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Analysis of Barrier Properties of Low Density Polyethylene films (LDPE) after addition of natural Polyphenolic extract

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Abstract: Packaging industry plays a vital role in Pakistan for safe transportation and handling of processed and unprocessed food items. Various types of packaging materials are available in the market but Plastic films are the most popular of material due to low cost of manufacturing and good barrier properties. The shelf life of various food items are dependent on the barrier properties of plastic film i-e Oxygen transmission rate (OTR) and WVTR(water vapor transmission rate).The usage of natural antioxidants(active packaging) in the packaging industry is one of the emerging technology . The usage of active packaging has resulted in a better shelf life and also environment friendly. The main objective of this work is to compare the barrier properties of Low Density Polyethylene (LDPE) films (with natural Polyphenols) with control Films .The LDPE granules containing different concentration of green tea(1% ,2% and 5%) extracts were extruded from the extrusion blown film machine. The results shows that LDPE pellets which contained high concentration of green tea extract(5%) had better barrier properties as compared to low concentration and control films.

Key Words : Low Density Polyethylene, Cast Polypropylene, Extrusion, OTR and WVTR

INTRODUCTION

The use of appropriate packaging material for food items are always a basic requirement of food industry. The use of PVC (poly vinyl chloride) film, EVOH (ethylene vinyl alcohol) incorporated with propylene or polystyrene, LDPE (low density polyethylene), HDPE (high density polyethylene), poly ethylene coated paper board cartons, polyethylene coated paper pouches, aluminum foil paper, polyolefins coextruded films, polypropylene pouches, metalized polypropylene or polyester films have been in practice by the food manufacturers and distributors since long. Polyethylene terephthalate (PET) is a desirable packaging material due better properties[1,2] .However the LDPE films are commonly use as food packaging materials due to high sealing, low cost and lower reactivity with other materials. Whereas LDPE has less barrier for gases specially oxygen with less shelf life for some specific food items[3].

Previously scientist has worked on improvement of barrier properties and developed different technologies eg by using lamination technology, metallization, co- extrusion, adding synthetic and natural polyphenolic compounds etc The presence of oxygen in a packaged food is often a key factor that limits the shelf life of a product. Oxidation can cause changes in flavour, colour, and odour, as well as destroy nutrients and facilitate the growth of aerobic bacteria, moulds, and insects[4]. Red meat and poultry is packed in oxygen permeable flexible packaging film which permits O_2 into the package while retarding the passage of water vapour, therefore LDPE with good water vapour and high gas transmission is preferred for packing meat and poultry. On the other hand for cured meat O_2 barrier films are required for packaging. The barrier properties and capacity to protect foods depends largely on the permeability of the packaging material to gases and vapors[5].

To protect food lipid oxidation, antioxidants addition to food formulation and dipping food in antioxidants solution have limitations due to their specific activity in complex food system and lack of ability to target the food surface where most oxidation reactions occur [6]. Solutions to these problems have been found in active food packaging system which is based on the addition of antioxidants, antimicrobials and other functional components into the packaging polymer matrix with the target of extending the shelf life of food products. Active packaging material allows a controlled and steady release of the additives into the food over a long period of time with a surety of limiting the undesirable degradation of flavour, lipids and nutrients and side effects on human health.

Numerous attempts have been made to develop and improve active packaging films and with the discovery of more and more bioactive phytochemicals, this paper is based on the extra ordinary formulation of the LDPE active packaging films after adding natural polyphenolic extract from leaves, fruits and seeds in different concentration by using extrusion process and then analyzed their barrier properties with respect to other mechanical and optical properties.

MATERIALS AND METHODS

Low-density polyethylene (density of LDPE 0.929 g/cm3) pellets were purchased from Lotrene Ltd (Commercial name) .The dried extracts / fractions 1, 2 and 5 % w/w were mixed with LDPE pellets in mixer to get a uniform distribution of the extracts onto the surface of pellets before processing .

Extraction and fractionation of polyphenols from crude methanolic extract of 100 g of *T. catappa* fruit (TCc) into anthocyanins (TCa) and non-anthocyanins (TCna) were performed as described by Siddiqi *et al*. [7]. Similarly from ajwain oilseeds and green tea leaves (TAc, CSc for ajwain and green tea crude extract respectively) then both were fractionated into acidic (TAa, CSa for ajwain and green tea acidic fraction respectively) and neutral polyphenols (TAn, CSn for ajwain and green tea neutral fraction respectively) by using the procedure of Oszmianski and Lee[8] .

The LDPE granules with different concentrations , TCc-LDPE, TCa-LDPE, TCna-LDPE, CSc-LDPE, CSa-LDPE, CSn-LDPE, TAc-LDPE, TAa-LDPE and TAn-LDPE processed in a single screw (Chugai Boyeki Co Ltd, Japan) having diameter 44mm.with L/D of 28 mm. The Screw Speed for these samples was maintained at 65 rpm throughout the process to maintain the uniform thickness of the film. The extruder cylinder temperature profile: 165,175 and 185 ^{o}C.

The LDPE melted then completely homogenized and moved toward Die (small opening used with air pressure to form large bubble). Bubble was collapsed at the roller; film was stretched and collected at the takeoff device. The film was wound and removed from winding roll after completion of film extrusion of each sample. The samples were collected in triplicate for further analysis.

Film thickness was measured by using thickness gauge (model TH-104, Sangyo Co. Ltd. Japan). Mechanical properties were determined by using Universal Testing Machine (AG-X Shimasdzu, Autograph, Japan) according to ASTM D 882.

Optical properties of modified LDPE films tests were conducted by Spherical Haze-Meter (D.S. Model 57, England). The values presented were the average of 5 measurements. The water vapor transmission rate (WVP) were carried out at 90% relative humidity (RH) and 25^{o}C in accordance with ISO 2528 and as described by Lopez-de-Dicastillo *et al*.[9,10].

The oxygen transmission rate of control and modified LDPE films has been measured by Oxygen Permeation Analyzer (Model BR-1/BT-1, Toyoseiki Seisaku. Ltd., Japan), calibrated at 23.0 °C and 0 % relative humidity with a standard Mylar film of known OTR of 65 cm^3/m^2 /day. N2 flow through the bottom chamber was 19 cm^3/min and O2 flow through the top chamber was 20 cm^3/min. A masking plate with a diameter of 2.5 cm (4.91 cm^2 surface area) was used. Control and modified LDPE films (n = 3) were measured for OTR (cm^3/m^2/day) at 23.0 °C, 90% RH, and atmospheric pressure.

RESULT AND DISCUSSION

The crude extracts of C. *sinensis* and *T. ammi* were fractionated into neutral and acidic fractions while *T. catappa* was fractionated into anthocyanin and non-anthocyanin fraction. All the fractions were then analyzed for total phenolics. The total phenolic contents were much higher in neutral fraction compared to acidic in *C. sinensis* and *T. ammi* leaves ($p < 0.01$) while much higher amount was estimated in non anthocyanin fraction compared to anthocyanin in *T. catappa* fruit ($p < 0.01$) (**Table 1).** This is may be due to a non-linear nature of LDPE or it has high degree of short and long chain branching. This branching prevents the regular lining up of the polymer molecules and as a result the chains do not pack well into the crystal structure. This allows the suitable permeation of water vapors across the film. Incorporation of polyphenolic extract at 5% level into the extruded films caused higher and even distribution of the polyphenols into the interstitial spaces within small, defective crystal structures and hence resulted in significant decrease in WVP of the films.

Lopez-de-Dicastillo *et al*.[11] used catechin and quercetin to with ethylene-vinyl alcohol (EVOH) films and reported an increase of up to 30% in WVP at 100% RH with respect to control but at 75% RH permeation declined by a factor of 4 with respect to blank. Further in his findings, the effect of % RH was more pronounced as compared to increasing the concentration of catechin and quercetin from 1 to 5%. Our studies were performed on LDPE at 90% RH. From our results and previous studies, it may be concluded that WVP of polymer based packaging film depends upon several integrated factors and predominantly on the type of polymer, nature of polyphenolic additive, and the atmospheric conditions like relative humidity.

Table 1: Total phenolics from *T.catappa* fruit(TCc), *C. sinensis* (green) leaves(CSc) and *T. ammi* oilseeds(TAc) with fractions anthrocynic/nonantrocyne (TCa.TCna) and acidic and neutral.

Extract/Fractions	Total Phenolics (mg GAE/100 g)
TCc	1005±34.20
TCa	189±19.0
TCna	879±22.0
CSc	15300±23.9
CSa	1624±56.0
CSn	13430±13.8
TAc	6900± 12.2
TAa	2700±25.6

TAn	4070±74.5

Table 2: Tensile strength of the LDPE films produced by extrusion with 1,2 and 5% Polyphenolic extract and fractions derived from *T.catappa* fruit, *C.sinensis* (green) leaves and *T.ammi* oilseeds.

Type	Tensile Strength (Mpa)			E-Modulus (Mpa)			% Elongation at Break		
	1%	2%	5%	1%	2%	5%	1%	2%	5%
TCc-LDPE	20.4±0.20	19.3±0.26	17.2±0.20	309±3.0	317±3.5	330±1.5	610±1.20	599±1.23	582±2.34
TCa-LDPE	20.9±0.18	19.8±0.12	17.8±0.21	311±3.3	320±2.5	333±3.0	609±0.24	598±1.34	585±3.20
TCna-LDPE	21.4±0.16	19.4±0.25	17.7±0.15	310±3.0	322±3.0	331±4.0	609±0.25	599±2.32	585±3.20
CSc-LDPE	20.8±0.34	19.7±0.27	17.6±0.11	309±2.0	323±1.23	332±3.0	610±1.33	600±0.22	589±2.98
CSa-LDPE	20.9±0.16	19.3±0.16	17.7±0.12	309±1.8	327±2.5	333±2.0	609±1.09	597±0.24	583±1.79
CSn-LDPE	21.2±0.19	19.5±0.34	17.0±0.21	310±2.0	330±2.4	335±2.3	607±1.53	596±1.22	588±2.00
TAc-LDPE	21.4±0.20	19.5±0.22	17.7±0.20	311±2.5	322±2.6	334±1.7	609±3.01	596±1.68	587±2.20
TAa-LDPE	20.3±0.20	19.6±0.25	17.6±0.14	308±3.5	319±3.0	330±2.4	609±2.33	598±1.79	586±2.07
TAn-LDPE	20.9±0.15	19.3±0.30	17.0±0.20	307±2.3	321±1.9	335±2.0	608±1.22	599±3.01	585±1.68
LDPE(Control)	20.5±0.56			310±3.12			611±3.45		

It follows that if any of the selected food packaging material is required but with limited water permeation, an antioxidant coating that could be stabilized on the surface of polymer, limit the water permeability and provide additional benefit of food protection against oxidative decomposition could be one of the options.

Water vapors barrier ability of packaging materials is a very important factor to ensure the shelf life of food products. A certain level of moisture is needed for a particular product. Food products sensitive to hydrolytic rancidity need careful protection to avoid off flavors and smells. Water permeability also becomes critical when there are issues of microbiological degradations and enzymatic changes.

OTR refers to the steady state rate at which oxygen gas permeates through a packaging film under specified conditions of temperature and relative humidity. Like WVP, OTR was also decreased in all four types of LDPE films as a result of incorporation of Polyphenolic extracts/fractions as compared to controls. The reason is same as for WVP i.e. the polyphenolic antioxidants got the chance to enter the

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polymer network while the polymer was being heated (in case of heat pressed and extruded-blown films) which resulted in settling of the additive molecules into irregular or defective crystalline structure. This hindered the more easy passage of oxygen as compared to control.

Table 3: % Haze and % Transmittance of the LDPE films produced by extrusion with 1, 2 and 5% of polyphenolic extract and fractions derived from *T.catappa* fruit, *C.sinensis* (green) leaves and *T.ammi* oilseeds.

Formulations	**%Haze**			**% Transmittance**		
	1%[a]	2%[b]	5%[c]	1%[a]	2%[b]	5%[c]
TCc-LDPE	11.4±0.15	11.8±0.34	13.8±0.45	88.7±0.33	88.0±0.3	86.2±0.56
TCa-LDPE	11.0±0.20	11.7±0.11	13.5±0.67	89.0±0.09	88.4±0.34	86.3±0.23
TCna-LDPE	11.2±0.18	11.3±0.09	12.8±0.23	88.7±0.50	88.5±0.23	87.0±0.18
CSc-LDPE	11.0±0.12	11.6±0.09	13.8±0.9	88.8±0.30	88.2±0.22	86.1±0.09
CSa-LDPE	11.4±0.11	11.9±0.08	12.8±0.08	88.3±0.20	88.0±0.32	87.0±0.34
CSn-LDPE	11.2±0.11	11.8±0.03	12.7±0.05	88.6±0.40	88.0±0.10	87.0±0.06
TAc-LDPE	11.4±0.12	11.6±0.2	13.5±0.05	87.5±0.20	88.3±0.08	86.2±0.05
TAa-LDPE	11.3±0.20	11.8±0.18	12.9±0.03	88.6±0.30	88.0±0.05	87.2±0.56
TAn-LDPE	11.2±0.22	11.5±0.09	12.6±0.04	88.7±0.40	88.3±0.05	87.2±0.45
LDPE(Control)	11±0.2			88.7±1.20		

Table 4: Oxygen Transmission Rate (OTR, cc/m^2/24hours) of LDPE films (RH 90%) produced by extrusion with 1, 2 and 5% of polyphenolic extract and fractions derived from *T. catappa* fruit, *C. sinensis* (green) leaves and *T. ammi* oilseeds.

Formulations	**Oxygen Transmission Rate (OTR, cc/m^2/24hours)**		
	1%[a]	2%[b]	5%[c]
TCc-LDPE	7232±25	7110±33	6816±25
TCa-LDPE	7233±38	7130±55	6900±44
TCna-LDPE	7226±26	7129±35	6928±35
CSc-LDPE	7230±28	7144±25	6933±42
CSa-LDPE	7238±24	7130±65	6921±40
CSn-LDPE	7236±30	7139±50	6927±31
TAc-LDPE	7214±29	7149±51	6910±29

TAa-LDPE	7212±33	7137±45	6898±41
TAn-LDPE	7240±34	7149±34	6905±37
LDPE(Control)	7200±66		

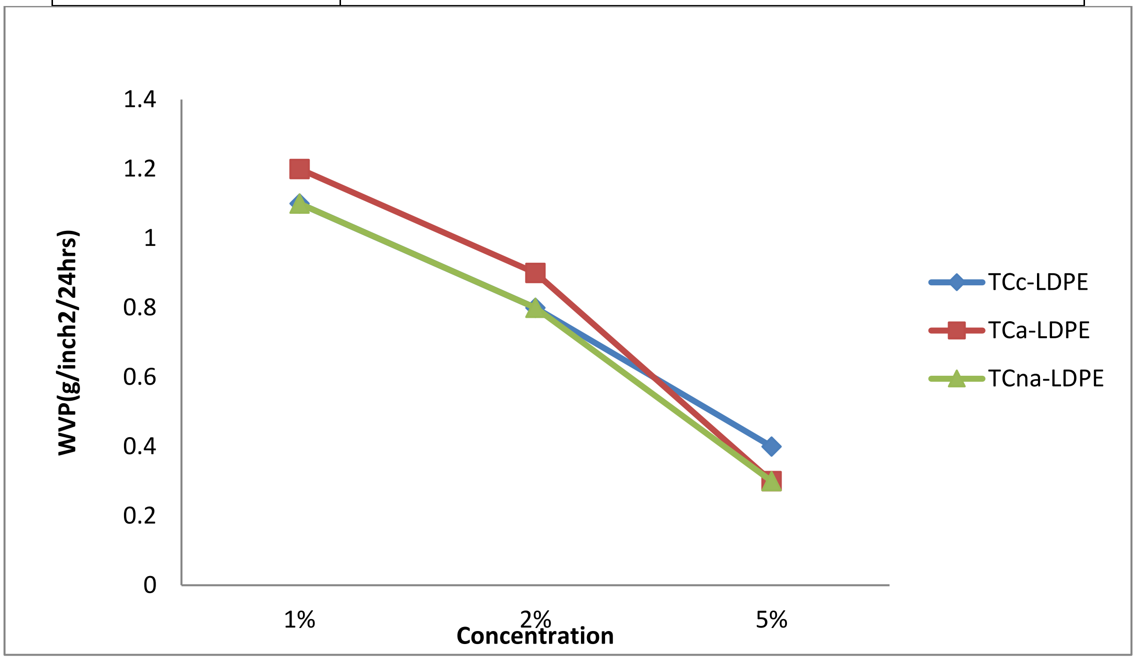

Figure 1: Effect of adding polyphenolic extract and fractions of *T. catappa* fruit on WVP of extruded LDPE films.

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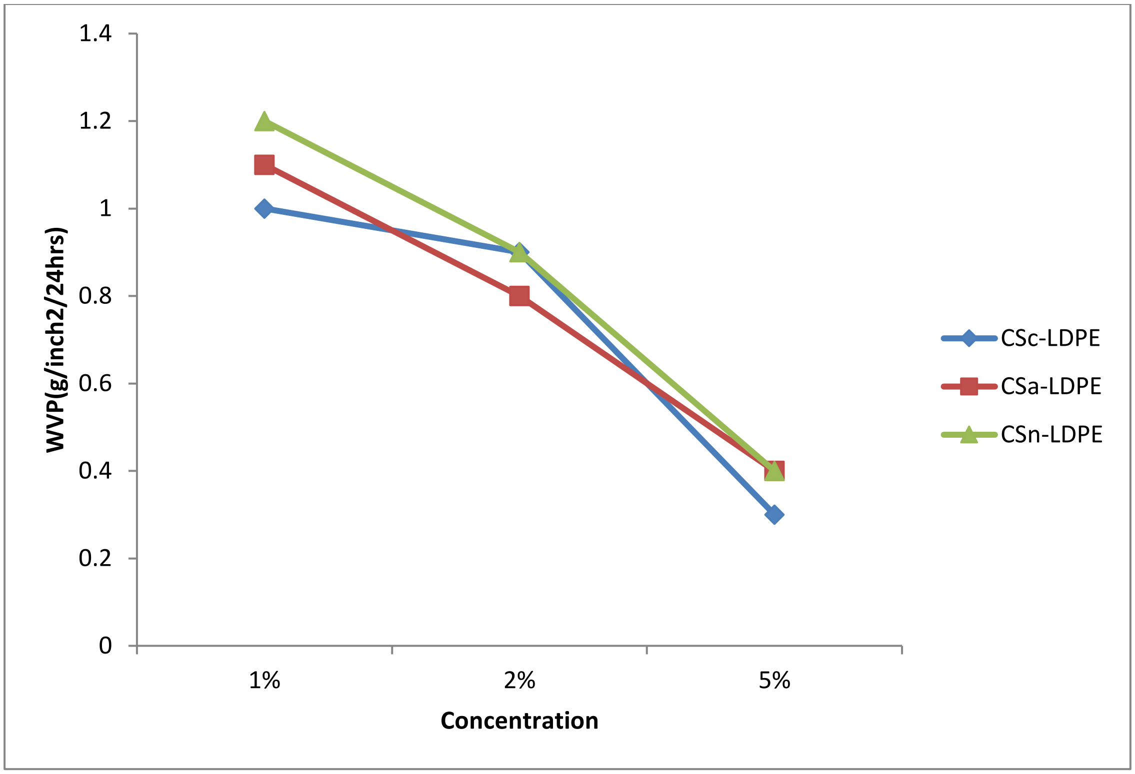

Figure 2: Effect of adding polyphenolic extract and fractions of *C. sinensis* green leaves on WVP of extruded LDPE films.

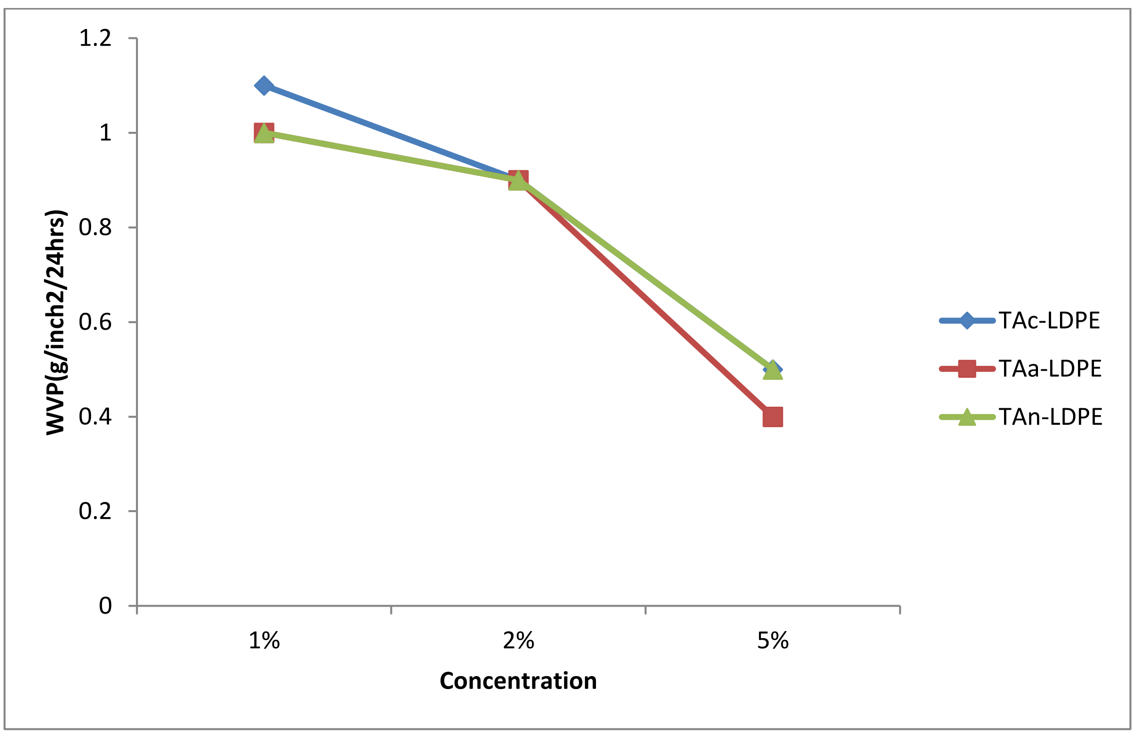

Figure 3: Effect of adding polyphenolic extract and fractions of *T. ammi* seed on WVP of extruded LDPE films

CONCLUSION

LDPE films are commonly use as food packaging materials due to high sealing, low cost and lower reactivity with other materials. LDPE has less barrier for gases specially oxygen with less shelf life for some specific food items. Active packaging material allows a controlled and steady release of the additives into the food over a long period of time with a surety of limiting the undesirable degradation of flavor, lipids and nutrients and side effects on human health. Prepared the extra ordinary formulation of the LDPE active packaging films after adding natural polyphenolic extract from leaves, fruits and seeds in different concentration by using extrusion process and then analyzed their barrier properties with respect to other mechanical and optical properties. Performed the extraction and fractionation of polyphenols from crude methanolic extract. The LDPE granules with different concentrations have processed in a single screw having diameter 44mm.with L/D of 28 mm.Film thickness was measured and Optical properties of modified LDPE films tested. Finally concluded that WVP of polymer based packaging film depends upon several integrated factors and predominantly on the type of polymer, nature of polyphenolic additive, and the atmospheric conditions like relative humidity

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