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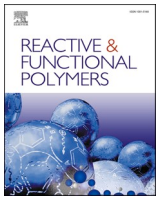

Formulation of poly(butylene adipate-*co*-terephthalate)/caffeic acid composites for vegetable packaging applications

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ABSTRACT

Poly(butylene adipate-*co*-terephthalate) (PBAT) is widely used as a bioplastic owing to its commendable water-barrier properties. In this work, PBAT was blended with caffeic acid (CA) (1–3 wt%) by solution mixing using chloroform as a solvent through solvent casting method. UV–Visible spectroscopy results show a decrease in transmittance from 100 % in PBAT to 6 % PBAT/3CA. The film's elongation was notably improved with an increase in the CA ratio, reaching up to 1055.4 %. Moreover, the tensile strength experienced a significant enhancement upon the inclusion of CA (3 wt%) up to 25.5 MPa. The decrease in water vapor permeability (WVP) ($3.05 \pm 0.1 \times 10^{-11}$ g.m/m^2.Pa.s) and water contact angle (WCA) ($60.5^{\circ} \pm 1.34^{\circ}$) was observed in PBAT/3CA. PBAT film containing 3 wt% CA exhibited remarkable scavenging action against $ABTS^{\bullet+}$ and $DPPH^{\bullet}$, recording values of 100 % and 98.5 %, respectively. When subjected to testing against foodborne pathogens such as *Escherichia coli* (*E. coli*) and *Listeria monocytogenes* (*L. monocytogenes*), the fabricated films displayed excellent antibacterial activity. The active films comprising PBAT/CA possess the potential to serve as a synergistic solution for food packaging, combining the UV barrier property, mechanical properties, flexibility, peeling resistance, and renowned biodegradability of PBAT with the ability to repurpose industrial waste.

1. Introduction

Packaging plays a central role in modern food and beverages trading, aiming to assure the preservation of food quality and nutritional value. The packing materials produced using biodegradable plastic is an innovative way to minimize plastic waste [1]. Innovation in this field is often driven by the constant need to protect edible goods against external factors such as light, temperature, and moisture, which can compromise the quality and safety of the products throughout their transportation and storage [1,2]. Marketing strategies, customers' tastes and demands are also key driving forces behind these developments. The main advancements in packaging, particularly in the sector of food containers, have been focused on the creation of eco-friendly systems with active ingredients that have antioxidant, antimicrobial, as well as antifungal properties [3]. Some of these ingredients might even be capable of simultaneously decreasing environmental pollution along with extending shelf life. Active packaging constitutes an example of the cutting-edge methods for food packaging that have been created in

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reaction to recent changes in current patterns and developments in both the market and the customers' needs [4]. The terminology of "active packaging" is usually given to forms of packaging which changes their physical condition to enhance security, sensory, or longevity properties while maintaining the integrity of the food [5,6]. To be considered active packaging materials, antioxidants along with antibacterial chemicals must be integrated within the polymer substance [6,7]. Current research trends in this field aim to replace petroleum-based polymers that are currently used in the packaging business, due to their high environmental impact. Therefore, it is necessary to improve the properties of PBAT material, to increase its potential applications and replace environmentally harmful polymers.

PBAT is copolymer of adipic acid, 1,4-butanediol and terephthalic acid, designed as a biodegradable material which requires simple molding processes. PBAT has excellent elasticity, exceptional tear resistance, outstanding processability, and great biodegradability characteristics [8]. Due to its exceptional mechanical and optical properties, PBAT has become the most alluring polymer for applications related to food packaging [8]. The PBAT is susceptible to enzymatic degradation and can easily blend with the host materials as it has a higher tendency to be completely soluble in solvents such as chloroform [9]. Excellent biodegradability and excellent mechanical characteristics are provided by the aliphatic and aromatic portions of PBAT, respectively [9,10]. For applications requiring flexible packaging, PBAT's exceptional flexibility is useful [11]. Even though PBAT has useful functional properties, its poor barrier properties can often lead to limitations in its usage. This makes the application of natural bioactive chemicals to enhance PBAT film characteristics an appealing area of study [12–14].

Caffeic acid (CA) (3,4-dihydroxycinnamic acid) is a hydroxycinnamate metabolite that is found in edible goods such as blueberries, apple slices, cider, as well as coffee-based drinks and in plant materials [15]. This natural product has already demonstrated a wide range of biological activities in vitro, such as carcinogenesis inhibition, antioxidant and antibacterial activities, and cardiovascular protection [15,16]. Natural phenolic compounds, such as CA, are attracting a lot of interest as prospective photoprotective agents for dermatological products, due to their powerful antioxidant ability and overall safety [17].

With this work, we aim to formulate a PBAT/CA-based composite through solution blending. To the best of our knowledge, this is the first report to analyze the impact of the incorporation of different concentrations of CA (1, 2, and 3 wt%) in a PBAT film, including the UV barrier ability, antioxidant and antibacterial activities, and physical properties, namely the examination of structural, operational, and thermal characteristics of the resulting composites.

2. Materials and methods

2.1. Materials

PBAT granules were obtained from M/s BASF Ltd. in Tokyo, Japan. Caffeic acid (CA) was purchased from TCI, Japan. 2,2-Diphenyl-1-picrylhydrazyl (DPPH), 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) were purchased from Sigma-Aldrich (USA). Bacteria *Escherichia coli* (*E. coli*) O157: H7 (ATCC 43895) and *Listeria monocytogenes* (*L. monocytogenes*) (ATCC 15313) were acquired through the Korean Collection for Type Culture (KCTC). Anhydrous ethanol 99.9 % was purchased from Samchun Chemicals, Seoul, Korea.

2.2. Preparation of PBAT/CA blend films

PBAT granules were pre-dried in an oven at 60 °C for 24 h before film preparation. Pristine PBAT films were created by dissolving 2 g of PBAT in 50 mL of chloroform, stirring the solution for 12 h at room temperature. Various concentrations of optimized CA (1, 2, and 3 wt% of PBAT) were prepared by dissolving in 5 mL of anhydrous ethanol solvent. Using solvent casting method, a plan PBAT and blend films comprising PBAT and CA were developed [18]. The active films were produced by blending the CA solution with the PBAT solution and stirring for 12 h at room temperature. The resulting films were categorized as PBAT, PBAT/1CA, PBAT/2CA, and PBAT/3CA. The prepared PBAT and PBAT/CA blend solutions were poured into a Teflon mold and allowed to dry for 24 h. After air-drying, the fabricated PBAT films were removed from the molds and stored in a chamber at 25 °C with 50 % relative humidity (RH) until further experiments. A schematic diagram for the fabrication of PBAT/CA films through the solvent casing method is presented in Fig. S1.

2.3. Characterization of PBAT/CA films

2.3.1. Surface morphology

Surface morphology was examined using field emission scanning electron microscopy FE-SEM (Hitachi S-4800, Minato-ku, Tokyo) operated at an acceleration voltage of 5 kV. For this study, a small piece of the film sample was coated with gold using a sputter coater for 60 s and mounted on the SEM specimen holder.

2.3.2. Surface color properties

The color properties of the fabricated films were measured through Chroma meter (Konica Minolta, CR-400, Tokyo, Japan). The Hunter color (L, a, b) of film sample was determined and the total color - difference (ΔE) was calculated via eq. (1).

$$\Delta E = \left[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2\right]^{0.5} \quad (1)$$

where ΔL, Δa, and Δb are the difference of each color values between the standard color plate and film sample respectively.

2.3.3. Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR)

The functional groups present in the PBAT and blends of PBAT/CA films were analyzed by using Fourier transform infrared (FTIR) (Perkin Elmer, USA) spectroscopy at a resolution of 4 cm^{-1} in the wavenumber ranges of 4000 cm^{-1} to 500 cm^{-1}.

2.3.4. Thermal analysis

The thermal stability of the films was evaluated using a thermogravimetric analyzer (TGA) Instruments (SDT Q600, USA). The film samples were exposed to a heating rate of 10 °C/min under a nitrogen (N_2) gas atmosphere and scanned over a temperature range from 30 °C to 700 °C.

2.3.5. Thickness and mechanical properties

The thickness of the film was measured using digital micrometer (Digimatic Micrometer, Quantu Mike IP 65, Mitutoyo, Japan) with a precision of 0.001 mm. Measurements were taken at five different selected locations on the film, and the average of these measurements was calculated. Each film's mechanical properties, including its elongation at break (EB), elastic modulus (EM), and tensile strength (TS) (MPa), were measured. The film specimens were cut into rectangular strips of 2 cm by 5 cm for this purpose. The Instron instrument (500 N) was operated at 50 mm/min crosshead speed according to ASTM D882–12 [19,20].

2.3.6. Water contact angle

The water contact angle (WCA) was used to evaluate the hydrophobicity of the surface of the composite film using drop method by utilizing the FTA-200 instrument systems. Rectangular pieces of films (3 cm × 8 cm) were placed on a movable platform that was fastened with a WCA analyzer. One droplet of water, about 10 μL in volume, was applied to the sample film using micro syringe. Next, the horizontal level and

symmetry on both sides of the water droplet were considered in order to calculate the WCA.

2.3.7. Water vapor permeability

Using the ASTM E96–16 standard procedure, the films' water vapor permeability (WVP) was ascertained [19,20]. The film samples, which measured 75 mm by 75 mm, were placed on top of a tester cup. The cups were put in a humidity chamber (RHFX1077, Jeio Tech Co. Ltd., Ansan, Gyeonggi-do, Korea), that was adjusted to a temperature of 25 °C and 50 % relative humidity. The weight variations of the water-filled cups were observed every hour. Water vapor transmission rate (WVTR) (g/m^2·s) of the film was determined from the slope of the linear plot of the change in weight of the WVP cup vs. time. The provided formula (2) was used to determine the films' WVP (g.m/m^2.Pa.s).

$$WVP = (WVTR \times L)/\Delta p \quad (2)$$

Where, L and Δp are the mean film thickness (m) and was the partial water vapor pressure (pa) difference across the two sides of the films respectively [21].

2.3.8. Antioxidant activity

The films antioxidant activities were performed using free radicals 2,2-diphenyl-1-picrylhydrazyl ($DPPH^{\bullet}$) and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) ($ABTS^{\bullet+}$) assays, using scavenging techniques previously reported in the literature [21]. In the free radical scavenging test, a predetermined amount of the prepared film samples was mixed with 10 mL of DPPH in methanol solution (0.004 %, OD ~ 1) and 7 mM ABTS solution. The absorbance was then measured after 24 h at wavelengths of 517 nm and 734 nm, respectively. Furthermore, a control experiment was carried out using the identical procedure, however without a film sample. The radical scavenging activity had been assessed in both instances using the subsequent formula (3).

Free radical scavenging activity (%) = $(A_0 - A_T)/A_0 \times 100$ (3).

where A_0 and A_T are the DPPH/ABTS solution absorbances of the control and test samples, respectively.

2.3.9. Antibacterial activity

The antimicrobial efficacy of the PBAT-based films against the foodborne pathogenic bacteria *E. coli* and L. *monocytogenes* was assessed using colony-forming unit (CFU) methodology [19]. To examine the antibacterial properties, bacteria were incubated for 16 h at a temperature of 37 °C with gentle agitation after being introduced into the TSB (tryptic soy broth) and BHI (brain heart infusion) broths using sterile techniques. To attain a concentration of approximately 10^5–10^6 CFU/mL in the culture broth containing 200 mg of each film sample, the initial concentration of bacteria (10^8–10^9 CFU/mL) was diluted and introduced into 20 mL of TSB and BHI broth. A total of 12 h was dedicated to the incubation phase at a temperature of 37 °C, with mild agitation maintained at 100 rpm. Samples were collected at predetermined intervals and diluted and grown on agar plates to read the number of viable cells.

2.4. Real-time packaging study

The ability of the PBAT composite film to prevent the carrot pieces from becoming hazardous was examined by looking into its food packing characteristics. Peeling and chopping the fresh carrots into small pieces, the carrots were then wrapped with the following materials: (i) commercially marked polyethylene bags, (ii) PBAT film, and (iii) PBAT/3CA composite film. After that, each of these was set aside on a sterilized dish. A five-person peer group performed the physical evaluation, examining the carrot pieces after they had been stored for one, five, nine, and eleven days. They evaluated the appearance based on color, texture, and smell.

2.5. Statistical analysis

All properties of films measured in triplicates. The results were presented as mean ± SD (standard deviation). ANOVA test was performed, and the significant differences ($p < 0.05$) among treatment groups was separated by Duncan's multiple range test using the SPSS computer program (SPSS Inc., Chicago, IL, USA).

3. Results and discussion

3.1. Morphological studies

The surface uniformity of the films and the dispersion of CA were analyzed using SEM. The optical images of the films are shown in Fig. 1. The surface of the neat PBAT (Fig. 1(a)) film exhibits uniformity, indicating the solubility of PBAT in chloroform without agglomeration. The PBAT/CA surface uniformity increases with an increase in CA concentration. The lower CA concentrations PBAT/CA1 (Fig. 1(b)) and PBAT/CA2 (Fig. 1(c)) do not showcase uniformity. This can be due to insufficient interaction between the CA and PBAT matrix which results in an uneven surface. The PBAT/CA3 (Fig. 1(d)) shows uniformity which indicates that, at higher concentrations, chain interactions become more efficient, resulting in surface uniformity. The PBAT/CA films demonstrate uniformity without any aggregation, with an increase in roughness on the film surface, suggesting compatibility between CA and PBAT.

3.2. Surface color

Consumer acceptance of packaged food is significantly influenced by the color of the film used for packaging. The neat PBAT film was transparent and lacked any coloration (Fig. 2(a)). The film's color gradually transformed into a light yellowish hue with the addition of 1–3 wt% caffeic acid, attributed to the yellowish color of CA fillers (Fig. 2(b-c)). Notably, the composite films displayed a consistent coloration, indicating a good distribution of caffeic acid throughout the PBAT matrix. The effect of CA addition on the color parameters of the PBAT-based films is presented in Table S1 in terms of L, a, b, and ΔE values.

The neat PBAT film was bright with an L-value of 91.2 ± 0.7. The integration of caffeic acid significantly ($p < 0.05$) reduced the brightness. The addition of 1, 2, and 3 wt% of caffeic acid enhanced redness (increased a-value) and yellowness (increased b-value) due to the yellowish color of the CA, and the alteration in color values is contingent upon the concentration of CA. The ΔE values of the CA-added films were significantly higher ($p < 0.05$) than the PBAT film, suggesting the PBAT/CA were more colorful and caffeic acid could interact with the polymer matrix through different molecular interactions. The color change was mainly due to the selective absorption of light by the incorporated fillers [21]. The increase in filler concentration caused the scattering effects, diminishing the transmission of light through the films and subsequently reducing the lightness [19].

The UV (ultraviolet)-visible light barrier features of the PBAT/CA composite films were investigated by UV–Vis spectroscopy (Fig. 2(d)). The pure PBAT film shows higher 15 % at the UV range of 280 nm, whereas at the visible wavelength, 650 nm the transmittance was more than 88 %. The effective UV barrier properties of PBAT films were ascribed to the involvement of π electrons from benzene functional groups and UV light absorption of carbonyl groups [22]. The addition of CA from 1 to 3 % has decreased the transmission range from 13 % to 6 % at UV range 280 nm and 80 % to 43 % at the visible range 680 nm. The CA contains conjugated double bonds and functional groups like hydroxy (-OH) and carbonyl (C=O), which can absorb light in the ultraviolet and visible regions [23]. Table S1 represents the values obtained from the UV–vis curve in Fig. 2(d). This shows increasing the concentration of caffeic acid increases UV barrier properties. The UV shielding

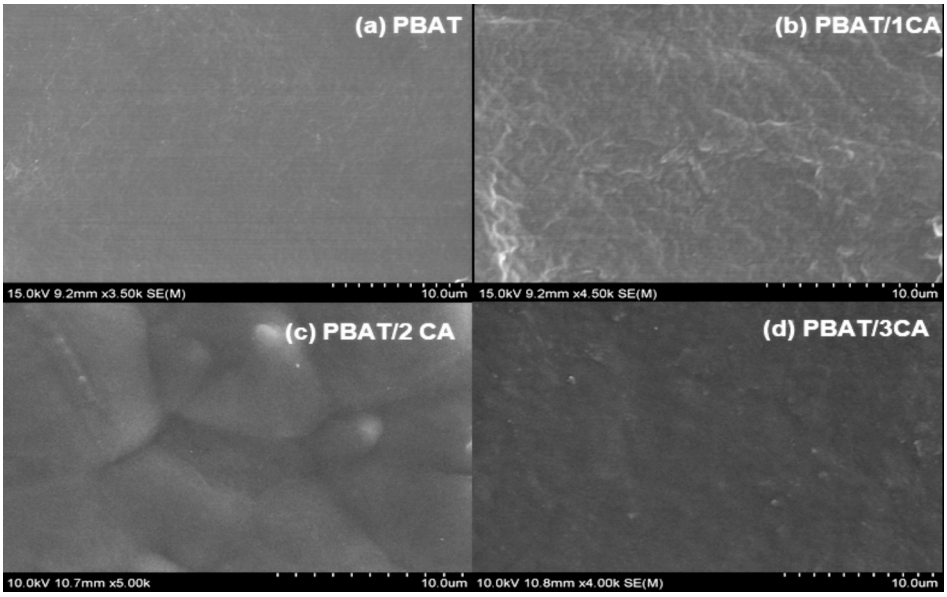

Fig. 1. (a) FE-SEM images of PBAT film, (b) PBAT/1CA, (c) PBAT/2CA, and (d) PBAT/3CA.

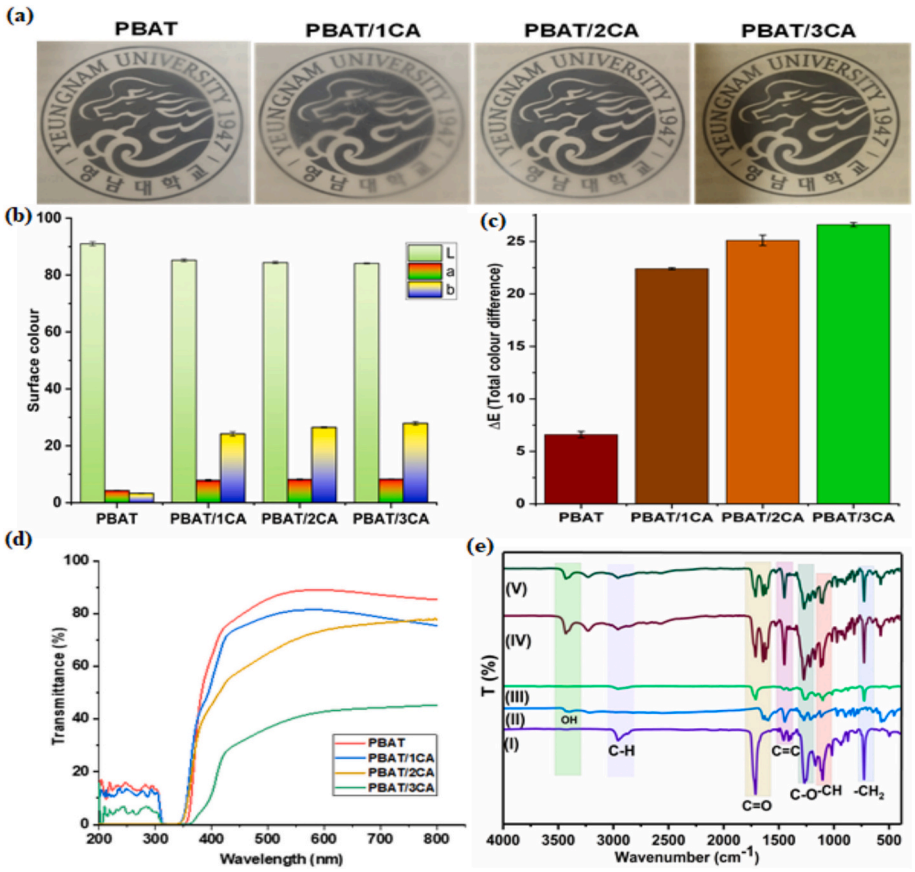

Fig. 2. (a) PBAT and PBAT/CA films, (b) surface color, (c) total color difference, (d) UV–Vis transmittance, (e) FTIR spectrum (I-PBAT, II-Caffeic acid, III-PBAT/1CA, IV-PBAT/2CA and V-PBAT/3CA).

films have the advantage of extending the life film as well as storing the quality and nutrients of food for the long term [23].

3.3. FTIR analysis

The FTIR spectra of PBAT, CA, and their various composites (PBAT/1CA, PBAT/2CA, and PBAT/3CA) reveal the presence of different functional groups within the spectrum range of 4000–500 cm^{-1} (Fig. 2 (e)). A band observed at 3435–3428 cm^{-1} in the FTIR spectra corresponds to the hydroxy group (-OH) present in CA (Fig. 2(e.II)). In PBAT/CA films, the absence of the -OH band suggests that PBAT suppresses the hydroxy group of CA at lower concentrations. The characteristic

stretching vibration observed at 2971–2963 cm^{-1} is attributed to the C—H group. An intense band observed at 1716–1714 cm^{-1} is associated with the carbonyl group (C=O) of PBAT [24]. The intense band observed at 1650–1614 cm^{-1} is associated with the carbonyl group (C=O) of CA. Bands at 1635–1647 cm^{-1} and 1451–1461 cm^{-1} are attributed to bending vibrations of the.

C=C group [25]. Band at 1279–1271 cm^{-1} correspond to the C—O linkage. Bands at 1116 and 1110 cm^{-1} indicate the -CH linkage in the polymer. Lastly, the peak ranging from 728 to 729 cm^{-1} is attributed to the methylene ($-CH_2$) groups present in the polymer backbone chains [26].

3.4. Thermal properties

In the packaging industry, additives are often used to decrease the impact of temperature changes in food [26]. The results of TGA and derivative thermo-gravimetric (DTG) presented in Fig. 3 (a-b) and Table 1. The thermal stability of a material mostly depends on the bond-breaking energy with respect to heat. The PBAT and PBAT/CA composite films are stable with minimal weight loss up to 300 °C. The maximum weight loss in PBAT occurs at 377 °C. After the addition of CA from 1 to 3 % the maximum weight loss is observed between 399 °C and 400 °C. It is well known that during thermal degradation processes, free radicals are generated [27]. The phenolic nature of CA provides anti-radical activity, and therefore we can hypothesize that including this natural product in the composite can work as a free radical scavenger and therefore enhance thermal stability when compared to PBAT film. The residue obtained at 600 °C in PBAT is 4 % and after the addition of caffeic acid, the residue percentage increased up to 7 %.

Table 1
Mechanical properties and TGA values of films.

Film	Thickness (μm)	TS (MPa)	EB (%)	T_{min} (°C)	T_{max} (°C)	$R_{\%}$
PBAT	109.1 ± 3.5[a]	18.1 ± 1.1[a]	846.3 ± 15.4[a]	351	377	4.0
PBAT/1CA	116.8 ± 2.6[b]	22.6 ± 0.6[b]	939.9 ± 22.8[b]	368	398	4.1
PBAT/2CA	120.5 ± 1.7[b]	23.1 ± 0.8[b]	988.0 ± 11.7[c]	370	399	7.2
PBAT/3CA	122.2 ± 3.0[b]	25.5 ± 0.5[c]	1055.4 ± 10.5[d]	370	400	7.4

3.5. Mechanical properties

The mechanical strength of packaging material is an important aspect concerning storage and processing [21]. Fig. 3(c) represents stress versus strain curves after blending of CA. The tensile strength of PBAT is 18.1 ± 1.1 MPa with thickness of 109.1 ± 3.5 μm as shown in Table S1, PBAT/CA1, PBAT/CA2 and PBAT/CA3 show 22.6 ± 0.6 MPa, 23.1 ± 0.8 MPa and 25.5 ± 0.5 MPa tensile strength with the thickness of 116.8 ± 2.6, 120.5 ± 1.7, and 122.2 ± 3.0 μm, respectively. The curve shows that PBAT has lower tensile strength compared to PBAT/CA composite. The PBAT shows a lower elongation break of 846.3 ± 15.4 %. The influence of the CA ratio can be observed, which shows that as the ratio of CA increases the elasticity in the film increases gradually from 939.9 ± 22.8 % to 1055.4 ± 10.5 %. This shows that increasing the CA ratio leads to an increase in the mechanical bond-breaking energy, due to an increase in hydrogen bond interactions [23]. The tensile strength of the film has not much influence by an increase in the CA ratio. The results were depicted in Table 1.

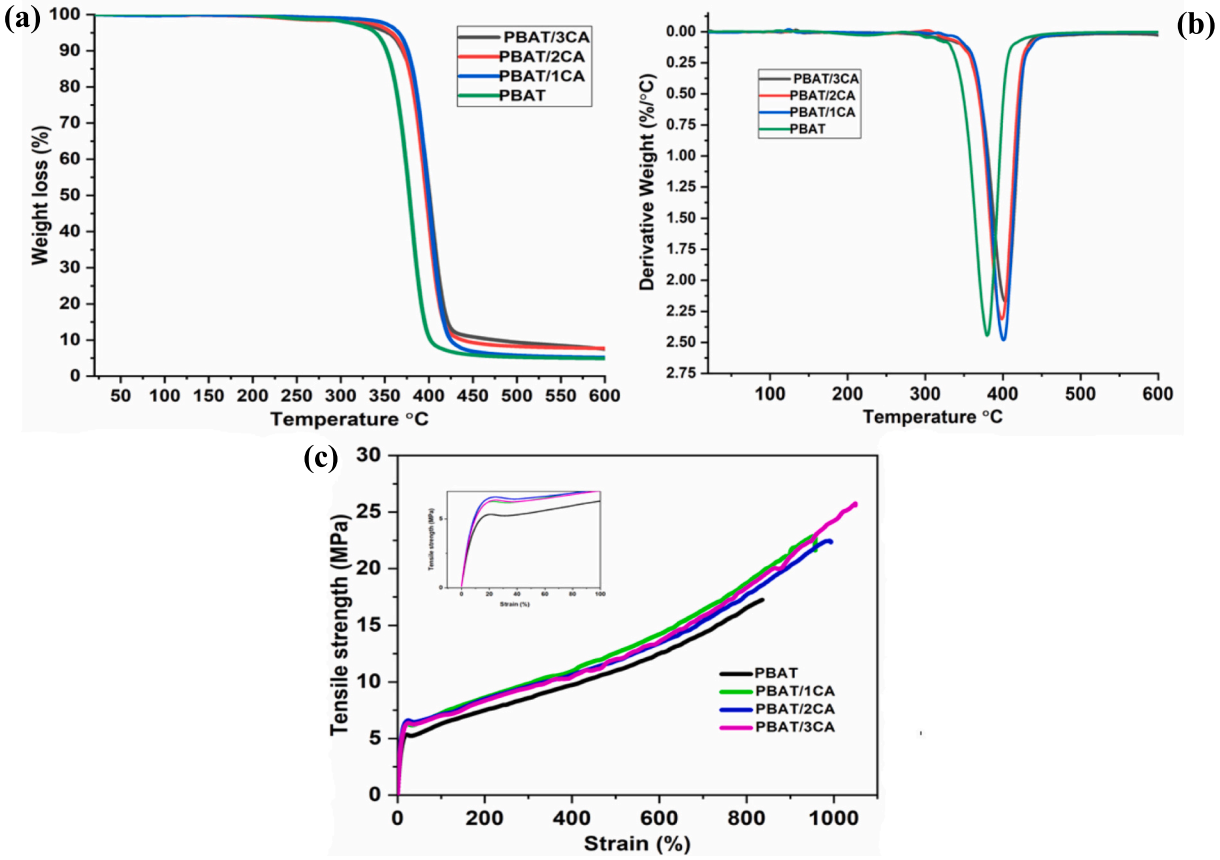

Fig. 3. (a) TGA curve of PBAT and PBAT/CA (1,2,3) blends; (b) DTG curve of PBAT and PBAT/CA (1, 2, 3) blends; and (c) Stress and strain curve of PBAT, and PBAT/CA (1, 2, 3) blends (inset: expansion from 0 to 100 %).

3.6. Water contact angle

The WCA of the PBAT-based films are presented in Table S2. The water contact angle determines the surface wettability. Fig. 4(a) represents the water contact angle of PBAT (84.4° ± 4.9°) which shows higher WCA that is due to its hydrophobic nature. Fig. 4(b, c, d) WCA of PBAT/CA1 (76.4° ± 3.5°), PBAT/CA2 (70.1° ± 1.5°) and PBAT/CA3 (60.5° ± 1.34°) indicates an increase in CA, decreases WCA. The hydrophilic group present in CA, as well as carboxyl group (-COOH), might increase the surface energy in PBAT/CA blends which leads to an increase in interaction with water molecules. The CA increase the surface smoothness with little irregularities, which lowers the WCA.

3.7. Water vapor permeability

Fig. 4(e) shows the WVP results of PBAT and its blend films. The WVP of the neat PBAT film was $4.12 \pm 0.3 \times 10^{-11}$ g.m/m^2.Pa.s, which was decreased significantly ($p < 0.05$) by the addition of different concentrations of CA and reached $3.05 \pm 0.1 \times 10^{-11}$ g.m/m^2.Pa.s for PBAT/3CA.The incorporation of CA creates a non-continuous phase in the polymer matrix, changing the free volume of the polymer interface and thereby reducing the passage of polar water vapor molecules. Moreover, the incorporation of CA can occupy interchain voids, forming a compact network structure that enhances the film's barrier characteristics against water vapor diffusion [23]. The reduced WVP in packaging films plays a crucial role in extending food shelf life by slowing down the transfer rate of atmospheric vapors to packaged food, consequently minimizing oxidative spoilage [28].

3.8. Antibacterial activity

The antibacterial activity is an important criterion in the field of food packaging [28]. As anticipated, the PBAT film, which was kept tidy, exhibited no bactericidal properties. However, the films that had CA added to them showed significant antibacterial activity against both L. *monocytogenes* and *E. coli*, as seen in Fig. 5 (a) and (b) respectively. The ability of CA to cause environmental hyper acidification has been linked to its antibacterial properties. By donating protons to the plasma membrane, bacteria cells are destroyed. Similar action on the intracellular cytosolic results in the suppression of the enzyme H^+- ATPase, which is required for the generation of ATP [29]. It has been suggested that the phenolic hydroxy group may function as a proton exchanger and reduce the pH gradient across the cytoplasmic membrane. The proton-driven force collapses as a result, and the ATP pool is depleted. CA can also alter the bacterial membrane's electric potential by quenching free electrons from the electron transport chain or by interfering with proton outflow by inactivating dehydrogenases. Since the oxidative phosphorylation reaction cannot take place, the growth of the bacteria may be hindered or even inhibited as a result [30]. The possible mechanism of the CA is presented in Fig. 6. Our research shows that higher CA content in the composites leads to higher antibacterial activity and as a result, all manufactured materials were categorized as antibacterial.

3.9. Antioxidant activity

Evaluating the antioxidant properties is crucial for packaging films as it can potentially extend the food's shelf life by halting the oxidation of lipids and other food components [31,32]. Fig. 5(c) shows the antioxidant effect of the PBAT/CA films. The neat PBAT film exhibited negligible antioxidant activity. The PBAT film with 1 wt% CA exhibited 100 % DPPH$^\bullet$ scavenging capacity and 98.5 % ABTS$^{\bullet+}$. With the addition of 2 and 3 wt% of CA, the radical scavenging capacity of composite films reached 100 % for ABTS$^{\bullet+}$ radical scavenging assay. The superb antioxidant capacity of the composite films is due to the radical scavenging capacity of the added CA. The fundamental factor contributing to CA's superior free radical scavenging ability is its possession of a catechol moiety within its molecular structure. Phenolic hydroxy groups can act as a potent electron donor, imparting antioxidant performance to the CA. Furthermore, the steric hindrance effect between the hydroxy groups at the C3 and C4 positions of the caffeic acid molecule facilitates the electron contribution of the phenolic hydroxyl group [29]. The obtained results suggest the potential of the designed PBAT/CA film for various industrial applications, particularly for oxidation-sensitive or oxidation-prone food items. Comparison of antioxidant property of proposed PBAT/CA with published reports presented in Table S3.

3.10. Real-time application

It has been demonstrated that the UV barrier and antioxidant properties play an essential role in food packaging. To analyze the capability of PBAT/CA film in vegetable (carrot) packaging applications, sliced carrots were wrapped in the developed films. Sliced carrot test samples have been stored and evaluated for antimicrobial resistance to gauge the potential for food preservation. The differences between preserving the chopped carrot fragments within the commercial polyethylene and wrapping them in PBAT/3CA film for 11 days in terms of the visual modifications are depicted in Fig. 7. Carrot slices that were stored for 11 days and exposed to air revealed a higher level of bacterial growth when wrapped in commercial film than exposed carrot pieces enclosed with

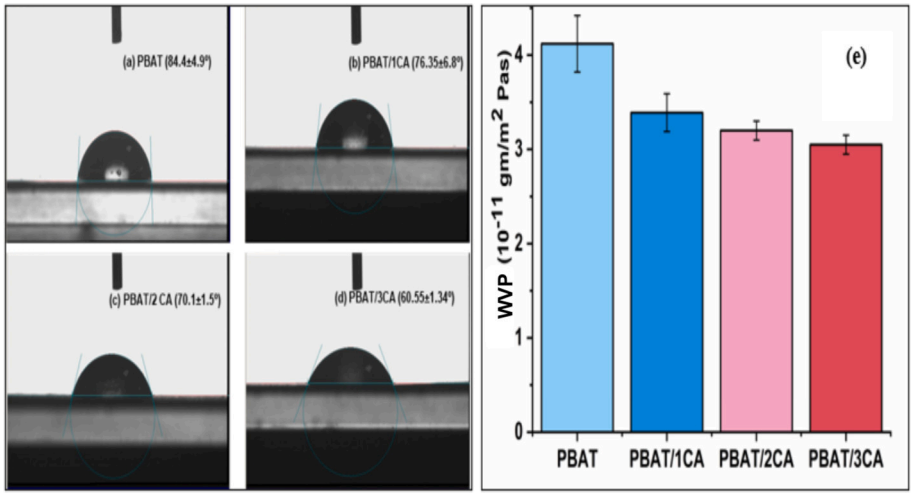

Fig. 4. (a) Water contact angle of PBAT, (b) PBAT/1CA, (c) PBAT/2CA, (d) PBAT/3CA, and (e) WVP of PBAT and PBAT/CA (1, 2, 3 %) blends.

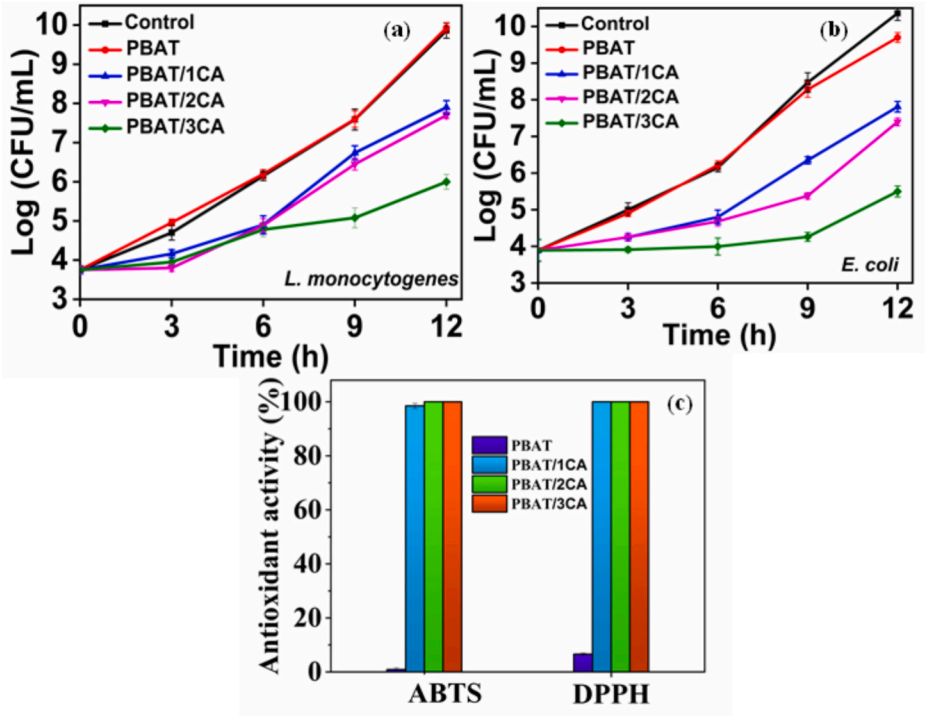

Fig. 5. Antibacterial activity against (a) *L. monocytogenes*, (b) *E. coli* and (c) antioxidant activity results of PBAT, PBAT/CA (1, 2, 3) blends.

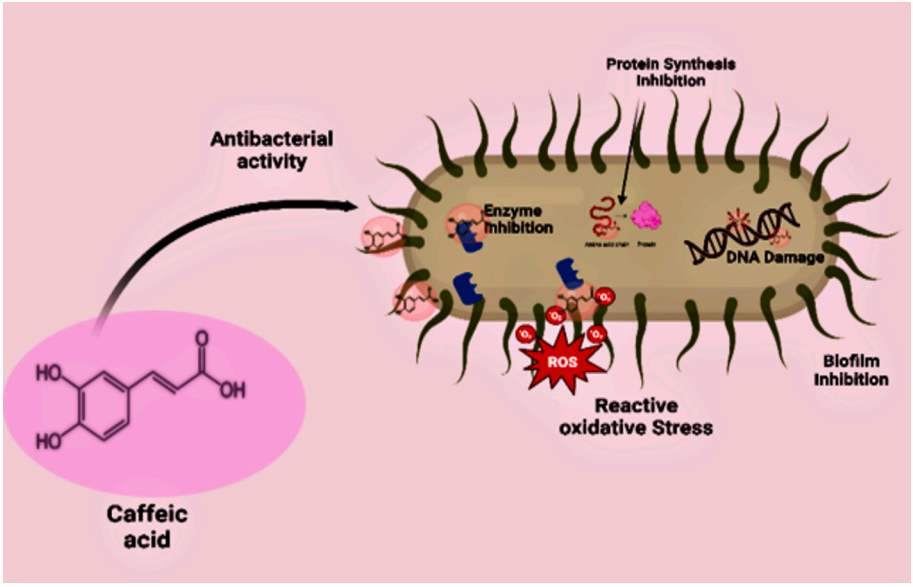

Fig. 6. Hypothesized antibacterial mechanism of CA.

PBAT/3CA composite film. Furthermore, compared to the other two samples, the carrot pieces covered in PBAT/3CA film typically had a greater odor, color, and texture. Thus, the PBAT/3CA film comes under the category of food packaging films that have excellent antibacterial properties and food preservation qualities. As a result, the coating keeps food safe and harmless while protecting it from external factors. Accordingly, the prepared PBAT/3CA composite materials are appropriate for applications requiring active food packaging. Notable variations are evident in the antimicrobial effectiveness of each treatment within an invitro model system for fresh carrot slices. The PBAT/3CA film control the growth of microorganisms during 11 days storage, validating the antimicrobial activity of the fabricated film toward food born pathogenic bacteria. As depicted in Fig. 8, all groups faced an increase in weight loss during storage, with control (openair) showing a more noticeable effect compared to those wrapped in PBAT/3CA blend films. The main cause for weight loss in packed fresh carrot slice is attributed to loss of water due to moisture evaporation [33]. The slice shrinkage observed in the open-air group sample and the accumulation of moisture in the commercial film highlight the significant water loss in the carrot slice. The newly fabricated PBAT/3CA films reduce the weight loss of slice due to control the moisture evaporation from the carrot slice.

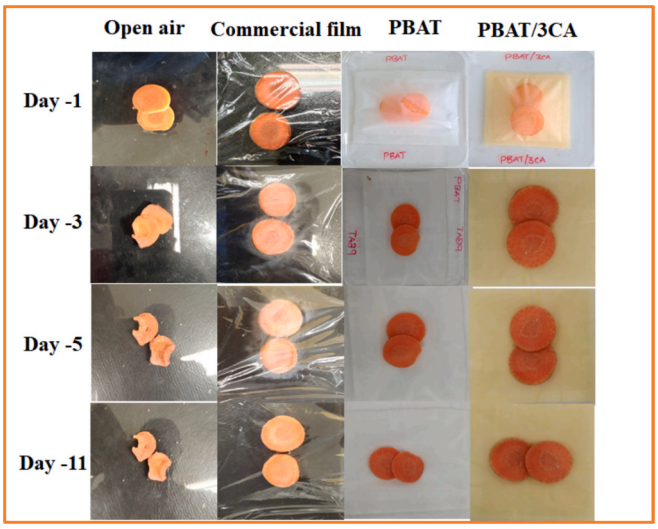

Fig. 7. Images of food quality test using carrot with open air, commercial film, PBAT, and PBAT/3CA composites.

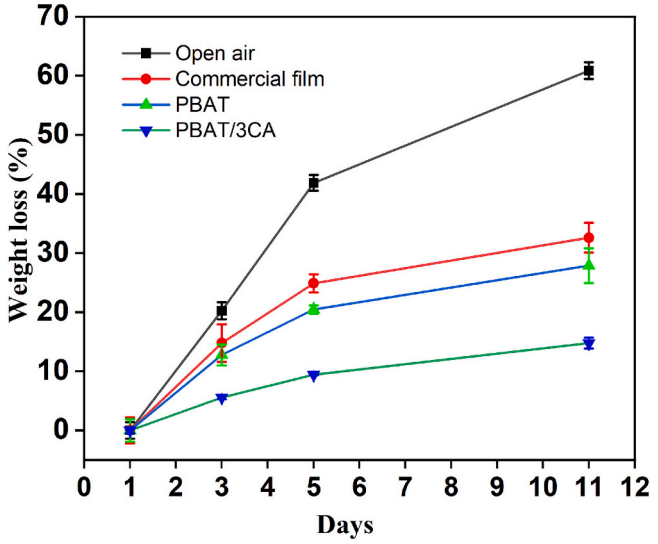

Fig. 8. Weight loss of carrot slice during the storage.

4. Conclusions

PBAT/CA composite films were formulated using solution-casting method. The influence of CA on PBAT was analyzed using SEM, optical, antibacterial, antioxidant, mechanical, and thermal methodologies. The morphological study shows that increasing CA content in the PBAT can lead to surface roughness. The addition of CA shows excellent UV barrier properties, as well as thermal and mechanical stability. The WVP of PBAT film was $4.12 \pm 0.3 \times 10^{-11}$ g.m/m^2.Pa.s, decreased to $3.05 \pm 0.1 \times 10^{-11}$ g.m/m^2.Pa.s, for PBAT/3CA and water contact angle decreases with increasing the CA concentration. The antibacterial efficacy against L. *monocytogenes* and *E. coli* has been shown to significantly increase with the inclusion of the studied natural product in the PBAT film. Thus, PBAT film combined with CA has demonstrated excellent antioxidant activity against $ABTS^{\bullet+}$ and DPPH radical assay, which can prevent undesirable photochemical reactions and the growth of harmful bacteria in edible goods. All the aforementioned attributes indicate the immense potential of PBAT/CA films in the food packaging sector.

CRediT authorship contribution statement

Siva Sankar Sana: Writing – original draft, Methodology, Investigation, Conceptualization. **Zohreh Riahi:** Writing – review & editing, Writing – original draft, Conceptualization. **Vijayalaxmi Mishra:** Writing – review & editing. **Jun Tae Kim:** Writing – review & editing, Formal analysis, Data curation. **Ramakrishna Vadde:** Writing – review & editing. **Pedro Brandão:** Writing – review & editing, Writing – original draft. **Seong-Cheol Kim:** Supervision, Resources. **Pedro Fonte:** Resources, Project administration, Funding acquisition.

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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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.reactfunctpolym.2025.106413.

Data availability

Data will be made available on request.

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