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Influence of addition of a mixture of manganese and iron carboxylate on the degradation process of LDPE films

Abstract: A study was made of the degradation of polyethylene packaging film modified with Mn(II) and Fe(III) carboxylate at additive content of 0.5 and 1 wt%. A comparison was made between the effectiveness of manganese and iron carboxylate at molar ratio of Mn:Fe 1.5 and the photodegradative effects of mixed carboxylate salts of these metals of various content of the individual fatty acids. We compared the effects of degradation of films obtained under the same processing variables and aged under the same conditions. In this way we have studied the effect of chemical composition of the carboxylates on their effectiveness and the usefulness of technical grade stearin in obtaining an effective and thermally durable prodegradant.

Keywords: pro-degradant additives, LDPE film, manganese carboxylate, iron carboxylate

WPLYW DODATKU MIESZANINY KARBOKSYLANÓW MANGANU I ŻELAZA NA PROCES DEGRADACJI FOLII PE-LD

Streszczenie: Przedstawiono wyniki badań degradacji opakowaniowej folii polietylenowej modyfikowanej karboksylanami Mn(II) i Fe(III) przy zawartości tego dodatku w polimerze 0.5 i 1% mas. Porównano skuteczność karboksylanu manganu i żelaza o stosunku molowym Mn:Fe 1.5 na działanie fotodegradacyjne mieszanych soli karboksylowych tych metali o różnym składzie indywidualnych kwasów tłuszczowych. Porównano efekty degradacji folii uzyskanych w tych samych warunkach przetwórstwa i poddawanych starzeniu. Badano wpływ składu chemicznego karboksylanów na ich skuteczność oraz przydatność stearyny technicznej do uzyskania skutecznego i termicznie trwałego prodegradanta.

Słowa kluczowe: prodegradanty, folie PE-LD, karboksylan manganu, karboksylan żelaza

INTRODUCTION

Low manufacturing cost, good mechanical properties and low density are the advantages of plastics that increase their usage. Plastics are a waste which is difficult to degrade and thus pollutes the environment and disturbs the ecosystem. The increase in the amount of waste polyolefin films, including packaging films, is particularly high. Chemically the polyolefines are un-reactive at room temperature and they do not readily degrade in natural environment. One of the possible solutions to this problem is the use of additives which can accelerate the decomposition of plastics in the natural environment without significantly affecting their

properties [1–3]. The mechanisms of polymer decomposition and the used additive types can be different. Of large commercial importance are Transition Metal Carboxylates (TMC). These compounds have the ability to initiate the breaking of hydroperoxy bonds that are formed during polymer oxidation, leading in consequence to the fragmentation of long polymer chains into more readily degraded shorter entities [2, 4–8]. During oxo-(bio) degradation process, UV light, heat and catalytic metals help in oxidative chain scission with the help of atmospheric oxygen, followed by biodegradation phase [9]. Of commercial importance are notably the stearates of: iron, manganese, cobalt, titanium, vanadium, chromium, zinc and copper. Studies

of the effects of the pro-oxidative action of TMCs in polyethylene have indicated that iron(III) stearate was most effective at an early stage of polyethylene photodegradation [4], whereas manganese(II) stearate played mainly the role of a thermo-oxidant [7].

Photo-oxidation has also been reported to be enhanced by incorporating photoinitiators such as chromophores into the materials or by copolymerization with a small amount of monomers that contain carbonyl groups, or by using transition metal compounds such as metal stearate and dithiocarbamates [10]. Some literature studies have analysed the photo-oxidation (or oxo-degradation) of PE in the presence of pro-oxidants based on metal ions [5–8,11].

Aerobic biodegradation of the product of thermo-oxidative degradation of polyethylene films containing pro-oxidant under controlled composting conditions was analyzed by Jakubowicz [12]. The degree of bio-assimilation after 6 months incubation was about 60% and depending on the amount of prodegradant present in sample. The effect of amount of metal ion based pro-oxidant and different fillers on the mechanical and thermal performance as well as photo-degradation of thick PE moldings was investigated [13]. The filler particles were observed to delay the time needed to attain embrittlement due to reduction in oxygen permeation in the matrix as well as UV absorption, however, these materials confirmed that degradation of the materials could be successfully tuned without sacrificing the mechanical, thermal and rheological properties of the nanocomposites.

Previous investigations of the authors of this paper have shown that combined action of Mn^{2+} and Fe^{3+} carboxylates produced better degradation effects than those of each of these compounds separately [14–16]. It was also found on the basis of the authors' research that it was possible to obtain a compound catalyst/oxo-biodegradant – manganese and iron carboxylate in one process, wherein the manganese to iron ratio could be varied in a broad range to be adjusted to anticipated conditions of degradation [15].

This paper presents results of research on the preparation and behaviour of a compound catalyst which comprises of iron and manganese carboxylates obtained from pure stearic acid and from various technical grade stearin in polyethylene films.

Technical grade stearin is a complex product consisting of various saturated fatty acids, mainly stearic and palmitic acid, wherein the composition and relative content of the various acids depend on the grade of stearin and on the manufacturer. The reactivity of stearin in the process of soap synthesis depends on the number of active carboxyl bonds and on the length of the alkyl chain and, to a lesser degree, on accompanying impurities. Direct reactions in an aqueous environment between saturated C16 and higher carboxylic acids and transition metal hydroxides, including Fe^{3+} and Mn^{2+} , have very low yields. For this reason synthesis of transition metal carboxylates is carried out in two steps: in the first step the carboxylic acid is saponified with a strong base of a monovalent metal, e.g. NaOH, and immediately after that exchange reaction is carried out between sodium carboxylates and salts of transition metals (e.g. chlorides, sulphates, acetates) to obtain carboxylates of these metals [17–19]. The yield of the synthesis depends on the molar ratio of the base (NaOH) to acid carboxylic groups, wherein a slight stoichiometric excess of the base is favourable. The presence of unreacted acid in the product lowers its melting point, which is an undesirable feature when the product is used in polyolefins. Excess lye, in its turn, disadvantageously increases the pH of the product and causes it to absorb moisture impeding thereby its processing into polymer concentrate and film [19].

Film degradation in the natural environment is caused by abiotic and biotic factors. Some investigators have found synergy in such factors as: exposition to sunlight, thermal ageing and biological action of fungi, mould and soil bacteria on the degradation rate of PE film containing a prodegradant [20, 21].

It is generally believed that the LDPE films containing prooxidants enter into embrittlement stage when the Mn is near 5 000 [6]. The oxidized PE with lower molecular weight and higher hydrophilicity is thus more susceptible to microbial attack. Reduction of the molecular weight of polyethylene to values around 40 000, combined with the introduction of oxygen-containing functional groups, leads to biodegradable products [22–24]. According to ASTM D 3826 the plastic attains its so-called brittle point, when its elongation at rupture reaches 5% (or less) of the initial value of an unaged sample. Upon attaining the brittle point the polymer is considered susceptible to microbial attack. In accordance with that standard the degradation time was determined as the time after which elongation at rupture is reduced to 5% of its initial value.

In the current study, the effect of chemical composition of the carboxylates on their effectiveness and the usefulness of technical grade stearin in obtaining an effective and thermally durable prodegradant was investigated. Prodegradants obtained from stearic acid and technical grade stearins of various content of saturated carboxylic acids contained cations of TMC: Mn^{2+} and Fe^{3+} with Mn:Fe molar ratio being equal to 1.5.

The effects of degradation under natural and accelerated weathering conditions of PE-LD films on the mechanical properties was compared.

EXPERIMENTAL SECTION

SYNTHESIS OF PRODEGRADANT ADDITIVE

Sodium hydroxide (0.25 n solution), manganese(II) chloride tetrahydrate, iron(III) chloride (POCH), stearic acid or technical grade stearin (two samples), were used for the synthesis of iron manganese carboxylates TMC.

Immediately after saponifying with soda lye, the molten carboxylic acids (C) were subjected to the reaction of sodium cation exchange

for manganese and iron using manganese(II) chloride and iron(III) chloride, respectively. The reaction was carried out at 80–85°C under continuous stirring using 5% stoichiometric excess of lye in relation to the acids content. A solution of $MnCl_2$ (0.25 n) was added to the reaction suspension at 70–80°C while stirring continuously. After ca. 30 minutes a solution of $FeCl_3$ (0.25 n) was added to the reaction suspension. The reaction suspension was stirred for another 0.5 hour at 70–80°C. The precipitate was separated and washed with water to remove chlorides. The product (TMC) was dried at 60°C.

SUBSTRATE AND PRODUCT TESTING METHODS

The metal content in obtained carboxylates was determined in optical emission spectrometry technique ICP- OES.

The thermal transformations (melting and degradation) of the obtained MnFeC additives were investigated using thermal analysis on a Mettler Toledo TGA/SDTA 851e analyzer: Particle size analysis (Coulter LS Particle Size Analyzer) was applied to determine the size of product grains obtained by precipitation. Specific surface was determined by means of a Gemini VII Micromeritics analyzer.

PE-LD FILMS

The PE-LD (Malen E GGNX 18-D003 from Lyondell Basell) films (0.03–0.05mm thick) contained TMC in the amounts of 0.5 and 1.0 wt% were obtained on a Plasti-Corder PLV 151 Brabender extruder (extrusion blow moulding).

METHODS OF FILM AGEING INVESTIGATIONS

The obtained films were subjected to natural weathering tests (according to EN ISO 877–1:2010) and to accelerated

ageing tests using a Xenon Weather-Ometer (EN ISO 4892-2:2013, method A). Susceptibility of LDPE films with prodegradant by the bacteria strain was evaluated on the basis EN ISO 846:20021 during a period of 84 days. The film samples, after the period of abiotic degradation, were sterilized by immersion in 70% isopropyl alcohol, washed in sterile distilled water and placed on a Czapek-Doxa substrate with no saccharose. Then the polymers were occluded with a suspension of spores of *Bacillus mycoides* with a concentration of $10^6/\text{cm}^3$. At the same time the film that has not undergone abiotic ageing was also subjected to biological degradation. After conditioning, the films were washed with distilled water, immersed in a 1% solution of mercury(II) chloride, washed again with water and dried to constant weight.

The surface morphology of the polymers was characterized by means of a Tesla BS 340 scanning electron microscope (SEM). Samples were coated with technical gold by metal evaporation in a Pelco SC-6 sputter coater ($t=40\text{s}$, $I=25\text{ mA}$, $p=80\text{ Pa}$).

Changes in strength properties of the film in the course of ageing were examined by an Instron Model D 7418 mechanical testing machine (test rate: 100 mm/min, specimen test length: 50 mm, temp. $23\pm 2^\circ\text{C}$ in accordance with EN ISO 527-3). On the basis of the ASTM D 3826 standard, it is accepted that the final point of degradation, which is the brittle point of a plastic material, occurs when the relative elongation of a plastic material at rupture is 5% or less. When the brittle point is reached, it is considered that the polymer can be susceptible to attack by microorganisms. In accordance with the previously mentioned standard, the time of decomposition of individual samples can be predicted by accepting that the brittle point equals 5% of elongation at rupture and by assuming that mechanical properties, during exposure to atmospheric conditions, change linearly.

The carbonyl index (CI), which reflects oxidation processes that occur in aged films, was determined according to ASTM D 6954-04.

RESULTS AND DISCUSSION

SYNTHESIS OF CARBOXYLATES

Manganese(II) and iron(III) carboxylates were synthesized by reacting carboxylic acid, sodium hydroxide, manganese(II) chloride and iron(III) chloride, wherein the molten acid was saponified with soda lye immediately prior to the exchange reaction. Afterwards chlorides of manganese and iron, respectively, were used to obtain the carboxylates (TMC-1, TMC-2, TMC-3). One half of the sodium carboxylate obtained was treated with stoichiometric amount of MnCl_2 , the other half was treated with stoichiometric amount of FeCl_3 .

The thermal resistance of the individual TMC carboxylates, as determined by DTG, is poorly differentiated. The degradation start points of TMC was similar for all samples and was close to 300°C . Oxobiodegradants are usually mixed with polyethylene at $170\text{--}190^\circ\text{C}$ [12]. This means that all carboxylates obtained had sufficient thermal stability, particularly when used in polyethylene, the processing temperature of which is much lower than 300°C .

The uniform morphological structure of TMC carboxylates, which is an important indicator of the quality of additives for packaging films, was confirmed by particle size distribution analysis, specific surface determination and calculated inhomogeneity coefficient, which was virtually identical in all samples. Other important parameters include particle size distribution and specific surface area (Table 1). The mean particle size varies within 10 to 15 μm .

Table 1. Morphological characteristics of the obtained carboxylates

Characteristics	TMC-1	TMC-2	TMC-3
Mean, μm	14.2	10.8	13.2
Median, μm	13.7	10.4	12.8
Mode, μm	17.9	11.3	16.4
Inhomogeneity coefficients, %	49.8	49.5	49.7
Bulk density, g/cm^3	0.13	0.21	0.15
Specific surface area A, m^2/g	5.49	8.99	6.78

EFFECT OF MNFEC ADDITION ON THE DEGRADATION OF PE FILM

For ageing testing PE-LD films with an addition of 0.5% (PE-a) or 1.0% (PE-b) of the metal carboxylates were selected. Samples obtained from MnFeC carboxylates were designated as follows: from TMC-1 in PE1; TMC-2 in PE2 and TMC-3 in PE3. The films were tested as prescribed in the adopted methodology [4,6,7,13]. The parameter which changes most rapidly in the case of atmospheric weathering is elongation (Fig. 1a), and tensile strength of the film during accelerated ageing (Fig. 1b). The percentage change in the proper mechanical parameter after given period of ageing has been adopted as a criterion of assessment of the process of destruction.

The films were aged in atmospheric conditions during Spring-Summer period (Silesia, Poland). After 3 months of exposition in atmospheric

conditions, complete degradation was observed for samples with an addition of TMC-1 obtained from pure stearic acid. In the other cases degradation proceeded slightly slower. The suitability of the film for use is determined by the time necessary for to obtain a change of the relative elongation by 50% compared to its initial value.

It has been observed the increase of the carbonyl index (Table 2), which confirms the oxidation and degradation process in the polymer matrix. With increase of the content of palmitic acids in TMC carboxylate the lower carbonyl index values were obtained in PE film sample after the same ageing time. The rate of increase of carbonyl index was proportional to the initial content of unreacted acid in TMC sample.

For samples subjected to accelerated ageing, the loss of weight of polymers depended mainly on the exposure conditions (Tab.2). The weight loss values obtained were affected by the quality

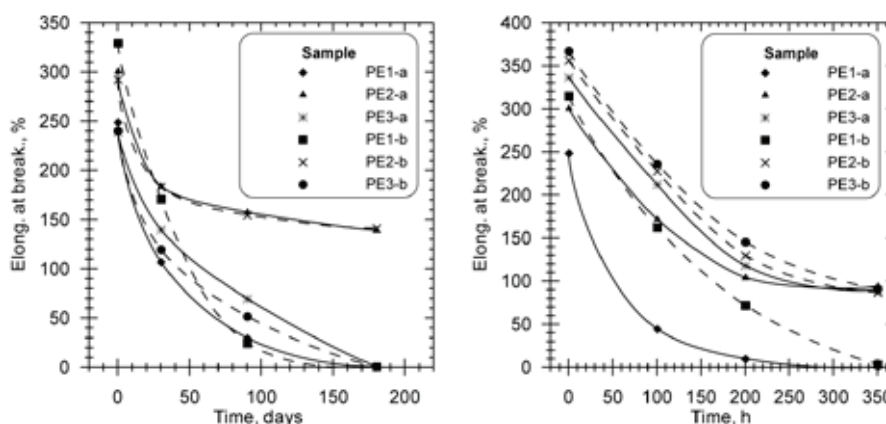


Figure 1: Change in ultimate relative elongation during (a) atmospheric weathering, (b) accelerated ageing

Tab.2. Degradation time, mass loss and carbonyl index of the film samples aged in Xenon Weather – Ometer

Sample	Degradation time, days	carbonyl index			Mass loss, %
		150h	200h	350h	
PE1 – a	50	0,053	0,134	0,160	1,489
PE2- a	48	0,101	0,158	0,187	2,055
PE3- a	323	0,085	0,090	0,114	0,997
PE1 – b	239	0,089	0,097	0,119	1,351
PE2- b	140	0,051	0,214	0,356	0,893
PE3- b	91	0,116	0,258	0,387	1,097

of the acid used to synthesize carboxylates and by the amount of additive introduced. It was confirmed that weight loss in the sample obtained from pure acid was in both ageing tests higher than that in samples obtained from a mixture of carboxylic acids. The lowering of this value makes the products of film oxidation assimilable by bacteria and other microorganisms.

No changes in the surface of the films were observed after degradation of samples under atmospheric and accelerating conditions (Xenotest). In the case of biological degradation of non-aged samples with added carboxylates, no changes were observed on the surface of the film, but there was clear flaking and formation of cracks in abiotically degraded samples after degradation (Fig. 2). Noticeable is also the formation of bacterial colonies in cracks in the film. Film degradation proceeded in laminar manner and the film was increasingly thinner.

CONCLUSIONS

We have verified the practicability of using technical grade stearins of various acid content to obtain quality oxodegradants for plastics, where the oxodegradants contained Mn^{+2} and Fe^{+3} at Mn:Fe molar ratio of ca. 1.5. The use of a mixture of saturated carboxylic acids of lower melting point instead of pure stearic acid has not changed substantially the physicochemical properties, including thermal stability, of the obtained carboxylates. These compounds are characterized by thermal degradation temperature ranging from 297°C to 364°C, which is much higher than the processing temperature of polyethylenes. The obtained MnFeC carboxylates had uniform structure and particle size distribution, suitable for application in packaging film. The use of iron and manganese carboxylates proved to be effective additives

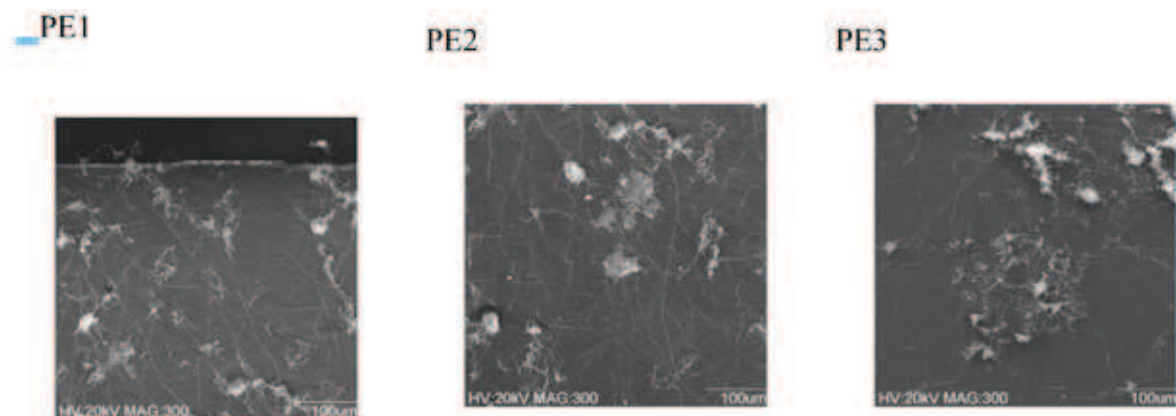


Figure 2. Comparison of film after acceleration ageing (150h) and influence of bacteria strain

Changes in the mechanical properties exposed to atmospheric weathering and to accelerated ageing prove degradation process in all films under influence of light, temperature and atmospheric oxygen. It is probable that the tested films (after exposure to UV light) will degrade to such an extent that they can also be biodegradable (consumable by microorganisms present in soil and water) approximately after 6 months to 1 year.

for initiating accelerated decomposition of the film. Manganese and iron carboxylate (TMC) that contained 28% palmitate (C16) and 52% stearate (C18) changed the brittle point of polyethylene in a similar way as did manganese and iron stearate (ca. 98% C18) of the same Mn:Fe ratio. Some amount of unreacted carboxylic acids present in the degradation additive had slightly affected the increase rate of carbonyl index in the aged samples.

Increased amounts of lower carboxylates (C16-C14) in the pro-degradant sample caused lower weight loss after ageing investigations.

Changes in the mechanical properties and the chemical structure of films subjected to accelerated ageing or atmospheric weathering confirmed that degradation proceeds in all films under the action of light, heat and atmospheric oxygen. In preliminary studies it was observed that oxidation products of polyethylene with TMC may be biodegradable. Manganese and iron carboxylates comprising various acid radicals proved to be as effective oxodegradants as chemically pure stearates of these metals.

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