

BIODEGRADABLE POLYMERS BASED ON SELECTED POLYOLEFINS AND POTATO STARCH

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Summary

This work deals with the biodegradable polymers, more particularly polyolefins, which contain different amounts of starch. Starch accelerates microbial degradation and thus shortens the time of polymer degradation in the environment. The tested materials were the most frequently used blends of polyolefins (polyethylene¹ and polypropylene²) containing 2, 5 and 10 wt.% of starch in the blend. Testing plates and bodies were prepared from the blend and were subjected to simulated weathering. The rate of degradation for both types of blends was measured and evaluated by standard analyzes and mechanical tests.

Keywords: polyolefins, starch, biodegradation, polymer degradation, mechanical properties

1 Introduction

The contemporary style of consumer society produces an excessive amount of materials; almost every fourth product is polymer-based. The situation urges global solutions to find a material that not only has the characteristics of the polymer from which it was created, such as strength, hardness, toughness and sufficient durability. It should also possess characteristics of the natural polymer and the ability to be degraded and decomposed into substances in the suitable environment comprising micro-macro organisms, humidity, UV radiation and other factors, which are inherent by natural and are a part of the natural cycle. Fulfilling all the above mentioned requirements for the final product is achieved by selecting the proper ratio between the base polymer and the degradable component. The various combinations of components are usually tested and monitored for several years to final their ideal ratio for achieving optimal product material and application characteristics.

2 Description, preparation and degradation of sample

Polyethylene (HDPE) and polypropylene (PP), being the mostly used polyolefins, were the main component of the tested samples. The second component was starch as a degradable element with the increasing concentration of 0, 2, 5 and 10 wt.% in the blend. Polymer blends of polyolefins and starch were homogenized (using the extruder W&D ZDS-K28) and a method of injection molding (injection molding NEO80) has been performed and standardized testing plates and bodies were prepared. Samples were subjected to artificial aging in a QUV-panel at 340 nm for 440 and 726 hours, respectively, which corresponds to the 4 and 6 months, respectively of natural weather aging in the territory of the central Europe. Brinell hardness and tensile properties using the unit MTS[®] 4/M force transducer at 20 kN were determined. Furthermore, the yellowness index was evaluated and the samples were visually evaluated.

3 Results and discussion

3.1 Brinell hardness

Results of hardness are presented as the mean in units of MPa and are expressed by parameters HK/5/153/60. The measurement was performed 10 times according to ČSN EN ISO 6506³ for plates with a thickness of 2 mm. The resulting values are shown in the Figure 1.

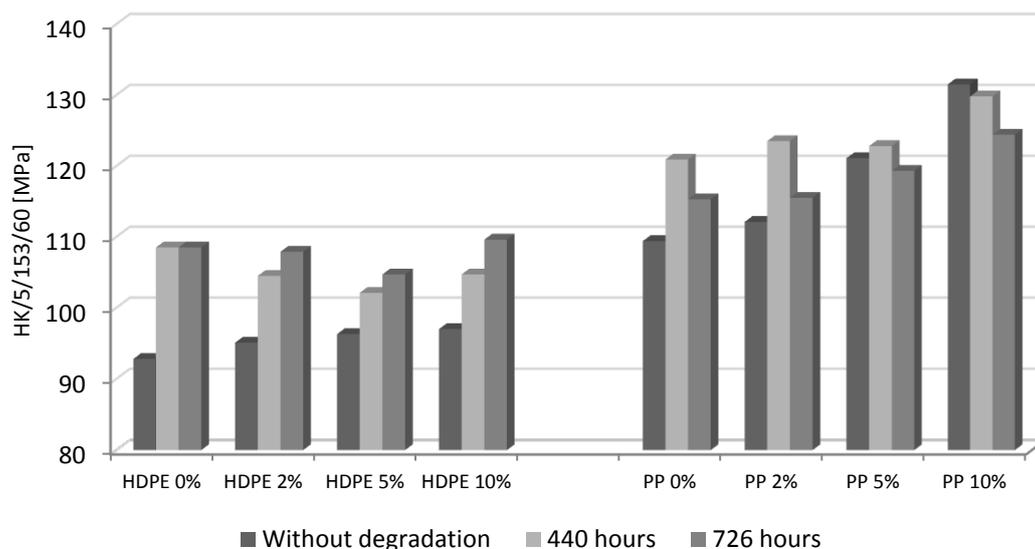


Figure 1. Comparison of Brinell hardness for the tested samples in QUV-panel

The starch content was shown to exhibit a negligible effect on the hardness of polyethylene, whereas in the case of polypropylene starch blends the hardness increased slightly, with the increase of the starch concentration.

The hardness polyethylene based samples grew almost linearly with the increasing exposure time in QUV-panel, see Figure 1. In the case of pure polyethylene, a significant shift of hardness depending on the exposure time in QUV-panel was not recorded.

The pure polypropylene and the sample with a low concentration of starch after 440 hours of exposure in a QUV-panel exhibited hardening, whereas a longer exposure time exhibited decreased hardness which was still higher than the initial hardness of samples without UV exposure. The hardness of blend samples decreased with increase in the concentration of starch and prolonged UV irradiation exposure.

3.2 Tensile properties

Elongation at break values of initial and exposed samples is shown in Figure 2. Results are presented as the averages of 10 measured values. The strength of testing bodies was measured according to ČSN EN ISO 527⁴.

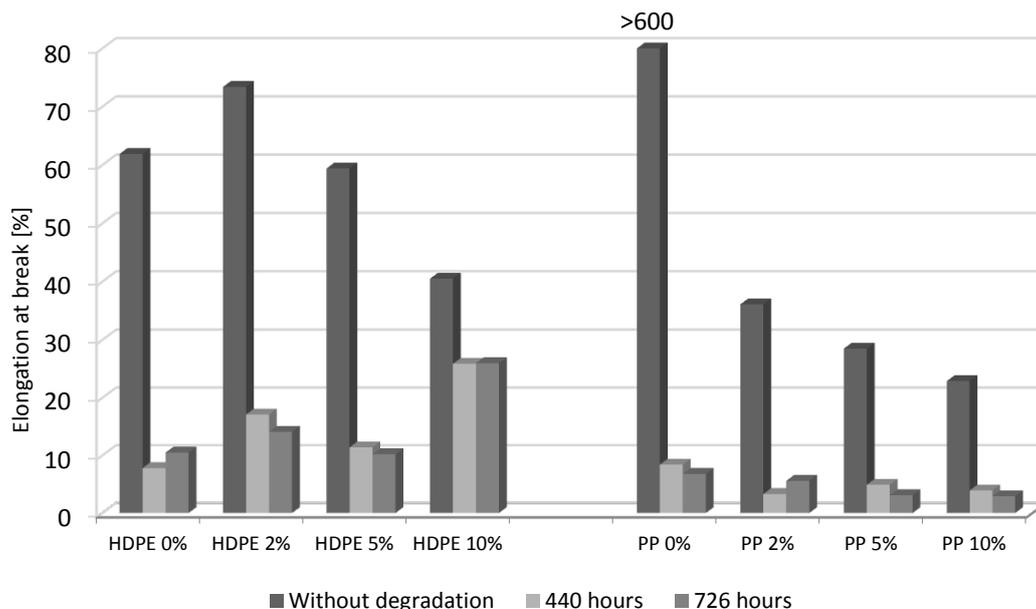


Figure 2. Comparison of elongation at break for the tested samples in QUV-panel

The effect of concentration of starch in polyethylene blends is reflected by the downward lowering of ductility, except the HDPE blend containing starch in the concentration of 2% that exhibited an enhancement of elongation compared with the pure polyethylene. In the case of polypropylene blends, starch was found to affect tensile properties significantly. Pure polypropylene after the tensile test did not break, but a long "neck" appeared. Already 2 wt.% of starch caused a pronounced reduction in ductility and with a further increase of starch concentration a linear decrease was found.

The exposure in QUV-panel of samples of polyethylene and its blends showed a significant reduction in ductility. More significant decrease was observed in pure polyethylene and its blends with 2% and 5% of starch concentration. In the case of HDPE containing 10% of starch the decrease was milder. All values of elongation at break of the pure polypropylene and its blends decreased significantly, by up to order. The most significant changes occurred in the case of mechanical properties when exposed for 440 hours in QUV-panel. After a further exposure the properties were not significantly changed.

3.3 Yellowness index

The method of determining the degree of yellowing is governed by ASTM D1925⁵. Yellowness index (YI) is a dimensionless number expressed from spectrophotometric data Figure 3 is shows spectrophotometric determination of PP containing 10 wt.% of starch. These data are evaluated using the Kubelka-Munk⁶ method (assuming an infinitely thick layer of the material) and the color change of the test sample from clear or white towards yellow is described. This test is most commonly used to evaluate color changes in the material due to simulated or actual weather conditions.

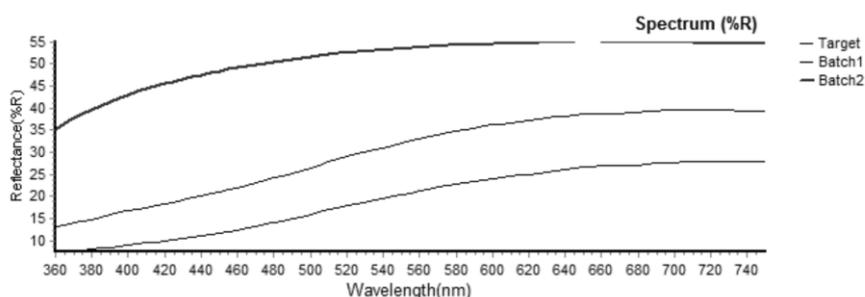


Figure 3. Evaluation of yellowness index for PP containing 10 wt.% of starch. Target: sample without degradation, Batch1: sample exposed in QUV-panel for 440 hours, Batch2: sample exposed in QUV-panel for 726 hours

Assessed spectrophotometric data are inscribed on the color gamut of the CIE L*a*b*. Yellowness index values are coordinates of the movement in the color range on the axis, see Figure 4. The collected data are shown in Table 1.

Table 1. Yellowness index of HDPE and PP samples

Samples	Yellowness Index		
	Without degradation	440 hours	726 hours
HDPE 0%	-8.21	-9.48	-8.66
HDPE 2%	27.98	22.33	12.83
HDPE 5%	55.76	18.48	15.67
HDPE 10%	49.13	31.87	18.02
PP 0%	-2.17	4.35	4.35
PP 2%	19.12	12.71	12.54
PP 5%	38.71	19.70	15.54
PP 10%	58.16	47.42	17.54

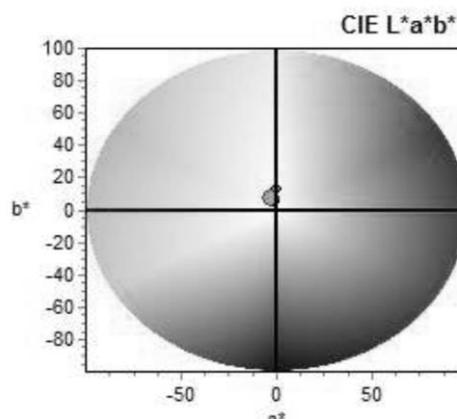


Figure 4. The color range CIE L*a*b* for the sample based on PP and starch in the content of 10 wt.% exposed in QUV-panel for 726 hours

The effect of the addition of starch to polyethylene is significantly manifested by a color change, which after two thermal extrusions turned from yellow to brown. After UV irradiation of the surface of the testing body the "chalk appearance" was observed, hence the tint changed from colored to white.

The proportion of starch in the polypropylene blends and the effect of ultraviolet irradiation were shown to affect the samples similarly as in the case of polyethylene, but the color transition was not so significant.

3.4 Visual assessment

The degradation of polyethylene in QUV - panel showed a noticeable cracking of the sample surface, as shown the in Figure 5. These cracks were longer, deeper with larger spacing than in the case of polypropylene. The "chalk appearance" of the surface accompanied by a color change from yellow to white tint was observed as well. This phenomenon is also related with a loss of surface gloss. The intensity of these visual changes grew with the starch content in the blend and the with UV exposure time. These factors mainly affected the depth of degraded surface layer. The samples based on polyethylene exhibited no flaking of the material.

Similar transformations of the observed surface are for polypropylene, see Figure 6., but compared to polyethylene samples, the rate of degradation was much larger. Cracks on the surface were much thicker forming a fine cracking network even in the case of the pure polypropylene. The rate of "chalk appearance" formation increased with increasing starch concentration, but it was also noticeable in the pure polypropylene samples. The "chalk appearance" took place simultaneously with the color change turning to white tint. The phenomenon of "chalk appearance" was several times pronounced for polypropylene samples than for the samples based on polyethylene, which is also related with mechanical flaking of the material that was observed in the case of pure polypropylene after 440 hours of exposure in a QUV-panel. With increasing exposure time and the starch content, the above described effects of aging were heightened.



Figure 5. Visual assessment for the sample based on HDPE and starch in the content of 10 wt.% A) sample exposed in QUV-panel for 726 hours B) sample exposed in QUV-panel for 440 hours C) sample without degradation



Figure 6. Visual assessment for the sample based on PP and starch in the content of 10 wt.% A) sample exposed in QUV-panel for 726 hours B) sample exposed in QUV-panel for 440 hours C) sample without degradation

4 Conclusions

The prepared polyolefin blends were subjected to accelerated aging in a QUV-panel for 440 hours and 726 hours. Changes in hardness in both types of samples were showed more significantly after the exposure for 440 hours in QUV-panel than after 726 hours of exposure in QUV-panel. In the case polyethylene blends, a significant decrease in ductility and tensile strength of the material was observed. The polypropylene blends exhibited a significant influence of the starch content on the ductility; the addition of 2 wt.% of starch caused a significant drop in ductility. The testing bodies of pure polypropylene withstood the tensile test, whereas after the addition of starch the tensile test specimens were broken. The ductility of samples decreased significantly after the exposure to UV irradiation. The addition of starch to the both types of polyolefins was manifested not only in the case of mechanical properties of the studied materials, but also in the case of surface appearance. After the exposure, the surfaces of samples dramatically changed color (turned white); "chalk appearance" and visible cracks appeared.

5 Literatures

1. Cerclé C., Sarazin P., Favis D.B.: Carbohydrate Polymers 92, 138 (2013)
2. González J., Albano C., Perera R., Ichazo M.N., Hernández M., Alvarez I.: ANTEC 1405, (2005)
3. ČSN EN ISO 6506: *Brinella hardness test*; 420359
4. ČSN EN ISO 527: *Plastics – Determination of tensile properties*; 640604
5. ASTM D1925: *Test Method for Yellowness Index of Plastics*
6. Torrent J., Barrón V.: Soil Science Society of America, 677, 367 (2008)