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OXO-BIODEGRADABILITY OF POLYETHYLENE BLENDS WITH STARCH, CELLULOSE AND SYNTHETIC ADDITIVES

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Abstract. Polyethylene (PE) is a pollutant packaging and mulch material. Therefore, it is necessary to raise its oxo-biodegradability by additives. Oxo-biodegradation is the degradation of PE in two steps: oxidation followed by microorganisms biodegradation. In this study, starch and cellulose are compared with synthetic additives. The results reveal that starch and cellulose cannot increase oxygen absorption and oxygenation as good as synthetic additives. However, they increase water absorption and make the surface of the bulk polymer more porous. Hence, the blends with starch and cellulose can be attacked more easily by microorganisms.

Keywords: Oxo-biodegradability, biodegradation, polyethylene blends, synthetic additives, starch, cellulose.

1. Introduction

Polyethylene (PE) is a polyolefin that can be found in packaging material and agricultural mulch films [1]. It is synthesized by polymerization of ethylene monomers. This ethylene gas is usually produced in a petrochemical process.

PE is in general resistant to degradation under environmental conditions and causes a lot of waste, because PE is a high-molecular-weight polymer. It contains very large molecules which cannot be attacked by microbial enzymes. Furthermore, it is not degraded by UV or heat under environmental conditions [1]. In fact, polyolefins pollute the environment at the rate of 25 million tons per year [2].

In order to protect the environment from more pollution by PE, its degradability must be raised. Polyolefins are usually degraded into low molecular weight compounds before biodegradation by micro-

organisms and their enzymes takes place. Microorganisms are able to degrade polyolefins with a *MW* lower than 5000 Da [1]. For example, filamentous fungi damage the polyolefins [9]. However, not all microorganisms that degrade polyolefins have been identified by now [1]. In order to accelerate biodegradation of polyolefins, additives have been developed by several research groups and companies. There exist synthetic additives as well as natural ones.

Polyolefins are degraded by oxo- biodegradation which consists of two stages of degradation. The initial step is the autoxidation of the polyolefin. The *n*-alkane chains are oxidized to ketones which are readily cleaved by hydrolysis to yield the corresponding acid [2]. In this way, hydrophilic polymers are created. These oxidation products are degraded by enzymes of microorganisms [1]. This second step is therefore known as biodegradation.

The radical mechanism of oxidation consists of three major steps: radical formation, chain propagation and finally the recombination of free radicals to end the reaction.

The initiation reaction delivers free alkyl radicals. Thus impurities support the initial radical formation in the PE. These alkyl radicals are oxidized to deliver peroxy radicals. Then, these peroxy radicals attack further polyolefin chains. In this way, hydroperoxides and new alkyl radicals are created and the radical chain reaction is propagated. If there is enough oxygen available, the termination reaction takes place [4].

In general, the final products of the polyolefins autoxidation depend on the available amount of oxygen and terminal double bonds. Moreover, the heterogeneous reaction of polyethylene on air is also determined by transport processes. If the polymer absorbs oxygen, the diffusion of oxygen is possible [4]. In general, the final

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The mechanism of PE oxo-biodegradation is not fully understood. Nevertheless, it is shown that abiotic oxidation delivers molecules with less weight, but they are still too large to pass the cell membrane. So they are further oxidized by extracellular enzymes or cell wall associated enzymes. These enzymes attack the surface of the polymer and the surface is eroded. The resulting smaller molecules are transported into the living cell. In an aerobic atmosphere, they are totally degraded into H₂O, CO₂ and biomass [6].

In general, the biotic degradation of polymers is a complex reaction. Hence, its kinetics is described by a Freundlich or modified Langmuir isotherm instead of Michaelis-Menten kinetics [3]. Considering the whole oxo-biodegradation, the first abiotic stage is the rate determining one. It can be accelerated by UV light (photodegradation) or by heating (thermal degradation). In addition to thermal degradation and photodegradation, the mechanical stress can be applied to accelerate degradation [8]. Furthermore, several additives improve the rate of this step. Their application in the first step of oxo-biodegradation is called a prodegradant technology [1].

In general, the synthetic additives help to oxidize the carbon backbone of the polyolefin. There exist two major groups of synthetic additives for prodegradant technology.

The first group consists of transition metal complexes of Mn, Fe and Co with organic ligands as well as metal oxides like TiO₂ combined with Mn. Usually, TiO₂ is added to whiten the polymer. Since it absorbs UV, this additive can accelerate the oxo-biodegradation. Commercial examples for transition metal based additives are d₂W by the manufacturer *Symphony Environmental*, TDPA by EPI or Addi-Flex by Addi-Biotech.

The second group includes transition metal free systems. For example, ketone copolymers, alkali metal carboxylates, unsaturated alcohols and esters, 1,3-diones, special amines like guanidine and peroxides like t-butyl hydroperoxide can be mentioned [1]. Example for this kind of additives are PDQ-H and UV-H by *Willow Ridge Plastics*.

The second stage of oxo-biodegradation is the degradation by microbes or enzymes. It was shown that blends of low density polyethylene (LDPE) with starch are more biodegradable than LDPE alone [1]. When the blends are exposed to UV radiation and buried in biotic

soil, higher carbonyl content can be measured by FT-IR than for LDPE alone. This indicates a higher oxidation yield. Consequently, starch facilitates biodegradation.

However, starch does not generally raise the biodegradability of the synthetic polymer matrix [10]. But it is possible for LDPE. Starch allows the microorganisms to attack the filler and in this way tension on the PE chains is created. Breaking of chain due to this tension creates shorter parts that can be attacked by microorganisms.

Basically, polymers can be degraded by hydrolysis of labile bonds. This reaction is enabled by enzymes from microorganisms. In biopolymers like starch, bonds labile towards hydrolysis are present. They can be blended with synthetic polymers like PE. This combination of PE with low cost biopolymers delivers biodegradable and in the meantime functional polymers. Further examples of convenient biopolymers are cellulose, soybean meal or pellet.

In several studies it was shown that starch accelerates the degradation of PE by moisture or microorganisms [1]. Starch is a natural polymer that is used by plants to save energy. It consists of two homopolymers of D-Glucose. One of them is amylose which is a linear α -D-(1,4')-glycan. The other one is amylopectin which contains the same linear chains but also α -D-(1,6') bonds. These glucose chains carry hydroxyl groups that can react chemically. As a superordinate structure, the polysaccharide forms granules that are hydrophilic. Due to the hydroxyl groups, hydrogen bonds between the granules occur. This hydrophilicity causes changes of physical features (T_g and mechanical properties) when exposed to moisture [7].

Cellulose is also a polysaccharide that consists of β -D-(1,4) linked glucose monomers. It is the major cell wall component of several plants. It is also biodegradable and carries hydrophilic hydroxyl groups. These groups interact with oxygen atoms from another cellulose chain. Hence, the cellulose chains built up microfibrils with a high tensile strength.

Starch and cellulose are biodegradable and decomposed biotically into CO₂ and H₂O. These products are metabolized by photosynthesis in plants. In this way, there are no pollutants produced by biodegradation.

A known problem is that the polar starch granules are immiscible in the hydrophobic PE chains. This determines the mechanical properties of the blends. The morphology can be studied by light microscopy [11]. Hydrophilic modifications of PE (e.g. vinyl acetate) allow better miscibility of starch in PE [9].

However, the dimensional stability and mechanical properties of starch and cellulose are poor compared to

synthetic polymers. Their mechanical properties depend on the blending process [7].

In future, comparative studies about the biodegradation of LDPE/starch blends will be of interest. They will reveal the quality of starch as a natural additive to improve biodegradation.

Biodegradation can be measured by examining the physical appearance, molecular weight, developing CO₂ and microbial growth on the polymer surface in soil, compost, marine water and distilled water [1]. The suitable analytical technique for a given sample is chosen according to its morphology, physiology and the degradation criteria. For example, the polymer might be a film, powder, liquid or coating and the inoculums can be soil, water or oxygen. Common analytic techniques are gravimetry for a wide range of applications, respirometry of O₂ consumed or CO₂ produced, surface hydrolysis by pure enzymes, radio labeling for all kinds of inoculums and materials, gel chromatography, mass spectrometry, NMR spectroscopy and FT-IR as a fingerprinting technique. These methods are usually employed to monitor degradation over time [3]. Furthermore, gel permeation chromatography is employed to determine the MW of polymers as well as their MW distribution and polydispersity.

In this work, several low-density polyethylene (LDPE) blends were examined. The samples consisted of LDPE alone and LDPE with different additives: UV-H, d₂W and PDQ-H which are synthetic additives as well as starch (30 %) and cellulose (10 %).

The synthetic additive d₂W by Symphony Environmental consists of metal stearates and stabilizers. The transition metal is typically Mn [1]. The weight percentage should be between 1 and 3 % according to the manufacturer.

PDQ-H and UV-H fabricated by *Willow Ridge Plastics* do not contain heavy metals [12]. Their composition is kept secret by the company. PDQ-H helps to raise oxo- biodegradability. The optimal load is between 1–3 %. UV-H accelerates photodegradation of PE. The load should be between 2–4 %.

The amount of 10 % of cellulose in LDPE has been found to be the best for maintaining the mechanical properties of the polymer. For starch, 30 % is a rather high amount that is essential to accelerate biodegradation.

The physical and chemical properties of the blends were monitored by different methods. To examine the morphology of different blends, the light microscopy was used. The mechanical properties were determined by using ISO 527-3. The kinetics of oxidation at 363 K was measured by FT-IR. Moreover, the absorption of oxygen at 403 K was observed in order to evaluate the oxygen

barrier properties of the blends. Finally, the blends were compared regarding their capability to absorb water at 303 K.

The obtained results allow a comparison between natural and synthetic additives in general. Moreover, a comparison between starch and cellulose is possible as well as between UV-H, PDQ-H and d₂W.

The purpose of this paper is to study the effect of PE films of different nature additives on the oxo-biodegradation. These additions served as starch, cellulose (natural) and D2W, UV-H, PDQ-H (industrial synthetic additives). Identify the influence of additives on the properties of the film at different trials.

2. Experimental

A commercially available cornstarch, HI-Maize 1043, distributed by National Starch Food Innovation was used. Natural cellulose fibers were purchased from Arbocel. UV-H and PDQ-H were provided by Willow Rich Plastics. The additive d₂W is fabricated by Symphony Environmental. The matrix material was LDPE from JSC Neftekhimsevilen.

Low density polyethylene (LDPE) was blended with different additives in a laboratory melt in a thermal melt extruder at 413 K (Fig. 1). This extruder was built at the institute.

The LDPE granulates were given into the extruder and the grinding rate was adjusted to 28 rpm. They were totally molten after 2 min and the additive was added. The mixture was grinded for 6 min longer at 35 rpm.

The foils were produced in a thermal press from beads of the following blends: LDPE/UV-H, LDPE/d₂W, LDPE/PDQ-H, LDPE/starch (30 %) and LDPE/cellulose (10 %).

The press was heated to 413 K. Before they pressed, the beads were covered with polyamide overlays. Each sample was molten at 0 N/cm² for 1 min, 600 N/cm² for 1 min, again 0 N/cm² for 1 min and at last 60 N/cm² for 1 min until a clear film was obtained. The resulting films were between 90 and 225 μm thick.

In order to analyze the morphology of the PE blends, an imager Z2m by Zeiss was used with a magnification 5x.

For each sample, three photos from transmitted light, reflected light and polarized light were taken.

The bulk properties of a polymer can be determined by measuring their mechanical stability. These properties are very important for describing their behavior on a macromolecular scale. Consequently, they limit the actual usage of a certain polymer or polymer blends.



Fig. 1. Twin screw melt extruder for blending of PE at 413 K: motor (1); temperature control (2) and cover plate (3) for the twin-screw extruder (4)

ISO 527-3 or ASTM D882 are standard methods that are used to monitor the tensile properties of a polymer sample. The strength of the sample must be below 1 mm. With this standard method, the tensile strength, elongation at breaking and the modulus of elastic were determined.

The testing machine was fabricated in-house. Its crosshead speed was adjusted to $100 \text{ mm}\cdot\text{min}^{-1}$. Three

measurements were conducted for each sample ($10\times 50 \text{ mm}$) and the results were averaged to obtain a mean value. The strength of each sample was determined and taken into account.

In order to compare different additives, the kinetics of thermo-oxidation at 363 K is determined. As described above, this step is the rate determining one for oxo-biodegradation of polyolefins. The kinetic measurements will reveal the capability of the additives to accelerate oxidation.

Each blend was measured by IR spectrometry. For this purpose, a FT-IR spectrometer Spectrometer100 by PerkinElmer was used. Each sample was measured once before the thermo-oxidation was started. Then, the samples were stored at 363 C on air for 3 h. After 1, 2 and 3 h FT-IR spectra were taken. The samples were tested by the transmission method.

For observing the oxidation process, the absorption carbonyl stretch around approximately 1718 cm^{-1} was analyzed. Therefore the background of each spectrum was cancelled by baseline correction. Then, the absorption A was determined.

The absorption of oxygen of different blends is examined with a manometric aperture. The atmosphere of the PE stripes consists of pure oxygen. The overall O_2 pressure is adjusted to $\approx 80 \text{ kPa}$. The small manometers measured the difference ΔP from 80 kPa after oxygen absorption by the sample. The process was monitored for 15 h. In this way, the kinetics of oxygen absorption can be compared.

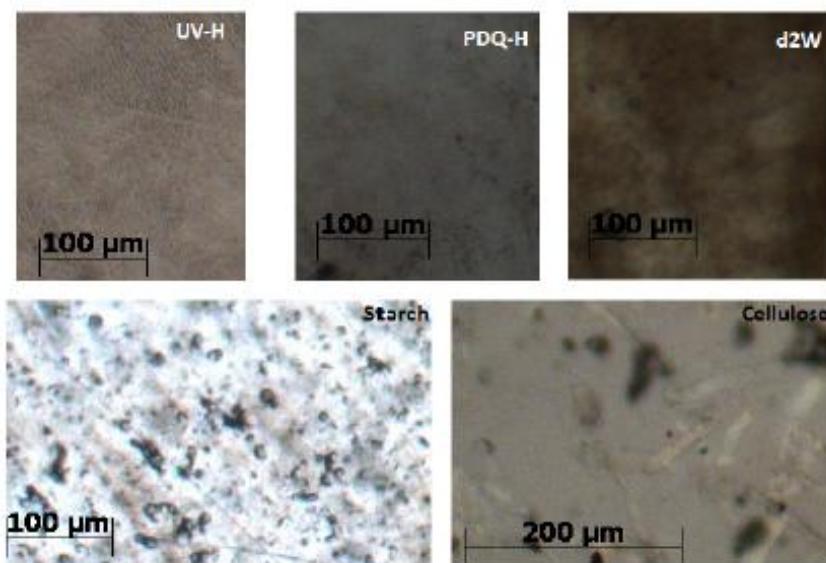


Fig. 2. Photos of of different LDPE blends surfaces with UV-H, PDQ-H, d_2W , starch (30 %) and cellulose (10 %)

The rate of water absorption was measured by weighing the blend samples every day. Before starting the experiment, the quadratic (2.0×2.0 cm) samples were weighed. Then, they were put into distilled H₂O and incubated at 303 K by a thermostat. For weighing the water absorption, the samples were dried using the absorbing paper.

3. Results and Discussion

The results are visualized in diagrams and graphs.

3.1. Microscopy

The morphology of the blends was studied by light microscopy (Fig. 2).

Fig. 2 shows that the synthetic additives UV-H, PDQ-H and d₂W have a homogeneous surface.

The surface of LDPE/starch (30 %) blend has pores that are approximately 10 μm in diameter. These pores containing polar starch granules are immiscible with the hydrophobic PE chains. This determines the mechanical properties of the blends. Cellulose forms patches of about 150×10 μm. These patches are not as evenly distributed as the pores from starch. In other words, cellulose does not penetrate PE as well as starch.

3.2. Mechanical Properties

In order to describe the mechanical properties of different blends, their elongation at breaking, ultimate tensile strength, and elastic modulus were determined.

Fig. 3 shows that the elongation at breaking of blends is in general shorter for blends compared with LDPE alone. However, the synthetic additives restore some durability. In contrast, the durability is around 100 % less for natural additives. This can be explained by taking into account the more brittle morphology of the blends with starch and cellulose. Their surfaces are more porous and therefore the polymers break more easily. Hence, the elongation at breaking is very short compared with more homogeneous blends.

The tensile strength of the blends with natural additives is 64 % of the strength of LDPE alone (Fig. 4). For LDPE/UV-H, the tensile strength is 91 % of the strength of LDPE and 84 % for LDPE/d₂W. For LDPE/PDQ-H, the ultimate tensile strength is even higher (118 %). In summary, UV-H does not change the tensile strength of LDPE as much as the other additives.

The modulus of elasticity E states the tendency of the sample to be deformed elastically. It was determined from the raw graphs. The angle α is the angle between the

curve and the abscissa during the initial linear stage of elongation.

$$E = \tan \alpha \quad (1)$$

According to the data visualized in Fig. 5, the modulus of elasticity is very low for pure LDPE compared with all blends. The value for starch is 100 times higher. For other additives it is even approx. 1000 times higher.

The elastic modulus is a value for the stiffness of the sample. Consequently, LDPE alone changes its dimensions when exposed to force faster as the blends. Among the blends, LDPE/starch (30 %) is the one with the lowest elastic modulus. Especially cellulose and UV-H have very high elastic moduli and change their dimensions slowly.

To sum up, all these additives change the mechanical properties of LDPE. According to Fig. 4, the natural additives make LDPE more brittle. The blend with starch (30 %) is usually more similar to LDPE alone than the blend with cellulose (10 %). Moreover, the blends with natural additives are not as strong as LDPE alone or with synthetic additives (Fig. 4). The synthetic additives and cellulose make LDPE stiffer (Fig. 5).

3.3. Kinetics of Oxidation by FT-IR

In general, FT-IR is used to identify the chemical composition of a sample. Functional groups deliver characteristic bands. The intensities of these bands are consummated to the concentration of the functional group as described by Lambert-Beer's Law.

In order to monitor the oxidation process at 363 K, the intensity of the carbonyl stretch at approx. 1718 cm⁻¹ is compared. The relative increase in intensity I_r at 1718 cm⁻¹ can be calculated from the raw spectra using Eq. (2). The initial absorption I_0 is used to determine the relative increase of intensity I_r after 1, 2 and 3 h. This increase is visualized in Fig. 7.

$$I_r = 100 \frac{I_n - I_0}{I_0} \quad (2)$$

Fig. 6 shows that LDPE alone is not oxidized on air at 363 K. For synthetic additives, the absorption at the carbonyl stretching signal increases. For d₂W, the increase is 200 %, for PDQ-H it is 87 % and for UV-H it is 17 %. However, for natural additives, the absorption does not increase. This indicates that they do not accelerate oxidation of LDPE. For cellulose, not even a carbonyl band is found in the spectrum. The oxygen in cellulose is incorporated as hydroxyl groups. Hence, a band at 3348 cm⁻¹ is observed.

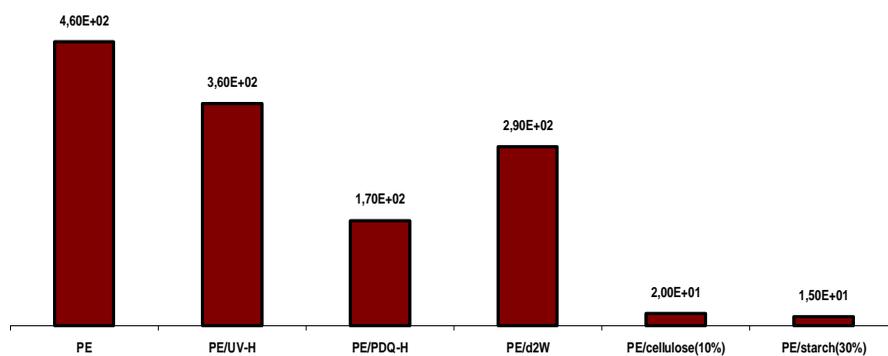


Fig. 3. Comparison of elongation at breaking (%)

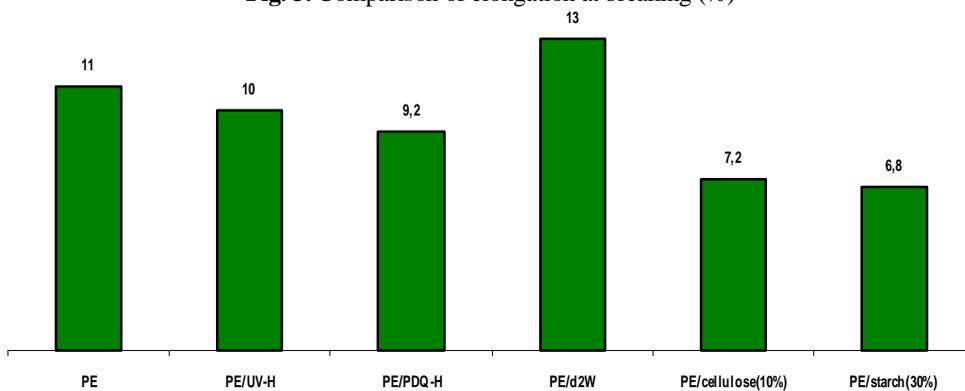


Fig. 4. Comparison of ultimate tensile strength (MPa)

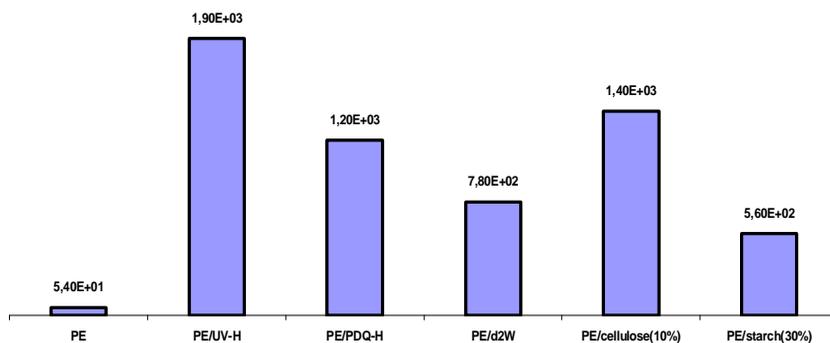


Fig. 5. Modulus of elasticity (a.u.) determined by Eq. (1) from the raw graphs (data are not shown)

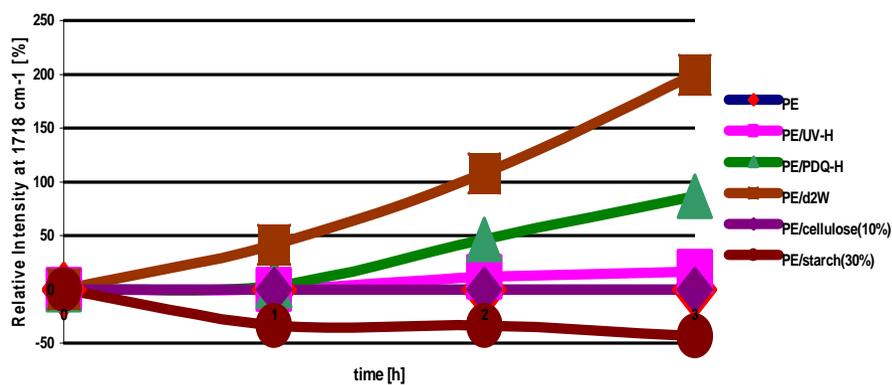


Fig. 6. Relative intensity in FT-IR at the ketone carbonyl band (appr. 1718 cm⁻¹) during oxidation on air at 363 K

The only effect that heating has on LDPE/starch (30 %) is a reduction of the water content (Fig. 7). The band at 1641 cm^{-1} can be attributed to water absorbed by the starch granules [5]. During the experiment, the band decreases (Table 1). Consequently, water is released at 363 K. In the meantime, relative absorption at 1712 cm^{-1} after baseline correction is not changed.

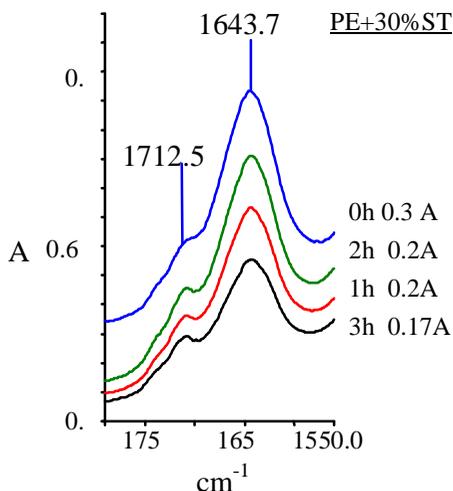


Fig. 7. FT-IR spectra of LDPE/starch (30 %) at 363 K on air over time

Table 1

Intensity at 1718 cm^{-1} during oxidation on air at 363 K

| Blend | Time, h | | | |
|---------------------|---------|------|-------|------|
| | 0 | 1 | 2 | 3 |
| PE/UV-H | 0.06 | 0.06 | 0.067 | 0.07 |
| PE/d ₂ W | 0.12 | 0.17 | 0.25 | 0.36 |
| PE/PDQ-H | 0.3 | 0.31 | 0.44 | 0.56 |
| PE/starch (30 %) | 0.3 | 0.2 | 0.2 | 0.17 |
| PE/cellulose (10 %) | 0 | 0 | 0 | 0 |
| PE | 0 | 0 | 0 | 0 |

In the spectrum of LDPE/cellulose (10 %), a water band at 1639 cm^{-1} was observed in the initial measurement, too. It had a very low intensity and was not observed in the later measurements. This fact shows that the cellulose blend contained less water which was also evaporated during the heating process.

The differences during the oxidation process can be explained by the nature of the additives. The synthetic additives d₂W, PDQ-H and UV-H are transition metal compounds. These compounds catalyze the decomposition of hydroperoxides into free radicals. Hence, the radical oxidation

is accelerated. The natural additives starch and cellulose have no catalytic function on the radical chain reaction.

3.4. Absorption of Oxygen

The measurement of oxygen absorption was carried out at 403 K. This temperature allows to measure the kinetics in a suitable time frame. The result is ΔP of oxygen compared with 80 kPa. This ΔP can be converted into the amount of oxygen absorbed Δn (mol/kg) by using Eq. (3), where 50 is weight of the sample.

$$\Delta n = \frac{\Delta P}{50} \cdot 100 \cdot 0.01 \quad (3)$$

$$r = \frac{\Delta h}{\Delta t} \cdot \frac{c}{60s} \quad (4)$$

The resulting isotherms are shown in Fig. 8. From these curves the rate r can be determined by the slope $\Delta h/\Delta t$ of the linear region by using Eq. (4). In Table 2 the resulting rates are summarized.

Table 2

Rate of oxygen absorption

| Blend | Rate of oxygen absorption, mol/(kg·s) |
|---------------------|---------------------------------------|
| PE/UV-H | $1.03 \cdot 10^{-5}$ |
| PE/d ₂ W | $1.96 \cdot 10^{-5}$ |
| PE/PDQ-H | $1.3 \cdot 10^{-4}$ |
| PE/starch (30 %) | $8.57 \cdot 10^{-6}$ |
| PE/cellulose (10 %) | $8.33 \cdot 10^{-6}$ |

Data from Table 2 shows, that the rates of oxygen absorption are higher for synthetic additives. For the natural additives, the rates are lower. LDPE/PDQ-H absorbs 100 times faster than the blends with cellulose and starch. This indicates that starch and cellulose films have high barriers for the penetration of oxygen.

3.5. Absorption of Water

The relative gain in weight during water absorption is shown in Fig. 9. For each blend, two samples were stored in distilled water and the average weight was determined. The relative weight was calculated with respect to the initial average weight (Eq. (5)).

$$K = \frac{W_2 - W_1}{W_1} \cdot 100\% \quad (5)$$

The graph (Fig. 9) shows that the natural additives accelerate water absorption. Synthetic additives do not enhance water absorption. The fluctuations of the measurements can be caused by single drops attached to the sample after drying it with a paper towel. Despite these fluctuations, the trend of weight gain for natural additives can be clearly seen in Fig. 9.

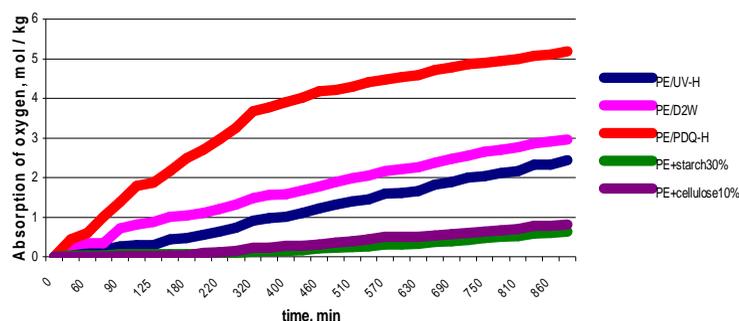


Fig. 8. Kinetics of oxygen absorption at 403 K at an oxygen pressure of 80 kPa

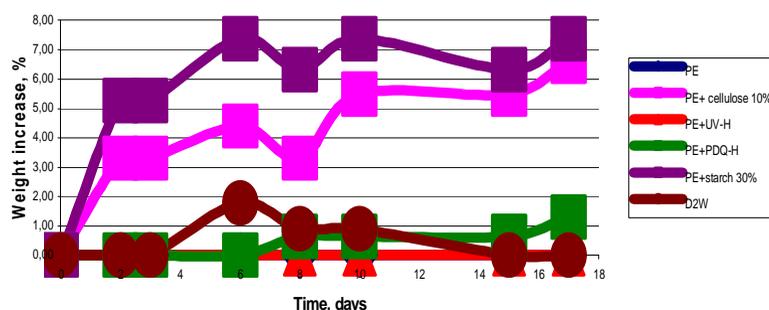


Fig. 9. Relative increase in weight during storage in distilled water at 303 K for 17 days

The cause for this water absorption for PE blends with natural additives is certainly their hydrophilicity. Since they consist of polysaccharides, they carry a lot of polar groups. However, the synthetic additives cannot raise the hydrophilic character of PE.

A consequence of this accelerated water absorption is the acceleration of biodegradation. After the polyolefins were oxidized, they can be cleaved by hydrolysis. During the oxo-biodegradation of PE in soil, it is exposed to oxygen and water. Consequently, the ability to absorb water raises the probability of fraction of the polymer.

Moreover, water molecules disturb the microstructure of the polymer. In this way, water allows microbial enzymes to further penetrate the polymer. These cell wall associated enzymes oxidize polymer. So the PE is further fractioned. In summary, absorbed water helps microorganisms and their enzymes during the surface erosion process.

4. Conclusions

The results obtained in this work allow to compare different additives that are available to accelerate oxo-biodegradation. The blends with synthetic additives exhibit a homogeneous surface. In contrast, the non-miscible natural additives cellulose and starch create pores

in the LDPE surface. These inhomogenities on the PE surface allow attacks by microorganisms. The mechanical properties of LDPE blends are changed by every kind of additives: the synthetic additives and cellulose make the material stiffer; natural additives make it more brittle and less strong.

It was shown, that the natural additives starch and cellulose do not accelerate oxidation at 363 K. However, synthetic additives are prooxidants and catalyze the oxidation of PE. The additive D_2W was identified as the one which catalyzes oxidation at 363 K best. The thermo-oxidation experiment and the observation of oxygen absorption have shown that oxidation is not accelerated by natural additives. Their role in acceleration of oxo-biodegradation is caused by their ability to absorb water. Whereas the blends of LDPE with synthetic additives maintain their hydrophobic character, the blends with starch and cellulose absorb water quickly. Since the cleavage of the oxidized PE chains is a hydrolysis reaction, water absorption raises the probability of cleavage.

The natural additives have an advantage that they are renewable, ecological and economical. During their biodegradation in soil, CO_2 , H_2O and biomass are developing. The addition of natural polymers decreases the petrochemically produced part of the polymers which can generally reduce the costs for PE in 14 times.

Consequently, it is useful to investigate further the mechanism and optimization of oxo-biodegradability accelerated by natural additives like starch and cellulose. The next step consecutive to this work is the comparison of different blends biodegradation.

References

- [1] Bateman S., Dean K. and Petinakis E.: *Progr. Polym. Sci.*, 2011, **36**, 1015.
[2] Eubeler J., Bernhard M. and Knepper T.: *Trends in Anal. Chem.*, 2010, **29**, 84.
[3] Eubeler J., Zok S., Bernhard M. and Knepper T.: *Trends in Anal. Chem.*, 2009, **28**, 1057.
[4] Jansen K.: Säureeinfluss auf die photochemische Alterung, Dissertation, UV-stabilisierter Polyethylenfolien, FU Berlin 2003.
[5] Kizil R., Irudayaraj J. and Seetharaman K.: *J. Agricult. Food Chem.*, 2002, **50**, 3912.
[6] Koutny M., Lemaire J. and Delort A.-M.: *Chemosphere*, 2006, **64**, 1243.
[7] Lu D., Xiao C. and Xu S.: *eXPRESS Polym. Lett.*, 2009, **3**, 366.
[8] Mueller R.: *Biopolymers*, 2010, **10**, 365.
[9] Popov A. and Koroleva A.: *Ecologia i Promyshlennost Rossii*, 2010, **12**, 37.
[10] Walker A., Tao Y. and Torkelson J.: *Polymer*, 2007, **48**, 1066.

[11] Ning W., Jiugao Y., Xiaofei M and Ying W.: *Carbohydrate Polymers*, 2007, **67**, 446.

[12] www.williwridgeplastics.com.

ОКСИ-БИОРОЗКЛАД ПОЛІЕТИЛЕНОВИХ СУМІШЕЙ З КРОХМАЛЕМ, ЦЕЛЮЛОЗОЮ ТА СИНТЕТИЧНИМИ ДОДАТКАМИ

Анотація. Показана можливість збільшення окси-біорозкладу поліетилену (ПЕ), який слугує матеріалом для пакування та забруднює довкілля після його використання, за допомогою введення в полімер різних додатків. Окси-біодеградація ПЕ здійснюється в 2 етапи: окиснення з наступною біодеградацією мікроорганізмами. Порівняно крохмаль і целюлозу (природні наповнювачі) та синтетичні додатки. Встановлено, що крохмаль і целюлоза не сприяють збільшенню поглинання кисню у порівнянні з синтетичними додатками, але підвищують поглинання води і приводять до утворення більш поруватої поверхні полімеру. Введення в ПЕ крохмалю або целюлози покращує здатність до проникнення мікроорганізмів в об'єм матеріалу та прискорення його розкладу.

Ключові слова: окси-біорозклад, біодеградація, поліетиленові суміші, синтетичні додатки, крохмаль, целюлоза.