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Physical Properties and Biodegradable Study of Metalized and Non-Metalized Polypropylene (PP) Films: A Comparative Research

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Abstract

Packaging industry plays vital role in the economy of Pakistan. Food packaging industries needs plastic films with well-defined barrier properties with respect to gases, humidity and aroma. The basic goal of this study was to assess the difference between barrier properties of metalized and non-metalized Polypropylene (PP) plastic films with respect of degradation. The PP films of 20 microns were produced by standard cast film extrusion process i.e. metalized PP films coated by aluminum and other without any coating.

The main objective of this work is to compare the environmental impact of metalized and non-metalized CPP films. The samples were manufactured on industrial scale and to meet the food industry requirement metalized films has excellent barrier properties but it has taken about 30 days for small degradation (1 by 1cm metalized CPP). However the barrier properties of non-metalized CPP films shows poor result but it has been easily degraded as compare to metalize films.

barrier properties of non-metalized with metallized PP films. Two types of Polypropylene (PP) films were manufactured by cast co-extrusion process on industrial scale. Barrier properties finished PP films were tested by using ASTMD-3985, D 882 and F1249standard methods. Results shows that non-metallized film has range of Water vapor transmission rate (WVTR) 6-8g/m^2/day and Oxygen Transmission Rate (OTR) range 2300-2500cc/m^2/atm/day. The obtained barrier properties data were considered from practical point of view. However metalized PP film shows about 50% to 80%improvement in the OTR and WVTR. It was estimated that metallization with aluminum has improved the barrier properties.

Biodegradation of polymer is governing by nature of polymer and types of microorganism utilized it. In current studies the extend of degradation of plastic by fungal colonization (Aspergillus and Penicilliums) was measure by the structure investigation using FTIR spectroscopy, results indicate fewer changes in the peak after exposed to the fungi in synthetic media. The spectrum peak in the control on non-metalized film observe at 37736 cm^{-1} ,38913 cm^{-1}, and 6742 cm^{-1}, which are absent after degradation. Similarly, in metalized plastic peaks at 3779.8 cm^{-1} ,3771.1 cm^{-1} ,2357.2 cm^{-1} and 2007.2 cm^{-1} were disappeared after degradation. This indicates fungi use the plastic as the source of carbon and degrade it.

Keywords: Barrier Properties; OTR; WVTR; Co-extrusion and Polypropylene films

Abbrevations: PP: Polypropylene; HDPE: High Density Polyethylene; LDPE: Low Density Polyethylene; PET: Polyethylene Terephthalate; EVOH: Ethylene Vinyl alcohol; GHS: Green House gases; WVTR: Water Vapor Transmission Rate; RH: Relative Humidity; Al: Aluminum; ALOx: Aluminum Oxide; SiOx: Silicon Oxide; Mgox: Magnesium Oxide; OTR: Oxygen Transmission Rate

Introduction

The basic purpose of packaging is to provide protection from environmental condition by maintaining the quality of food items from the manufacturing industry to the normal consumers. The most important physical property in flexible packaging materials are water vapor and oxygen gas transfer rate [1]. The transfer rate depends on the type of the plastic, gas molecules quantity, interacting time between gas and plastic [2]. Therefore, special barrier packaging materials are on the high demand for the packaging of oxygen sensitive food items. Whereas other properties like tensile strength, optical properties, thickness, gloss, printability, transparency, international and local food legislations [3]. Currently to meet such requirements plastic manufacturing industries use additives, multilayers formation by using different polymers only few can be utilized due to crystal structure.

The co-extrusion technique is mostly used for manufacturing of multilayer plastic films based on polypropylene (PP), High Density Polyethylene (HDPE), Low Density Polyethylene (LDPE), Polyethylene Terephthalate (PET) etc. with suitable oxygen barrier material like Ethylene Vinyl alcohol (EVOH) etc. However traditionally low-cost aluminum coating with (Cast polypropylene) CPP, PET etc. has been used as good barrier just by increasing few micrometer thicknesses by metallization process [4]. But aluminum will restrict gas and water if the thickness of plastic sheet above 25.4 μm [5]. Whereas, it may produce small hole or stress if manufactured in less thickness. Incorporation of aluminum into film by lamination process better option but costly as compared to co-extrusion (Figures 1-3).

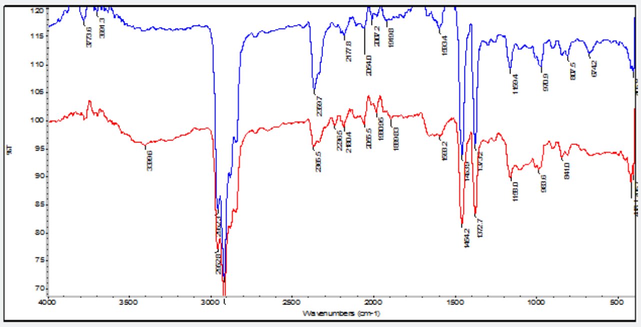

Figure 1 : FTIR result of Non-metalized PP with control (Red) and treated.

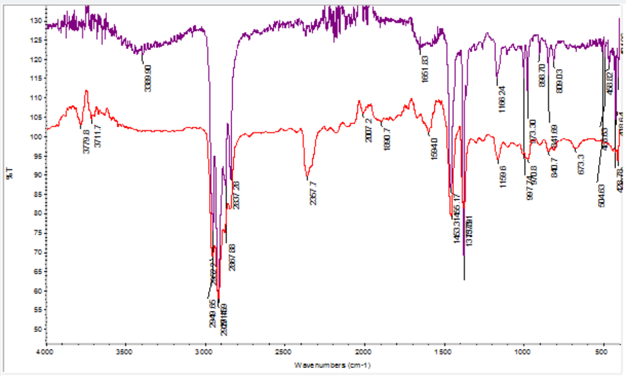

Figure 2 : FTIR result of metalized (red spectrum) and metallized film (purple spectrum) after treated with fungi.

It is also very important to mention here that aluminum coated plastic materials are not recyclable and hence causes excess wastage [6]. The key objective of sustainable food packaging system is to maintain excellent quality of the packaged items, safe handling, minimizing post harvested based loses and wastages. In developing countries like Pakistan about 25 to 50% food losses occurs due to improper food processing and packaging problems [7]. However, it is also proven that chemicals from packaging also migrate to the food items after some time of packing which can be minimize after adding some additives or improving shelf life by coating aluminum. The monitoring of migration is an important aspect of food quality [8].

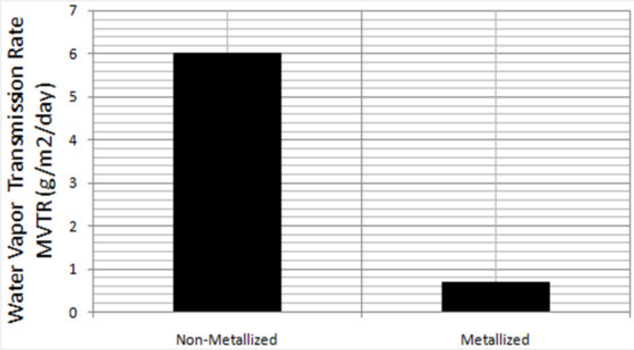

Figure 3 : Graph based on test result of CPP films based on water vapor transmission rate(WTR) result .

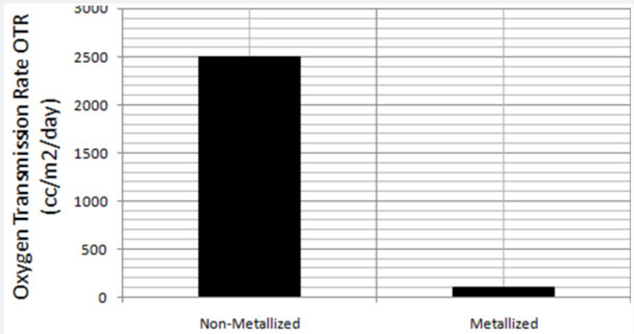

Figure 4 : Graph based on test result of CPP films based on Oxygen Transmission rate result

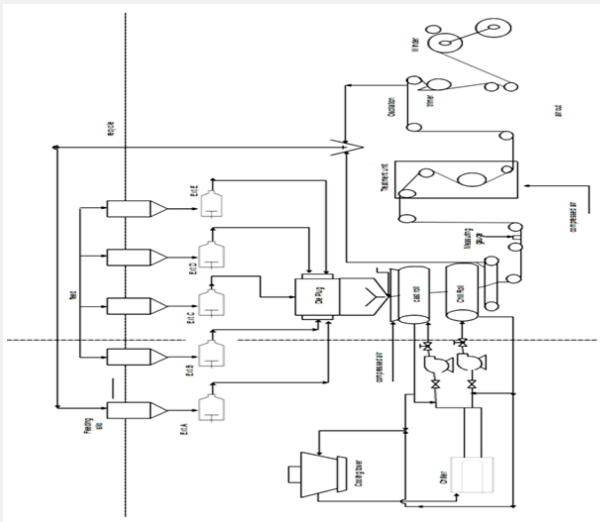

Figure 5 : Process Flow Diagram of CPP films

Plastic film with new intelligent technologies is one of the fastest growing forms of packaging with number of benefits. At that minute, it is seen as an environmental burden, emission of Green House gases (GHS) and wasting resources. The high hydrophobic level and the high molecular weight of Plastic make

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it non-biodegradable and lethal of marine biota and vector of harmful algae and, bacteria species transportation in floating water bodies. By natural cycle degradation of PP is slow it is initiated by both biotic and abiotic factors of environment. On molecular symmetric continuous chain of methylene and absence of functional groups make it poor to microbial attachment thus resistant to biodegradation. The aim of the present research is to investigate and understand the physical properties of materialized and non-materialized film used in packaging industries with its potential effects in environment (Figures 4 & 5).

Material and Method

Preparation of polypropylene (PP)

In this study, the PP granules purchased from Chemicals supplier Ltd. With densities 0.9g/cc and melt flow index 8g/10min were used. Metalized and non-metalized types of PP films were manufactured by standard cast co-extrusion (co extruder prefilmic, Japan) process.

Physical test of film

PP films were tested by using ASTM standard methods for Barrier properties. The physical properties of both types of plastic samples were characterized by tensile strength, break point elongation, swelling behavior and thermo gravimetric analysis. The Water Vapor Transmission Rate (WVTR) of the PP non-metallized and metallized films was measured at 38 °C with 90% Relative Humidity (RH). All the measurements were performed according to ASTM F1249 with Systech7001 model analyzer. Flat film samples were clamped in a diffusion chamber. Nitrogen with generated RH was then introduced into the upper half of the chamber while a moisture free (99.99% zero grade N2) carrier gas flows through the lower half. Molecules of water vapor diffusing through the film into the lower chamber were conveyed to the sensor by the carrier gas. This allows a direct measurement of the water vapor without using complex extrapolations. The water vapor transmission rate of the test film is displayed as (g/m^2/day).

However, thickness was analyzed by gauge mounted on the machine. Similarly, tensile properties of samples measured by ASTM-D 882, Universal Tensile tester (Model No PH-VE-ID). Haze test of samples measured by Haze meter (ASTM-D 1003, Model No. D65).

The oxygen transmission rate (OTR) of the PP non-metallized and metallized films was measured at 23°C with 0% Relative Humidity (RH). All the measurements were performed according ASTM D-3985with (Stitch 8001model. Flat film samples were clamped in a diffusion chamber. Pure oxygen 99.9% is then introduced into the upper half of the chamber with an oxygen free (99.999 % zero grade N_2) carrier gas flows through the lower half. Molecules of oxygen diffusing through the film into the lower chamber were conveyed to the sensor by the carrier gas. This allows a direct measurement of the oxygen without using complex extrapolations. The oxygen transmission rate of the test film was displayed as (cc/m^2/atm/day).

Degradation test

The samples of plastic were collected by plastic manufacturing company. The samples were washed aseptically with alcohol and poured into sterile Sabered Dextrose Agar and consortium of *Aspergillus* and *Penicilliums* respectively. The plates were incubated at 28 °C for one week. After incubation, the plastic with fungus growth transfer into the minimal media ($MgSo_4$. $7H_2O$ (1gm/L), $FeSO_4$ (0.002g/L), NaCl (0.2g/l), $K_2HPO_4$1O.5 g/l), KH_2PO_4 (0.08 gm/l), NH_4NO_3 (2.0 g/l) and Agar (0.7%) containing no source of carbon accept plastic [9-13]. After the interval of two months the weight of plastic measured by gravimetric method by using ASTM D6003-96 [14]. Change in the chemical structure of plastic film were recorded by using Fourier Transform infrared (FT-IR) (Thermo Scientific Nicolet TM iS10), from a wavenumber of 400–4000 cm^{-1}.

Results and Discussion

Table 1: Comparative study of the Tensile and Barrier Properties of the Non metalized and Metalized PP Films.

	Non-Metallized				Metallized			
Samples	Thickness (micron)	Oxygen transmission rate (cc/m^2/day)	Water vapor transmis-sion rate(g/m^2/day)	Tensile strength (N/mm^2)	Thickness (micron)	Oxygen transmission rate (cc/m^2/day)	Water vapor transmission rate(g/m^2/day)	Tensile strength N/mm^2)
1	20	2500	6	$\frac{MD\ 53}{TD\ 25}$	60	90	0.7	$\frac{MD\ 50}{TD\ 25}$
2	20	2500	6	$\frac{MD\ 52}{TD\ 26}$	60	98	0.72	$\frac{MD\ 51}{TD\ 26}$
3	20	2490	6.1	$\frac{MD\ 54}{TD\ 22}$	60	95	0.68	$\frac{MD\ 50}{TD\ 24}$
4	20	2450	6	$\frac{MD\ 52}{TD\ 23}$	60	91	0.7	$\frac{MD\ 49}{TD\ 24}$

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5	20	2480	6.2	$\frac{MD}{TD}\frac{54}{24}$	60	98	0.71	$\frac{MD}{TD}\frac{51}{26}$
6	20	2500	6	$\frac{MD}{TD}\frac{55}{25}$	60	100	0.71	$\frac{MD}{TD}\frac{50}{25}$

Since barrier properties of packaging material are responsible for product quality deterioration, the detailed understanding of the characteristics of coated films is great practical and commercial importance. Generally polypropylene film has good barrier to moisture vapors and low barrier to oxygen transmission [15-19]. But by manufacturing the film with above specified pp grades and additives with metalized coating shows better results in terms of OTR barrier as well as other properties. Results are based on the six samples of each metalized and non-metalized cast polypropylene film. From data given in Table 1 substantial differences between the barrier properties of the investigated coated and uncoated cast PP films were estimated. To make the polymer more stable in terms of barrier properties a thin layer of metal i.e Aluminum (Al), Aluminum Oxide (AlOx), Silicon Oxide (SiOx), or Magnesium Oxide (MgOx)is used [20]. Table 1 includes the properties of non-metalized and metalized cast polypropylene film with aluminum. Results show that cast polypropylene film without metallization has the value of ORT and WVTR 2500 cc/m^2/day and 6 g/m^2/day respectively. The value of tensile strength is 53.5 N/mm^2. These all values are good instead of OTR value which is very high. But when we metalized this film with aluminum coating the results are better. Cast polypropylene film with metallization has the value of ORT and WVTR 100 cc/m^2/day and 7 g/m^2/day respectively. The value of tensile strength is 50 N/mm^2.

Synthetic polymeric materials have been widely used because of low density, cheap in cost and good possibility. To make the polymer more stable in environmental condition a thin layer of metal i.e. Al is used [20]. However, the biodegradability is considerably less, and the materials easily accumulate in environment. Polypropylene (PP) is one of such synthetic polymeric constituents and is known as a non-biodegradable one. Generally large molecule such as PP cannot easily enter cells of microorganisms. Therefore, PP is hard to be metabolized in microorganisms [9,10]. The microorganism once attached to the surface on plastic used it as the sole source of carbon, leading to formation of low molecular fragment of polymer i.e. oligomer or monomers [12].

The biodegradation of plastics by bacteria and fungi proceeds differently under different conditions according to their properties. The different factors that rules biodegradation is type of organism, polymer characteristics [11]. Our result is somehow is the same in case of metalized and non-metalized pp film, FTIR results show very few changes in the peak after exposed to the fungi in mineral media. The spectrum peak in the control of non-metalized film observe at 37736 cm^{-1}, 38913 cm^{-1} and 6742 cm^{-1}, which are absent after degradation with fungi consortium namely *Aspergillus spp* and *Pencillium spp.* Similarly in metalized plastic peaks at 3779.8 cm^{-1} ,3771.1 cm^{-1} ,2357.2 cm^{-1} and 2007.2 cm^{-1} were disappear after degradation with fungal species. Peak shifted is also recorded in the region of 1500-1000 cm^{-1} (Figure 2). The results indicated the far acceptable degradation of metalized film as compare to un-metalized, but somehow it can be due to the removal of metallization layer on pp film. The shift of peaks and new peak formation in the spectrum is the sign of degradation which is due to the enzymes produce by microorganism once it attached to the surface and used the subtract as a source of their food. *Aspergillus spy* were reported as the degrading agent of Polyethylene film, the rate of degradation reported as 26% in 6 months [12]. Khan et al. [13] proved that the degradation of Polyurethane film (PU) up to 90%by *Aspergillus tubingensis.* He observed the changes in spectrum at 3321 cm^{-1} as hydrogen bond (NH),which is absent in control. He reported these changes as a sign of degradation and formation of new products in degradation. Similar week band generate at the shoulder of band 2954.8 cm^{-1} in the sample spectrum which is also absent in control.

Conclusion

From the above-mentioned results and discussion, we can assess that the film with aluminum metallization has excellent barrier properties than non-metalized. Therefore, it is concluded that use cast polypropylene film with aluminum coating for the better shelf life of food products. It is also concluded that specified grades of polypropylene and additives have also some impact on the properties of the film. Therefore, it is better to use mentioned polypropylene grades and additives. However, from the environmental point of view they are persistent in nature and not easily biodegradable. Therefore, in this era of innovation technology design material should be manufacture as must be resistant during their use and must biodegrade at the end of their useful life.

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