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The influence of storage time of oxo-degradable polyethylene film on the mechanical properties

Summary: *A method for the preparation of prodegradant, the transition metal compound containing iron and manganese, in a one-step manufacturing process was described. The catalytic system (prodegradant) iron-manganese stearate containing about 3-3.5% of each metal was selected to the application studies. To assess the resistance of plastic materials to weather condition, aging tests were applied, in which the plastic materials undergo destructive processes and afterwards strength tests were performed. The results of mechanical tests of polyethylene films with the addition of concentrated OXO-BIO aged under atmospheric conditions and accelerated weathering were described. Films containing 12.5% and 25% of OXO-BIO were stored for 6 months at room temperature in darkness, and then were subjected to atmospheric aging. The results of strength tests were described. After 6-month storage period, slight differences of initial mechanical properties of films (being within the tolerance limits of determined parameters) were noted.*

WPŁYW CZASU SKŁADOWANIA OXO-DEGRADOWALNEJ FOLII POLIETYLENOWEJ NA WŁAŚCIWOŚCI MECHANICZNE

Streszczenie: *Opracowano metodę otrzymywania mieszaniny prodegradanta, czyli związku zawierającego metale przejściowe żelaza i manganu, w jednoetapowym procesie produkcyjnym. Do badań aplikacyjnych wytypowano układ katalizujący (prodegradant), będący mieszaniną stearynianu żelaza(III) i stearynianu manganu(II), zawierający około 3-3,5% każdego z metali. Do oceny odporności materiałów z tworzyw sztucznych na działanie warunków atmosferycznych zastosowano testy starzeniowe, w których tworzywa ulegają procesom destrukcyjnym, a następnie wykonano badania wytrzymałościowe. Omówiono wyniki badań mechanicznych folii polietylenowych z dodatkiem koncentratu OXO-BIO starzonych w warunkach atmosferycznych i przyspieszonych. Folie zawierające 12.5% oraz 25% OXO-BIO magazynowano przez okres 6 miesięcy w temperaturze pokojowej w zaciemnieniu, a następnie poddano starzeniu atmosferycznemu. Omówiono wyniki badań wytrzymałościowych. Po 6-miesięcznym okresie składowania zauważono niewielkie różnice w wyjściowych parametrach mechanicznych folii, mieszczących się w granicach tolerancji wartości określonych parametrów.*

1. INTRODUCTION

Degradable polymers are materials which undergo degradation as a result of a variety of physical, chemical or biological agents. Some of these materials can be produced from renewable resources, such as polylactide PLA. The costs to manufacture synthetic polyolefins are by far lower than the costs needed to produce a biopolymer or biocomposite material, while the small share of an oxo-biodegradation agent in the formulation does not affect this relation [1,2].

The use of degradable polyolefins is an approach that has been recently developed to try to contribute to solve the environmental problem caused by the large quantities of these plastic wastes. There are many ways to increase the degradability of a polymer chain, which can undergo hydrolysis, oxidation, thermal-, photo-and biodegradation [3-6]. Photodegradation, which occurs under the influence of UV rays, involves the stimulation of radical reactions, which ultimately leads to the shortening of the polymeric chain. Chemical degradation involves cracking the polymeric chain and reducing its molecular weight, while biological degradation entails the use of the polymer as a source of energy and carbon for organisms which ultimately lead to its decomposition. The actual biodegradation process takes place as a result of the colonization of the polymer surface by microscopic fungi and bacteria [7]. Some polymers are susceptible to biodegradation by the action of enzymes or micro-organisms, while others become biodegradable only in advanced stages of decay. Each type of polymer degradation differs in terms of the molecular mechanism it is governed by. In addition, one kind of polymer degradation can be carried out by means of different mechanisms simultaneously [8]. The process of degradation of a composite in the natural environment consists of two stages: decay and mineralization. In the first stage, modification of the chemical structure and physical properties takes place. Mineralisation follows, during which microorganisms digest the compounds formed in the first stage. The first stage of degradation is a stage where the rate of oxo-biodegradation is limited, as the small molecule compounds created there prefer assimilation by micro-organisms [9]. This phase is different for oxo- and hydrodegradable polymers. The advantage of oxo-biodegradable plastics is the ability to „program" the life time of the final product. Depending on the nature and quantity of the additive, one can schedule when a plastic bag will start decomposing. Complete breakdown may occur within 1-5 years, irrespective of the place where the product ends up.

This work is aimed at investigating the entire degradation process of polyethylene containing a pro-oxidant/prodegradant additive, by subjecting it to UV-irradiation in Weater-O-Meter or natural acceleration in moderate climate (Silesia, Poland) and subsequently to investigation of mechanical properties. Also performed the study of accelerated aging films with prodegradant, that previously were stored 6 months in a dark place at room temperature.

2. EXPERIMENTAL PART

2.1. Research methodology

The studied film was made of polyethylene, which is widely used in the manufacture of packaging film. Its formulation contains OXO-BIO concentrate, the exact composition of which is described in previous work [1, 10].

The raw materials used for the production of OXO-BIO include:

— PE FGAN polyethylene, 18-D003 (Lyondell Basell); density = 0.918-0.921 g/cm^3; MFR = 0.20-0.35 g/10 min;
— OXO-BIO concentrate:
  • Mass flow rate (MFR) – 1 g/10 min (190°C; 2.16 kg)
  • The percentage share of manganese (Mn) and iron (Fe):
    a. Manganese content: 0.11 – 0.15 %,
    b. Iron content: 0.9 – 1.0 %.

Two BIO films containing 12.5 and 25% w/w of OXO-BIO concentrate were made. Each of them contained a mixture of iron and manganese stearates in the amounts of 0.5 and 1% w/w respectively.

The film was made by extrusion blow moulding of low density polyethylene (PE-LD). The foil can be extruded in the form of a sleeve, a sleeve cut on one side, or in the form of tape (a sleeve cut on both sides).

Extrusion parameters:

• type of extruded product: 0.03 mm thick film
• melt temperature: 175 – 180 °C
• temperature of cylinder areas: 165 – 190 °C
• temperature of the head: 190 °C.

2.2. Analysis of BIO film obtained using OXO-BIO concentrate

The aim of the study was to determine the time of degradation of polyethylene containing an addition of OXO-BIO concentrate in natural weathering conditions and accelerated aging (Xenotest) and to assess the degree of degradation on the basis of strength tests.

Oxo-and photodegradation tests of the film were carried out according to the following methodology:

a) natural aging in temperate climate (Silesia) (1, 3, and 6 months) according to standard PN-EN ISO 877:2001;

b) accelerated aging in a Xenon Weather-O-Meter according to standard PN-EN ISO 5193-2:2009 (method A).

The following measurements were employed to monitor the oxo- and photodegradation processes in the course of aging (in accordance with the standard BS 8472:2011):

— changes of mechanical properties (strength) (according to standard PN-EN ISO 527-3:1998).
— evaluation of the surface of the film using a scanning microscope (after biodegradation).

3. TEST RESULTS

The changes in the parameters of strength as a result of atmospheric aging and accelerated aging are listed in Tables 1 to 3.

Testing conditions:

• testing machine Instron Model D 7418;
• testing speed: 100 mm/min; gauge length: 50 mm; temperature 23±2°C.

Changes in the parameters of strength as a result of accelerating aging are listed in Table 1. Changes in the parameters of strength as a result of atmospheric aging are listed in Table 2 (Winter period) and table 3 (Summer period).

4. RESULTS AND DISCUSSION

One of the criteria used in the assessment of the destructive processes taking place in plastic materials as a result of the action of UV radiation is the change of a film's strength parameters. In the case of natural aging, the conditions of exposure are complex and variable. Important factors which cause aging are climate, season, industrial pollution, etc. As it is impossible to make a precise determination of the factors causing the destruction of plastic materials, the results of the test are only informative in nature.

Depending on the polymer, particular properties change in different ways. The parameter which changes

Table 1. Changes in the parameters of strength as a result of accelerating aging

Film		0		100 h			150 h			250 h			400 h		
		Tensile strength [MPa]	Elong. at break [%]	[MPa]	[%]	ε [%]	[MPa]	[%]	ε [%]	[MPa]	[%]	ε [%]	[MPa]	[%]	ε [%]
1. **25% BIO**	MD	25.4	270.0	22.6	164	61	22.1	225	83	19.9	157	58	16.9	87	32
	TD	15.0	538.0	17.0	489	91	14.6	257	48	13.6	345	64	12.5	61	11
2. **12.5% BIO**	MD	27.0	260.0	20.8	108	42	19.3	135	52	14.6	106	41	-	-	-
	TD	18.0	608.0	16.4	490	81	11.9	65	11	10.1	44	7	13.2	67	11

MD – machine direction; TD – traverse direction

Table 2. Changes in the parameters of strength as a result of atmospheric aging (Winter period)

Film		0		1 month			3 months			6 months		
		Tensile strength [MPa]	Elong. at break [%]	[MPa]	[%]	ε [%]	[MPa]	[%]	ε [%]	[MPa]	[%]	ε [%]
1. **25% BIO** (outside)	MD	25.4	270.0	16.3	95.0	35.2	20.08	143.4	53.10	16.8	141.6	52.4
	TD	15.0	538.0	11.5	88.0	16.4	19.0	167.6	31.1	14.3	170.3	31.6
1. **25% BIO** (inside)	MD	25.4	270.0	20.3	126.0	46.7	15.9	117.3	43.4	14.7	116.0	43.0
	TD	15.0	538.0	8.74	93.0	17.3	12.4	220.0	40.9	13.2	273.0	50.7
2. **12.5% BIO** (outside)	MD	27.0	260.0	22.5	126.7	48.7	20.4	253.0	97.3	20.3	235.4	90.5
	TD	18.0	608.0	12.7	166.2	27.4	13.5	209.0	34.4	12.0	164.9	27.1
2. **12.5% BIO** (inside)	MD	27.0	260.0	25.0	144.0	55.4	21.3	220.7	84.9	19.8	214.6	82.5
	TD	18.0	608.0	14.1	291.0	47.9	14.7	418.9	68.9	13.7	330.0	54.3

Table 3. Changes in the parameters of strength as a result of atmospheric aging following 6 months of storage (Summer period).

Film		0		1 month			3 months		
		Tensile strength [MPa]	Elong. at break [%]	[MPa]	[%]	ε [%]	[MPa]	[%]	ε [%]
1. **25% BIO** (outside)	MD	24.5	265.7	21.4	177.3	66.7	14.4	137.0	51.6
	TD	14.3	551.8	11.6	184.4	33.4	11.8	23.7	4.3
1. **25% BIO** (inside)	MD	24.5	265.7	19.8	190.7	71.8	13.1	113.0	42.5
	TD	14.3	551.8	14.7	542.0	98.2	12.5	44.4	8.0
2. **12.5% BIO** (outside)	MD	25.3	249.4	23.4	184.0	73.8	14.5	179.7	72.0
	TD	15.5	521.6	17.4	569.1	101.8	11.7	40.5	7.8
2. **12.5% BIO** (inside)	MD	25.3	249.4	23.6	228.3	11.5	15.7	176.1	70.6
	TD	15.5	521.6	17.7	573.5	109.9	10.8	42.0	8.1

the fastest in the case of PE-LD is elongation at rupture. As a criterion for the assessment of the processes of destruction, the percentage change in the relative elongation after a given period of aging has been adopted, which is expressed by the formula:

$$K_\varepsilon = \frac{K_t}{K_0} \cdot 100\%$$

where:

K_t – relative elongation after a given period of aging

K_0 – elongation of the sample not subjected to aging, the reference elongation

As a result of aging in a Xenon Weather-O-Meter after 50, 100, 150, 250 and 400 hours of exposure, it is noted that strength deteriorates faster across than along the direction of extrusion of the film (Table 1). For 12.5% BIO film (across) after 100 hours, elongation falls by 20%, and after 400 hours-up to 90%, while for the 25% BIO film (across) after 100 hours, relative elongation is down by 9%, while after 400 hours – p to 90%.

The films were aged in atmospheric conditions during the Autumn-Winter period, which is characterized by low sunlight (Silesia, Gliwice). As a result of atmospheric aging after 1, 3 and 6 months of exposure, it is noted that degradation takes place on both films with OXO-BIO concentrate.

After 6 months of aging in atmospheric conditions (Silesia), relative elongation decreases by ca. 50% for the film containing a 1% mixture of SFe and SMn (25% BIO) (measurement along the direction of extrusion) and up to ca. 70% when the measurement is made across the direction of extrusion. For films containing 0.5% SFe and SMn (12.5% BIO), elongation decreases by ca. 10% when measured along the direction of extrusion (by ca. 75% across).

The following graph shows the falling trend in the strength parameters of the film aged in atmospheric conditions (Figure 1 and 2).

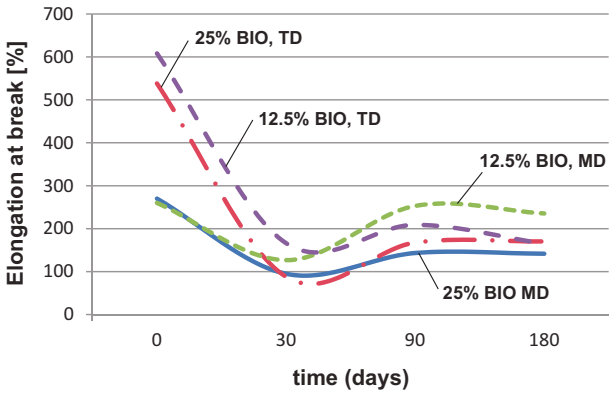

Figure 1. Dependence between relative elongation and exposure time in atmospheric conditions (Silesia)

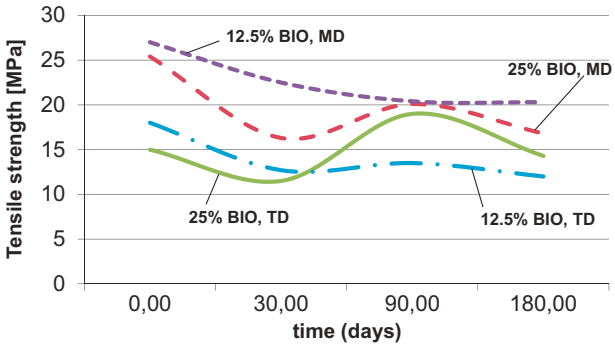

Figure 2. Dependence between tensile strength and exposure time in atmospheric conditions (Silesia)

Films containing 12.5% and 25% of OXO-BIO were stored for a period of 6 months at room temperature in the dark, and then were subjected to atmospheric ageing (Spring-Summer with high sun exposure). Strength test results are presented in Table 3. After 6-months of storage, slight differences were observed in the baseline mechanical parameters of the film (Table 2 and 3), which fell within the tolerances of the specified parameters (according to PN-C-89258-2:1997).

After 3 months of aging in atmospheric conditions (following 6 months of storage) (Silesia) relative elongation decreased by ca. 50% for the film containing a 1% mixture of SFe and SMn (25% BIO) (measurement along the direction of the extrusion) and up to ca. 95% when the measurement was made across the direction of extrusion. For the film containing 0.5% of SFe and SMn (12.5% BIO), relative elongation decreased by 28% when measured along the direction of the extrusion (up to ca. 92% across). After storage and subsequent aging in atmospheric conditions, a reduction in the strength parameters was observed, the reason for which was heavy exposure to sunlight in the atmospheric aging stage (April-June).

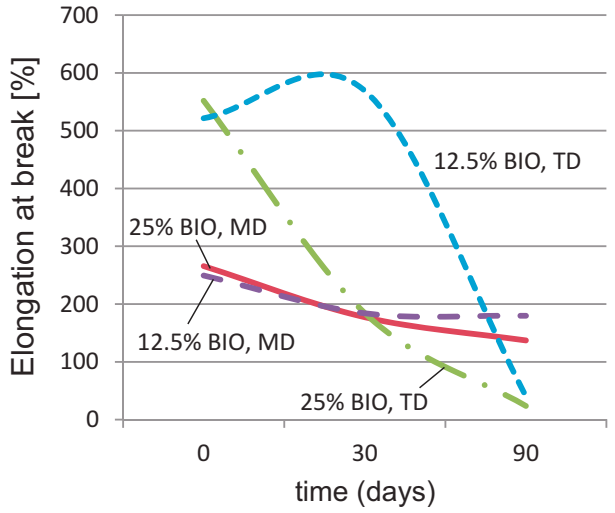

Figure 3. Dependence of relative elongation on the exposure time in atmospheric aging (Silesia)

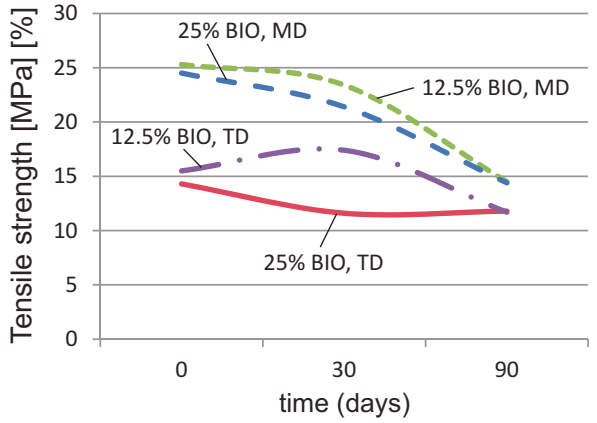

Figure 4. Dependence of tensile strength on the exposure time in atmospheric aging (Silesia)

The following graph shows the falling trend in the strength parameters of the film aged (following storage) in atmospheric conditions (Figure 3 and 4).

Degradation of the polymer matrix in films containing a prodegradant, i.e. a mixture of iron and manganese stearates, is rapid. However, such a mixture and the degradation products formed in the first stage, have a plasticizing effect (increase in relative elongation). As a result, the film degrades slightly longer. Nevertheless, the time of degradation can be programmed by adjusting the right transition metal ion concentration (iron and manganese).

Table 4. Estimated time of degradation of oxo-biodegradable films

No.	Sample	Degradation time (film achieve 5% of the inital relative elongation at break)
1.	1. 25% BIO	15 months
2.	2. 12.5% BIO	5 years

Table 5. Estimated time of degradation of oxo-biodegradable films (stored for 6 months)

No.	Sample	Degradation time (film achieve 5% of the inital relative elongation at break)
1.	1. 25% BIO	6 months
2.	2. 12.5% BIO	1 year

On the basis of the ASTM D 3826 standard, it is accepted that the final point of degradation, which is the brittleness point of a plastic material, occurs when the relative elongation of a plastic material at rupture is 5% or less. When the brittleness point is reached, it is considered that the polymer is susceptible to attack by microorganisms. In accordance with the previously mentioned standard, the time of decomposition of individual samples (Table 4 and 5) can be predicted by accepting that the brittleness point equals 5% of elongation at rupture and by assuming that mechanical properties, during exposure to atmospheric conditions, change linearly.

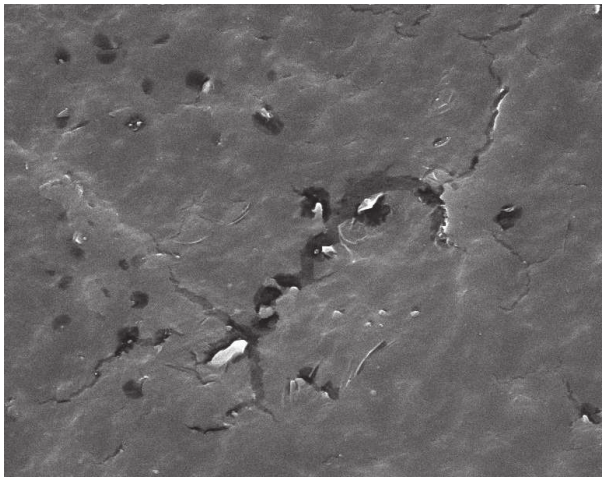

Figure 5. Photo of 25% BIO film (sample 1) aged for 250 hours in a Xenon Weather-Ometer

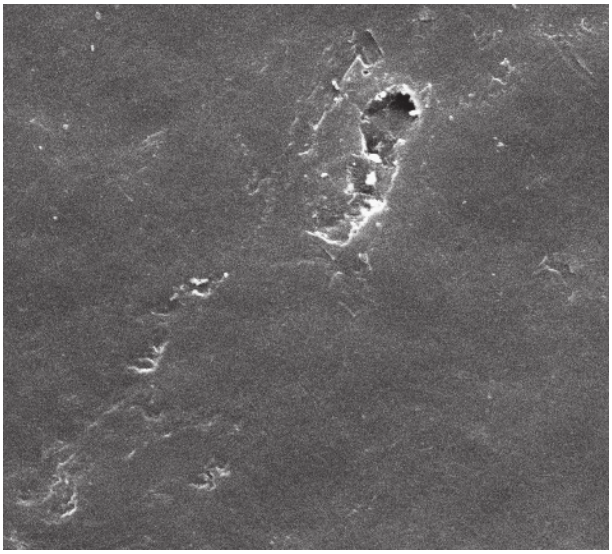

Figure 6. Photo of 25% BIO film (sample 2) aged for 250 hours in a Xenon Weather-Ometer

As a result of the degradation of samples aged in atmospheric and accelerated conditions, cracks on the surface of the film were observed (Figure 5 and 6).

Changes observed in the strength parameters and in the chemical structure of polyethylene subjected to atmospheric and accelerated ageing are indicative that degradation is the result of the action of light and oxygen in the air.

Films are suitable for use up to a value of 50% of their relative elongation at rupture in relation to the baseline value.

5. CONCLUSIONS

Oxo-biodegradability is heavily dependent on the prodegradant used (more specifically on the transition metal it contains) and on its concentration. The rate of oxo-degradation increases along with the content of the prodegradant in the final product. Transition metal compounds used: iron and manganese were found to be effective prodegradants in oxo-degrading processes.

The needed for a film to degrade, that is the time until the point of brittleness is achieved (5% of the baseline strength parameters) depends on the content of the active substance of the prodegradant present in the film and amounts to, respectively:

— 0.5% of the active substance of the prodegradant – 5 years
— 1% of the active substance of the prodegradant – 15 months.

Films are suitable for use until a 50% relative elongation at rupture in relation to the baseline value is achieved. For this reason, the actual service life of oxo-degradable film is reduced and it is accepted that for a film with an addition of:

— 0.5% of the active substance of the prodegradant, this period totals 2-3 years
— 1% of the active substance of the prodegradant, this period totals 8-12 months.

The degradation time can be programmed at the production stage, by dosing the right amount of prodegradant. The time of degradation may be slightly longer, if antioxidants are present in the system, which weaken the action of oxygen on the polymer chain, and capture oxygen radicals responsible for initiating the oxidation of the polymer. By selecting the right amount of antioxidant in the formula, the service life of the final product can also be programmed. Changes observed in the strength parameters and in the chemical structure of polyethylene subjected to atmospheric and accelerated aging are indicative that degradation is caused by the action of light and oxygen in the air.

Storage of OXO-BIO enriched film for a period of 6 months without light and at a temperature below 30°C does not lower its mechanical parameters. Storage of film in a dark warehouse for a period of 6 months leads to acceleration of oxo-degrading processes and a reduction of the service life of the film by 50% in relation to the baseline value.

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