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PREVENTING OF MIGRATION IN FOOD CONTACT POLYVINYL CHLORIDE-BASED STRETCH FILMS WITH POLYLACTIC ACID LAYER

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ABSTRACT

In this study, the effectiveness of biodegradable polylactic acid (PLA) coatings for the prevention of residues migrating through polyvinyl chloride (PVC) films was investigated. PLA films prepared in chloroform at concentrations of 5, 10, 15 and 20 wt% were heat sealed to PVC film surfaces in a hot press (130 °C, 5 min, 5 tons). Physical, mechanical, FTIR and migration analyses were performed on these two-layer films. With PLA coating, the thickness of the films increased, mechanical properties decreased and some changes in color values occurred. It was determined by FTIR that there was no structural change on both surfaces of the films as a result of hot pressing. From the overall migration analysis, no migration was observed in the tests with aqueous food simulants, while migration was detected in fatty food simulants. In the specific migration analysis by GC-MS, di-2-ethylhexyl phthalate (DEHP) migration decreased by 50% with PLA coating. It is concluded that PLA coating of PVC stretch films may be a promising application to reduce migration.

Keywords: PVC, PLA, film, coating, migration, functional barrier

GIDA İLE TEMAS EDEN POLİVİNİL KLORÜR BAZLI STREÇ FİLMLERDEKİ MİGRASYONUN POLİLAKTİK ASİT KATMANI İLE ENGELLENMESİ

ÖZ

Bu çalışmada, Polivinil klorür (PVC) filmlerden geçen kalıntıların engellenmesi için biyobozunur polilaktik asit (PLA) kaplamaların etkinlikleri araştırılmıştır. Kloroform içerisinde ağırlıkça %5, 10, 15 ve 20 konsantrasyonlarda hazırlanan PLA filmler, sıcak preste (130 °C, 5 dk., 5 t) PVC film yüzeylerine ısıl olarak yapıştırılmıştır. Hazırlanan bu iki katlı filmlerde fiziksel, mekanik, FTIR ve migrasyon analizleri gerçekleştirilmiştir. PLA kaplama ile birlikte filmlerin kalınlıklar artmış, mekanik özellikleri azalmış ve renk değerlerinde bazı değişikler meydana gelmiştir. Sıcak pres sonucu filmlerin her iki yüzeyinde de yapısal bir değişiklik olmadığı FTIR ile tespit edilmiştir. Toplam migrasyon

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analizlerinden sulu gıda benzerlerini ile yapılan testlerde migrasyon gözlenmezken, yağlı gıda benzerlerinde migrasyon tespit edilmiştir. GC-MS ile yapılan spesifik migrasyon analizinde ise di-2-etilhekzil ftalat (DEHP) migrasyonu PLA kaplama ile birlikte %50 oranında azalmıştır. PVC streç filmlerin PLA ile kaplanmasının migrasyonu azaltmak için umut verici bir uygulama olabileceği sonucuna varılmıştır.
Anahtar kelimeler: PVC, PLA, film, kaplama, migrasyon, fonksiyonel bariyer

INTRODUCTION

Ensuring the safety of food contact materials, determining the effect on food quality/safety, and identifying the health risks arising from these materials are extremely important in terms of protecting consumer rights. However, some substances in the composition of these materials can pass into foods (migration) and reach levels that are harmful to human health (Üçüncü, 2007; Arvanitoyannis and Kotsanopoulos, 2014; Brunazzi et al., 2014; Castle, 2017; Cruz et al., 2018; Hahladakisa et al., 2018). Plastic materials are widely consumed in many sectors, especially packaging, due to their technological advantages. However, the use of many additives in the production of these materials and their reuse/recycling may cause some undesirable residues to pass into the food (Tice, 2003; Ackerman et al., 2009; Saçak, 2010; Piergiovanni and Limbo, 2016; Castle, 2017; Cruz et al., 2018; Hahladakisa et al., 2018; Baur et al., 2019; Groh et al., 2019).

Polyvinyl chloride (PVC) is used in some areas that come into contact with food, including stretch films, lid seals and tin can lacquers. In addition, it is a type of plastic that contains the most additives such as stabilizers, modifiers, plasticizers, lubricants, colorants, and emulsifiers (Howick et al., 2005; Bradley and Coulier, 2007; FSA, 2007; Üçüncü, 2007; Hanušová et al., 2013; Brunazzi et al., 2014; Piergiovanni and Limbo, 2016; Petersen and Jensen, 2016; Villanueva et al., 2016). Due to the hydrophobic surface structure of PVC materials, no migration is observed in contact with aqueous foods, while migration values may occur above legal limits in contact with fatty foods. Plastic food stretch films are packaging materials used for the short-term preservation of perishable foods such as fresh meats, vegetables, and fruits. It is widely used in markets and homes due to its advantages such as its flexibility, tear, puncture-resistant structure, transparency, and low price. Films that provide these features are in the market based on PVC or polyethylene (PE). PVC-based films have some mechanical and price advantages compared to PE-based films. However, inconvenient migration may occur in contact with PVC films with food. The level of migration varies depending on some parameters, such as the properties of the food (fatty, aqueous, acidic, dry), the type and amount of additives in the composition of the films, the contact time and temperature (Coltro et al., 2014). There are many studies on the migration of some residues from PVC-based materials to food. Phthalate derivatives have an important place among these residues. In addition, many of them have been banned or their usage levels have been limited due to their adverse health effects (López-Cervantes and Paseiro-Losada, 2003; Coltro et al., 2013; Li et al., 2015; Petersen and Jensen, 2016; Bernard et al., 2017; Raeisi et al., 2017).

Biodegradable polymer systems represent an alternative to improve new eco-friendly systems that can reduce the amount of waste concerning petroleum-based polymers. Support to traditional green-based polymer systems can reduce greenhouse gas emissions. Polylactic acid (PLA), the most widely used among biopolymers, is a biodegradable plastic produced by lactic acid polymerization obtained by fermentation of sugar in sources with rich polysaccharide content (such as corn, wheat, and molasses). It is a bioplastic that can be easily used in traditional thermoplastic lines and whose thermal and mechanical properties are similar to those of many synthetic polymers such as polyethylene terephthalate (PET) and polystyrene (PS). In addition, it can be used in processes such as film, bottle, container, and lamination due to its advantages such as low temperature adhesion, strong sealing properties, and printing capability (Üçüncü, 2007;

Niaounakis, 2015; Scarfato et al., 2017; Baur et al., 2019; Ilyas et al., 2020).

Various methods can be used to prevent the migration of substances from plastics to food. Examples of these are coated or lamination of the surface, crosslinking on the surface, changes in the hydrophilic/lipophilic properties of the surface and covalent bonding of additives (Messori et al. 2004; Ito et al., 2005; McGinty and Brittain, 2008; Reddy et al., 2009; Wen et al., 2010; Xiong et al., 2016; Raeisi et al., 2017;). In this study, it is aimed to use PLA layer, a biodegradable polymer suitable for food contact, to reduce the migration of PVC stretch films. Although different applications have been used to reduce migration in previous studies, there is no research on the use of a biodegradable layer for this purpose. Therefore, this study aims to examine the effect of the PLA layer in reducing the migration of PVC stretch films. This research may offer a new approach to reducing migration in food packaging and contribute to more sustainable packaging options.

MATERIALS AND METHODS

Materials

The PVC stretch film, which is produced for food contact (50 cm x 30 m) and PLA pellets (PLA, L175, low viscosity resin suitable for film extrusion) to be used in the study were obtained from a local supplier. Chloroform, glycerol, ethanol, isooctane, and glacial acetic acid were obtained from Merck (Darmstadt, Germany) in analytical grade.

Preparation of films

PLA pellets were dried in an oven (Memmert, UN55, Germany) at 40 °C for 24 h before the preparation of PLA films. PLA solutions at 5, 10, and 20 % (w/v) are prepared by dissolving PLA pellets in 100 mL of chloroform on a magnetic stirrer (Daihan, MSH-20D, South Korea) for 6 h. Glycerol at 50 % (w/w) was added as a plasticizer based on PLA content. The solutions were poured on the glass plates (40 x 40 cm) and adjusted to a constant thickness with a drum bar at 0.88 mm and left to dry at room temperature for 1 night. The drum bar thickness was set to 0.88 mm (determined by a preliminary experiments) for all PLA solutions so that the dried films could be peeled off the surface without tearing. To obtain double-layer films, PVC film and the varied concentration PLA layers were placed and compressed at 130 °C for 5 min at a pressure of 5 tons between the heated plates (30 x 30 cm) of the hot press (Carver 12 Manual Heated Press, USA) and followed cooling. The productions were carried out on the same day for each formula in quantities sufficient for the analyses. Four kinds of films were obtained: PVC stretch film (PVC), as a control, and other bilayer films (PVC+5%PLA, PVC+10%PLA, and PVC+20%PLA).

Characterization

Thickness of films

The thickness of the films was calculated by measuring from 15 different points using a digital micrometer (Mitutoyo, 293-IP-54, Japan) with ± 0.003 mm accuracy.

Mechanical properties

Elongation at break (EAB), tensile strength (TS), puncture deformation (PD), and puncture force (PF) of the films were determined by Texture Analyzer (TA-HD Plus, Stable Micro Systems, UK). For EAB and TS analyses, 6 test specimens of certain sizes (20 x 50 mm) were prepared from films and kept in a desiccator at 23 ± 2 °C with 50 % ± 10 humidity for 48 h. Then, the test specimens were tested with a drawing speed of 2 mm/s (ASTM, 2018).

For PF and PD analysis, 5 samples of 50 mm diameter were prepared from the films and kept in a desiccator at 23 ± 2 °C with 50 % ± 10 humidity for 48 hours. The test specimens were tested with a speed of 0.2 mm/s of the spherical probe (diameter 10 mm) attached to the movable arm (ASTM, 2020).

Color properties of films

Film color parameters

(L*, a*, and b*) were measured using a color spectrophotometer (Konica-Minolta, CR-400). The color was determined by the CIE system, in which L*, a*, and b* represent lightness-darkness,

redness-greenness, and yellowness-blueness, respectively. Measurements were made at eight different locations of the films and placed on a reference white plate. Before measurement, the instrument was calibrated with a reference white plate (L* = 94.63, a* = 0.38, b* = 0.34). The total color difference (ΔE*) was calculated according to the equation below (ASTM, 2022):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

FTIR spectroscopy analysis

The bond structure analyses in films were performed with attenuated total reflection (ATR) equipment of Fourier Transform Infrared Spectroscopy (FTIR) (Spectrum Two, Perkin Elmer, USA). Measurements were taken on the PLA-coated surface in the wavelength range of 400-4000 cm^{-1} (ASTM, 2007). Three replicate tests were carried out on each film.

Migration analysis

The migration analyzes were applied in compliance with the requirements of EN 1186 and EN 13130 standards and the EU 10/2011 regulation, into contact with all types of foodstuffs and for long-term storage. Specimens of 100 x 100 mm (± 1 mm) were prepared from the films. From these, test samples were prepared with a thermal sealing machine (Lavion, FS200, Turkey), with the PVC surfaces on the inside. These test samples with 1 dm^2 area and PLA outer surface were immersed in 100 ± 2 mL food simulants. Test samples were removed from food simulants after being kept in the oven under test conditions (Memmert, UN55, Germany).

Overall and specific migration analyzes were performed in food simulants. Food simulants and contact conditions used in analyzes; FS-A (10 % Ethanol), FS-B (3 % Acetic acid), FS-D_{21} (95 % Ethanol), and FS-D_{22} (Isooctane) were used as a food simulant. For FS-D_{22} and other food simulants 2 days exposure at 20 °C and 10 days exposure at 40 °C respectively were used as a contact condition. Hydrophilic substances are extracted by hydrophilic food simulants A and B. Lipophilic substances are extracted by food simulants D_{21} and D_{22} that have lipophilic characters. Three replicate tests were carried out on each film (CEN, 2002, 2004; EU, 2011).

Overall migration analysis

After these food simulants were evaporated in the weighing dishes, the constant weighing value was recorded. Expressed the overall migration as milligram residues per square decimeter of sample surface intended to come into contact with foodstuffs, calculated for each test specimen using the formula below (CEN, 2002):

$$X = ((ma\text{-}mb) \times 1000) / S \quad (2)$$

X: is the overall migration into the food simulant, in milligrams per square decimeter of the surface area of the film sample (mg/dm^2)
ma: is the mass of the residue from the film sample after evaporation of the food simulant (g)
mb: is the mass of the residue from the blank food simulant (g)
S: is the surface area of the film sample (dm^2)

Specific migration analysis

Due to the hydrophobic surface structure of PVC materials, no migration is observed in contact with aqueous foods, while migration values may occur above legal limits in contact with fatty foods. Therefore, only FS-D_{21} and FS-D_{22} food simulants were used in specific migration analysis. These simulants were put into 2 mL vials after being passed through a 0.45 μm pore diameter PVDF filter. After the contact with the samples, the chromatographic analysis of the food simulants was carried out in a GC-MS (Agilent Technologies 7890B and 5977MSD, USA), operating with HP 5 MS capillary column (30 m x 0.25 mm x 0.25 μm). Chromatographic conditions were adopted: Helium carrier gas flow rate of 1 mL/min. The detector and injector temperatures were 300 °C and 250 °C, respectively. The temperature of the column was programmed at 60 °C (hold 1 min), from 60 °C to 220 °C with 20 °C/min heating, at 220 °C (hold 1 min), from 220 °C to 280 °C with 5 °C/min heating and hold 4 min. 1 μL injected in splitless mode. The acquisition in two parallel was performed on full-scan (m/z = 50–500). Among the peaks in the chromatogram which have certain properties (field and noise factors of peaks above 1/80 and

1/300, respectively) were identified with the support of certified MS libraries (NIST 2005 Standard Reference Database and Wiley 7 Nist 05 Mass Spectral Database). In addition, the total ion concentration (TIC) was calculated over the areas of these peaks (Nerin et al., 2003; Bentayeb et al., 2013; Kassouf et al., 2013; Yavuz, 2013). Three replicate tests were performed for each fatty food simulant.

Statistical analysis

The obtained data were evaluated statistically using IBM SPSS (22.0, USA) program. In the data conforming to a normal distribution, Oneway-ANOVA was used for comparisons of groups and Tukey multiple comparison test was used whether there was a significant difference between the groups at a 95 % confidence interval ($P < 0.05$).

RESULTS AND DISCUSSION

Thickness of films

The results of the thickness are shown in Table 1. The thickness of the films was measured between 0.014 and 0.090 mm. As expected, the thickness of the bilayer film significantly increased with increasing the thickness of the PLA layer. This was associated with the increase in the amount of PLA and glycerol in the film solution and the increase in the total amount of solids in the polymer matrix ($P < 0.05$).

Table 1. Thickness and mechanical properties of films.

	Thickness	Tensile		Puncture	
Films	(mm)	TS (Mpa)	EAB (%)	PF (N)	PD (mm)
PVC (control)	0.014±0.001^{d}	53.62±2.92^{a}	544.78±50.76^{a}	517.66±25.67^{a}	13.09±0.91^{a}
PVC+5%PLA	0.034±0.001^{c}	17.30±1.91^{c}	115.80±5.16^{b}	367.36±16.73^{c}	1.82±0.05^{b}
PVC+10%PLA	0.063±0.003^{b}	18.51±0.94^{c}	123.52±4.57^{b}	418.66±58.39^{bc}	1.59±0.07^{b}
PVC+20%PLA	0.090±0.003^{a}	24.55±1.34^{b}	117.45±14.58^{b}	459.72±46.48^{ab}	1.36±0.08^{b}

Results are expressed as mean ± standard deviation. Different letters in the same column indicate significant differences ($P < 0.05$).

Abbreviations: TS, tensile strength; EAB, elongation at break; PF, puncture force; PD, puncture deformation

Mechanical properties

The mechanical properties of the packaging materials represent their ability to protect their unity and tolerate outside stress during transportation, processing, storage, and handling. Sufficient extensibility and mechanical strength are generally needed for use in applications of food packaging (Sothornvit and Krochta, 2000; Briassoulis and Giannoulis, 2018; Haghighi et al., 2019; Zhou et al., 2019; Pirinc et al., 2020). It is expected that the films to be used as packaging materials have high elongation at break (EAB) and puncture deformation (PD) values to be flexible during wrapping, and high tensile strength (TS) and puncture force (PF) values to ensure product integrity during transportation (Nuthong et al., 2009). It has been reported that using combinations of different polymers (blends or multilayer) to improve some mechanical properties have better or less values than single component materials (Chieng et al., 2014; Liu et al., 2017; Patwa et al., 2018; Iglesias Montes et al., 2019; Al-Shalchy et al., 2020; Oksiuta et al., 2020;).

EAB, and TS of the films were measured and listed in Table 1. The PVC film had higher resistance to break (TS of 53.62 MPa), and stretchability (EAB of 544.78 %) than those of the other films. In a study by Coltro et al. (2013); they reported TS and EAB values in PVC stretch films (16-20 μm thickness) in the range of 24.5-36.8 MPa and 190-227 %, respectively. Park et al. (2020) reported these values in the range of 23.4-28.3 MPa and 635-741 %, respectively. The results obtained for uncoated PVC films are difficult to compare with the literature due to the wide variety of relevant variables (different thickness and compositions).

These values decreased rapidly with the application of PLA coating to PVC films ($P < 0.05$). When PLA, which has lower TS and EAB values compared to PVC, was coated on the PVC surface, it caused a significant decrease in both values of the bilayer films. In studies on bilayer films reported that using a second layer in films decreases the TS value (Jiang et al., 2018; Park et al., 2020). The lowest values were observed as 17.3 MPa and 115.8 % in the PVC+5%PLA sample. Among the bilayer films, the TS value also increased with the increasing PLA concentration in the coating ($P < 0.05$). The highest TS value among PLA-coated PVC films was determined as 24.55 MPa in the films coded PVC+20%PLA. The increase in TS value was due to the increase in the PLA concentration of the PLA layer in bilayer films, similar findings were reported by Zhou et al. (2019). No significant change was observed in the EAB value of PLA-coated PVC films ($P > 0.05$). However, Zhou et al. (2019) reported that the EAB value decreased due to the increase in PLA concentration.

Puncture properties such as force and deformation of packaging materials are other important mechanical properties. Puncture force (PF) indicates the ability of packaging material to inhibit the intrusion of a foreign object, and puncture deformation (PD) is the expression of the amount of elongation before the burst of packaging by this foreign substance (Pirinc et al., 2020). The puncture properties of bilayer films are shown in Table 1. When the puncture properties of the films were examined, the highest PF (517.66 N) and PD (13.09 mm) values were obtained in uncoated PVC films. PF and PD values of PVC films significantly decreased with PLA coating ($P < 0.05$). The decreasing trend of PF and PD values could be related to the PLA layer which produces films having a lower tensile, and puncture force. However, the puncture strength of the multilayered materials was higher than those of the conventional blend (monolayer) and the puncture mechanisms of multilayered materials were more complex. It has been stated that due to the tensile and shear stress differences between the adjacent layers during the puncture, interfacial delamination will occur and exhibit gradual rupture behavior (He et al., 2016).

The lowest PF value (367.36 N) was obtained in the PVC+5%PLA film, and the lowest PD value (1.36 mm) was obtained in the PVC+20%PLA film. In PLA-coated films, with increasing PLA concentration, PF value increased significantly($P < 0.05$), and PD value decreased, but did not significantly affect ($P > 0.05$). The increase in PLA concentration in the second layer of multilayer packaging films resulted in an increase in TS and PF, while there was no significant change in EAB and PD values. Although the literature suggests that an increase in the thickness of the second layer would lead to significant changes in mechanical properties, the effect of an increase in polymer concentration in the second layer has not been investigated. Therefore, we can only explain the results of our study as follows: It is known that the elongation capability of films is directly related to the amount and type of plasticizer incorporated into the film structure. In our study, glycerol used as a plasticizer for PLA film layers was added to the formulation based on PLA mass and kept constant at 50% (w/w). This explains why there was an increase in TS and PF values due to an increase in surface area resulting from an increased thickness of all PLA layers, but no significant change occurred in elongation values (EAB and PD) because the proportional amount of plasticizer remains consistent across all PLA layers.

Color properties of films

The color and transparency of the packaging material have a significant impact on consumer expectations. Normally, transparent film packaging has higher demands in market as customer would like to have clear view on the colors, textures and quality of the food's ingredients that they are consuming (Bourtoom and Chinnan, 2008; Khoshgozaran-Abras et al., 2012; Lee et al, 2019; Zhao et al., 2022; Guzman-Puyol et al. 2022; Abdullah et al., 2022; González-López et al, 2023). The color results of the films are given in Table 2. As is seen, the highest L*, a*, and b* values were determined from the PVC (control), PVC+5%PLA, and PVC+20%PLA

films, respectively. With the increase in the PLA concentration decreased the L* values compared to the control film. All films had positive a* and b* values, meaning the films showed very slight redness and yellowness. In addition, increasing the PLA concentration in the layer slightly increased the a* and b* values. The lowest a* and b* values were determined in PVC (control) film. The total color difference (ΔE*) of the films was calculated based on the reference plate. With the increase of PLA concentration in the films, ΔE* values increased in general, and the lowest results were obtained for the PVC (control) film. According to the classification of ΔE* values by Silva and Silva (1999), PVC control films showed a "very small (between 0.2 and 0.5)" color difference, while PLA-coated bi-layer films showed "small (between 0.5 and 1.5), and distinct (between 1.5 and 3.0)" ΔE* values.

Table 2. Color properties of films.

Films	L*	a*	b*	ΔE*
PVC (control)	94.83±0.07^{a}	0.37±0.02^{c}	0.63±0.09^{c}	0.36±0.05^{c}
PVC+5%PLA	94.12±0.09^{b}	0.55±0.04^{a}	1.10±0.09^{b}	0.93±0.08^{b}
PVC+10%PLA	94.09±0.12^{b}	0.49±0.02^{b}	1.09±0.10^{b}	0.93±0.13^{b}
PVC+20%PLA	92.85±0.15^{c}	0.46±0.04^{b}	1.27±0.14^{a}	2.02±0.13^{a}

Results are expressed as mean ± standard deviation. Different letters in the same column indicate significant differences (P <0.05).
Abbreviations: L*, darkness (0) – lightness (100); a*, greenness (-) – redness (+); b*, blueness (-) – yellowness (+); ΔE*****, color difference

There are many factors that affect the color of packaging films. Some of them are the type of polymer material, the additives used, the thickness of the films and film production methods (Guzman-Puyol et al. 2022). In our study, color values changed depending on the increase in PLA layer thickness. This situation has been observed in some studies; in multilayer polyethylene films, the thickness of each layer and the total layer thickness are effective on color values (Kondratov et al., 2018), and in some films, opacity or darkness values increase as the thickness increases (Galdeano et al, 2013; Nilsuwan et al., 2017; Lee et al, 2019), and in gelatin/PLA bilayer films, increasing PLA layer thickness causes an increase in L* and a* values and a decrease in b* and ΔE* values (Nilsuwan et al., 2018).

FTIR spectroscopy results

FT-IR is a well-known and widely used method to investigate the phase behavior and intermolecular interaction between polymers. In this study, the FTIR-ATR spectra along with characteristic transmittance bands for PVC and PLA surfaces of the films are shown in Figure 1. Accordingly, PVC surfaces detected characteristic stretching vibrations for C-H, C-C, and C-Cl at 2958/2927/2857 cm^{-1}, 1089 cm^{-1}, and 835/692/635/608 cm^{-1}, respectively. CH_2 scissoring and CH_2 rocking vibrations were observed at 1425 cm^{-1} and 959 cm^{-1}, respectively. Other peaks seen in PVC stretch films were attributed by the additives in the composition of PVC, especially phthalate derivatives. The C=O and C-O-C stretching vibrations were observed at 1730 cm^{-1} and 1461/1174 cm^{-1}. Similar results have also been reported by other researchers (Coltro et al., 2013; Kerr et al., 2013; Ludwig et al., 2018; Sharma et al., 2019; Al-Shalchy et al., 2020; IRSAT, 2024).

PLA shows characteristic stretching vibrations for C-H, C=O, C-O, C-CH_3 and C-C at 2998/2947 cm^{-1}, 1756 cm^{-1}, 1180/1130/1080cm^{-1}, 1043cm^{-1}, and 871/755cm^{-1}, respectively. Bending vibrations for C-H have been identified at 1455/1359/1383 cm^{-1}. -CH_3 rocking and C=O bond vibrations were observed at 957 and 694 cm^{-1}, respectively. Similar results have also been reported by other researchers (Zakaria et al., 2013; Chieng et al., 2014; Yuniarto et al., 2016; Rocca-Smith et al., 2016; Râpă et al., 2016; Patwa et al., 2018; Olejnik and Masek, 2020; IRSAT, 2024).

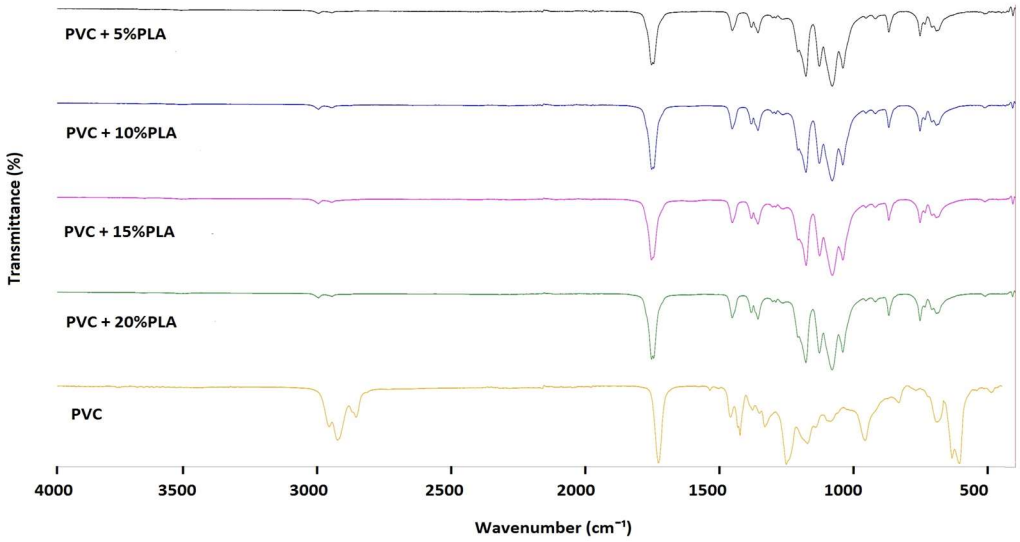

Figure 1. FTIR spectra of PVC and PLA surfaces of films

When the FTIR spectra collected from both surfaces of the films are examined, the characteristic wavelengths of both polymers were seen only on their surfaces. This situation can be explained by the fact that the thermal sealing process does not cause any structural deformation and interactions between the PVC and PLA layer; shows that the films were formed by physical interaction rather than chemical interaction on their surfaces.

Overall migration results

When the results of the overall migration analysis of the films are analyzed; no migration was observed in contact with FS-A and FS-B representing aqueous foods. In this case, it shows that no adverse situation will occur in the long-term contact of the films with aqueous foodstuffs. In FS-D_{21} and FS-D_{22} food simulants, overall migration was observed in the range of 0.80-8.13 mg/dm² and 0.87-6.33 mg/dm², respectively (Figure 2). In the control PVC films obtained from the market in the study, the overall migration level was 0.80 and 6.33 mg/dm² for FS-D_{21} and FS-D_{22}, respectively. Overall migration in PVC films has been reported to range between 13 and 720 mg/dm² (Petersen et al. 1995; 1997; 2004).

The migrations occurring in FS-D_{21} (polar) and FS-D_{22} (apolar) representing fatty foods were measured below the legal limit (10 mg/dm²). This indicates that the produced multilayer films can be in contact with such foodstuffs for a long time without exceeding the permitted migration limits. In contact of the films with FS-D_{21}, there was an increase in the migration level due to the increase in PLA concentration ($P < 0.05$). This may be due to the migration of lactic acid monomers/oligomers in the structure of the PLA as a result of the strong affinity of PLA to FS-D_{21}, or the dissolution of the glycerol, which is used as a plasticizer, in FS-D_{21} (Conn et al., 1995; Mutsuga et al., 2008; Bor et al., 2012; Scarfato et al., 2017; Ubeda et al., 2019).

The test results with the apolar FS-D_{22} showed that the overall migration level in the PVC film with the PLA layer decreased significantly ($P<0.05$). However, the increase in PLA concentration in the PLA-coated PVC films did not have a significant effect on overall migration ($P>0.05$). Previous studies (López-Cervantes and Paseiro-Losada, 2003; Coltro et al., 2013; Li et al., 2015; Petersen and Jensen, 2016; Bernard et al., 2017; Raeisi et al., 2017) have shown that the PLA layer acts as a functional barrier, preventing nonpolar substances from diffusing into the PVC films.

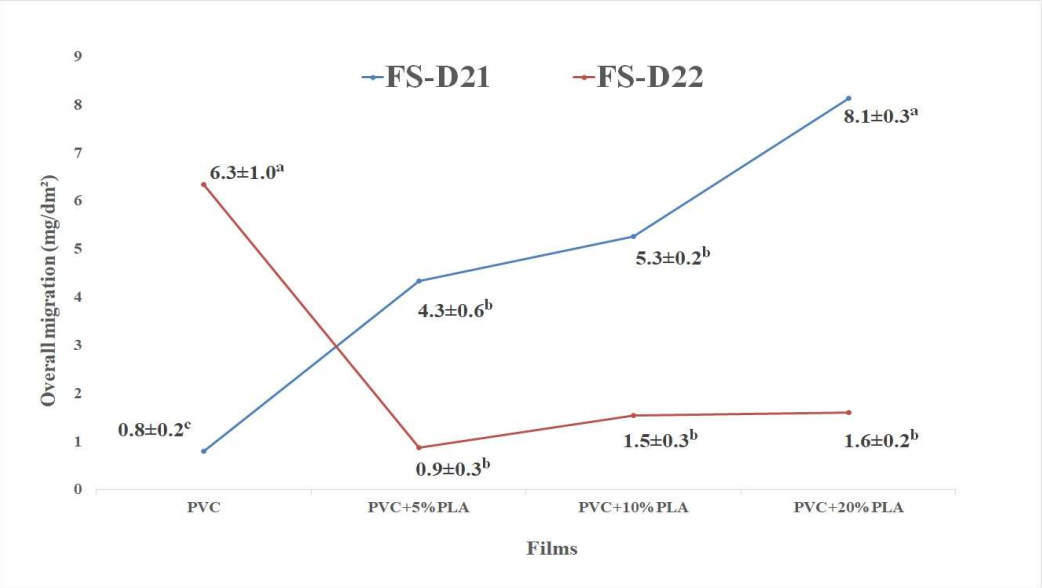

Figure 2. Overall migration analysis results with FS-D_{21} (%95 EtOH) and FS-D_{22} (isooctane) food simulants in films

Specific migration results

As a result of the contact of films with FS-D_{21} and FS-D_{22} under test conditions, polar and apolar specific migrants diffusing to these food simulants were determined qualitatively by GC-MS. Total ion concentrations (TIC) were determined by calculating the areas of the peaks of each migrant as m/z (Figure 3). TIC levels in FS-D_{21} and FS-D_{22} were determined in the range of 0.5-5.6 x 10^8 m/z and 2.5-8.7 x 10^8 m/z, respectively. PLA layer significantly reduced migration in PVC films ($P < 0.05$). In the study reported by Bradley and Coulier (2007) for the determination of residues migration from "Food contact PVC materials" to food simulants (ethanol and isooctane) with GC-MS; residues were detected at similar retention times.

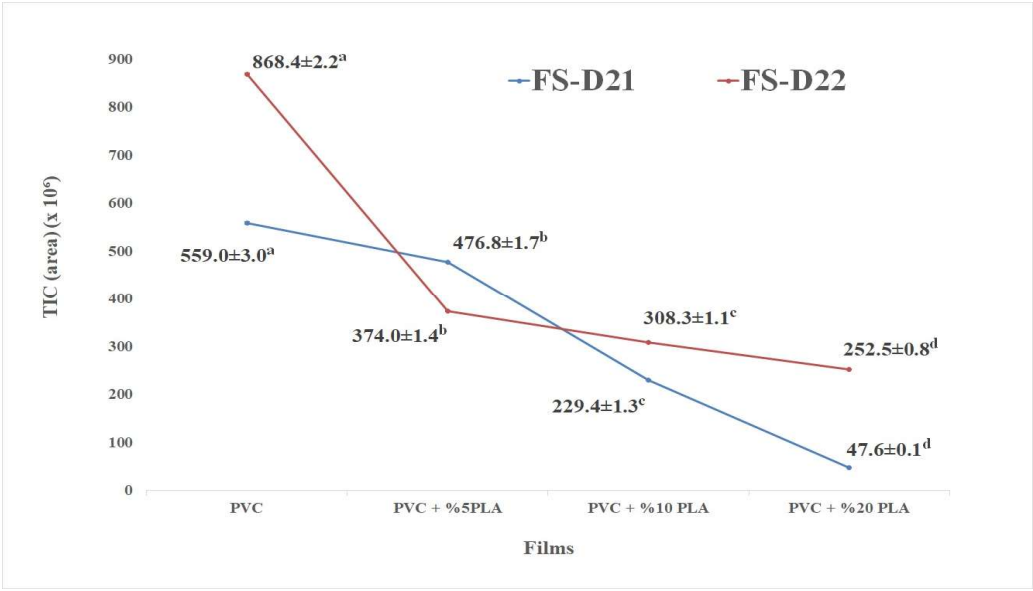

Figure 3. Total ion concentration (TIC) migration analysis results by GC-MS

Among the detected peaks, only di-2-ethylhexyl phthalate (DEHP) could be identified by the MS library. The concentration (in the area) of this migrant, which is the most commonly used phthalate derivative in PVC films, in FS-D_{21} and FS-D_{22} was determined in the ranges of 0.2-3.2x10^8 m/z and 2.1-5.1x10^8 m/z, respectively (Figure 4). PLA layer significantly reduced DEHP migration in PVC films ($P < 0.05$). This shows that phthalate derivatives, which are used to ensure the processability of PVC-based stretch films and improve some mechanical properties (flexibility, physical strength, barrier, etc.), but can pose a risk to human health, are prevented to migrate by the PLA layer. There are various studies to reduce DEHP migration from PVCs. In these studies, methods used nano inhibitors (Raeisi et al., 2017), films made by micro-layer co-extrusion technology (Xiong et al., 2016), by covalently attaching hydrophilic monomers onto the hydrophobic PVC surface (Wen et al., 2010), plasma and UV application on the surface (Ito et al., 2005; McGinty and Brittain, 2008), and coating the surface (Messori et al. 2004; Reddy et al., 2009). Especially, there was a considerable reduction in the plasticizer migration with coated PVC sheets versus uncoated PVC sheets (Reddy et al., 2009).

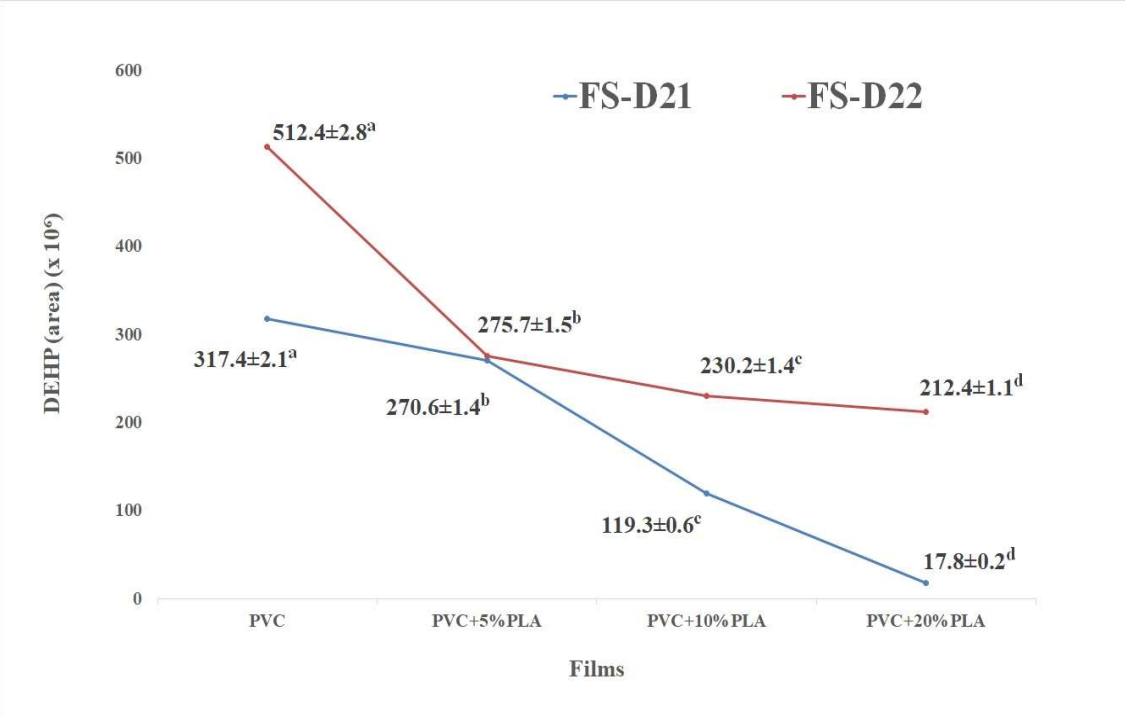

Figure 4. Di-2-ethylhexyl phthalate (DEPH) migration analysis results by GC-MS

According to EU 10/2011 regulation; a functional barrier 'means a barrier consisting of one or more layers of any type of material which ensures that the final material or article (EU, 2011). In this case, the PLA coating exhibited functional barrier properties by preventing the migration of PVC films.

CONCLUSION

In this study, PVC stretch films were coated with a PLA layer to prevent the migration of plasticizers such as phthalate. The physical, mechanical, migration, and FTIR properties of films were also determined. The physical and mechanical analysis of the films revealed that the tensile (TS and EAB) and puncture (PF and PD)

properties of the PVC films have weakened with the coating of the PLA layer. This situation negatively affected the flexibility and strength of the films.

The color values of the films were quite similar to those of the PVC control films, and a low level of change occurred. This change is "not perceptible by the human eyes ($\Delta E^* \leq 1$)" or "detectable only by close observation ($\Delta E^* = 1\text{-}2$)".

The migration analysis indicated that there was a considerable reduction in the overall and specific migration with PLA-coated PVC films when compared to uncoated PVC films. All PVC films coated with the PLA layer showed a lower overall migration to all food simulants than the limit set in the legislation. Overall migration analysis is a practical and simple method used to check the safety of food contact materials. However, even if the results obtained by overall migration analysis are appropriate, the safety of the materials should be checked by specific migration analysis. In our study, although the overall migration result with FS-D_{21} increased with PLA layer thickness, it reduced the migration of residues such as DEHP, which may pose a risk in terms of specific migration. This indicates that PLA can be used as a functional barrier to prevent the migration of hazardous residues such as plasticizers into food.

As a result, the addition of a PLA layer to the PVC film caused a weakening in the mechanical, and color properties of the films. However, given that it can be an effective way to reduce the risk of migration from PVC-based packaging to foods, this situation may be acceptable in certain applications for improved food safety.

In future studies, it can be recommended to add different plasticizers at various concentrations to PLA films to improve the flexibility and strength of bi-layer PVC films.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

AUTHOR CONTRIBUTIONS

Conceptualization, A.F.D; Writing and Original Draft Preparation, A.F.D. and F.T.S.; Writing and Review and Editing, A.F.D., F.T.K.D., F.T.S.; Visualization, A.F.D.; Funding Acquisition, A.F.D. All authors have read and agreed to the published version of the manuscript.

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