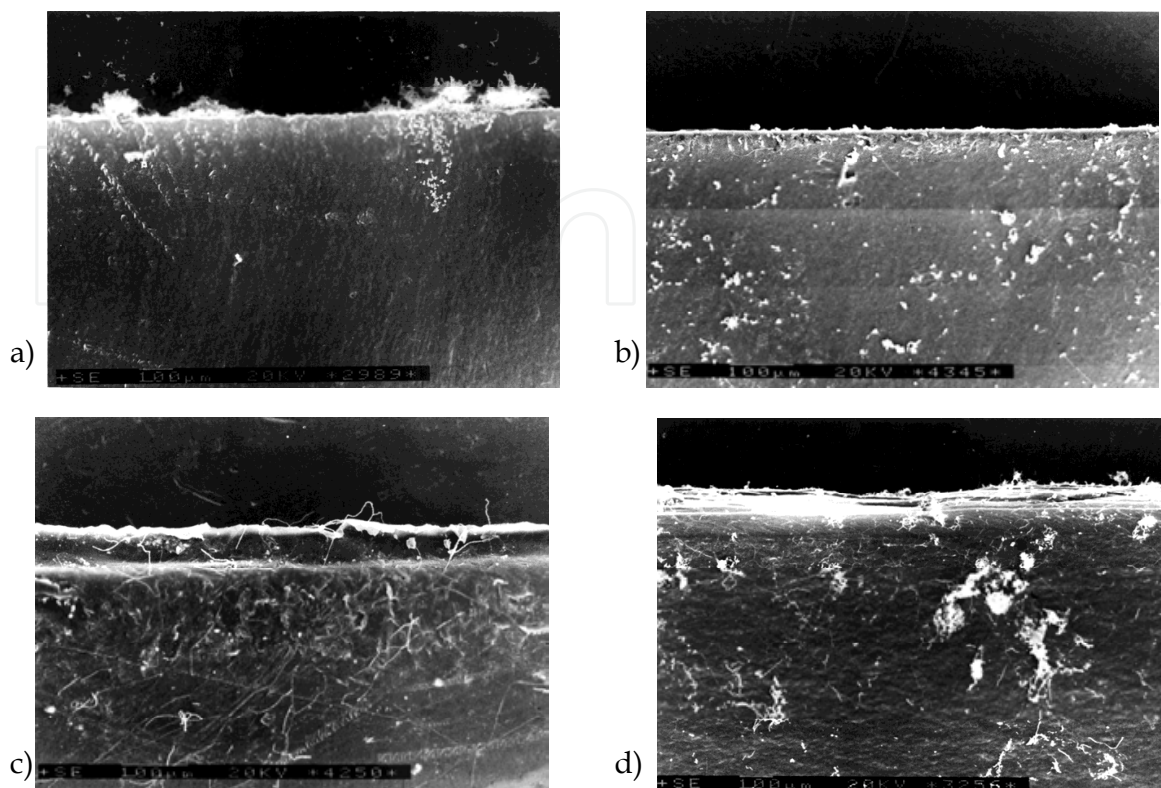


Fig. 3. SEM micrographs of neat LDPE film after biodegradation with a) *Aspergillus niger* b) *Aureobasidium pullulans* c) *Paecilomyces varioti* d) *Penicillium funiculosum*

As a result of fungal degradation, peeling and cracking in texture of film containing 15% Bionolle® were visible (Figure 4). The entire surface of film was densely covered with spores belonging to *Aspergillus niger* (Figure 4a) and *Aureobasidium pullulans* (Figure 4b). Scarce hyphae of *Paecilomyces varioti* (Figure 4c), *Penicillium funiculosum* (Figure 4d) and mixed population of fungi (Figure 4f) colonised both the edges and the surface of film. Agglomerations of *Trichoderma viride* conidiophores (Figure 4e) inhabited primarily the edges of the sample.

The destructive process of biodegradation was very prominent in film containing 30% Bionolle®. Small holes and cracks, surface irregularities, peeling and exfoliation appeared. *Aspergillus niger* (Figure 5a), *Paecilomyces varioti* (Figure 5c), *Penicillium funiculosum* (Figure 5d) and mixed population of fungi (Figure 5h) produced a well-developed mycelium over the entire surface of the film. Hyphae and conidiophores of *Penicillium ochrochloron* (Figure 5e), *Scopulariopsis brevicaulis* (Figure 5f) and *Trichoderma viride* (Figure 5g) was scattered on the film surface. *Aspergillus terreus* (Figure 5b), almost unable to colonise 85/15 composition, introduced deep cracks and holes, suggesting that the fungi penetrate into the sample matrix during degradation.

After 84-day incubation with filamentous fungi the most intense changes were found on the surface of 40/60 composition. Hyphae and conidiophores of *Aspergillus niger* (Figure 6a), *Aspergillus terreus* (Figure 6b), *Aureobasidium pullulans* (Figure 6c) and *Trichoderma viride*

(Figure 6g) grew out directly from the polymer sample. However, changes induced by the action of these microorganisms deep and distinct. Dense network of fractures was particularly visible after incubation with *Aspergillus terreus*. *Aspergillus niger* and *Aureobasidium pullulans* caused massive exfoliation of the plastic edges. Although *Penicillium ochrochloron* (Figure 6e) and *Scopulariopsis brevicaulis* (Figure 6f) created mycelium, a considerable part of the film surface was found to be unaffected. Loss of integrity of film resulted into fragile surface entirely covered by dense mycelia of *Penicillium funiculosum* (Figure 6d) and mixed population of fungi (Figure 6h).

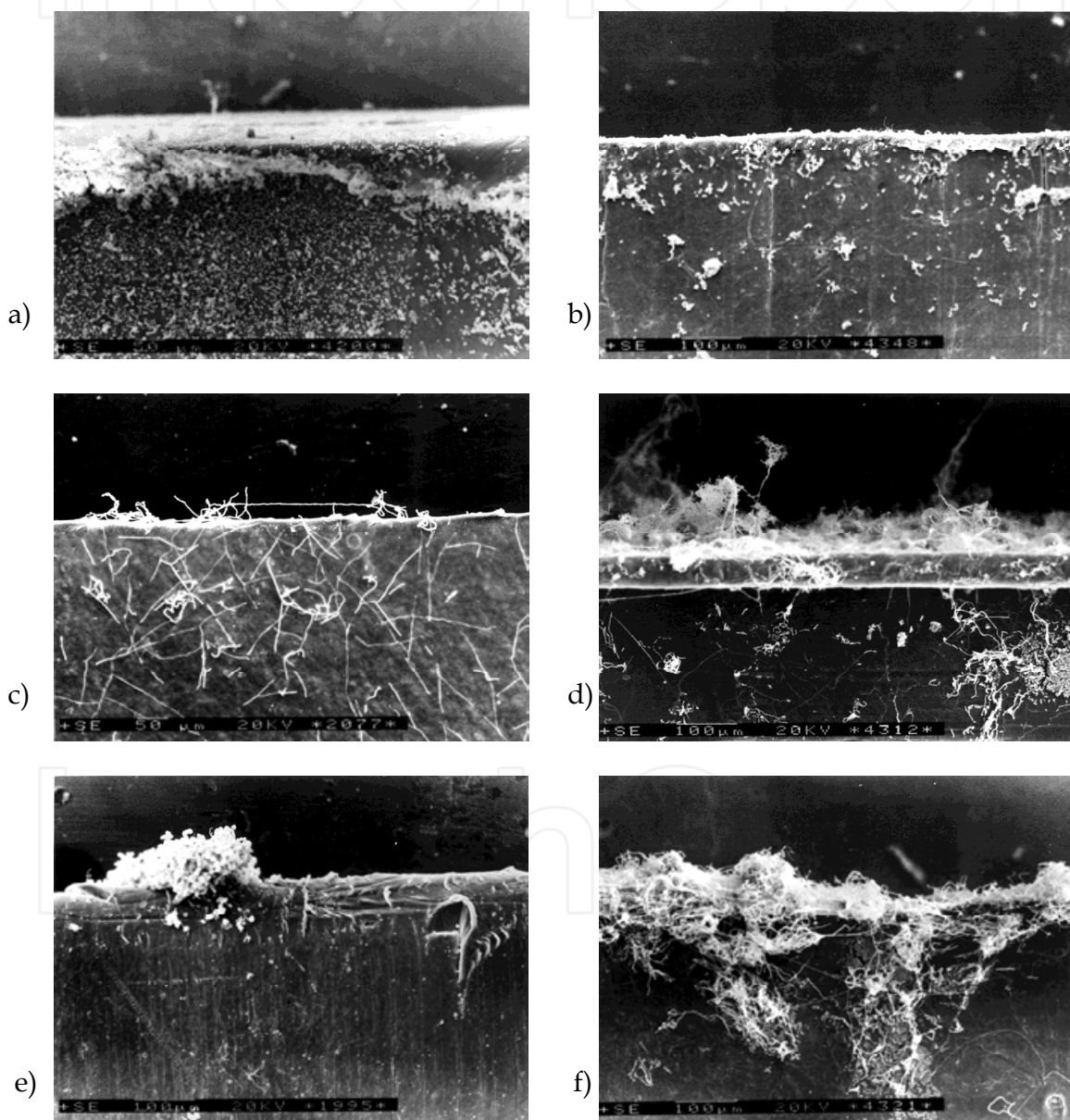


Fig. 4. SEM micrographs of neat 85/15 composition after biodegradation with a) *Aspergillus niger* b) *Aureobasidium pullulans* c) *Paecilomyces varioti* d) *Penicillium funiculosum* e) *Trichoderma viride* f) mixed fungal population

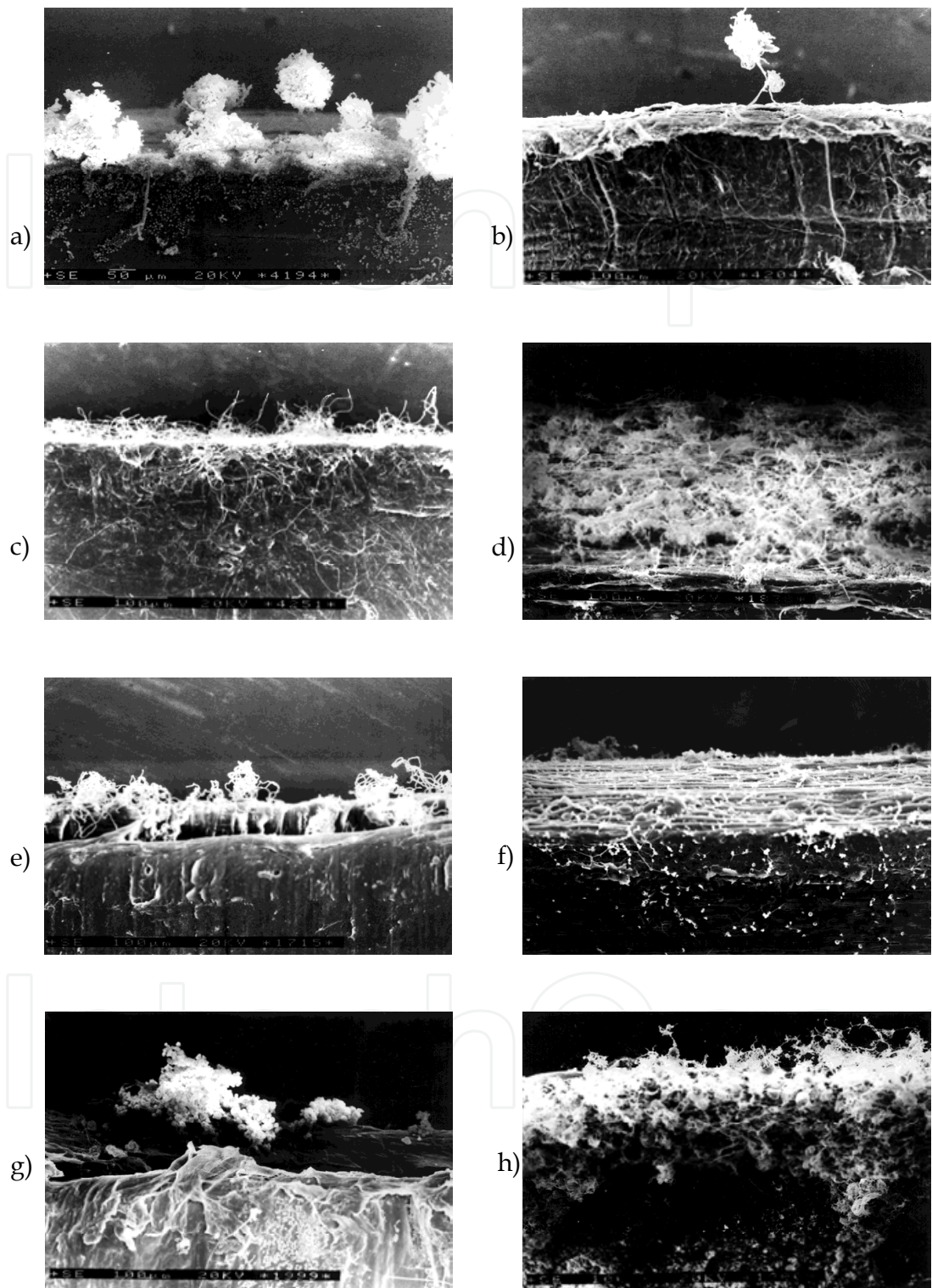


Fig. 5. SEM micrographs of neat 70/30 composition after biodegradation with a) *Aspergillus niger* b) *Aspergillus terreus* c) *Paecilomyces varioti* d) *Penicillium funiculosum* e) *Penicillium ochrochloron* f) *Scopulariopsis brevicaulis* g) *Trichoderma viride* h) mixed fungal population

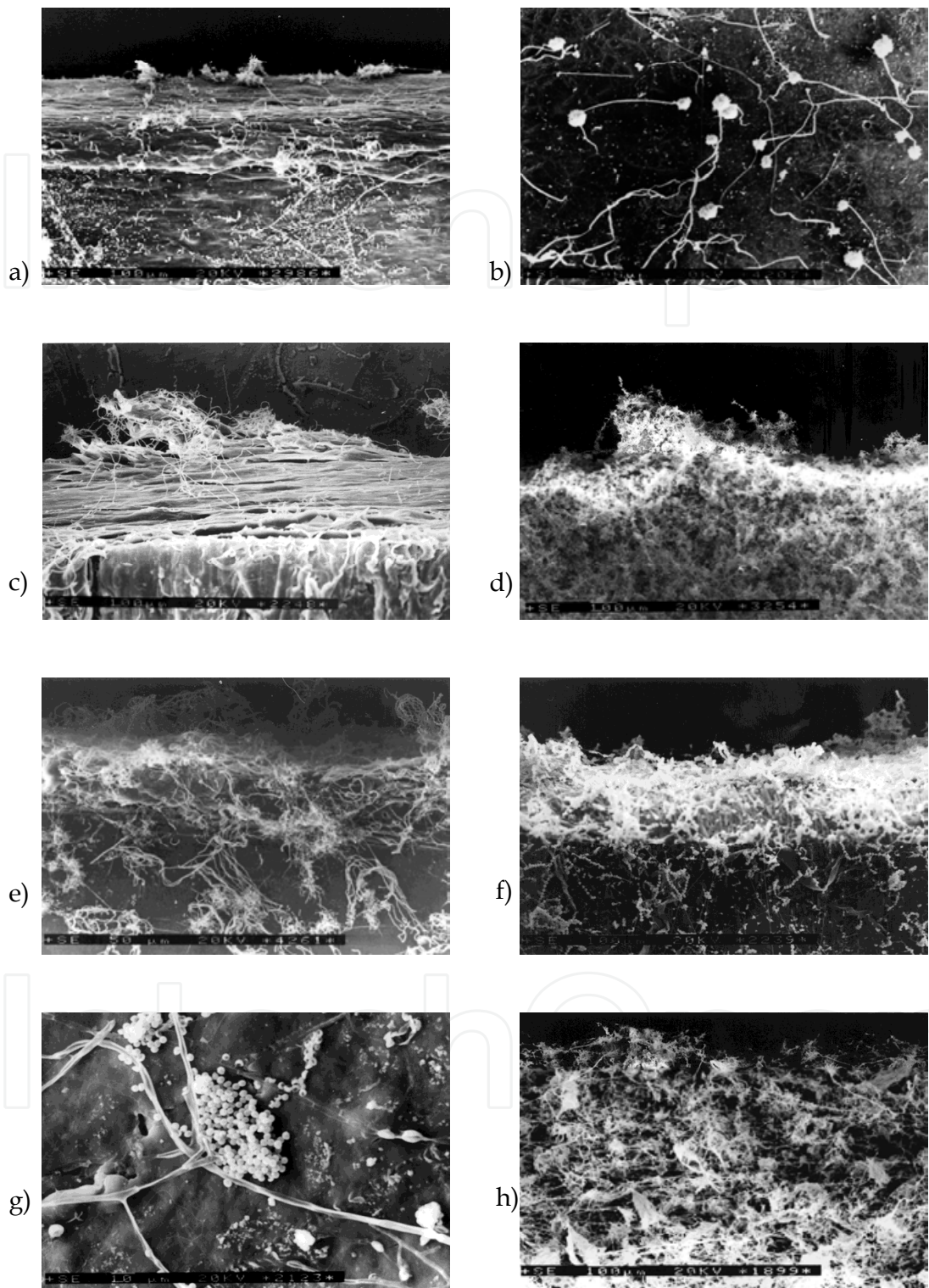


Fig. 6. SEM micrographs of neat 40/60 composition after biodegradation with a) *Aspergillus niger* b) *Aspergillus terreus* c) *Aureobasidium pullulans* d) *Penicillium funiculosum* e) *Penicillium ochrochloron* f) *Scopulariopsis brevicaulis* g) *Trichoderma viride* h) mixed fungal population

3.2 Abiotic degradation

Weight variations of LDPE film and LDPE/Bionolle® compositions recorded after exposing to abiotic treatment are shown in Table 3.

Abiotic degradation processes	LDPE/Bionolle® film compositions			
	100/0	85/15	70/30	40/60
	Weight loss, %			
Photodegradation	0,06	0,05	0,07	0,06
Thermodegradation	0,02	0,03	0,13	0,1
Photo- and thermodegradation	0,03	0,04	0,09	0,26
Hydrolysis	0	0,04	0,07	0,38
Photodegradation and hydrolysis	0,02	0,05	0,07	0,27
Thermodegradation and hydrolysis	0,02	0,03	0,08	0,34
Photo- thermodegradation and hydrolysis	0	0,04	0,09	0,31

Table 3. Weight loss of films after abiotic aging

Regardless of the type and combination of abiotic aging factors, there were no significant differences in weight loss observed for LDPE and its compositions containing up to 30% Bionolle®. More significant decrease of the weight in film containing 60% polyester was recorded not till then it was subjected to hydrolysis or when more than one aging factor was used during degradation experiments. Oxidative aging of films did not accelerate their loss of mass, most likely due to the presence of crosslinks evolved under the action of radiation and/or heat (Ojeda et al., 2011). It is often reported that, in LDPE films, crosslinking competes with the chain scission mechanism depending on the oxygen concentration at the reaction site (Feuilloley et al., 2005).

Changes in some mechanical properties of films after abiotic degradation are presented in Figure 7.

Values obtained by measuring elongation at break of polyethylene after photodegradation, thermodegradation and photothermodegradation slightly increased. As it was reported above, due to the formation of cross-linking bonds between the polyethylene chains. However, reduction in the mechanical properties after hydrolysis was observed. This decrease can be attributed to the chain scission of the polymer which, in this case, most intensively proceeded in films exposed earlier to both UV radiation and heat. This macromolecular chain scission is the cause of embrittlement of films (Abrusci et al., 2011). Amongst modified films, sensitivity toward abiotic treatment in terms of loss in the mechanical properties can be arranged as follows: 40/60>85/15>70/30. It seems that the exposure of the films containing 15% and 30% polyester to abiotic oxidation has accelerated their subsequent hydrolysis. On the contrary, in film consisted in most part of polyester, the most significant decrease in tensile strength by about 81% and elongation at break reduced by 99% was observed in samples subjected only to hydrolysis. From the above results it can be concluded that the samples with low content of Bionolle® behaved more like polyethylene while 40/60 composition more like polyester. It is known, that in hydrolytic degradation of biodegradable polyesters, elongation at break is the most sensitive property among the tensile properties (Tsuji et al., 2006).

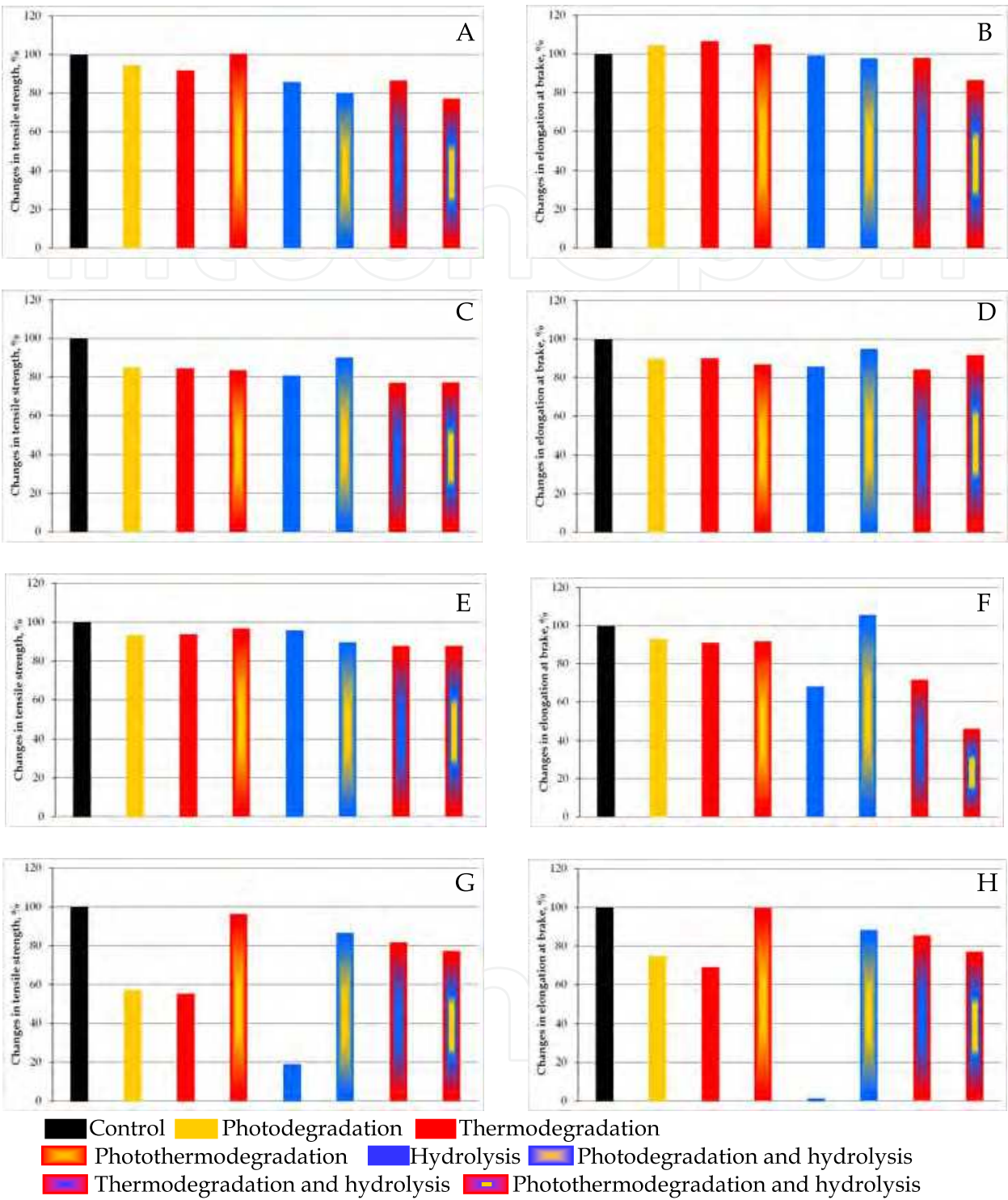


Fig. 7. Changes in some mechanical properties of films after abiotic degradation A) and B) LDPE C) and D) 85/15 blend E) and F) 70/30 blend G) and H) 40/60 blend

Figure 8 shows FTIR spectra of samples before and after exposing to selected abiotic and biotic factors.

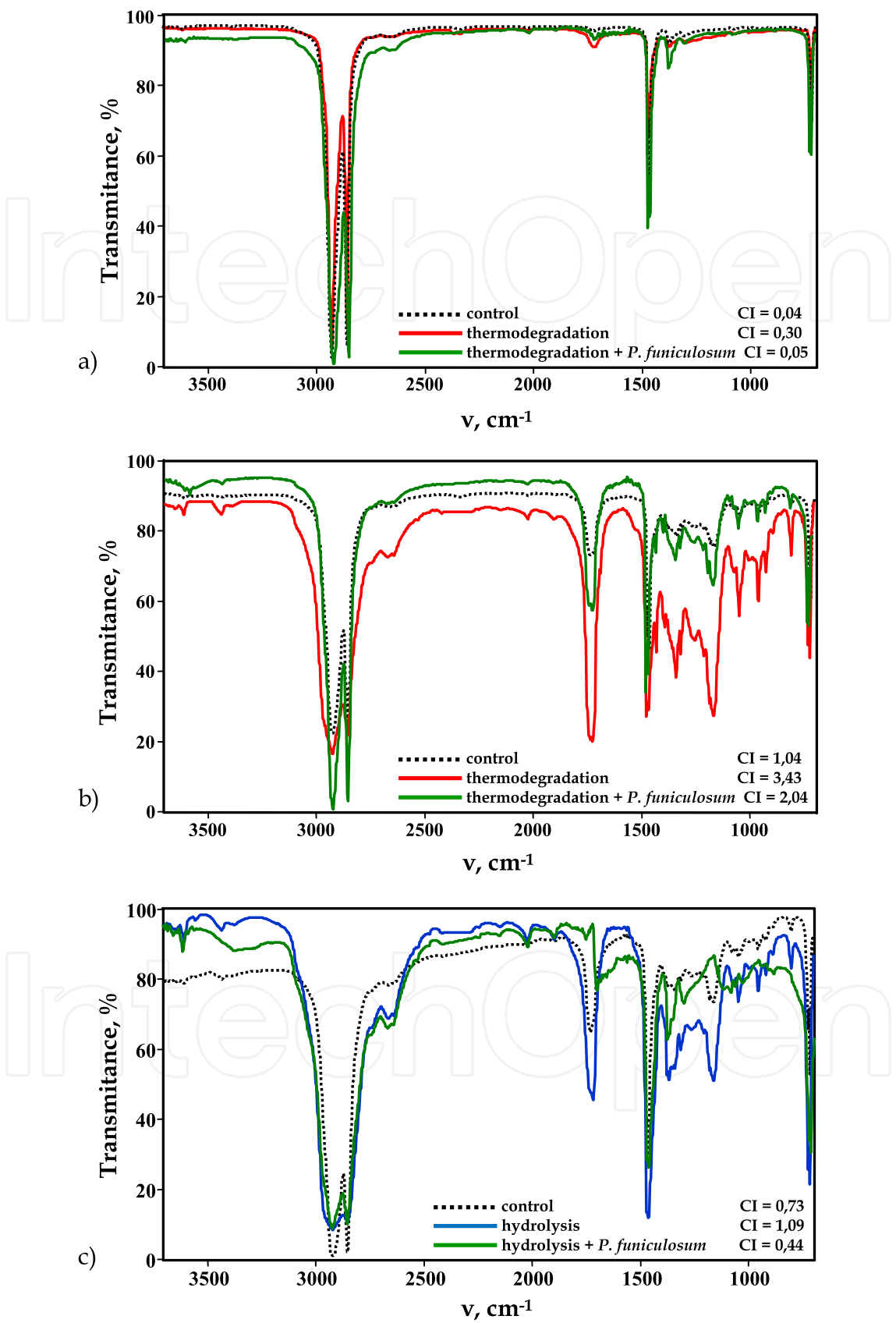


Fig. 8. FTIR spectra of films before and after degradation with selected abiotic and biotic factors a) LDPE b) 70/30 composition c) 40/60 composition

The data showed that the area corresponding to the carbonyl region has grown after abiotic degradation of all films indicating the formation of low molecular weight carbonyl compounds as a result of oxidation and/or hydrolysis. Carbonyl index of LDPE was increased by 25%(photothermodegradation)-650%(thermodegradation). As for polyethylene, the greatest impact on the oxidation of 70/30 composition had thermodegradation (230%) while the smallest - photothermodegradation (196%). Similar correlations were also observed for internal double bond index, which after thermodegradation of polyethylene and 70/30 composition increased by 167% and 316%, respectively. For film containing 60% Bionolle®, the largest increase in carbonyl index, amounting 50%, was found after hydrolysis. Such low degree of oxidation resulted probably from the fact that low-molecular fractions of polymer diffused out of the polymer matrix during the hydrolysis of film (Göpferich, 1996). The above findings suggest that single processes, especially thermo-oxidation, are more efficient in polymer degradation than simultaneous action of UV radiation and heat. These findings are in agreement with (Ram et al., 1980) who claims that the presence of oxygen in conjunction with high temperatures, plays more significant role in the increase of carbonyl concentration than when combined with UV exposure. Moreover, the air temperature as a critical factor increases the rate of various chemical reactions associated with degradation (Briassoulis et al., 2004). Additionally, as mentioned earlier, thermodegradation occurs throughout the bulk of polymer, not only on its surface.

Micrographs of films exposed to selected abiotic factors are presented in Figures 9 and 10.

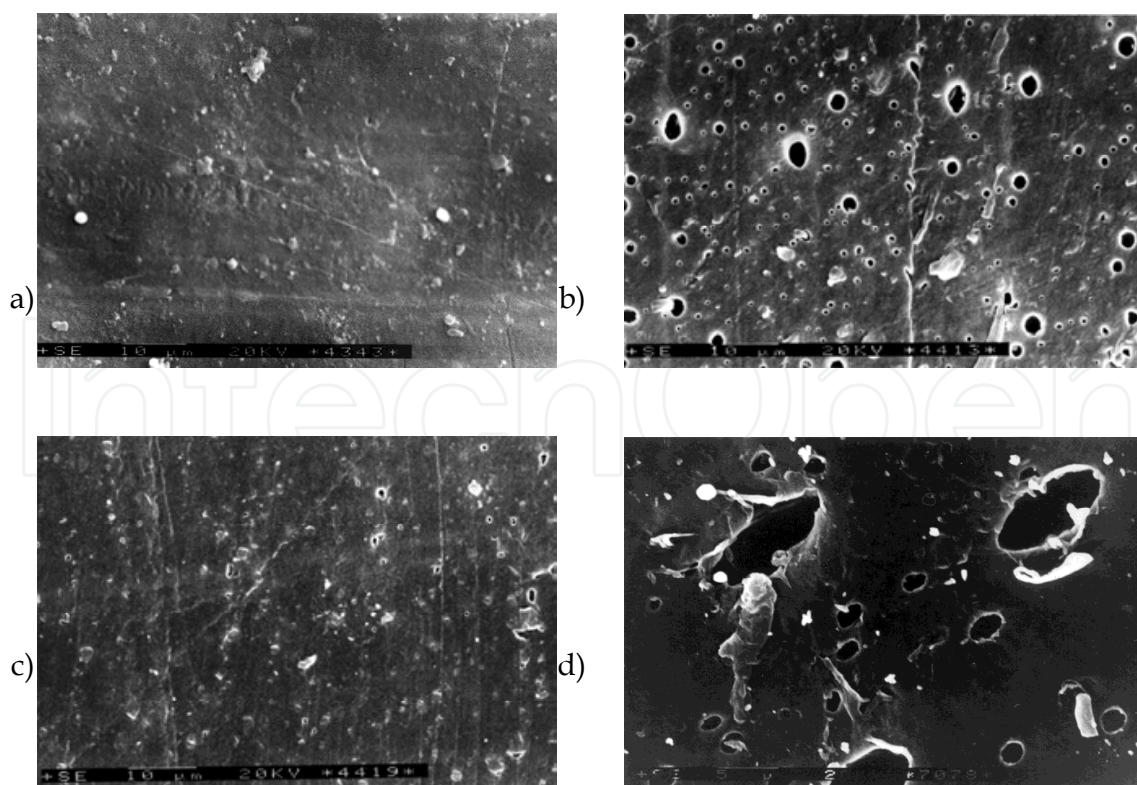


Fig. 9. SEM micrographs of 70/30 composition after a) photodegradation b) thermodegradation c) photothermodegradation d) hydrolysis

Compared to the smooth control film (Figure 2), only some irregularities were visible on the surface of 70/30 composition exposed to UV radiation (Figure 9a). After thermodegradation numerous and well distributed oval cavities with a diameter 1-8 mm were seen all over the surface (Figure 9b). Observations of changes resulting from the individual oxidative processes (photo- and thermodegradation) were helpful in interpreting the data obtained after simultaneous action of UV radiation and heat (Figure 9c). It is evident that both processes act antagonistically. This observation confirms the results obtained by other methods. The smallest weight loss and negligible increase in carbonyl index, probably resulted from the fact that sites of potential chain oxidation (macro radicals) were involved in the crosslinks formation (H-S. Kim & H-J Kim, 2008). Hence, observed reinforcement of plastics after photothermodegradation. However, the most pronounced changes were observed after hydrolysis of the film (Figure 9d). Holes on the surface were less in number but bigger in size than cavities observed after thermodegradation. Studies conducted by other researchers suggest that hydrolysis, in contrast to the photodegradation, occurred mainly in the amorphous region of polymer (Bikiaris et al., 2006; Tsuji et al., 2006). Judging by the size, shape and distribution of holes, identical to that observed after thermodegradation, it can be concluded, that during the heat-treatment, the amorphous phase breaks down in the first place. This is due to the fact that, under the impact of warmth, the mobility of macromolecules within amorphous region increases more significantly, therefore they become more prone to degradation.

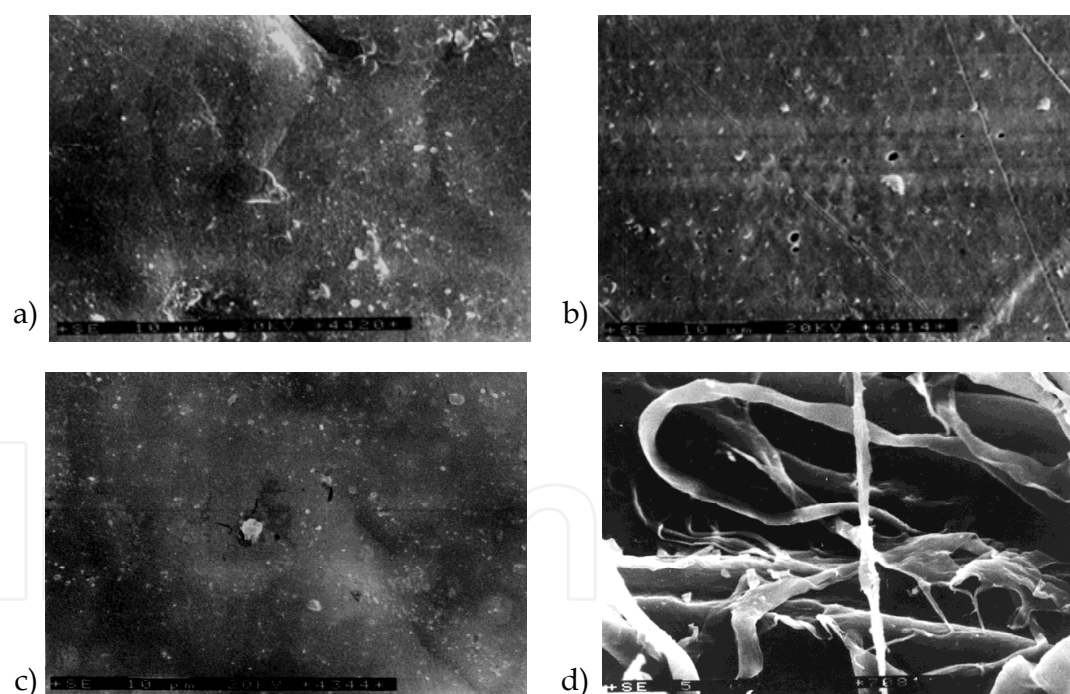


Fig. 10. SEM micrographs of 40/60 composition after a) photodegradation b) thermodegradation c) photothermodegradation d) hydrolysis

There were no visible changes of film texture after photo- and photothermodegradation (Figure 10a and c). Again, after another analysis of 40/60 composition, it could be stated that the behaviour of the composition under the influence of different factors is affected mainly by a large quantity of polyester in polyethylene. These findings are in agreement with our previous study on photodegradation of PBSA (Łabużek et al., 2006b). Thermodegradation of

film containing 60% Bionolle® resulted in the formation of regular holes in small quantities (Figure 10b). The most significant surface fragmentation was observed after hydrolysis of the film (Figure 10d). As is evident from SEM, amorphous regions are preferably hydrolysed, revealing the crystalline ones which in turn affects the mechanical properties. It is postulated that mechanical properties, especially elongation at break (see Figure 7G and H), depend more on changes occurring in the amorphous phase (Briassoulis et al., 2004).

3.3 Influence of abiotic degradation on the rate of biodegradation

Penicillium funiculosum and mixed population of fungi were used in studies on biodegradation of abiotically aged films, since, in previous stage of experiments, they exhibited the greatest ability to degrade examined plastics.

Table 4 shows the percentage weight loss of pre-aged LDPE film and LDPE/Bionolle® compositions after biodegradation with *Penicillium funiculosum* and mixed fungal population.

Process	Fungi	LDPE/Bionolle® film compositions			
		100/0	85/15	70/30	40/60
		Weight loss, %			
Photodegradation and biodegradation	<i>P. funiculosum</i>	0,13	0,26	1,43	69,19
	Mixed fungal population	0,07	0,18	1,38	65,61
Thermodegradation and biodegradation	<i>P. funiculosum</i>	0,28	0,28	1,48	71,61
	Mixed fungal population	0,04	0,23	1,56	74,14
Photo- and thermodegradation and biodegradation	<i>P. funiculosum</i>	0,08	0,14	1,45	70,16
	Mixed fungal population	0,12	0,15	1,27	60,38
Hydrolysis and biodegradation	<i>P. funiculosum</i>	0,17	0,45	2,18	74,62
	Mixed fungal population	0,13	0,32	1,86	59,32

Table 4. Weight loss of pre-aged films after biodegradation

Based on material weight loss it cannot be clearly determined what impact have abiotic processes had on subsequent biodegradation of the material. Contrary to LDPE, photodegradation, thermodegradation and photothermodegradation of modified polyethylene films accelerated their biodegradation. Percentage weight loss of LDPE films modified with 30% Bionolle® after biodegradation with *Penicillium funiculosum* and mixed population of fungi increased by 15% and 13%; 19% and 28%; 17% and 4% in comparison to weight loss of neat films, respectively. The biodegradative propensity of abiotically degraded 40/60 composition was also markedly affected. The pre-treated film after being exposed to *Penicillium funiculosum* and mixed population of fungi exhibit a mass loss of 15-19% and 4-28% higher than observed for control film. However, the biggest mass loss was observed after hydrolytic aging and biodegradation with *Penicillium funiculosum*. Biodegradation of films containing 15%, 30% and 60% polyester after prior hydrolysis increased by 104.5%, 75.8% and 24%, respectively. Considering percentage weight loss after hydrolysis and biodegradation of 40/60 composition, we have to remark, that any amount greater than 60% meant the degradation of polyethylene.

Changes in some mechanical properties of film samples after the abiotic degradation and biodegradation are shown in Figure 11.

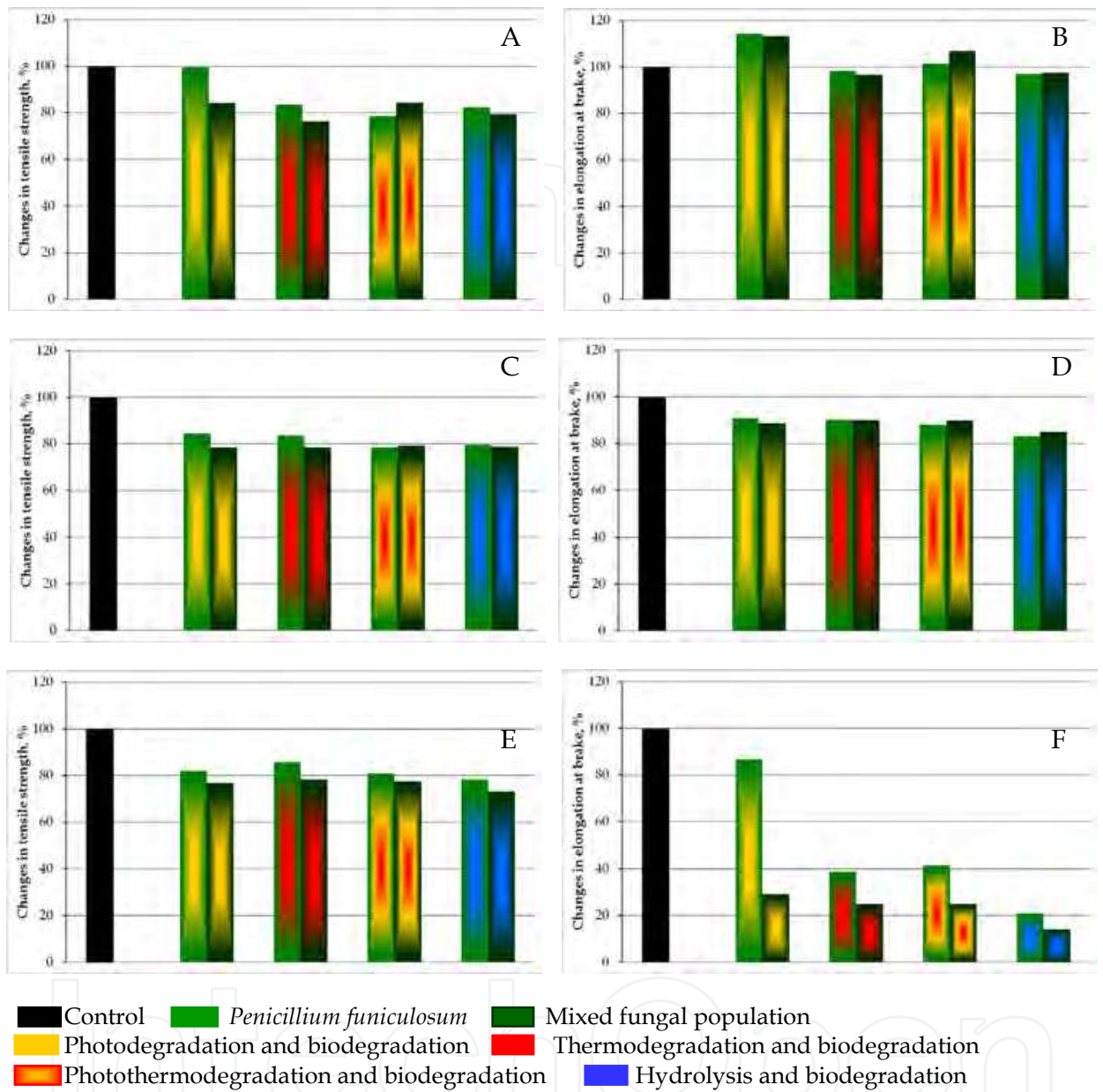


Fig. 11. Changes in some mechanical properties of films after abiotic and biotic degradation A) and B) LDPE C) and D) 85/15 blend E) and F) 70/30 blend.

A significant increase in elongation of LDPE after thermo-, photo-thermo- and biodegradation with both *Penicillium funiculosum* and mixed populations of fungi was noted. These values were significantly higher than observed after biodegradation of neat polyethylene. The highest impact of abiotic pretreatment on the subsequent biodegradability was observed for 85/15 composition which elongation decreased by 9,26%-16,82% as compared to 3,09%-8,49% for the film subjected only to biodegradation. As seen from Figure 11 there is a difference concerning the influence of abiotic aging to biodegradation of modified films between mixed fungi population and *Penicillium*

funiculosum. Contrary to mixed fungal population, assimilation of products of polymer oxidation during incubation with *Penicillium funiculosum* occurred less efficiently than depolymerisation of long LDPE chains. Far-advanced decomposition of 40/60 blend, prevented determination of its mechanical properties.

The amount of carbonyl groups, resulting from thermodegradation, decreased by 83% as a consequence of the assimilation of the degradation products by *Penicillium funiculosum*. Similar mechanism of biodegradation of abiotically aged polymers is repeatedly reported. Also Albertsson et al. (1987) found a synergistic effect between photooxidation and the biodegradation of polyethylene. Carbonyl residues completely disappeared after the incubation of the polymer samples in the presence of *Arthrobacter paraffineus*. Decrease of carbonyl index by 30-35% with respect to the starting materials was described for LDPE film samples containing pro-oxidant additives exposed to thermal- and biological degradation (Chiellini et al., 2007). The spectroscopic investigations led by Roy et al. revealed that the bacterial consortium consisted of *Bacillus pumilus*, *Bacillus halodenitrificans* and *Bacillus cereus* preferentially consumed the oxygenated products, thus leading to a decrease in the carbonyl index from 1,29 to 0,31 (Roy et al., 2008). In our study, internal double bonds also proved to be equally easily digested, since their amount after thermo- and biodegradation decreased by 92%. Interestingly, our study also shown that the number of carbonyl residues was about 80% lower than that observed during the biodegradation alone. The amount of carbonyl groups in the film with 30% content of polyester after thermo- and biodegradation compared to control film increased by 96%, while in relation to the film after thermodegradation decreased by 41%. As shown on Figure 8 carbonyl index of aged 40/60 composition after hydrolysis and subsequent biodegradation was lower by 40%, 93% and 60% than the value obtained for the control, after biodegradation and after hydrolysis, respectively.

These results implies that the filamentous fungi having at their disposal oxidised degradation products of polyethylene become less effective in degradation of macromolecules. Decrease in both indices (carbonyl and internal double bond) is a clear evidence that microorganisms use other set of enzymes during biodegradation of aged films than when they grow on high-molecular neat LDPE and polyester. Another conclusion is that the main enzymes involved in degradation of polymers are not constitutive proteins, expressed and secreted by microorganism independently of the substrate. On the contrary, the difference in mechanism of biodegradation clearly indicates the participation of inducible enzymes expressed only under specific conditions.

Micrographs of films exposed to selected abiotic factors and subsequent biodegradation are presented in Figure 12.

Compared to the film exposed only to biodegradation, observations of LDPE after thermo- and biodegradation revealed filamentous fungi growing over the entire surface of the film (Figure 12a). Rough, peeling surface of the material was seen at higher magnification. It is likely that the fungi inhabiting film, used the degradation products of LDPE as a carbon and energy source. This surveillance was supported by a decrease of carbonyl index (Figure 8) and elongation at break (Figure 11) indicating fungal assimilation of low-molecular weight fractions.

SEM micrographs of 85/15 composition revealed deep cracks and holes with diameter 5-50 mm. The cavities on the surface suggested that microorganisms penetrated the polymer matrix during the degradation process.

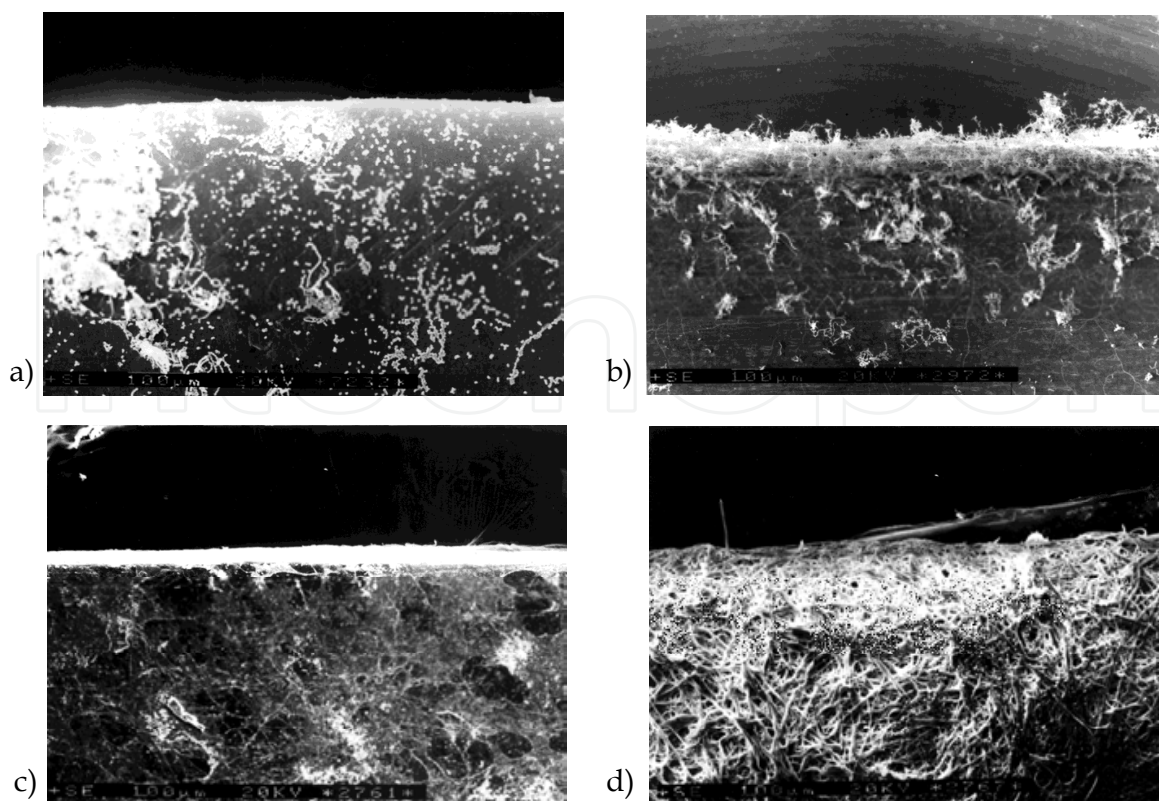


Fig. 12. SEM micrographs of films after exposing to different abiotic factors and subsequent biodegradation with mixed fungal population a) LDPE after thermo- and biodegradation b) 85/15 composition after photo- and biodegradation c) 70/30 composition after photo-thermo- and biodegradation d) 40/60 composition after hydrolysis and biodegradation

Massive erosion (holes with diameter about 200 μm) of film 70/30 and dense network of fungal hyphae indicated that, after abiotic degradation, surface of film become at least as available to microorganism as unaged 40/60 blend.

It was impossible to separate fungal hyphae from the residual 40/60 composition after 84 days of hydrolysis and subsequent biodegradation. As revealed earlier (Table 4), weight loss of film exposed to both factors increased slightly compared to film subjected only to biodegradation. In order to describe the possible mechanism of degradation of this material, it is essential that a few facts should be given. Firstly, hydrolytic degradation (abiotic or biotic) of the polymer occurs predominantly in the amorphous regions (H-S. Kim & H-J Kim, 2008). Secondly, hydrolysis of the crystalline material is slow, because of the limited water diffusion rates into the crystalline domains and stereochemical limitations (Bikiaris et al., 2006). In our study, after inoculation of the composition with fungi, developing hyphae at first assimilated low-molecular products of polymer hydrolysis then attacked its crystalline region (Tserki et al., 2006). Moreover, by taking into account the weight loss of the composition (59-75%), it can be assumed that fungi (long before the end of the experiment) completely assimilated polyester. Remaining LDPE fibres are clearly visible in the micrographs. Hence, decrease in the rate of biodegradation could be the result of (i) slow biodegradation of crystalline phase of polyester (ii) complex biodegradation of LDPE and (iii) penetration of fungi into the depths of the polymer matrix.

4. Conclusion

In the environment plastics decompose under the influence of different abiotic and biotic factors. The abiotic factors such as radiation, temperature, humidity, chemical pollution and wind can act synergistically or antagonistically causing various types of structural and chemical changes in the polymer. Microorganisms, especially bacteria or fungi, play a crucial role in biological degradation of polymers.

Scanning electron microscopy (SEM) is an invaluable tool for polymer analysis, since it is extensively used to study changes in the texture and composition of biodegradable polymer materials exposed to various environmental factors. It allows for the exploration of large surfaces with excellent resolution of topographic features.

Especially the new generation of SEM technology, known as ultra-high resolution field emission SEM (UHR FE-SEM) presents a promising technique for polymer morphological characterization, and provides complementary data to other microscopic methods.

One of the possible ways to accelerate the degradation of so-called “stable polymers” in the environment is their blending with polymers containing ester, ether, carboxyl and hydroxyl groups that are susceptible to hydrolytic attack of microorganisms. The chapter describes studies on biodegradation of LDPE/Bionolle® blends. It was shown that the addition of polyester significantly accelerated biodegradation of material.

Another way to sensitize the polymer is to expose it to the abiotic aging (action of abiotic factors) followed by the action of microbes. Abiotically modified surface of plastics promotes growth of microorganisms thus accelerates biodegradation.

Indeed, examined films underwent rapid biodegradation, but the course of the process was significantly different from that seen earlier. Further investigation on the mechanism of biodegradation revealed that fungi secreted different sets of enzymes depending on molecular weight of substrate. Unlike some other researchers, we have shown that filamentous fungi used in our study, were capable of efficient oxidation and degradation of the high-molecular weight LDPE. However, when pre-degraded, low-molecular weight chains of polyethylene served as a source of carbon and energy, microorganisms assimilated only short oligomers resulted from prior abiotic degradation. They did not show strong oxidising activity.

In our opinion, LDPE/Bionolle® blends can be used in the production of environmentally degradable packagings. Particularly noteworthy is composition containing 60% Bionolle®, which decompose several dozen percent within 84 days.

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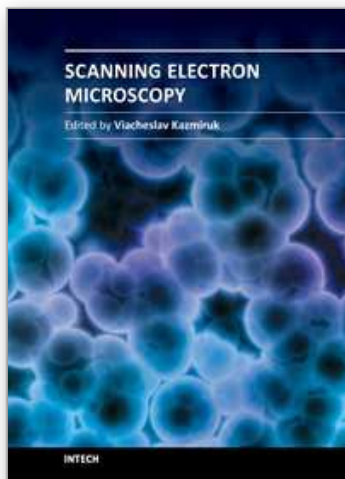
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