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ORIGINAL ARTICLE

Effects of Green Tea Extract on Physicochemical and Antioxidant Properties of Polyamide Packaging Film

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KEYWORDS

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ABSTRACT: Polyamide 6 has been widely used in food packaging applications and also green tea contains amounts of antioxidant compounds. The aim of this study was investigation of green tea effects on properties of polyamide packaging polymer. Polyamide 6 was dissolved in methanol which was saturated with calcium chloride. The active packaging film was produced by incorporation of methanol green tea extracts at levels of 2.5, 5, 10 and 20% in polyamide solution by solution casting method. Mechanical and barrier properties of polyamide films were investigated using ASTM standards and antioxidant activity of polyamide films was evaluated using DPPH method. Results indicated that green tea extract increased antioxidant properties and tensile and young modulus of polyamide films. Oxygen and water vapor permeability of films were decreased by incorporation of green tea extract into polyamide matrix. Green tea extract improved barrier and tensile properties of polyamide films, however elongation at break reduced as increasing of green tea extract in polyamide-based films significantly (P<0.05).

INTRODUCTION

The field of active packaging, one of the innovative food packaging concepts, has been the subject of substantial research in the fields of food preservation. Antioxidant packaging, a promising form of active packaging, defines as incorporation of antioxidant agent into polymer packaging matrix. Green tea contains amounts of antioxidant compounds and is considered as effective agent in active antioxidant packaging [1, 2, and 3]. Consumer concerns of food safety lead to the development of active packaging, which is an innovative packaging concept, attracting so much interest in recent researches. The purpose of active packaging is not only to protect food quality but also to improve food properties and extend shelf life [4]. Active

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packaging has been defined as ‘a type of packaging that changes the condition of the packaging to extend shelf life or improve safety or sensory properties while maintaining the quality of the food’ (European FAIR-project CT 98-4170)[4]. “Active compounds and ingredients can be incorporated into packaging materials to provide several functions that do not exist in conventional packaging systems” [5]. “Active packaging may carry antioxidants, antimicrobial, oxygen scavenger, moisture regulator and ethylene scavenger characteristics. Due to the health concerns of the consumers and environmental problems, current research in active packaging has focused on the use of natural preservatives” [1]. Incorporation of antioxidants into packaging materials has become significant because oxidation is a major problem affecting the food quality and safety properties. Currently, the most frequently used antioxidants in active packaging are butylated hydroxyl anisole (BHA) and butylated hydroxyl toluene (BHT). Although these synthetic antioxidants can efficiently be used in active packaging because of high stability, low cost and effectiveness, there are significant concerns related to their toxicological and carcinogenic effects. Therefore, widespread researches have been performed to use some natural antioxidants such as green tea compounds instead of synthetic antioxidants [1].

Green tea is a good source of polyphenolic compounds. Catechins (also known as flavanols), including epicatechin (EC), epigallocatechin (EGC), epicatechin gallate (ECG), epigallocatechin gallate (EGCG), catechin (C), gallocatechin gallate (GCG), catechin gallate (CG), and gallocatechin (GC), are the dominant phenolic compounds in tea leaves. Besides flavanols, various flavonols, such as quercetin, kaempferol, and quercetagetin, and flavones, such as rutin and chrysin, are also present in tea leaves [6]. Green tea has been reported to delay lipid oxidation due to scavenging reactive oxygen and nitrogen species as well as chelating heavy metal particles [7].

Polyamides are chain thermoplastics contain monomers with amine and carboxylic functional groups which cause mechanical and barrier resistance. Various solvents for polyamide polymers are reported such as formic acid, sulfuric acid, halogenated alcohols, aromatic hydroxyl compounds like phenols and some electron withdrawing molecules like arsenic and antimony tri –chlorides [8].

Siripatrawan and Harte incorporated green tea extract into chitosan film. They showed green tea improved water vapor barrier characteristics and increased antioxidant activity and also phenolic content of chitosan films. FTIR results indicated that some interactions between chitosan functional groups and green tea compounds occurred. Addition of green tea extract increased *a* and *b* values while *L* values reduced with increasing green tea concentration [1].

An active film from silver carp skin gelatin incorporated with green tea extract was studied. The findings of this study showed that the incorporation of green tea extract into gelatin films increased the total phenolic content, DPPH radical scavenging activity and reducing power. The higher concentration of green tea content incorporated into gelatin films caused higher tensile strength and lower elongation at break, water solubility and water vapor permeability. FTIR spectra indicated that protein–polyphenol interactions were involved in the green tea contained gelatin films. Therefore, the addition of green tea extract into gelatin film improved the antioxidant activity and affected the physicochemical properties of gelatin films because of interactions between gelatin and green tea extract [2].

In another study green tea extract incorporated into chitosan film in order to extension of pork sausages shelf life. It was found that samples wrapped with active film contained green tea extract showed lower changes in color, texture, TBA value, microbial growth, and

sensory characteristics than controls. Successful inhibition of lipid oxidation and microbial growth in the refrigerated pork sausages was possible with chitosan film incorporating green tea extract. The results suggested that incorporation of green tea extract into chitosan film could enhance the antioxidant and antimicrobial properties of the film and thus maintained the quality and prolonged the shelf life of the sausages [3]. Delay in lipid oxidation of smoked sardines when they are kept in gelatin based film with rosmary aqueous extracts [9]. A gelatin film with an added borage extract was also effective in reducing lipid oxidation of frozen fish patties [10].

The aims of this study was i) incorporation of green tea extract into polyamide 6 film as active packaging film and ii) evaluation of green tea extract effects on mechanical, opacity, barrier and antioxidant properties of polyamide films.

MATERIALES AND METHODS

Green tea extract

According to Chan and colleagues [6], 10 gram green tea powder purchased from Tala Company, Iran was mixed in 100 methanols (0.790 gr/cm^3, Dr Mojallali Co., Iran) with 750 rpm stirring speed for 12 h and then clarified solution was stored at -20°C.

Film preparation

Polyamide film was prepared with calcium chloride saturated methanol using solution casting method. Five gr polyamide 6 pellets (1.313 gr/cm^3, 223°C melting point, Eurotec Co., New Zealand) was dissolved in saturated methanol alcohol using stirring at room temperature for 12 h. The resulted solution was casted into plates and then films were removed after 12 h from plates (256 cm^2). The concentration of green tea extract considered as 2.5, 5, 10 and 20% on dry basis. The thickness of films was about 250 µm.

Water vapor permeability

Water vapor permeability of the films was carried out according to the modified method of weight cup of ASTM standard E96/E96M-05. The test cups were filled with deionized water and covered with films. Weight of cups was determined every 2 h. A plot of weight gained versus time was used to determine the water vapor transmission rate. The slope of the linear portion of this plot represented the steady state amount of water vapor transmission through the film per unit time (g/h). Three samples were tested per treatment. The water vapor permeability was calculated as follow [11].

$$WVP = \frac{\mathrm{TR} \times \mathrm{L}}{\Delta \mathrm{p}} \quad (1)$$

Where WVP is water vapor permeability, TR is transmission rate which is determined by the slope of linear regression plot, L is the film thickness and Δp is water vapor pressure differential across the film (4362 Pa).

Oxygen permeability

Oxygen permeability of films was determined according to Ou and colleagues method [12]. This method is based on peroxide value determination of antioxidant free soybean oil. 10 gr of antioxidant free soybean oil was filled in the test cups and covered with films and then sealed with silicon. Peroxide values of oil were determined every 4 days during 12 days storage following the procedure of national standard 4179. The tests were performed in triplicates.

Antioxidant activity

Antioxidant activity of films was evaluated using DPPH (2, 2-diphenyl-1-picrylhydrazyl) free radical scavenging assay according to Blois with slight modification [13]. Briefly, the films (1×3 cm) were dissolved in 4.5 ml methanol. Three ml of film extract solution was mixed with 1 ml of 1m methanolic solution of DPPH. The mixture was centrifuged at 4500 rpm rotation speed for 10 min and then incubated in the dark at ambient temperature for 30 min. The absorbance was then

measured at 517 nm. The percentage of DPPH free radical was determined using the following equation:

$$DPPH\ scavenging\ effect\% = \frac{Abs_{DPPH} - Abs_{extract}}{Abs_{DPPH}} 100 \quad (2)$$

Where Abs $_{DPPH}$ is the absorbance value at 517 nm of the methanolic solution of DPPH and Abs $_{extract}$ is the absorbance value at 517nm for the sample extracts. Each sample was assayed at least three times.

Mechanical properties

Mechanical tests of LBL deposited films were performed on an Instron Machine (Zwick model, England). The samples were tested according to ASTM D0882-02 standard [14]. The films were cut to 2×10 cm and conditioned at 50% relative humidity and 25 $^{\circ}$C for 48 hours. The tensile tests of the films were carried at a crosshead speed of 60 mm/min, 30°C and with a load capacity of 1 kN. Each test was repeated seven times and results (tensile, elongation at break and Young modulus) are expressed as means ± standard deviation.

Film color

Color of films was evaluated using hunter chormameter (C4-400, Japan). a*(redness/greenness), b*(yellowness/blueness) and L*(lightness/darkness) values determined at three replications. C*(sauternes) calculated as following equation:

$$C^{*} = \sqrt{a^2 + b^2} \quad (3)$$

STATISTICAL ANALYSIS

The means of treatments were subjected to one-way analysis of variance (ANOVA) at 95% confidence level using Minitab 16.0 software

RESULTS AND DISCUSSION

Antioxidant film based on polyamide polymer containing green tea extract (GTE) was produced using solution casting method. The water vapor and oxygen permeability results were shown in Table 1 and 2, respectively. Results indicated that GTE affected oxygen and water vapor barrier properties of polyamide films significantly (P<0.05). Water vapor permeability decreased from 6.16 g/m.s. Pa for control film to 5.02 for polyamide film containing 20% GTE. Reduction of water vapor permeability can be attributed to covalence and hydrogen bonding between polyamide polar groups and phenolic compounds of GTE. Interaction between polyamide polymer and GTE groups leads to reduce availability of hydrophilic groups of polymer and consequently reduce water permeability [1]. As shown in Table 2, peroxide values of antioxidant-free soybean oil decreased significantly (P<0.05) as GTE concentration of polyamide films increased. Peroxide values of antioxidant-free soybean oil decreased from 3.97 to 1.47 in day 12 as increasing of GTE concentration up to 20%. Linkage between free hydroxyl groups of phenolic compounds in GTE and hydrogen groups of polyamide leads to less penetration of oxygen molecules across the films [15]. This result is corroborated by earlier findings [2, 15] who studied on green tea contained biodegradable polymer.

Table1. Water vapor permeability results of polyamide films

Films	Water vapor permeability×10^{-7} (g/m.s.Pa)
Polyamide (control)	6.16±0.16[a]
PA + 2.5% GTE[1]	5.93±0.19[a]
PA + 5% GTE	5.53±0.04[b]
PA + 10% GTE	5.265±0.039[bc]
PA + 20% GTE	5.027±0.047[c]

[1]GTE: green tea extract

Values are recorded as mean ± standard deviation

Means followed by different superscripts in each column are significantly different ($p<0.05$)

Table 2. Peroxide values of soybean oil regarding to oxygen permeability of films

Films	Day 0	Day 4	Day 8	Day 12
Polyamide (control)	0[a]	1.850±0.135[a]	3.224±0.133[a]	3.970±0.099[a]
PA + 2.5% GTE[1]	0[a]	1.321±0.113[b]	2.548±0.021[b]	3.560±0.018[b]
PA + 5% GTE	0[a]	1.045±0.107[bc]	1.843±0.135[c]	2.883±0.132[c]
PA + 10% GTE	0[a]	0.800±0.016[cd]	1.592±0.002[d]	2.510±0.092[d]
PA + 20% GTE	0[a]	0.715±0.112[a]	1.178±0.11[e]	1497±0.103[e]

[1]GTE: green tea extract

Values are recorded as mean ± standard deviation

Means followed by different superscripts in each column are significantly different ($p<0.05$)

Antioxidant activity of films was evaluated using DPPH scavenging assay. Free radical scavenging effects enhanced from 67.2% to 88.75% as incorporation of GTE increased from 2.5 to 20% into polyamide film as shown in Table 3. DPPH scavenging effect of GTE attributed to phenolic content of GTE and high regression relationship between phenolic compounds and antioxidant activity. Green tea contained major phenolic compounds such as epicatechin (EC), epigallocatechin (EGC), epicatechin gallate (ECG), epigallocatechin gallate (EGCG), catechin (C), gallocatechin gallate (GCG), catechin gallate (CG), and gallocatechin (GC). Phenolic compounds scavenge free radicals due to electron-donating groups and subsequent prevention of radical chain initiation, binding of transition metal ion catalysts, and interaction with the free radicals to inhibit lipid oxidation [3].

Table3. Antioxidant activity of films

Films	Scavenging effect%
Polyamide (control)	0.0±0.0[e]
PA + 2.5% GTE[1]	67.250±1.500[d]
PA + 5% GTE	76.250±1.893[c]
PA + 10% GTE	83.750±0.957[b]
PA + 20% GTE	88.750±0.57[a]

[1]GTE: green tea extract

Values are recorded as mean ± standard deviation

Means followed by different superscripts in each column are significantly different (p<0.05)

Mechanical properties of films revealed in Table 4. Results indicated that GTE affected tensile, elongation at break and Young 'modulus of polyamide films significantly (*P*<0.05). Tensile strength is the maximum tension supported by the film until the moment it collapses. Elongation is a measure of the flexibility of the film and can be considered as a characteristic that defines the ability of the film deform in place before it collapses and Young modulus is elasticity coefficient and describes stiffness of the material. These measurements are important due to mechanical characteristics of the films [16]. There is no significant difference between tensile strength of control films and active films containing 2.5, 5 and 10% GTE (*P*>0.05). The significant improvement in tensile strength was observed only in film samples contained 20% GTE from 3.3 to 6.59 Mpa. Elongation at break of films ±decreased significantly (*P*<0.05) upon GTE concentration increased from 255 mm to 38 mm. In fact, incorporation of GTE provides less flexible structure and more stiffness property of polyamide. Changes in mechanical properties of polyamide films due to GTE addition can be attributed to chemical interaction between phenolic compounds of GTE and hydrophilic groups of polyamide polymer which support the findings of [1, 2] who studied on green tea extract effect on chitosan film and silver carp skin gelatin.

Table 4. Mechanical properties of films

Films	Tensile Mpa	Elongation Mm	Young 'modulus Mpa
PA (control)	3.3±0.947[b]	255.44±6.05[a]	1.35±1.51[b]
PA + 2.5% GTE[1]	3.91±0.155[b]	248.90±3.76[a]	4.15±5.75[b]
PA + 5% GTE	3.98±0.198[b]	132.09±9.26[b]	11.73±1.17[b]
PA + 10% GTE	4.63±0.891[ab]	80.38±2.35[c]	111.89±1.28[a]
PA + 20% GTE	6.59±0.339[a]	38.30±6.68[d]	129.55±18.79[a]

[1]GTE: green tea extract ,Values are recorded as mean ± standard deviation

Means followed by different superscripts in each column are significantly different (*P*<0.05)

Color values of films were shown in Table5. The results indicated that GTE changed opacity properties of polyamide films significantly (P<0.05). Adding GTE into polyamide films significantly affected (P<0.05) L*(lightness/darkness), a*(redness/greenness) and b*(yellowness/blueness) values of the films.

Films without GTE were lighter (higher L* value). L* values of the films decreased from 54.36 to 30.80, but a* increased from 0.650 to -1.928 which indicates tendency toward greenness and b* values increased from -1.382 to 15.12 which indicates tendency towards yellowness, as the GTE concentrations increased from 0to20%. It was also observed that C* values increased from 1.527 to 15.244. It means incorporation of GTE caused more turbidity of polyamide films. This findings support similar studies in the literature which revealed color parameters increased as consequence of antioxidant addition to polymers [1, 2].

Table 5. Color parameters of films

Films	a*	b*	L*	C*
PA (control)	0.650±0.031^{a}	-1.382±0.076^{e}	54.364±1.594^{a}	1.527±0.076^{e}
PA + 2.5% GTE[1]	-0.192±0.061^{b}	8.190±0.129^{d}	46.426±0.730^{b}	8.276±0.128^{d}
PA + 5% GTE	-1.596±0.156^{c}	12.900±0.127^{c}	39.362±1.474^{c}	12.999±0.113^{c}
PA + 10% GTE	-1.726±0.194^{cd}	14.17±0.068^{b}	35.756±0.636^{d}	14.275±0.08^{b}
PA + 20% GTE	-1.928±0.042^{d}	15.122±0.066^{a}	30.802±0.796^{e}	15.244±0.061^{a}

[1]GTE: green tea extract

Values are recorded as mean ± standard deviation

Means followed by different superscripts in each column are significantly different (P<0.05)

CONCLUSION

Antioxidant polyamide-based packaging film including green tea extract was developed. Incorporation of green tea extract improved barrier and antioxidant properties but decreased the mechanical strength of polyamide films. Polyamide films incorporated with green tea extract exhibited antioxidant activity and improved barrier characteristics which could render them for active food packaging application.

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The authors declare that there is no conflict of interests.

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