Modification of low density polyethylene for manufacturing of oxo-biodegradable films (*Rapid Communication*)

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Abstract: The effect of various additives on oxo-biodegradation of films made of low density polyethylene (PE-LD) compositions has been investigated. Twelve compositions were made with varying contents of a prodegradant. Masterbatches acting as a prodegradant consisted of: PE-LD, iron(II) stearate ($FeSt_2$) as a catalyst for decomposition, ethylene-propylene-diene copolymer Royaltuf® 485 (Roy) as an agent reducing ferric ions, quaternary ammonium salt modified bentonite (ZR2) as a nanofiller, and compatibilizer Fusabond® E226 (Fus). Reference material consisted of PE-LD film which was not supplemented with the above additives. Assessment focused on the impact of nanofiller and copolymer on functional properties and oxo-biodegradation processes in the obtained films. The impact was assessed by taking into account changes in external appearance, mechanical properties, location and incidence of bands in infrared spectra, values of surface free energy (*SFE*) and effect of microorganisms on the film surfaces. The findings showed that addition of ZR2 resulted in improved initial strength characteristics of the films, and iron stearate accelerated the degradation process in the polyethylene whereby its hydrophilicity and susceptibility to microorganisms were increased. Addition of Roy promoted acceleration of oxo-degradation process.

Keywords: polyethylene film, oxo-biodegradation, prodegradant, nanofiller.

Modyfikacja polietylenu małej gęstości do wytwarzania folii oksy-biodegradowalnych

Streszczenie: W pracy badano wpływ różnych dodatków na oksy-biodegradację folii wykonanych z kompozycji polietylenu małej gęstości. Sporządzono 12 kompozycji zawierających różne zawartości prodegradantu. W skład przedmieszki stanowiącej prodegradant wchodziły: PE-LD, stearynian żelaza(II) ($FeSt_2$) jako katalizator degradacji, kopolimer etylenu z propylenem i dienem Royaltuf® 485 (Roy) jako reduktor jonów żelaza, bentonit modyfikowany IV-rzędową solą amoniową (ZR2) jako nanonapełniacz i kompatybilizator Fusabond® E226 (Fus). W celu porównania przygotowano również folię z PE-LD nienapełnionego wspomnianymi dodatkami. Zbadano wpływ nanonapełniacza oraz kopolimeru na właściwości użytkowe i proces oksy-biodegradacji otrzymanych folii. Wpływ ten określano na podstawie zmian wyglądu zewnętrznego, właściwości mechanicznych, położenia i pojawiania się pasm w widmach w podczerwieni, wartości swobodnej energii powierzchniowej (*SEP*) oraz śladów oddziaływania mikroorganizmów na powierzchnię folii. Stwierdzono, że dodatek ZR2 poprawiał wyjściowe właściwości wytrzymałościowe folii, zaś stearynian żelaza przyśpieszał proces degradacji badanego polietylenu, przez co zwiększał hydrofilowość i jej podatność na atak mikroorganizmów. Zastosowanie dodatku Roy miało także pozytywny wpływ na przyśpieszenie procesu oksydegradacji.

Słowa kluczowe: folia polietylenowa, oksy-biodegradacja, prodegradant, nanonapełniacz.

Due to their beneficial functional properties and easy processing, polyolefins, and in particular polyethylene, are widely used as packaging material, for instance as disposable plastic bags. Following their short term use, plastic films are landfilled as waste which is slow to degrade and remains in the environment for a very long time [1, 2]. This is because they are resistant to oxidation and biodegradation due to the chemical structure of the polymer used in their production [3, 4]. By applying specific additives, or the so-called prodegradants, which do not significantly alter the original properties of films, it may be possible to obtain oxo-biodegradable polymers [5]. The most frequently used prodegradants include salts and complexes of transition metals: iron, manganese or cobalt [6]. These compounds display varied activity in both photo- and thermodegradation [7—9]. Polymers

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with these additives undergo much faster degradation, which is confirmed by increased carbonyl index, degree of crystallinity, and deteriorating strength characteristics [10]. The level of degradation depends on the timing of exposition to abiotic action and on whether or not the catalyst action has been initiated with sun's rays — UV radiation [11, 12]. Numerous studies also investigated addition of nanofiller in the form of modified or unmodified montmorillonite which may be responsible for initiating autoxidation in polymer matrix and which does not significantly alter the oxidation mechanism in the reaction of polyethylene oxo-biodegradation [13]. It has also been demonstrated that modified layered aluminosilicates (organoclay) impact microbial growth in polymers by stimulating growth of microorganisms, while maintaining ambient pH at the level beneficial for their long-term development [14, 15].

The pattern of polyethylene biodegradation, called oxo-biodegradation, consists of two stages. These are: abiotic degradation and microbial biodegradation [3, 15]. Abiotic oxidation leads to formation of functional, *i.e.* acidic, alcohol, aldehyde and ketone groups [13, 16—17]. Due to increased hydrophilicity and the occurrence of low molecular weight chains, film decomposing in this way is more susceptible to microbial attack than films which are not subjected to initial degradation [6, 18]. The second stage should be preceded with abiotic oxidation accompanied with exposition to light and/or heat before transfer to the biotic environment [3, 8, 19]. Groups created in the abiotic process may be utilized by microorganisms as nutrients for production of biomass [20, 21]. The process carried out in compost is more effective than that conducted in soil [22—24]. Bio-erosion results in decreased mass of film and a thin layer of biofilm. Reduction in carbonyl index and occurrence of double bonds indicate there is a progress in biodegradation thanks to microbial activity [19, 25].

The main purpose of this study was to select additives and identify their impact on the progress in oxo-biodegradation. Two novel solutions have been used in course of the research. The first one involved obtaining biodegradable films, which are more accessible for microorganisms, by using ammonium salt modified montmorillonite and ethylene-propylene-diene copolymer Royaltuf® which promotes maintenance of iron at the second stage of oxidation due to the reducing action of double bonds present in the diene mers of this copolymer. It was assumed according to our earlier studies that these additives would enhance the process of low density polyethylene oxo-biodegradation [26].

EXPERIMENTAL PART

Materials

Low-density polyethylene (PE-LD, Lyondell Basell) with trade bane Malen E FGAN 18-D003 was characterized by melt flow rate *MFR* = 0.4 g/10 min and density $d = 0.92$ g/cm^3.

Bentonite modified with quaternary ammonium salt (QAS), containing two aliphatic substituents with the number of carbon atoms C10—C12, and two methyl substituents was an experimental product named Nanobent® ZR2 (denoted ZR2), manufactured in accordance with a technology developed under targeted project No. 03933/C ZR7-6/2007) in ZGM "Zębiec" SA.

Sodium stearate iron(II) sulphate(VI) and acetone (all lab grade purity) were produced by CHEMPUR (Piekary Śląskie).

Ethylene-propylene-diene copolymer (EPDM), with trade name Royaltuf® 485 (denoted Roy) was manufactured by Chemtura.

As a compatibilizer improving mutual miscibility of ZR2 and PE-LD was used Fusabond® E226 (denoted Fus) manufactured by DuPont (USA).

Preparation of prodegradant

Iron(II) stearate (FeSt$_2$), used as a catalyst, was obtained through the reaction of ion exchange between iron(II) sulphate(VI) and sodium stearate. The reaction was carried out by mixing at the temperature of 90 °C in a round-bottom flask using equimolar quantities of reagents introduced in the form of solutions. The obtained, water-insoluble product was dried for 24 hours, in a dryer at the temperature of 60 °C. In course of the drying process the precipitate changed its color into brownish, which meant, that iron(II) was partly oxidized to iron(III).

Subsequently, the obtained catalyst was mixed with acetone suspension of ZR2, using equal weight ratio of both components. The suspension was mixed long enough to achieve a homogenous mixture of thick cream consistency. After the solvent was evaporated, the residue was dried for 48 hours at the temperature of 60 °C and then it was milled and sifted through 0.06 mm sieve, which made it possible to obtain FeSt$_2$ embedded on ZR2 (abbr.: Fe/ZR2).

PE-LD masterbatches containing the relevant additives were obtained during extrusion blending process performed by a line consisting of: co-rotating twin screw extruder (ZSK 18ML from Coperion, Germany), water cooling tank and pelletizer. Four kinds of masterbatches were prepared, with composition shown in Table 1.

Table 1. Composition of the masterbatches used as prodegradants

Masterbatch symbol	Content of component, wt %				
	PE-LD	ZR2	FeSt$_2$	Roy	Fus
M1	80	0	10	0	10
M2	70	10	10	0	10
M3	70	0	10	10	10
M4	60	10	10	10	10

Further on, the prepared masterbatch pellets, now referred to as prodegradants, were introduced at the amount of 5, 10 or 15 wt % to PE-LD. These compositions were used to obtain films by extrusion blow molding performed by T32 extruder (manufactured by Metalchem Gliwice) and a laboratory line for blown films (manufactured by IPTPiB in Toruń). This way twelve types of film were obtained, three per each masterbatch. The film used as the reference sample was obtained from commercial PE-LD (with no additives).

Methods of testing

All kinds of prepared films were subjected to abiotic aging in climatic test chamber XENONTEST ALPHA+ from ATLAS. Strips used as test samples had dimensions of 13.5 × 4.5 cm. Aging test was performed in accordance with the applicable standard, PN-EN ISO 4892-2, method A, point 1. Films were subjected to aging for 50, 100 and 125 h.

Static tensile strength of the films was determined according to PN-EN ISO 527-1:1998 standard using INSTRON 5967 testing machine (Instron Corporation, United Kingdom), at the speed of pulling set at 100 mm/min.

FT-IR analysis of the films was performed using Nicolet 6700 spectrophotometer, manufactured by ThermoScientific (USA), equipped with ATR module with a diamond accessory. Interferograms were made for thirty two scans. Spectra were subjected to advanced ATR correction, atmospheric correction, and baseline correction. Carbonyl index is defined as a ratio of intensity of the band originating from carbonyl group vibrations (1714 cm^{-1}) to the band of wagging vibrations of -CH$_2$- group (1472 cm^{-1}) [27].

Wetting angle for the film was determined using Zismann's method [28] by means of optical goniometer. Images of drops were taken with C-3020 Olympus camera. Surface free energy for the film surfaces (γ_s) was calculated using Owens-Wendt's method [29]. Wetting angles were determined for two reference liquids: water (γ_L = 72,8 mJ/m^2, γ_L^d = 21,8 mJ/m^2, γ_L^p = 51,0 mJ/m^2) and diiodomethane (γ_L = 50.8 mJ/m^2, γ_L^d = 48.58 mJ/m^2, γ_L^p = 2.38 mJ/m^2).

Tests of film biodegradation, following the initial abiotic degradation, were conducted in compost originating from mushroom cultivation, obtained from Grzyb-Mix Company in Bratkowice near Rzeszów. The films were covered with compost layers, and wetted with distilled water, aerated from the bottom, by means of barbotage, and subjected to thermostating at 40 °C for 30 days.

RESULTS AND DISCUSSION

All the films presented good homogeneity and transparency and they had neither agglomerates nor inclusions. The films were subjected to a number of strength tests, and visual as well as structural assessments, before aging and after abiotic aging in the climatic test chamber and after biodegradation in compost, in order to compare the influence of abiotic and biotic factors on the films.

Mechanical properties

The dependence of tensile strength and elongation at break, in the direction parallel to that of extrusion and

Table 2. Strength characteristics and carbonyl index of prepared films before and after aging

Symbol of composition	Type of masterbatch added	Content of masterbatch added wt %	Mechanical properties				Carbonyl index				
			Before aging		After 50 h of aging						
			Tensile strength MPa	Elongation at break mm	Tensile strength MPa	Elongation at break mm	Before aging	After 50 h of aging	After 100 h of aging	After 125 h of aging	Biodegradation
PE_unfilled	–	0	26.2	113.0	23.5	96	1.8	1.9	3.8	6.8	2.6
PE_5M1	M1	5	18.8	184.5	12.4	62	4.1	10.1	18.5	26.1	17.5
PE_10M1	M1	10	19.0	179.1	12.1	89	5.5	6.1	14.9	14.8	13.4
PE_15M1	M1	15	19.3	145.5	10.1	68	7.6	10.0	31.5	36.6	32.0
PE_5M2	M2	5	24.5	101.0	14.9	68	0.5	2.7	8.1	11.5	10.3
PE_10M2	M2	10	24.8	98.0	14.6	67	1.5	5.9	14.1	21.7	16.1
PE_15M2	M2	15	25.5	110.0	14.3	65	1.8	13.1	27.7	46.5	37.2
PE_5M3	M3	5	14.3	130.5	9.3	81	4.2	3.6	10.0	16.0	14.9
PE_10M3	M3	10	15.0	173.0	9.6	60	5.6	12.3	35.5	49.7	41.0
PE_15M3	M3	15	17.3	156.0	8.9	50	9.5	28.5	49.7	61.2	43.2
PE_5M4	M4	5	22.1	63.0	10.7	12	5.3	11.5	23.7	31.6	29.5
PE_10M4	M4	10	18.8	99.5	12.9	25	12.9	14.2	31.3	32.8	30.4
PE_15M4	M4	15	18.1	80.3	11.2	25	15.9	14.9	35.9	40.4	35.7

blow molding, on the type and concentration of prodegradant determined before aging and 50 h afterwards, is presented in Table 2. It is clear that an addition of Roy in the form of M3 masterbatch results in decreased tensile strength of films in comparison to unfilled PE-LD film. On the other hand, addition of ZR2 in the form of M2 masterbatch improves this characteristic of films. It should also be emphasized that prior to aging all films were characterized with strength properties similar to film with no prodegradant (PE_unfilled), while the elongation parameters are similar or slightly higher. The effects of the additives in terms of these strength parameters are highly beneficial from the point of view of the functional properties of the films. This suggests that films with prodegradants may be as useful for daily-life purposes as the generally available films with no prodegradants. Films with a prodegradant are highly susceptible to abiotic degradation. It is possible to notice that initial, more rapid abiotic degradation quite significantly impacted strength properties of all films with prodegradants following their initial aging. Taking into account addition of ZR2 without Roy (M2 masterbatch), after 50 h of aging the films were found with higher resilience, while addition of Roy (M3 and M4 masterbatches) significantly decreased their strength properties. Therefore we can conclude that Roy copolymer may act as a reducing iron(III) ions agent. Films with Roy, whether or not with an addition of ZR2, show similar tensile strength, which is much lower than in the case of no Roy supplement. This proves that the addition enhances the degradation process. Besides that, an increase in the quantity of any prodegradant results in faster decomposition of film, and as a consequence in reduced value of tensile strength for samples subjected to initial abiotic aging.

FT-IR spectroscopy

The progress in decomposition of the films was verified with FT-IR spectroscopy. The contents of groups appearing in the process of oxo-biodegradation were assessed. It was expected that carbonyl and hydroxyl groups would emerge. The spectra of the films before the aging process as well as after 50, 100 and 125 hours of aging and after the process of biodegradation were analyzed. These spectra illustrate the changes occurring in course of the aging process in climatic chamber and the effects of microorganisms' activity in mushroom compost. Based on the intensity of corresponding bands in the spectra the values of carbonyl indices for the films, described their susceptibility to degradation, were calculated and listed in Table 2. The growth in the value of carbonyl index for each film coincided with longer duration of aging in the climatic chamber. Films with the lowest content of prodegradants were found with the lowest value of carbonyl index, and the rate increased with higher quantity of the prodegradant. Addition of Roy promoted significant acceleration of decomposition (faster increase in carbonyl index — Table 2). Addition of ZR2 produced similar, although less pronounced effect.

In most cases, after biodegradation the films were found with lower value of carbonyl index. This proves that these polar groups are more susceptible to the growth and action of microorganisms. Presence of ZR2 in the mixture used for extruding the films also promotes microbial growth.

Surface free energy — polar constituent

The polar constituent of surface free energy (*SFE*) for the coatings was determined using Owens-Wendt's model and measurements of wetting angles for film surfaces by means of model liquids. The results are presented in Fig. 1. The investigation focused on the effect of polarities of groups contained in the film structure on the value of *SFE*, and in particular the polar constituent, in order to determine hydrophilic susceptibility of the films to microbial action. It can be noticed instantly that in the case of water the wetting angle for film samples after aging was decreased (Fig. 1), which proved that more hydrophilic groups appeared in the film.

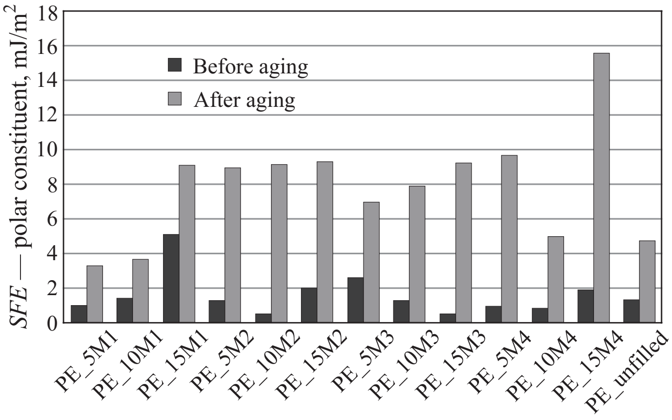

Fig. 1. Values of polar constituent of surface free energy (*SFE*) before aging and after 125 h of aging for all prepared films

Visual assessment

Exemplary microscopic photo of composite film (PE_15M4) before and after aging is shown in Fig. 2. As a result of abiotic degradation on the surface of PE_15M4 film numerous cracks were found, which additionally increased after the biotic process. After the film was extracted from the compost and rinsed with water, the biofilm remained on its surface. This shows that newly created conditions on the film surface promote adherence of microbial colonies which draw carbon and water necessary for biofilm synthesis from polyethylene.

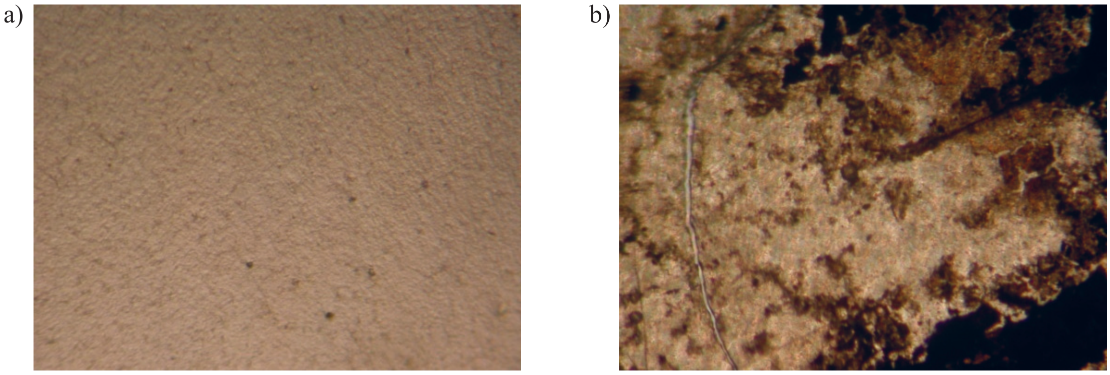

Fig. 2. Microscopic photo (enlargement 40×) of PE_15M4 film: a) before aging, b) after 125 h of aging and 30-day biodegradation in mushroom compost

CONCLUSIONS

— Application of Fusabond® E226 compatibilizer visually improved homogenization of the additives. The prepared films were uniform, with no inclusions; they contained no visible agglomerates of iron(II) stearate or Nanobent® ZR2 filler.

— The use of iron(II) stearate significantly increased the speed of polyethylene oxo-degradation.

— Nanobent® ZR2 filled composite films had strength characteristics similar to films made of unmodified PE-LD.

— Addition of Royaltuf® 485 copolymer increased the speed of oxo-degradation and films with this additive had strength characteristics after initial aging. It can be assumed that Royaltuf® 485 acted as an agent reducing iron(III) to iron(II).

— During initial abiotic aging polar functional groups emerged and there was an increase in hydrophilicity of films and as a consequence a greater chance for microbial attack. Following abiotic aging each film was found with a higher value of surface free energy.

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