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A Comparitive Study of Physical Behaviour and Biodegradation of Metalized and Non-Metalized Polypropylene Films

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Abstract

The goal of this study was to analyze the physical properties of metalized and non metalized cast PolyPropylene (CPP) plastic films with respect of its degradation and environmental pollution. The PP films of 20 microns were produced by standard cast film extrusion process i.e. metalized PP films coated by alumunium and other without any coating.The samples were manufactured at industry which produces food grade plastics made by cast co-extrusion process. Physical properties like Tensile strength, Oxygen transmison rate and water vapour transmission rate measured as per ASTM standard. Results shows that non-metallized film has range of WVTR 6-8g/m^2/day and OTR range 2300-2500 cc/m^2/atm/day. However metalized PP film shows about 50% to 80% improvement in the OTR and WVTR. It has been proven that metallization with aluminum has improved the physical properties but effect the rate of degradation. In current study the extend of degradation of plastic by fungal colonization(*Aspergillus* and *Pencillium spp*) was measure by the structure investigation using FTIR spectroscopy, results indicates 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 variation in peaks indicates fungi use the plastic as the source of carbon.These samples were tested for their degradation properties with respect to the physical properties. Both samples took for 30 days of degradation. It is found that non-metalized films degradaded effectively in the mean period of time.

Article History

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Keywords

Barrier Properties;
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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). However traditionally low cost aluminum coating with (Cast polypropylene) CPP, PET has been used as good barrier just by increasing few micrometer thickness 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 produces 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.

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, the main hazards of these types of migrations on food safety has several question if quantity of these migrated chemicals in food items greater than the specified standard, which can be minimized after adding some additives or metallic coating. The monitoring of migration is an important aspect of food quality.[8]

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 Greenhouse gases (GHS) and wasting resources. The high hydrophobic level and the high molecular weight of Plastic makes it non-biodegradable and lethal of marine biota and vector of harmful algae and bacteria species transportation in floating water bodies.[16,17] 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.[18] The aim of the present research is to investigate and understand the physical properties of metalized and non- metalized PP film used in packaging industries with its potential effects on environment.

Material and Method

Preparation of Polypropylene(PP)Samples

In this study, the PP mgranules purchased from Chemicals suppliers Ltd.with densities 0.9 g/cc and melt flow index 8 g/10min were used. Six samples of metalized and non-metalized types of PP films were manufactured by Cast extrusion process as shown in process flow diagram Fig 5. According to which PP granules additives enters through hoppers into extruder (Ext-01) of Filmax701 model, Mitsubishi , then melted (temperature 210 to 285 °C) PP granules introduces into the die Plug (D-0001). The finished plastic cools with chill roller machines (15 to 22 °C). Finally Corona treatments were used to increase the surface tension. After that PP Film moves to winding section where the extruded film converted into film rolls. Similarly metalized CPP films were produced by using Vacuum metalizer (Model No: K5000)by adding a thin film of aluminum to PP films. The thickness of non metalized (20 microns) and metalized PP films (60 microns) were measured by automatic gauge meter during the production.

Physical test of Manufactured Polypropylene Plastic Film

To analyze the biodgradation properties of metalized and non metalized PP films some physical test of sample were performed as per American standard testing methods(ASTM)

First of all tensile and elongation test of both types of PP films were conducted by universal tensile tester (AG-X Shimasdzu, Autograph, Japan) according to ASTM D- 882 method, the PP films were conditioned for 48 hours at 25 °C about 50% relative humidity (RH).The samples were cut in specific shape and strips (100 x 10 mm) then tensile strength measured in both directions i.e. in the machine(md) and transverse direction(td), since they can vary considerably from one direction to another, the Measurement was based on six replicate of each sample.

Similarly barrier properties in terms of water vapor transmission rate (WVTR) and oxygen transmission rate(OTR) of the sample were tested in accordance of American standard testing method. The PP samples tested for WVTR at 80 to 90% relative humidity (RH) and 20-25 °C by means of special type of permeability cups as per ISO 2528 and as mentioned by Lopez-de-Dicastillo.[23] These cups were filled specifically with silica gel then sealed with the sample pp films. However the cups were stored in desiccators to maintain the required humidity. The cups were weighed and the increase in weight versus time was used to calculate WVTR. These values were then divided by water vapour gradient and multiplied by sample thickness to obtain the exact value.

Similarly the oxygen transmission rate (OTR) of the non-metallized and metalized PP films was measured at 23 °C with 50 to 55% RH. First of all PP film samples were clamped in a diffusion chamber of the OTR analyzer. Pure oxygen (99.9%) was introduced into the upper half of the chamber where as nitrogen (99.999 % zero grade N_2) carrier gas flows through the lower half. The oxygen transmission rate of both types of PP films were displayed as (cc/m²/atm/day).

Degradation test

The samples of metalized and non metalized PP films were further analyzed for their biodegrdation properties.The samples were washed aseptically with alcohol and poured into sterile Sabouraud Dextrose Agar and consortium of *Aspergillusspp* and *Pencullium spp* 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.[19]

After the interval of 02 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

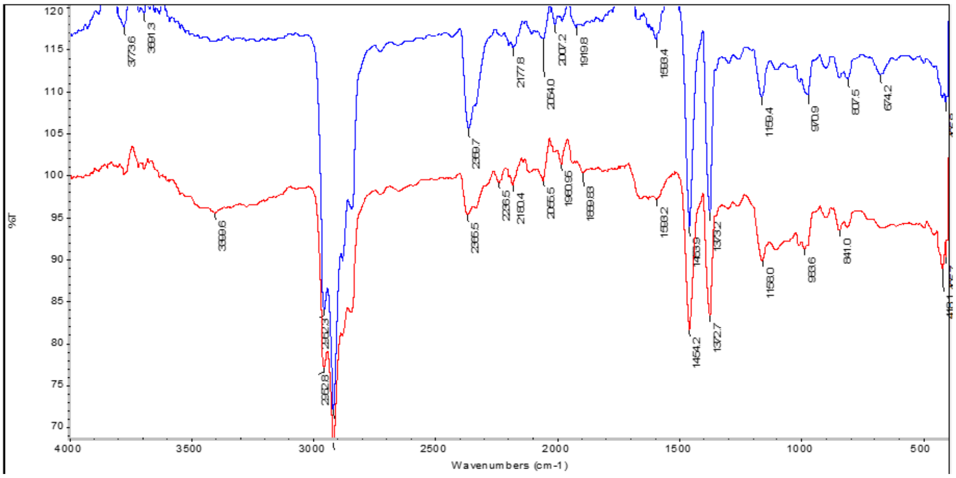

Fig. 1: FTIR result of Non-metalizedPP with control (Red) and treated with fungi (Blue) spectrum.

infrared (FT-IR) (Thermo Scientific Nicolet TM iS10), from a wavenumber of 400–4000 cm^{-}

Scanning Electron Microscopy (SEM)

The PP film after incubation period with fungal stains were removed and dried in Petri plate for 24 hours. The sample were coated with 300°A gold and analysis under high resolution electron microscope (Jsm-6380 A,Japan).

Strum test

Strum test (OECD 301B: ASTM D5209) was used for the evaluation of biodegradability of polymer material. The sterile piece of film was added to 300 mL basal salt medium as the only carbon source. Spore suspension of *Aspergillus niger* and *Penicillium spp* were used for the degradation of polyethylene. Control bottles were prepared without any plastic. degradation test was performed at room temperature for the duration of four weeks. Before set the system Ba $(OH)_2$ filtered and stored in the airtight bottles to prevent atmospheric contamination of CO_2 absorption in the system. Evolution of carbon dioxide, which was trapped in absorption bottle containing 0.01M, $Ba(OH)_2$ was monitored every week, The amount of CO_2 evolved during the test duration was measured by gravimetric method. As $BaCO_3$ is insoluble in water and formed precipitates as it is shown in Eq. 1.

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$$

Results and Discussion

Material Characteristics

The 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. But by manufacturing the CPP films with standard PP granules after 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), aluminium 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 coating. Results show that cast polypropylene film without metallization has high WVTR which is not acceptable for some food packaging industry. But after metalizeation with aluminum PP films results proved to be better.

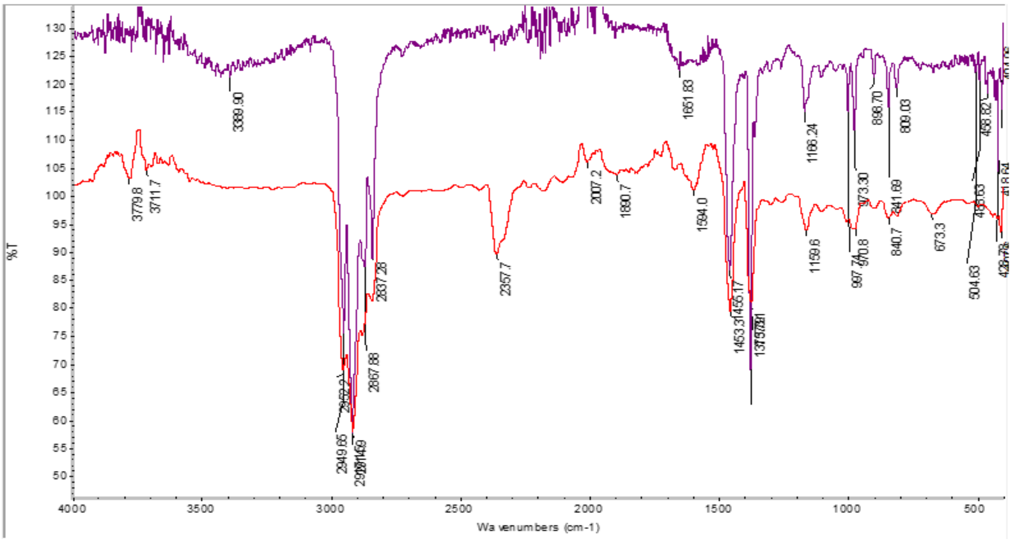

Fig. 2: FTIR analysis result of metalized (red spectrum control) and metallized film (purple spectrum) after treated with fungi.

Biodegradebilty Results

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 into 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 are 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 controlof 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} (Fig-1 and Fig 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 its attached to the surface and used the subtract as a source of their food. *Aspergillus spp* 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)upto 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. Similary weak band generate at the shoulder of band 2954.8 cm^{-1} in the sample spectrum which is also absent in control.

Table1: 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/m²/ day)	Water vapor transmission rate(g/m² /day)	Tensile strength (N/mm²)		Thickness (micron)	Oxygen transmission rate (cc/m² /day)	Water vapor transmission rate(g/m² /day)	Tensile strength) (N/mm²)	
1	20	2500	6	MD	53	60	90	0.7	MD	50
				TD	25				TD	25
2	20	2500	6	MD	52	60	98	0.72	MD	51
				TD	26				TD	26
3	20	2490	6.1	MD	54	60	95	0.68	MD	50
				TD	22				TD	24
4	20	2450	6	MD	52	60	91	0.70	MD	49
				TD	23				TD	24
5	20	2480	6.2	MD	55	60	98	0.71	MD	51
				TD	24				TD	26
6	20	2500	6	MD	55	60	100	0.71	MD	50
				TD	25				TD	25

Scanning electron microscopy (SEM) images of film samples after degradation test revealed the significate surface degradation and structural changes of Metalized and non metalized PP film at resolution of 500x to 15000x. In the present work Incubated Film colonized by fungi shows important morphological changes i.e formation of cavities and erosions (fig 4 & 5).The observed rough and erosion Surface by fungal is the primary reason of mass loss. SEM photographs of control polyethylene did not show any disruption on surface. These results show that *Aspergillus spp* and *Pencillium spp* could utilized metalized and non metalized film and promote their growth mechanism. The Cracks and holes appeared in film after degradation is due to the dispersion of fungal mycelium and penetration of hyphae (Khan *et al.,* 2017). Nature of microorganism and nature of pretreatment is the important factor of degradation. According to the Griffin 1980, growth of fungi cause cracking, bursting and swelling of plastic as fungi penetrate on the polymer.

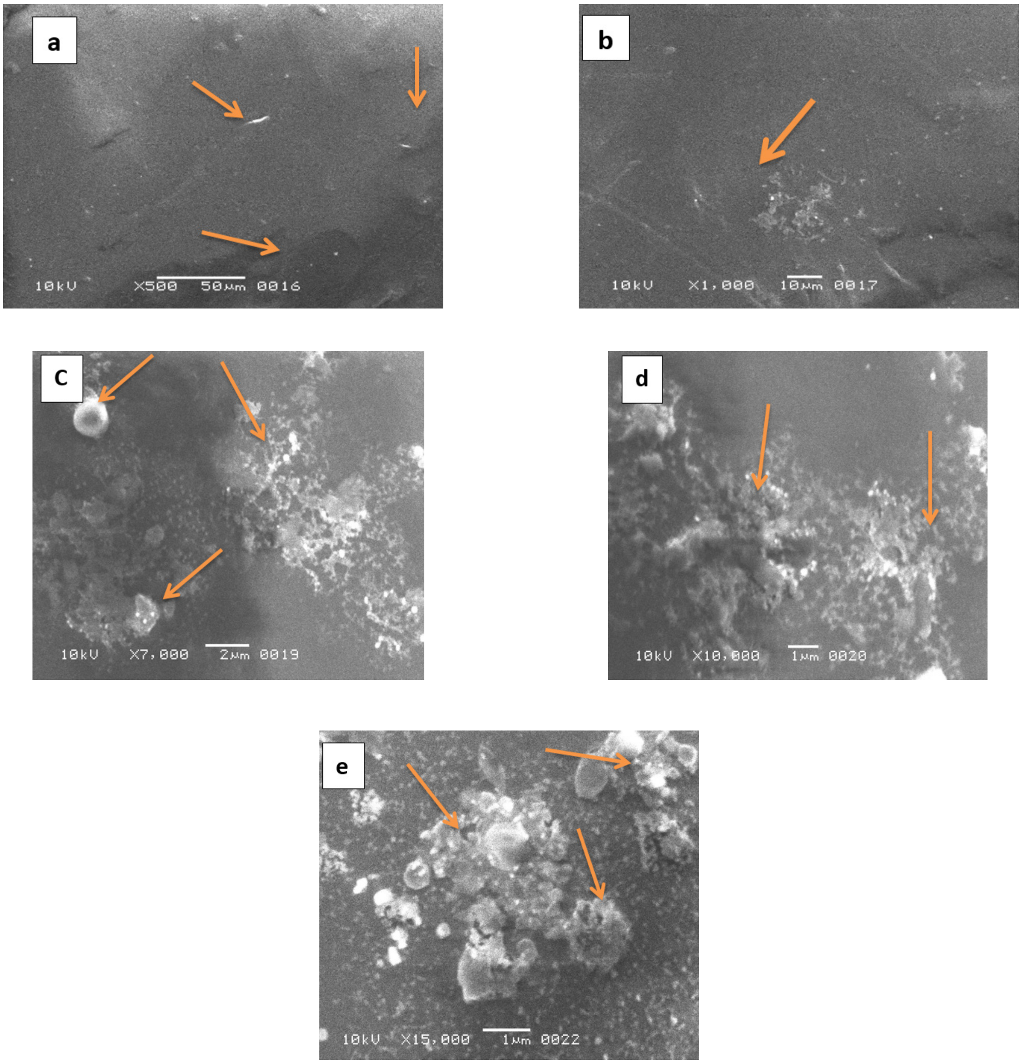

Fig 3: SEM photomicrographs of metalized cpp film exposed by *Aspergillus spp* and *Pencilliumsppat* (a)500x (b)1000X (c)7000x (d)10,000x (e)15000x respectively after 30 days of incubation

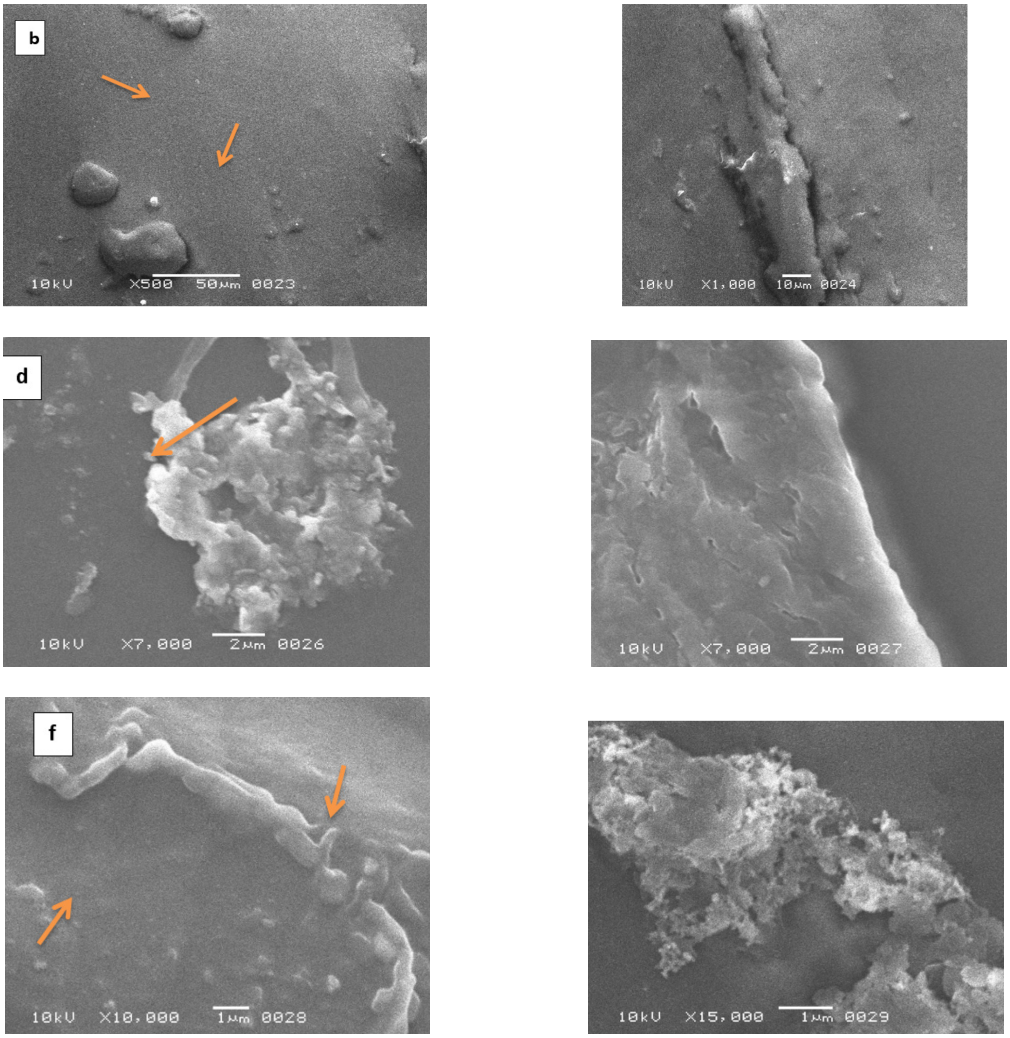

Fig. 4: SEM photomicrographs of Non-metalized cpp film exposed by *Aspergillus spp* and *Pencilliumsppat* (a)500x (b)1000X (c)7000x (d)10,000x (e)15000x respectively after 30 days of incubation

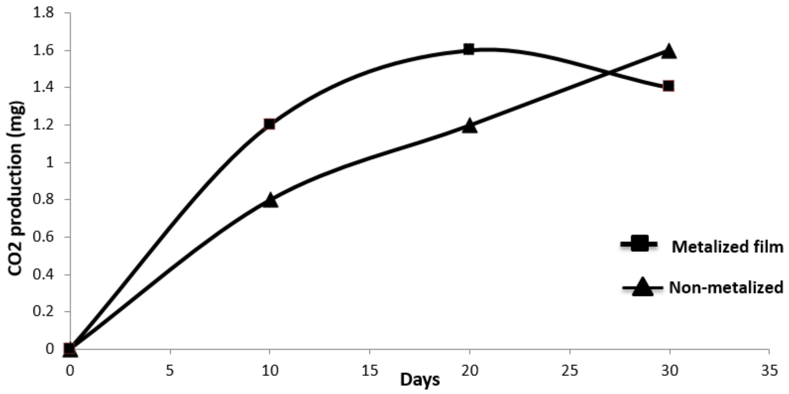

Fig. 5: Mean strum test result of metalized and non metalized film

Conclusion

- PP plastic are mostly used for packaging of materialpossibilyseprating the product from external environment. From the above mentioned results and discussion we can assessed that :
- The film with aluminum metallization has excellent barrier properties than non-metalized.
- 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.
- 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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