New Masterbatch for Barrier Films

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Abstract

The market for multi-layer barrier films in agricultural applications is constantly increasing. The two main applications are silage films (both stretch film and silo film) and mulch films that are used for fumigation. Today these films are produced with a polyamide (PA) layer or an ethylene vinyl alcohol (EVOH) layer. Because both polymers are not compatible with polyethylene (PE) in the adjacent layers, a tie layer is needed to allow for adherence of the PE and barrier layers. The accepted method for producing these films involves a five-layer extruder. Most agriculture films, however, are produced using a three-layer extruder, and if a converter wants to produce a barrier film they thus need to invest in a new and expensive production line.

Tosaf has developed a new barrier masterbatch (MB) that enables the production of barrier films without the need for a tie layer, thus a barrier film can be produced using a three-layer extruder. Tosaf's new MB reduces the oxygen transmission rate (OTR) by two orders of magnitude even with a very thin layer of 10 – 20 μm (0.4 – 0.8 mils). The films produced with Tosaf's new MB are more economical in terms of materials cost.

INTRODUCTION

The aerobic deterioration of silage was studied in depth. R. Muck[1] summarizes the known mechanism. When silage is exposed to oxygen aerobic microorganisms start growing. They first respire the soluble substrates and then more complex compounds. This reduces the nutrition level of the silage. The most common microorganisms that initiate the aerobic deterioration of silage are yeasts. They consume sugars and fermentation acids resulting in elevated silage temperatures and pH. With the increase of the pH, other aerobic bacteria grow increasing the temperature even further. The final stage of deterioration is the appearance of molds, making the silage unusable.

E. Tabacco et al[2,3] has studied the use of an oxygen barrier film to cover the silage compared to a standard LDPE (low density polyethylene) film. They monitored the level of different bacteria and also measured different parameters that indicate the quality of the silage. They found that when using a film with oxygen transmission rate (OTR) lower than 100 cm^3/m^2 per 24 hours, the microbiological quality of the silage can be increased. The oxygen barrier film they evaluated was of the older generation, using PA (polyamide) as the oxygen barrier. Today films with an EVOH barrier layer are produced and they have an even lower OTR.

T.F. Bernardes et al[4] studied the top spoilage losses in maize silage that is sealed with a plastic film. They evaluated 4 different films: PE + PA film having an oxygen transmission rate of 75 cm^3/m^2 per 24 hours, standard PE film with an oxygen transmission rate of 722 cm^3/m^2 per 24 hours, a PVC film with an oxygen transmission rate of 982 cm^3/m^2 per 24 hours and a coextruded PE/PVOH (polyvinyl alcohol) film with an oxygen transmission rate of 289 cm^3/m^2 per 24 hours. They found a direct correlation between the film's OTR to the quality of the silage stored. Because this parameter is relatively easily controlled there are existing norms and standards that define the oxygen transmission rate expected of a silage film. The most common ones are the German DIN 53380 -part 3 and the American ASTM D-3985.

Another agriculture application where the gas permeability of the film is important is the mulch film. A niche market for mulch films is targeted for soil fumigation and disinfection. The chemicals used to disinfect the soil from soilborn pests are not environmentally friendly or safe for workers. These chemicals are applied to the soil and then they are released back to the atmosphere. By using a mulch film with barrier properties the farmer can control the evaporation rate of the fumigants from the soil to the atmosphere, thus allowing the farmer to use lower levels of fumigants to get the same level of disinfection.

A. Gamliel[5] et al. studied the fumigant permeability of PA barrier films as compared to standard LDPE films and found that lower levels of fumigants could be used with the PA-barrier films in order to give the same disinfection results. Due to excessive exposure to the workers in the field, the barrier requirements have become more restrictive in recent years. As a result, barrier layers that fulfill these requirements are currently based on EVOH instead of PA.

Comparative measurements of PA-barrier films vs. EVOH-barrier films vs. standard LDPE films show that the permeability of the fumigants in an EVOH-based film is 3 – 6 orders of magnitude lower then a PA-based film and 4 – 7 orders of magnitude lower then a standard LDPE film. With regard to oxygen permeability, EVOH barrier film is 2 orders of magnitude lower than the PA-based film and 4 orders of magnitude lower than standard PE film.

Because neither EVOH nor PA are compatible with PE, a tie layer is required between the barrier layer and the PE layers, thus a barrier film typically contains at least 5 layers. Many producers of agricultural films prefer to utilize their existing 3 layer extruder equipment, in which case they cannot produce the barrier films discussed above without otherwise investing large sums in new equipment purchases.

We present results of a new masterbatch and compound that can be used to produce 3-layer agricultural films with good barrier properties without the need for a tie layer. The oxygen and fumigant barrier properties achieved are similar in performance to those of EVOH-based films.

EXPERIMENTAL

The plastic films were produced with a lab-scale three-layer blown film machine from Labtech. The equipment has 2 extruders LE 25 – 30/C, screw Ø 25 mm, 30 L/D and a die of A/B/A 50 mm.

Oxygen transmission rate (OTR) of the films was measured on a SYSTECH 8501 from Systech Illinois. The test was conducted according to DIN 53380-3.

Permeability of the films to the fumigant gases was measured using a A Hewlett-Packard (HP - SN: AA85D4BA-3178-40AD-BB01-90B1FA2F3B80) high- speed µGC with OV-1 Column, micro TC detector, and helium carrier gas.

RESULTS AND DISCUSSION

Oxygen barrier for the silage application

Both a MB and a compound were produced. The MB is IP7503PE and the compound is IP7502PE.

To evaluate these products 3 layer films were produced. The films contained either IP7502PE or IP7503PE mixed (melt blended) with LDPE and the ORT of the films was measured and compared to an LDPE film. The measurements are presented in table 1.

Table 1: OTR measurements of films containing IP7502PE and IP7503PE compared to LDPE films.

Film #	Skin Layer	Core Layer	%	Total film Thickness (μm)	Core Layer Thickness (μm)	OTR ($cm^3/m^2/day$)
1	LDPE	LDPE	100	170	N\A	299.3
2	LDPE	IP7503PE	72	160	40-50	3.1
		LDPE	28			
3	LDPE	IP7502PE	100	165	40-50	6.5
4	LDPE	IP7502PE	100	165	10-15	5.4
5	LDPE	LDPE	100	50	N\A	1142.9
6	LDPE	IP7503PE	72	55	20	4.6
		LDPE	28			
7	LDPE	IP7502PE	100	55	20	3.3

Reported OTR measurements by Nippon Gohsei (a EVOH polymer producer) are presented in table 2.

Table 2: Reported OTR measurements of a 20 micron film by Nippon Gohsei:

Polymer	OTR (CC.20 [illegible]/m^2/day.atm)
EVOH (44%)	1.2
LDPE	7900
PA	76

The measured OTR values for the films containing both IP7502PE and IP7503PE show a reduction of OTR similar to the one expected when using EVOH polymers.

Gas Permeability for the mulch application

A 50 micron 3 layer film was produced with the following composition: A\B\A LDPE\IP7502PE\LDPE 40%/20%/40%. The film was sent to Ajwa Analytical Laboratories in University of California Davis and its mass transfer coefficient (MTC) was measured in both high and low relative humidity (RH). The results are presented in tables 3 and 4.

Table 3: MTC of a film containing IP7502PE at low RH.

Fumigant	MTC (cm/hr)	Std
Methyl Bromide	0.0000	0.0000
Cis 1,3-D	0.0005	0.00011
Chloropicrin	0.00033	0.00028
Methyl isothiocyante	0.00248	0.00055
Dimethyl disulfide	0.00025	0.00043

Table 4: MTC of a film containing IP7502PE at high RH.

Fumigant	MTC (cm/hr)	Std
Methyl Bromide	0.00575	0.00185
Cis 1,3-D	0.01023	0.00282
Chloropicrin	0.00123	0.00044
Methyl isothiocyante	0.03751	0.00361
Dimethyl disulfide	0.00964	0.00202

Table 5 contains reported values by Kuraray group of the MTC at low RH for a mulch film containing EVOH as the barrier layer. All measurements were performed at the same laboratory in University of California Davis.

Table 5: MTC of a 40 micron film containing EVOH at low RH.

Fumigant	MTC (cm/hr)
Methyl Bromide	0.000004
Chloropicrin	0.00183
Cis 1,3-D	0.00428

The measured MTC values at low relative humidity are similar to the values reported by EVOH producers. The MTC values at high RH are also considered very low and are in accordance to the values reported to films containing EVOH as the barrier layer.

SUMMARY AND CONCLUSIONS

Barrier films are becoming more and more important in today's market where the demand on films performance is higher. There are exiting solutions available in the form of PA and EVOH based multi-layer films, however since they are not compatible with PE, producing these films requires the use of a tie layer and a structure involving a minimum of 5-layers. Most agriculture film producers still use 3 layer extruders, thus they do not have the ability to produce the barrier films using current 5 layer films solutions.

IP7502PE and IP7503PE enable the production of barrier films using a three layer extruder without the need for a tie layer. The barrier properties achieved when using these new products is equivalent to the ones achieved when using EVOH as the barrier polymer.

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