

Research Article

Increased Performance of Thermoplastic Packaging Materials by Using a Mild Oxidizing Biobased Additive

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Green additives such as prodegradants based on natural fatty acids and iron can improve the environmental profile of thermoplastic packaging materials. We present two studies in which this is demonstrated. In the first study, the addition of a green prodegradant to a 5-layer gas barrier laminate during processing provided a laminate with significantly reduced oxygen transmission due to the resulting oxygen-consuming degradation process. The result shows that material reduction and cost efficiency of packaging laminates can be combined, since 5-layer laminates with reduced oxygen barrier layer thickness and retained gas barrier properties are feasible. The products are interesting from an ecological and economic aspect. In the second study, the addition of a green prodegradant to several qualities of polypropylene that are used in packaging applications leads to materials that are readily degraded in accelerated weathering. The molecular weight of the modified polypropylenes after 830 hours of accelerated weathering is reduced from typically 80.000 g/mole to 1.500–2.500 g/mole. At such molecular weight levels, digestion by microorganisms is feasible. The mild prodegradant used in the study does not lead to degradation during processing. Thermoplastics containing such additives are therefore fully recyclable provided that they have not been exposed to a long period of weathering.

1. Introduction

Thermoplastic packaging materials have in the past three decades faced an increasing demand to improve their environmental profile. As a consequence, significantly increased amounts of renewables have been used in packaging materials [1–8]. Additionally such materials often exhibit a green profile due to their biodegradability [9–11]. Reduced material consumption is also an important approach. Packaging materials with reduced wall thickness but preserved mechanical and/or gas barrier properties lead to reduced carbon footprint and combine environmental friendliness with cost efficiency. Another route to packaging materials with increased environmental profile is to establish effective recycling procedures. Littering should be significantly reduced if users are aware of the value of post-consumer packaging [12]. Conventional thermoplastic packaging materials can

be turned into finally biodegradable materials by addition of prodegradant additives during processing into packaging products [13–15]. Prodegradants based on renewables such as fatty acid salts and environmentally friendly metals like iron are especially interesting. Thermoplastics containing such additives are fully recyclable [16].

In this paper we present the results of two studies in which green prodegradants based on ferric stearate are added to different thermoplastics. In the first study a green prodegradant is added to a 5-layer gas barrier laminate during processing in order to investigate changes of the oxygen transmission rate due to the presence of an oxygen-consuming degradation process. In the second study a green prodegradant is added to several qualities of polypropylene that are used in packaging applications. The goal is to investigate changes in tensile properties and molecular weight during accelerated weathering due to oxidative degradation.

2. Experimental

2.1. Prodegradant Additive in 5-Layer Oxygen Barrier Film.

In the first step a mixture of ferric(III) stearate and stearic acid was prepared which is the main prodegradant agent in both studies. The synthesis was conducted in an oil-thermostat-controlled 50-litre double-mantle glass reactor having two dosing pumps, a mechanically powered steel stirrer, a glass-mantled thermometer, a distillation cooler, a bottom valve, and a connected membrane vacuum pump. In advance a solution of 11.3 kg (41.8 moles) of ferric chloride hexahydrate in 10.5 L water and 0.11 L concentrated hydrochloric acid was prepared to produce a 21.9 kg aqueous ferric chloride solution with about 10.6% w/w iron. To provide the fat-soluble organic compound 12.9 kg (45.3 moles), stearic acid was melted in the reactor by adjusting the temperature of the oil thermostat to 190°C. Then 0.18 L low-aromatic white spirit (mixture of hydrocarbons, Statoil AS, Norway) and 0.35 L water were added, and the pressure reduced to 200 mbar. By means of one of the dosing pumps 6.1 kg of the in-advance-prepared ferric chloride solution was added over a 50-minute period. By means of one of the dosing pump 10 mL per minute of a 1% aqueous hydrogen peroxide solution was added to maintain a modest but continuous foaming in the reactor. The addition of the aqueous ferric chloride solution was adjusted so that the amount of distilled water and hydrogen chloride approximately corresponded to the amount of aqueous ferric chloride added. After complete addition of aqueous ferric chloride solution, the mixture was boiled and distilled under continuous addition of 25 mL per minute 1% aqueous hydrogen peroxide solution. The amount of distilled water and hydrogen chloride was larger than the amount of 1% hydrogen peroxide solution resulting in a decreased portion of water in the reaction mixture. When the temperature of the reaction mixture had reached 115°C, it was cooled to about 100°C and thereafter drained through the bottom valve into 100 litre of a 1% hydrogen peroxide solution. When the resulting gas development dropped off, the iron-containing additive was filtered from the liquid phase. The iron-containing additive was then dispersed in 1% aqueous hydrogen peroxide solution at 60–70°C for 2 hours by means of a dispersing rod. The dispersed iron-containing additive was filtered from the aqueous phase and dried in a convection oven at 50°C. The iron content was measured by total combustion to be 3.6% w/w.

In the second step, the mixture of ferric(III) stearate and stearic acid was compounded in a Clextral double-screw extruder together with other additives and a polypropylene quality. The compounding conditions are listed in Table 1 and Table 2. The compound is called “masterbatch 1” (MB 1), and its functionality is to introduce the main prodegradant into the thermoplastics in the 5-layer laminate. The composition of MB 1 is shown in Table 3.

In order to hinder degradation during processing of the thermoplastics, which form the 5-layer laminate, a second masterbatch, “masterbatch 2” (MB 2), has to be added. MB 2 has been prepared in a way similar to that of MB 1, and its composition is shown in Table 4.

TABLE 1: Description of the Clextral extruder.

Extruder type	Clextral double-screw extruder
Rotation frequency	150 [min ⁻¹]
Feeding	10 [g/min]
Dwell time	2-3 [min]
Heating zones	12
Temperature profile	see Table 2
Outlet nozzle	Circular/diameter 4 mm

TABLE 2: Compounding conditions on the Clextral extruder.

Zone	1	2	3	4	5	6	7	8	9	10	11	12
T [°C]	12	12	12	200	220	280	280	260	—*	240	230	220

* zone 9 is not heated.

TABLE 3: Composition of MB 1.

Component	Content (%)w/w	Description
Ferric(III) stearate/stearic acid	10	Iron content 3.6% w/w
Polyoxyethylene(20) stearyl ether	4	CAS (9005-00-9)
Stearyl amine	3	CAS (124-30-1)
Polypropylene	83	random copolymer R 451*

* Tiszai Vegyi Kombinát Plc., Hungary.

TABLE 4: Composition of MB 2.

Component	Content (%)w/w	Description
Pentaerythritol Tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionylpentaerythriol)	15	Irganox 1010, CAS [6683-19-8]
Polyethylene	85	Linear low density (Exact 0230, ExxonMobil, USA)

TABLE 5: Composition of the 5-layer laminate.

Layer no.	Type of polymer	Description of polymer
1	PE	Low-density polyethylene
2	Modified PE	Maleic-anhydride-modified PE (OREVAC, Arkema, France)
3	EVOH	Ethylene-vinyl alcohol copolymer with 38% mol ethylene (Soarnol ET 3802, Nippon Gohsei, Japan)
4	Modified PE	Maleic-anhydride-modified PE (OREVAC, Arkema, France)
5	PE	Low-density polyethylene

A 5-layer barrier film has been manufactured by 5-layer film blowing. The materials that constitute the 5 layers are listed in Table 5.

TABLE 6: Description of the polypropylene qualities.

PP quality	Manufacturer	Typical application area
BE 170 MO	Borealis, Belgium	Injection moulding
Tipplen H 681	TVK Plc., Hungary	Extrusion thermoforming
Tipplen K 948	TVK Plc., Hungary	Injection moulding
Tipplen K299	TVK Plc., Hungary	Injection moulding
Tipplen H 649	TVK Plc., Hungary	Bisoriented film

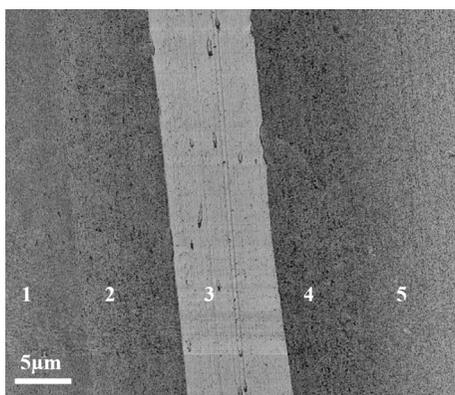


FIGURE 1: AFM characterization of 5-layer laminate.

The processing temperature was 190°C–230°C. The total thickness of the laminate was 60 μm. Two different amounts of a 9:1 blend of MB 1/MB 2 have been added to all layers during processing. The total addition was 1% and 2% w/w.

The oxygen transmission rate of the laminate was measured on an Ox-Tran device (MOCON Inc., USA) at 23°C and 50% relative humidity.

Atomic force microscopy was used to characterize the 5-layer laminate. Ultramicrotomy was used to cut the films perpendicular to the laminate plains and in the extrusion direction.

2.2. Prodegradant Additive in Polypropylene Qualities. In the second part of the study, a prodegradant additive was compounded into five different polypropylene qualities (Table 6) and their degradability was investigated. Atomic force microscopy (AFM) shows the different layers and regularly distributed spots of the prodegradant additive (Figure 1).

The prodegradant additive was prepared in the same way as described in the first study, however with a different content of iron. The synthesis was carried out in order to obtain a mixture of ferric(III) stearate and stearic acid with an iron content of 1.9% w/w. This mixture was compounded in a Clextral double-screw extruder together with other additives and a polypropylene quality in order to obtain the prodegradant masterbatch for the second study. The obtained masterbatch is called “masterbatch 3” (MB 3), and its composition is shown in Table 7.

Similar to the first study, a 9:1 blend of MB 3/MB 2 has been added to the polypropylene qualities during processing. The extruded tape samples were fixed to suitable

TABLE 7: Composition of MB 3.

Component	Content (%)w/w	Description
Ferric(III) stearate/stearic acid	16	Iron content 1.9% w/w
Polyoxyethylene(10) stearyl ether	8	CAS (9005-00-9)
Stearyl amine	5	CAS (124-30-1)
Polypropylene	71	Random copolymer R 451*

* Tiszai Vegyi Kombinát Plc., Hungary.

TABLE 8: SEC conditions.

Instrument type	PL-GPC 210
Columns type	4* PL gel 20 micron LS
Solvent	1,2,4-trichloro benzene
Temperature	145°C
Injection volume	0.20 mL
Sample concentration	2-3 mg/mL
Calibration	Polystyrene standards
Mark Houwink constants	$K = 14.1 * 10^{-4} \text{ dL/g}$, $a = 0.7$

TABLE 9: Oxygen transmission rate and elongation at break of the 5-layer laminate.

Thickness of EVOH layer	MB 1	MB 2	OTR ($\text{cm}^3\text{O}_2/\text{m}^2\cdot\text{day}$)	Elongation at break (%)
5 μm	0.9%	0.1%	$2, 12 \pm 0.03$	355 ± 55
5 μm	1.8%	0.2%	$1, 51 \pm 0.03$	318 ± 6
10 μm	0%	0%	$3 \pm 0.5^*$	—
5 μm	0%	0%	$5 \pm 1.0^*$	—

* Information from technical datasheet (Nippon Gohsei).

specimen holders (Atlas Electric Devices Company, Illinois, USA) and exposed for accelerated weathering in an UVCON WEATHER-O-METER (Atlas Electric Devices Company, Illinois, USA). The accelerated weathering device is equipped with 340 UVA fluorescent lamps and is suitable for testing procedures according to ISO 4892-3 (ASTM G154). The periodic testing cycle consisted of the following procedures:

- (i) 4 hours of dry UV exposure with 340 UVA fluorescent lamps at 60°C,
- (ii) 0.5 hours of water spray with deionized water at 8–10°C,
- (iii) 3.5 hours of condensation 40°C.

Degradation of the tape samples was followed by mechanical testing (ISO 527-2) and finally by SEC analysis. SEC was performed according to ISO 16014-1, 16014-2, and 16014-4. As specified in Table B.1 in ISO 16014-2, the same Mark Houwink constant was used for the polypropylene samples and the polystyrene standards. The SEC conditions are listed in Table 8.

TABLE 10: Elongation at break (%) depending on accelerated weathering time.

PP quality	Sum MB 2/MB 3	Accel. weathering				
		0 hours	24 hours	48 hours	72 hours	96 hours
BE 170 MO	2% w/w	12 ± 3	<5	<2	—	—
Tipplen H 681	2% w/w	349 ± 346	5 ± 3	6 ± 4	<5	<2
Tipplen K 948	2% w/w	23 ± 8	<5	<2	—	—
Tipplen K299	2% w/w	7 ± 3	<5	<2	—	—
Tipplen H 649	1% w/w	710 ± 94	700 ± 87	23 ± 32	<5	<2
Tipplen H 649	0% w/w	475 ± 314	706 ± 54	650 ± 94	676 ± 104	584 ± 76

TABLE 11: Strain at yield (N/mm²) depending on accelerated weathering time.

PP quality	Sum MB 2/MB 3	Accel. weathering				
		0 hours	24 hours	48 hours	72 hours	96 hours
BE 170 MO	2% w/w	29.3 ± 1.1	5.6 ± 3.9	1.7 ± 0.5	—	—
Tipplen H 681	2% w/w	27.9 ± 3.1	17.3 ± 4.2	14.9 ± 2.1	<10	<5
Tipplen K 948	2% w/w	21.6 ± 0.7	<10	<5	—	—
Tipplen K299	2% w/w	19.7 ± 1.7	2.7 ± 0.4	2.4 ± 1.6	—	—
Tipplen H 649	1% w/w	35.0 ± 4.6	33.0 ± 3.7	20.0 ± 3.2	<10	<5
Tipplen H 649	0% w/w	29.9 ± 3.4	35.2 ± 3.0	32.8 ± 3.1	31.4 ± 2.7	32.5 ± 3.5

3. Results and Discussion

3.1. Prodegradant Additive in 5-Layer Oxygen Barrier Film. Table 9 shows the results on oxygen transmission rate (OTR) and elongation at break (ISO 527-2) of the 5-layer laminate. Elongation at break was taken as an average of 10 samples.

The results show that the oxygen transmission rate is significantly improved by addition of the prodegradant additive. This can be explained by the oxygen consumption of a slow degradation process in the laminate which is induced by the prodegradant additive.

Doubling of the amount of prodegradant additive does not induce significant degradation during processing and short storage. Elongation at break is a very sensitive marker for ongoing degradation. The very narrow result distribution of elongation at break (low standard deviation) shows that the adhesion within the layers after addition of 2% of prodegradant additive is excellent and significantly better than with lower amounts.

Atomic force microscopy (AFM) shows the different layers and regularly distributed spots of the prodegradant additive. This is in good compliance with an oxygen-consuming slow degradation process around the prodegradant additive.

As a consequence, 5-layer laminates with reduced oxygen barrier layer thickness and retained gas barrier properties are feasible. This is interesting from an ecological aspect (material reduction) and economical aspect (cost reduction).

3.2. Prodegradant Additive in Polypropylene Qualities. Mechanical properties of 0.4 mm tape samples based on the

different polypropylene qualities after different periods of accelerated weathering are shown below. Elongation at break is listed in Table 10 and strain at yield is listed in Table 11.

A comparison of the mechanical properties elongation at break and strain at yield of polypropylene qualities with and without prodegradant indicates clearly that qualities with prodegradant do not suffer significant degradation during processing. The development of the mechanical properties also shows that all of the five PP qualities with prodegradant additive degrade rapidly when they are exposed to accelerated weathering. The typical mechanical properties of PP materials are lost after 72 hours of accelerated weathering. In some cases the majority of samples became too brittle due to proceeded degradation. Therefore accurate data on elongation at break or strain at yield could not be obtained. When the data are based on one or two samples, the values are expressed as “<(number)”. When all samples became too brittle, the expression “—” was used.

Additionally the molecular weight distribution of the PP qualities after 830 hours of accelerated weathering was measured by SEC. The results are listed in Table 12.

SEC analysis clearly indicates that the degradation of the five PP qualities with prodegradant additive continues after the loss of the typical mechanical properties. The average molecular weight of the modified polypropylenes after 830 hours of accelerated weathering is reduced from typically 80.000 g/mole to 1.500–2.500 g/mole. At these values average molecular weight levels are small enough to make the degraded PP qualities accessible for biodegradation.

TABLE 12: SEC average molecular weights M_w and M_n and polydispersity (M_w/M_n) after 830 hours of accelerated weathering.

PP quality	Sum MB 2/MB 3	M_n	M_w	Polymer dispersity
BE 170 MO	2% w/w	919 ± 10	2518 ± 30	2,7 ± 0,06
Tipplen H 681	2% w/w	695 ± 12	1554 ± 41	2,2 ± 0,02
Tipplen K 948	2% w/w	807 ± 16	1864 ± 44	2,3 ± 0,01
Tipplen K299	2% w/w	767 ± 0	1752 ± 8	2,3 ± 0,01
Tipplen H 649	1% w/w	707 ± 24	1572 ± 50	2,2 ± 0,00

4. Summary

Green additives such as prodegradants based on natural fatty acids and iron can improve the environmental profile of thermoplastic packaging materials. Reduced oxygen transmission rate of a 5-layer gas barrier laminate was observed and explained by the oxygen consumption of a slow degradation process in the laminate. The result shows that material reduction and cost efficiency of packaging laminates can be combined, since 5-layer laminates with reduced oxygen barrier layer thickness and retained gas barrier properties are feasible. The products are interesting from an ecological and economic aspect.

Additionally several qualities of polypropylene which are used in packaging applications are degraded in accelerated weathering to an extent which makes digestion by microorganism feasible. Mild prodegradant based on ferric stearate does not lead to degradation during processing. Thermoplastics containing such additives are fully recyclable, provided that they have not been exposed to a long period of weathering.

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