Articles

2020-02-27

Ferulic Acid Incorporated Active Films Based on Poly(lactide) /Poly(butylene Adipate-co-Terephthalate) Blend for Food Packaging

Shubham Sharma
Technological University Dublin, d17127955@mytudublin.ie

Amit Jaiswal
Technological University Dublin, amit.jaiswal@tudublin.ie

Brendan Duffy
CREST, TU Dublin, brendan.duffy@tudublin.ie

See next page for additional authors
Follow this and additional works at: https://arrow.tudublin.ie/schfsehart

Part of the Food Biotechnology Commons, Food Chemistry Commons, Food Microbiology Commons, and the Food Processing Commons

Recommended Citation

Authors

Shubham Sharma, Amit Jaiswal, Brendan Duffy, and Swarna Jaiswal
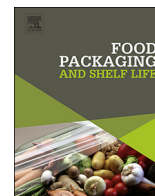
Ferulic acid incorporated active films based on poly(lactide) /poly(butylene adipate-co-terephthalate) blend for food packaging

Shubham Sharma[a,b], Amit K. Jaiswal[a,*], Brendan Duffy[b], Swarna Jaiswal[a]

[a] School of Food Science and Environmental Health, College of Sciences and Health, Technological University Dublin-City Campus, Cathal Brugha Street, Dublin, D01 HV58, Ireland
[b] Centre for Research in Engineering and Surface Technology (CREST), FOCAS Institute, Technological University Dublin-City Campus, Kevin Street, Dublin, D08 NF82, Ireland

ARTICLE INFO

ABSTRACT

Active natural antibacterial blend of poly(lactide) - poly(butylene adipate-co-terephthalate) (PLA-PBAT) incorporated with ferulic acid was formed by solvent casting method. The influences of FA on the structural, colour, optical, thermostability, and antibacterial efficiency of PLA-PBAT blend films were studied. On the incorporation of the FA, thickness of the film was increased by 1.5–10 %. The tensile strength (TS) of the FA incorporated blend film increased to a value of 10.78 MPa at 10 wt% as compared to the control film which has 5.42 MPa. The temperature of degradation of the film increases as the FA content increases in the film. Antibacterial activity has been observed to increase due to the inclusion of the phenolic compound in the composite film against *Listeria monocytogenes* and *Escherichia coli*. The composite film has a potential application as an active food packaging due to its antibacterial and UV-light barrier properties.

1. Introduction

Plastic materials have been an inevitable part of human life as they are convenient to use, lightweight, cheap, possess good physicochemical and processing properties. Use of plastics as a packaging material for food and beverages had increased widely in the form of cups, bottles, tubs, trays, sheets, and films. Plastics are conventionally manufactured from fossil fuels consuming finite and non- renewable resources. The increasing use of conventional plastics leads to an increase in the universal problem of plastic waste. A substantial volume of plastic waste has been deposited in the water bodies, landfill or the recovery sites where their classification or recovery demands both money and energy. The death records of the birds and sea animals have also increased due to the detrimental effect of plastics. As a result, focus is moved from conventional plastic which has limited disposal method and adverse environmental effect, to bioplastic which are bio-based and environmentally friendly.

Numerous polymers of biological or fossil origin (biodegradable/ non-biodegradable) are used in various applications such as textile, building and construction, packaging etc. According to Vert et al. (2012) bio-based plastics are composed of the biological product in parts or in whole derived from the biomass such as animal, plant, and marine materials. According to the reports, the largest application of

the bioplastics is in the area of packaging with almost 1.6 million tonnes (40 %) of the total bioplastics market in 2016 (Vert et al., 2012).

Biodegradable plastics are those polymeric substances which are susceptible to degradation under optimum conditions like temperature, humidity, pH and oxygen availability (Argente, 2018; Vert et al., 2012). The worldwide production capacities had significantly increased for the production of the bio-based (biodegradable and non-biodegradable) plastics such as bio-based polyethylene (PE), bio-based polyethylene terephthalate (PET), poly(butylene adipate-co-terephthalate) (PBAT), poly-hydroxy alkanoates (PHA) etc. in 2016 (Nova-Institute, 2016).

PLA shows properties like mechanical strength, light transmission, transparency, rigidity and low cost which makes it the most promising polymer; however, brittleness, low melt strength, and low thermal stability limit its application. It was observed that, these properties restrict its use in the processes like blow molding and blown film extrusion (Agwuncha, Ray, Jayaramudu, Khoathane, & Sadiku, 2015; Jiang, Wolcott, & Zhang, 2006; Zhang et al., 2015). Recent studies suggest that, the best solution to increase the properties of PLA is to blend with a flexible polymer (Al-Itry, Lamnawar, & Maazouz, 2012; Arruda, Magaton, Bretas, & Ueki, 2015; Chen, Abdelwahab, Misra, & Mohanty, 2014; Shankar & Rhim, 2018; Wang, Rhim, & Hong, 2016). Poly(butylene adipate-co-terephthalate) (PBAT) can be considered for its blending with PLA due to its properties like flexibility, resilience,

---

and biodegradability (Moustafa, El Kissi, Abou-Kandil, Abdel-Aziz, & Dufresne, 2017).

The composite blend could be enriched more by the incorporation of functional materials such as those which possess mechanical, antioxidant, or antibacterial property. Barbosa et al. (2019), had incorporated organoclay in the PLA-PBAT blend and observed that the addition of clay had changed the morphology of the PLA-PBAT blend hence enhancing the mechanical property of the bio-nanocomposites. The internal environment of the packed food is positively influenced by the active packaging (Sharma, Jaiswal, Duffy, & Jaiswal, 2019). The active functional property of the composite in the food packaging material may enhance the food shelf-life by protecting it from the physical, chemical and the biological degradation, reducing the risk of microbial contamination and subsequently illnesses caused by foodborne pathogens (Llorens, Lloret, Picouet, Trbojevich, & Fernandez, 2012; Argente, 2018). In order to form an antibacterial composite, a compound with antibacterial property can be blended with the base polymer. Shankar and Rhim (2019), had incorporated Zinc oxide Nanoparticle in the PLA-PBAT blend and observed that the composite film possess strong antibacterial property (Shankar & Rhim, 2019). Significant increase in recent years have been observed in the use of natural antibacterial agents from plant source such as polyphenols, essential oils etc. due to its eminent biological properties.

Ferulic Acid (FA) is also known as 4-hydroxy-3-methoxycinnamic acid; is an abundant phenolic acid, ubiquitously present in the plant cell wall (Ou & Kwok, 2004). FA possess cross-linking property with both polysaccharides and biopolymers, and can be utilized in the development of complex gels and films for food industry applications (Graf, 1992; Ou & Kwok, 2004). FA is observed to increase the mechanical properties of the film such as tensile strength, elastic modulus, elongation at break and the antioxidant property on the soy protein film and starch-chitosan films (Mathew & Abraham, 2008; Ou, Wang, Tang, Huang, & Jackson, 2005). Kasmi, Gallos, Beaugrand, Paës, and Allais (2019) had used FA as the biobased powder for appropriate plasticisation of PLA. In this study, FA reduces the stiffness of PLA without and chemical degradation. Moreover, the resultant film formed was observed to be more suitable for storage and processing with polymers by the hot melt process rather than the common plasticisers such as PEG, glycerol etc. (Kasmi et al., 2019). The FA has also promising broad spectrum antibacterial results in various studies (Kwon et al., 1997; Pernin, Bosc, Maillard, & Dubois-Brissonnet, 2019; Piotrowski et al., 2015).

In the present study, solution casting method is used to incorporate FA as an antibacterial agent in a PLA/PBAT blend film. To the best of our knowledge, it is the first report to incorporate FA at several concentration (1, 5 and 10 wt%) in the PLA-PBAT blend film. Property characterization by the influence of FA in the composite film was studied at various aspects such as structural, functional and thermal properties.

2. Materials and methods

2.1. Materials

Poly(lactide) (PLA, Synterra BF 2004; average molecular weight of 200 kDa) was purchased from Helian Polymer (Belfeld, Netherland). PBAT (Ecoworld PBAT003; m.p. $110-120\,^{\circ}$C, the density of 1.26 g/cm^3) was obtained from Helian Polymer (Belfeld, Netherland). Chloroform was obtained from Sigma Aldrich (Ireland) and ethanol was obtained from Merck KGaA (Germany). Ferulic acid (MW: 194.18 g/mol, MP: 168–172 °C) was obtained from Sigma Aldrich, Gillingham, UK. Brain heart infusion broth (BHI), tryptic soy broth (TSB), and agar powder were procured from Sigma Aldrich (Ireland). Foodborne bacterial pathogens, *Escherichia coli* (NCTC 9001) and *Listeria monocytogenes* (NCTC 7973) were used in the study. For further testing, strains were grown in the agar media and stored at 4 °C.

2.2. Preparation of composite films

Solvent casting method was used to form composite blend film of PLA/PBAT with ferulic acid. According to Wang et al. (2016) the bend was prepared in the ratio of 98:2 of the PLA and PBAT (Wang et al., 2016). 100 mg FA/mL absolute ethanol solution was formed by dissolving 10 g of FA in 100 mL of absolute ethanol. Various amount of FA solution (0.4 mL, 2.0 mL, and 4 mL which is equivalent to 1%, 5%, and 10 % of the Wt% of polymer resin) was added in 100 mL chloroform. The volume was made up to 4.0 mL by adding ethanol. PLA (3.92 g) and PBAT (0.08 g) were added to the prepared FA solution and the blend was dissolved by continuous stirring for 24 h at room temperature. By following same procedure PLA-PBAT control composite film was prepared by adding 4.0 mL ethanol (without FA). The solution formed was transferred on a Teflon coated glass plate (24 cm × 30 cm), evenly spread with the help of bent glass rod and dried at room temperature for 24 h. The dried film was casted off from the glass plate. The film was conditioned at 50 % relative humidity (RH) and 25 °C temperature for at least 48 h. The films prepared were labelled as PLA-PBAT, PLA-PBAT_FA[1%], PLA-PBAT_FA[5%], and PLA-PBAT_FA10 %.

2.3. Film characterization

2.3.1. Morphological observations

To analyse the microstructural morphology of the surface as well as the film cross-sectional area, scanning electron microscopy (SEM) (Hitachi SU70) was used. Liquid nitrogen was used to freeze fracture the film. A small piece of sample prepared was mounted on the sample holder of SEM for observing of the morphology of the surface. Analysis of the image was done with a 5-kV accelerating voltage.

2.3.2. Surface colour and optical properties

Colour of the films surface was measured using a colorimeter (ColorQuest XE, HunterLab) having a standard background plate of white colour. The colour parameters obtained through reflectance values were L (lightness), a (red-green) and b (yellow-blue). For the uniformity in the measurement of colour three readings were acquired for each duplicate by changing the position of the sample. Standard background values of white colour plate were set as L = 97.75, a = -0.42, and b = 1.83. Average of 5 readings were taken for the determination of Hunter colour values (L, a, and b) from each film sample. Determination of total colour difference (ΔE) was as follows:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

where ΔL, Δa, and Δb represents the differences between standard colour value of each colour plate and sample film, respectively (Wang et al., 2016).

UV-Vis spectrophotometer is used for measuring the optical properties using the light transmittance spectra. Rectangular films (3 cm × 7 cm) were cut and mounted between two magnetic cells of spectrophotometer. Percent transmittance at 280 nm (T280) and 660 nm (T660) was determined for the UV-light barrier and transparency.

Attenuated total reflectance-Fourier transform infrared (AT-FTIR) spectrophotometer was used for the measurement of Fourier transform infrared (FT-IR) spectra of the films, operated at a resolution of 4 cm^{-1}. 4 cm × 4 cm samples of the film were cut and placed directly on the ray exposing stage. The spectrum was recorded at wavenumber of 4000–500 cm^{-1}.

2.3.3. Thickness and mechanical properties of the films

Digital micrometer (Mitutoyo, Japan) having resolution 0.001 mm was used to measure the thickness of the film samples. Each film was assessed at three random locations with the sensitivity of 1 μm. Standard ASTM D 882–88 method was used by Instron Universal
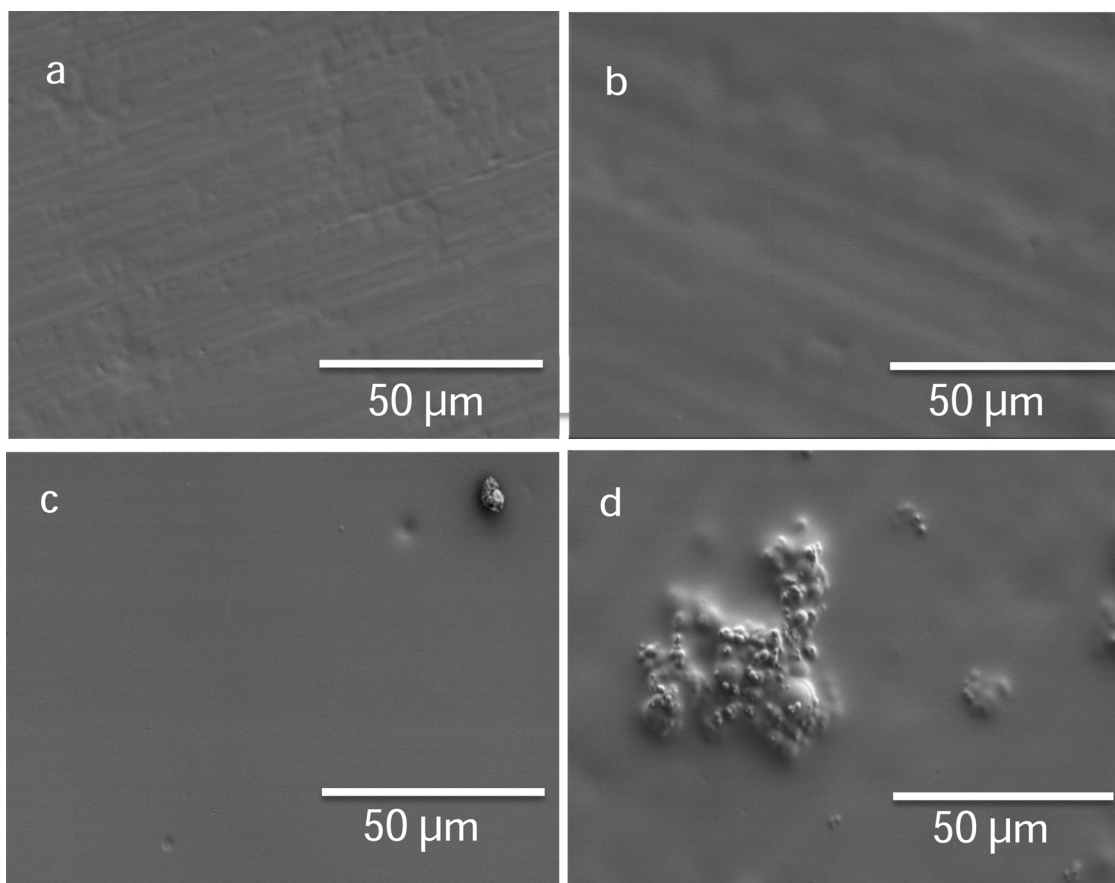
Fig. 1. SEM micrographs of the blend surface (a) PLA/PBAT (b) PLA/ PBAT-FA1%, (c) PLA/ PBAT-FA 5%, (d) PLA/ PBAT-FA10 %.

Testing (Model 5565, Instron Engineering Corporation, Canton, MA, USA). Tensile properties such as tensile strength (TS), elastic modulus (EM) and elongation at break (EB) of each film was measured. TS was measured in MPa. Film samples were cut into rectangular strips of 3 cm × 15 cm. 50 mm of grip length and a 50 mm/min crosshead speed using a 500 N load cell were used to operate the Instron Instrument. Following equation was used for the calculation:

$$TS = F/A$$

where F represents maximum force (N) required to pull the sample apart and A stands for the films initial cross-sectional area (m^2).

Tensile elongation at break (*EB*) or fracture strain was calculated as follows:

$$EB\ (\%) = [(X_f - X_o)/ X_o]\ x\ 100$$

X_f depicts elongation of the film at the failure and X_o is the initial grip separation (50 mm) of samples.

The EM (GPa) measures the resistance of the film from being elastically deformed. The stress–strain curve in the region of elastic deformation defines the elastic modulus which corresponds to the stress divided by the strain of the film sample. The average of the five measurements for each film was obtained.

2.3.4. Surface hydrophobicity

Water Contact Angle (WCA) was determined by using WCA analyser (FTA-200 systems) to determine surface hydrophobicity of the composite film. Rectangular strips (3 cm × 8 cm) was cut and placed on the moveable stage having WCA analyser attached. A micro syringe was used to place a drop of water (~ 10 μL) on the surface of the sample film and the WCA was determined on both sides of the water droplet considering horizontal level and symmetry. Water droplet of definite

volume was placed on the surface of the film sample in the horizontal position. High-speed camera recorded the formation of drop and final shape and the image processed by computer. All experiments were carried out in triplicate and the mean values reported.

2.3.5. Thermal stability

Thermogravimetric analyser (TGA) measured the thermal stability of the films. Film samples about 9 mg each was scanned at the temperature ranged from 30 to 500 °C at the heating rate of 10 °C/min. The weight loss (%) and the maximum decomposition temperature (Tmax) of films was determined from the TGA curve.

2.3.6. Antibacterial activity

The antibacterial property of the blend film was determined by using viable colony count method against foodborne pathogenic bacteria, *L. monocytogenes* (Gram-positive) and *E. coli* (Gram-negative) (Shankar, Rhim, & Won, 2018). For the sterilization of the film samples, 100 mg of the sample was measured and kept for 20 min. under ultraviolet light. Test microorganisms (*E. coli* (NCTC 900) and *L. monocytogenes* (NCTC 7973)) were inoculated aseptically in the Tryptic Soy Broth (TSB) and Brain Heart Infusion (BHI) broth, respectively, and incubated at 37 °C for 18 ± 2 h. The overnight culture was diluted to obtain 10^8 CFU/mL bacterial population. To obtain the initial bacterial population of 10^6 CFU/mL, 200 μL of the diluted inoculum was transferred aseptically to 20 mL of TSB and BHI broth to obtain the initial concentration of bacteria. 100 mg of the film samples were also added to the inoculated broth and incubated for 15 h at 37 °C at 200 rpm. In the interval of every three hours samples were taken from the broth culture, diluted appropriately and plated on agar plates for the determination of viable cell counts. Same procedure was used for the comparative testing of the culture broth without film, culture broth

with control film (without FA) and culture broth with FA (1%, 5% and 10 %) blend film. All antibacterial tests were performed in triplicate.

2.4. Statistical analysis

Determination of each property of the film's samples were performed in triplicate with individually prepared film samples. STATG-RAPHICS Centurion XV software (Stat Point Technologies Inc. Warrenton, VA, USA) was used for the study of significant difference by analysis of variance (ANOVA) and the multiple comparisons (Fischer's least significant difference test). For the significant value $p < 0.05$ was considered. All results are expressed as mean $\pm$ standard deviation.

3. Results and discussion

3.1. Characterization of blend films

3.1.1. Morphology of the surface

The microstructure of PLA/PBAT composite film and the effect of the incorporation of FA in the blend film was studied by SEM as shown in Fig. 1. Various authors has eminently reported the incompatibility between PLA and PBAT (Jiang et al., 2006; Yeh et al., 2010). The blend surface under high magnification had showed a slight rough surface of the PLA/PBAT blend film due to the uneven distribution of PBAT particle on the PLA matrix. Yeh et al. (2010) studied there may be solubility difference between PLA and PBAT polymer which may be due to the PBAT repeating units which are extended and has high flexibility as compared to PLA resins (Yeh et al., 2010). It might be due to the huge difference in the solubility constraints of PLA and PBAT (Moustafa et al., 2017; Siemann, 1992). Chloroform provides a common solubility platform to both PLA and PBAT resins but the phase separation between the them can occur due to the chloroform evaporation and drying of the films (Shankar & Rhim, 2018). A homogeneous film was observed at the low concentration of FA (1 and 5 wt%) in the blend film. The smoothness of the film also depends on the concentration of FA. At 1% and 5% FA concentration the film is observed to be clear and smooth similar to the control film (without FA). At 10 wt% FA concentration small FA particles were observed which were due to the increase in the FA content in the film.

3.1.2. Surface colour and optical properties

The control film and composite film with low concentration of FA (1 and 5 wt%) were visually transparent, smooth, and homogeneous while the composite film with higher FA concentration (10 %) was observed to be translucent and rough. The PLA/PBAT control film was colourless and transparent while the blend films incorporated with FA were slightly translucent with a tint of whitish colour. It was observed that as the concentration of FA is increased from 1% to 10 %, there was also enhancement in whiteness. The light transmittance property and the observations of surface colour are shown in Table 1.

No significant difference ($P < 0.05$) in the lightness was observed. The values of hunter a-value (greenness) and hunter b-value (yellowness) significantly increased after the incorporation of FA. The linear increase in the hunter b-value of PLA/PBAT was observed with increase in the FA content (1, 5 and 10 wt%) signifying the increase in

yellowness of the film samples.

UV blocking property of the packaging material is a necessity in order to avoid the deterioration of food due to photo-oxidation reaction caused by ultraviolet rays. Active packaging are developed which are having light absorber or blocking material in it (Kwon et al., 2018). But these blocking materials must not reduce the transparency of the packaging. PBAT film has low transparency while the PLA films has exhibited high transparency. The composite blend of PLA and PBAT is showing high transparency as the wt % ratio of PLA is higher than PBAT (98:2). Film transmittance was measured at 280 nm and 660 nm. Transmittance at 280 nm (T280) assessed the UV barrier property of the film while the transparency of the composite film was evaluated by measuring the transmittance at 660 nm (T660) as shown in Table 1.

The film of PLA/PBAT has shown high UV barrier property of 2.37 % at T280, which was due to the property of PBAT polymer to absorb UV (Shankar & Rhim, 2018; Wang et al., 2016). Incorporation of FA in the blend films led to the reduction in the UV Barrier property at T280 to 1.60 %. The reason of decrease could be absorption of UV light by the phenolic compounds of FA. Also, a substantial decrease in the transparency was found at T660. The PLA/PBAT film exhibited 78.61 % transparency while addition of FA to the film decreased the transmittance to 35.86 %, 35.75 % and 34.61 % at 1, 5 and 10 wt% of FA.

3.1.3. FTIR analysis

The FTIR spectra of the composite blend of PLA- PBAT, PLA-PBAT-FA[1%], PLA-PBAT-FA[5%], PLA-PBAT-FA10 % shows distinguishing peaks in the spectrum of 4000–500 cm^{-1} (Fig. 2). The carbonyl (C−O) stretching in the carboxylic group is represented around 1180 cm^{-1}. The peak in between the region of 1045 – 1185 cm^{-1} depicts the monosubstituted benzenes. The spectral band around 2599 cm^{-1} shows the stretching of the − OH group of the carboxylic acid which is formed because of the dehydration and the hydrolysis during the formation of PLA-PBAT blend. A stretch around 1746 cm^{-1} represents the occurrence of the stretching of carbonyl group ($> C = O$) in ester linkage. Deformation of O−H had depicted a strong peak which was also observed around 914 cm^{-1}. In all the films, a bending peak around 832 cm^{-1} was formed which depicts the presence of substituted benzene. Kumar, Mohanty, Nayak, and Parvaiz (2010) had also observed similar peaks stretching with respect to carboxylic group in the blend film (PLA-PBAT). Presence of ferulic acid is also defined by the characteristic peak of C−H stretching at 2951 – 3016 cm^{-1}. The C=C aromatic ring was observed around 1515 cm^{-1} which was not seen in the control blend film (PLA-PBAT).

3.1.4. Mechanical properties of the blend films

Mechanical strengths of the packaging film secure the food during the stress conditions such as storage, handling and processing of the food. Influence of FA incorporation on the mechanical properties of the composite films such as tensile strength (TS), fracture failure or elongation at break (EB), and elastic modulus (EM) were tested by standard ASTM D 882–88 method (Table 2). The flexibility and strength of film is defined by its TS and EB. Films thickness of the control film (PLA-PBAT) was measured at 55.27 μm which has increased from 1.5% to 7% after the integration of FA. Moreover, it was observed that the composite film thickness increased significantly ($p < 0.05$) as the FA concentration

Table 1
Light transmittance and surface colour of composite films.

Film	L (Lightness)	a (Red-Green)	b (Yellow-Blue)	Total Colour Difference (ΔE)	Transmittance T$_{(280)}$	Transmittance T$_{(660)}$
PLA/PBAT	93.4 ± 0.02[a]	− 0.38 ± 0.005[a]	2.34 ± 0.01[a]	4.38 ± 0.02[a]	2.37 ± 0.04[a]	78.61 ± 0.09[a]
PLA/ PBAT-FA[1%]	94.0 ± 0.01[b]	− 0.66 ± 0.01[b]	3.35 ± 0.05[b]	3.97 ± 0.01[b]	1.45 ± 0.06[b]	35.86 ± 0.05[b]
PLA/ PBAT-FA[5%]	94.2 ± 0.01[c]	− 0.78 ± 0.001[c]	3.63 ± 0.01[c]	3.87 ± 0.004[c]	1.62 ± 0.05[c]	35.75 ± 0.06[b]
PLA/ PBAT-FA[10%]	94.4 ± 0.02[d]	− 0.87 ± 0.01[d]	3.89 ± 0.01[d]	3.88 ± 0.01[c]	1.74 ± 0.04[d]	34.61 ± 0.12[c]

*The letters (a–d) at each concentration indicate groups that are significantly different ($P < 0.05$).
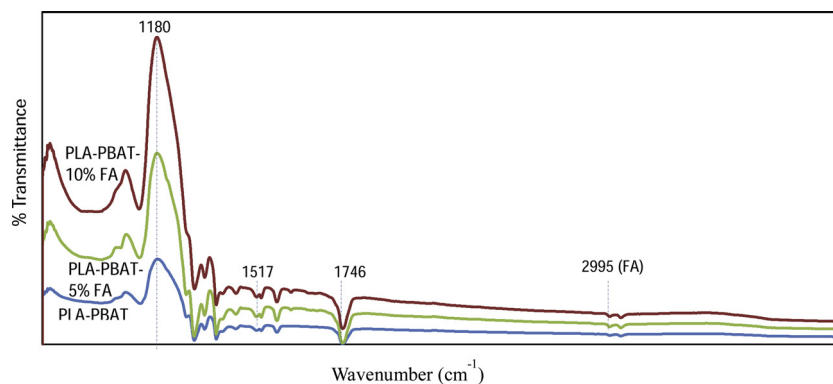
Fig. 2. FTIR spectra of PLA/PBAT blend film incorporated with FA (1%, 5% and 10 %).

increases from 1 to 10 wt%.

According to various studies individually PLA and PBAT shows distinctive mechanical properties such as PBAT is a flexible plastic with low elasticity modulus (100 MPa) and PLA is stiff plastic having greater modulus of elasticity (> 1000 MPa) (Al-Itry et al., 2012; Shankar & Rhim, 2016, 2018). The TS value of the FA incorporated blend film increased to a value of 10.78 MPa at 10 wt% as compared to the control film which has 5.42 MPa. The TS value was significantly higher ($p < 0.05$) as the FA concentratiom increases from 1 to 10 % wt%) (Table 2). Intensification in tensile strength of the blend could be due to the introduction of cross linkage by FA which results in the PLA and PBAT network stabilization (Mathew & Abraham, 2008).

Elongation at Break (EB) determines the flexibility of the blend film. The average value of EB control blend film was determined as 21.93 % which is found to be increased to 23.57 %, 22.42 % and 22.13 % of the composite film with FA concentration of 1, 5 and 10 wt% respectively. The results showed an increase in EB value of blend film in comparison to the control, however, the increment were statistically insignificant. While comparing EB value of blend films of 1, 5 and 10 wt% FA concentration, it was observed that the EB value was decreasing as the FA concentration increased (Table 2). The increase in the value of EB of the blend film containing FA in comparison to control film (without FA) can be due to the presence of FA which acts as a natural plasticizer in the blend film. Percentage decrease of EB with the increase of FA content might occur due to the decrease in the intermolecular distance and intensification of the intermolecular crosslinks (Mathew & Abraham, 2008). Study by Mattew et al. also showed the decrease in EB value due to the incorporation of ferulic acid in starch-chitosan blend film (Mathew & Abraham, 2008). Elastic Modulus (EM) measures the stiffness of the composite films. The EM value shows significant ($p < 0.05$) difference between 1 and 10 wt% of FA concentration while the FA concentration 1 and 5 wt% had shown no significant difference ($p < 0.05$).

3.1.5. Water contact angle (WCA)

Hydrophobicity of films surface was measured by water contact angle (WCA) (Table 2). The WCA of the control PLA-PBAT film was obtained to be 78.24° which is in the range (75.3° – 88.7°) obtained by Wang et al. (2016) in their study. According to the study of Vogler

(1998) the film is hydrophilic if the WCA is less than 65°. The film with low concentration of FA (1 and 5 wt%) were observed to be hydrophobic as the WCA was higher than 65° while at the incorporation of higher concentration (10 wt%) of FA the film showed slight hydrophilic nature as the WCA was observed to be less than 65° (Shankar & Rhim, 2018; Vogler, 1998). WCA of the composite film was observed to decrease significantly with the increase in the content of FA in the blend film. Woranuch and Yoksan (2013) also observed decrease in WCA on increase in the content of FA on ferulic acid-coupled chitosan film (Woranuch & Yoksan, 2013). The decrease in WCA of the film could be due to the incorporation of FA which is hydrophilic.

3.1.6. Thermogravimetric analysis

It is significant to study the thermal stability and thermal properties of the composite film in the food industry application as it may be subject to the process at higher temperature during the food packaging, transportation and storage. The TGA curve (Fig. 3) indicated the weight loss pattern of the PLA/PBAT control blend film and FA incorporated blend films at the concentration of 1%, 5% and 10 %. All the blend film exhibited decomposition in 2 stages. The first weight loss stage was observed around 60 to 80℃. This weight loss was ranging between 5 %–12 %, which was due to the solvent evaporation from the films. Similar values were found by Shankar et al. (2018), where the authors observed the first stage weight loss of 5–10 % at 70 to 90℃ in the grapeseed extract incorporated blend film.

The second stage for the weight loss was observed to be in between 280 – 400℃ which was attributed to the PLA and PBAT degradation. The temperature of degradation of the film increases as the concentration of the FA in the composite film increases. The control film shows the drop in second stage weight at 280–290℃ while FA incorporated film with concentration of 1, 5 and 10 wt% shows weight loss around 290–300℃, 330–340℃ and 370–380℃, respectively. The result of TGA shows that the thermal stability of the composite film increased significantly with the increase in the concentration of the FA which is indicated by increased final residue.

3.1.7. Antibacterial activity

L. monocytogenes (a Gram-positive bacterium which causes food borne disease) and *E. coli* (a Gram-negative bacterium which is a very

Table 2
Thickness and tensile properties of composite the films.

Film	Thickness (μm)	Tensile Strength TS (MPa)	Elongation at Break EB (%)	Elastic modulus EM (MPa)	Water Contact Angle (WCA)
PLA/ PBAT	55.27 ± 0.07[a]	5.42 ± 0.03[a]	21.93 ± 17.42[a]	200.44 ± 7.39[a]	78.24° ± 0.25[a]
PLA/ PBAT-FA[1%]	56.19 ± 0.02[b]	5.53 ± 0.85[a]	23.57 ± 19.75[a]	161.32 ± 5.61[b]	71.29° ± 0.27[b]
PLA/ PBAT-FA[5%]	58.38 ± 0.02[c]	6.82 ± 0.08[b]	22.42 ± 18.55[a]	176.20 ± 8.73[b]	71.25° ± 1.13[b]
PLA/ PBAT-FA[10%]	59.25 ± 0.015[d]	10.78 ± 0.83[c]	22.13 ± 21.34[a]	193.56 ± 38.7[a]	64.96° ± 0.65[c]

*The letters (a–d) at each concentration indicate groups that are significantly different ($P < 0.05$).
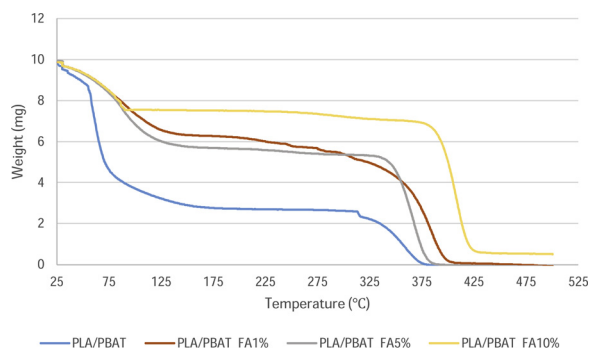
Fig. 3. TGA of PLA/PBAT blend films.

common indicator of food sanitation) are used for the *in-vitro* antibacterial efficency of the PLA/PBAT film incorporated with FA. Antibacterial activity was examined for the positive control, PLA-PBAT film without FA, PLA-PBAT film with 1% FA, PLA-PBAT film with 5% FA and PLA-PBAT film with 10 % FA. The average initial microbial count of both the bacteria were 6.5 CFU/ml.

The control sample showed a rapid growth, as the bacterial population reached to 9.5 and 9.0 log CFU/ml after 12 h for *L. monocytogenes* and *E. coli* respectively. The incorporation of FA in the film at different concentration (1, 5 and 10 wt%) inhibited the growth of *L. monocytogenes* and *E. coli* at different level. A significant increase in the antibacterial efficacy has been observed due the inclusion of the phenolic compound in the composite film.

Fig. 4(a) depicts the influence of FA on *L. monocytogenes* growth. FA has exhibited strong antibacterial activity on *L. moncytogenes* (grampositive bacteria). With 1 wt% of FA concentration the microbial degradation was observed low, while the microbial degradation was observed to increase as the concentration of FA increases (5 and 10 wt%). After 12 h the blend film with 5% FA was observed to reduce microbial growth from 6.5 log CFU/ml to 4.0 log CFU/ml and the blend film with 10 % FA demonstrated reduction from 6.5 log CFU/ml to 3.0 log CFU/
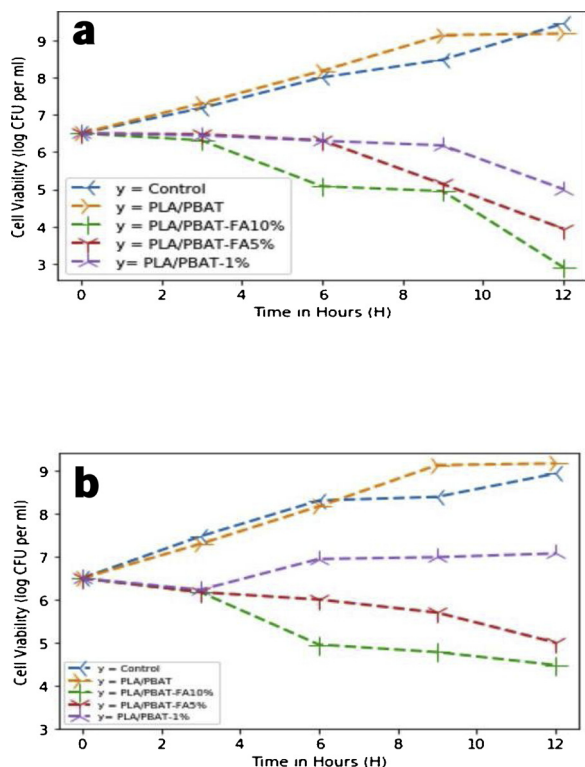

Fig. 4. Antibacterial activity of FA against (a.) *L. monocytogenes*, (b.) *E. coli*.

ml.

Fig. 4(b) shows the influence of FA on the growth of *E. coli*. FA composite films have not shown any bactericidal activity at its low concentration (1 wt%) against gram negative bacteria (*E. coli*). However, with the increased FA concentration (5 and 10 wt%) in the blend film, the antibacterial property against *E.coli* increases by 23 %–30 %. At 5 wt% FA blend film reduces the *E. coli* growth from 6.5 log CFU/ml to 5.0 log CFU/ml, whereas at 10 wt% FA it showed *E. coli* reduction from 6.5 log CFU/ml to 4.5 log CFU/ml. The bactericidal activity of FA composite films on *E. coli* was observed to be less than that on *L. monocytogenes*. Borges et al. (Borges, Ferreira, Saavedra, & Simoes, 2013) in their study stated that FA could be used as a green broad-spectrum antibacterial product which led to the irreversible changes in the microbial membrane properties. FA has shown strong antibacterial activity on the *L. monocytogenes* (gram-positive bacteria) than the *E. coli* (gram-negative bacteria).

4. Conclusions

Composite film of PLA-PBAT incorporated with FA was formed using solvent casting method. A very high influence of incorporation FA on the properties of the film such as morphological, optical, thermal stability, mechanical properties (tensile strength, elastic modulus and elongation at break) and antibacterial efficiency was observed. The blend films depicted a slight tint of yellow after incorporation of FA and significant UV-light barrier property. FA incorporation in the PLA-PBAT film had enhanced the physical, mechanical (tensile strength, fracture failure and elasticity) and antibacterial property. The film thickness was increased by 1.5–10 %, the tensile strength (TS) of the FA incorporated films increased to a value of 10.78 MPa at 10 wt% in comparison to the control film (5.42 MPa). Water contact angle (WCA) of the film has decreased significantly with the increment of FA concentration in the composite film. The thermal stability of the film was also observed to increase significantly. All the blend film exhibited thermal decomposition in 2 stages, where first stage weight loss of 5 %–12 % was observed around 60 °C–80 °C and the second stage of weight loss (complete degradation) was observed at 280 °C – 400 °C. The temperature of degradation of the film was observed to increase by the incorporation of FA in the film and as its concentration increases. Also, with the increase in the FA concentration from 1 to 10 wt% in the composite film had showed strong antibacterial activity against *L. monocytogenes* and *E. coli*. A significant increase in the antibacterialefficacy has been observed due to the inclusion of the phenolic compound (FA) in the composite film against *Listeria monocytogenes* and *E. coli*. Therefore, PLA-PBAT film incorporated with FA has shown high UV-barrier properties and strong antibacterial activity, which can avoid unwanted photochemical reaction and growth of pathogenic bacteria on the packed food, hence they can be used as an active packaging.

CRediT authorship contribution statement

Shubham Sharma: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Writing - original draft, Writing - review & editing. **Amit K. Jaiswal:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing - review & editing. **Brendan Duffy:** Funding acquisition, Resources, Supervision. **Swarna Jaiswal:** Formal analysis, Resources, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare no conflict of interest.

Acknowledgement

University Dublin - City Campus (formally Dublin Institute of Technology), Ireland under the Fiosraigh Scholarship programme, 2017.

References

Agwuncha, S. C., Ray, S. S., Jayaramudu, J., Khoathane, C., & Sadiku, R. (2015). Influence of boehmite nanoparticle loading on the mechanical, thermal, and rheological properties of biodegradable polylactide/poly (ε-caprolactone) blends. *Macromolecular Materials and Engineering, 300*(1), 31–47.

Al-Itry, R., Lamnawar, K., & Maazouz, A. (2012). Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy. *Polymer Degradation and Stability, 97*(10), 1898–1914.

Arruda, L. C., Magaton, M., Bretas, R. E. S., & Ueki, M. M. (2015). Influence of chain extender on mechanical, thermal and morphological properties of blown films of PLA/PBAT blends. *Polymer Testing, 43*, 27–37.

Barbosa, J. D. V., Azevedo, J. B., Araújo, E. M., Machado, B. A. S., Hodel, K. V. S., & Mélo, T. J. A. (2019). Bionanocomposites of PLA/PBAT/organophilic clay: Preparation and characterization. *Polímeros, 29*(3).

Borges, A., Ferreira, C., Saavedra, M. J., & Simoes, M. (2013). Antibacterial activity and mode of action of ferulic and gallic acids against pathogenic bacteria. *Microbial Drug Resistance, 19*(4), 256–265.

Chen, R., Abdelwahab, M. A., Misra, M., & Mohanty, A. K. (2014). Biobased ternary blends of lignin, poly (lactic acid), and poly (butylene adipate-co-terephthalate): The effect of lignin heterogeneity on blend morphology and compatibility. *Journal of Polymers and the Environment, 22*(4), 439–448.

Graf, E. (1992). Antioxidant potential of ferulic acid. *Free Radical Biology & Medicine, 13*(4), 435–448.

Jiang, L., Wolcott, M. P., & Zhang, J. (2006). Study of biodegradable polylactide/poly (butylene adipate-co-terephthalate) blends. *Biomacromolecules, 7*(1), 199–207.

Kasmi, S., Gallos, A., Beaugrand, J., Paës, G., & Allais, F. (2019). Ferulic acid derivatives used as biobased powders for a convenient plasticization of polylactic acid in continuous hot-melt process. *European Polymer Journal, 110*, 293–300.

Kumar, M., Mohanty, S., Nayak, S., & Parvaiz, M. R. (2010). Effect of glycidyl methacrylate (GMA) on the thermal, mechanical and morphological property of biodegradable PLA/PBAT blend and its nanocomposites. *Bioresource Technology, 101*(21), 8406–8415.

Kwon, S., Orsuwan, A., Bumbudsanpharoke, N., Yoon, C., Choi, J., & Ko, S. (2018). A short review of light barrier materials for food and beverage packaging. *Korean Journal of Packaging Science and Technology, 24*(3), 141–148.

Kwon, Y.-S., Kobayashi, A., Kajiyama, S.-I., Kawazu, K., Kanzaki, H., & Kim, C.-M. (1997). Antimicrobial constituents of Angelica dahurica roots. *Phytochemistry, 44*(5), 887–889.

Llorens, A., Lloret, E., Picouet, P. A., Trbojevich, R., & Fernandez, A. (2012). Metallic-based micro and nanocomposites in food contact materials and active food packaging. *Trends in Food Science & Technology, 24*(1), 19–29.

Mathew, S., & Abraham, T. E. (2008). Characterisation of ferulic acid incorporated starch–chitosan blend films. *Food Hydrocolloids, 22*(5), 826–835.

Moustafa, H., El Kissi, N., Abou-Kandil, A. I., Abdel-Aziz, M. S., & Dufresne, A. (2017). PLA/PBAT bionanocomposites with antimicrobial natural rosin for green packaging.

ACS Applied Materials & Interfaces, 9(23), 20132–20141.

Nova-Institute (2016). *Global production capacities of bioplastics 2016 - 2021.* European Bioplastics.

Ou, S., & Kwok, K. C. (2004). Ferulic acid: Pharmaceutical functions, preparation and applications in foods. *Journal of the Science of Food and Agriculture, 84*(11), 1261–1269.

Ou, S., Wang, Y., Tang, S., Huang, C., & Jackson, M. G. (2005). Role of ferulic acid in preparing edible films from soy protein isolate. *Journal of Food Engineering, 70*(2), 205–210.

Pernin, A., Bosc, V., Maillard, M.-N., & Dubois-Brissonnet, F. (2019). Ferulic acid and eugenol have different abilities to maintain their inhibitory activity against *Listeria monocytogenes* in emulsified systems. *Frontiers in Microbiology, 10*, 137.

Piotrowski, J. S., Lu, F., Kabbage, M., Ralph, J., & Landick, R. C. (2015). *Antimicrobial Ferulic Acid Derivatives and Uses Thereof: U.S. Patent Application No. 14/703,337.*

Shankar, S., & Rhim, J.-W. (2016). Tocopherol-mediated synthesis of silver nanoparticles and preparation of antimicrobial PBAT/silver nanoparticles composite films. *LWT-Food Science and Technology, 72*, 149–156.

Shankar, S., & Rhim, J.-W. (2018). Antimicrobial wrapping paper coated with a ternary blend of carbohydrates (alginate, carboxymethyl cellulose, carrageenan) and grapefruit seed extract. *Carbohydrate Polymers, 196*, 92–101.

Shankar, S., & Rhim, J. W. (2019). Effect of types of zinc oxide nanoparticles on structural, mechanical and antibacterial properties of poly (lactide)/poly (butylene adipate-co-terephthalate) composite films. *Food Packaging and Shelf Life, 21*, 100327.

Shankar, S., Rhim, J. W., & Won, K. (2018). Preparation of poly (lactide)/lignin/silver nanoparticles composite films with UV light barrier and antibacterial properties. *International Journal of Biological Macromolecules, 107*, 1724–1731.

Sharma, S., Jaiswal, S., Duffy, B., & Jaiswal, A. K. (2019). Nanostructured materials for food applications: Spectroscopy, microscopy and physical properties. *Bioengineering, 6*(1), 26.

Siemann, U. (1992). The solubility parameter of poly (DL-lactic acid). *European Polymer Journal, 28*(3), 293–297.

Argente, E. T. (2018). *Incorporation of active components in biopolymer-based films for food use (Doctoral dissertation, Universitat Politècnica de València).* Available at: https://pdfs.semanticscholar.org/9227/eb6fe8335092843a35dc6bbcf2881c5c5095.pdf (Accessed on 10th January 2020).

Vert, M., Doi, Y., Hellwich, K.-H., Hess, M., Hodge, P., Kubisa, P., et al. (2012). Terminology for biorelated polymers and applications (IUPAC Recommendations 2012). *Pure and Applied Chemistry, 84*(2), 377–410.

Vogler, E. A. (1998). Structure and reactivity of water at biomaterial surfaces. *Advances in Colloid and Interface Science, 74*(1-3), 69–117.

Wang, L.-F., Rhim, J.-W., & Hong, S.-I. (2016). Preparation of poly (lactide)/poly (butylene adipate-co-terephthalate) blend films using a solvent casting method and their food packaging application. *LWT-Food Science and Technology, 68*, 454–461.

Woranuch, S., & Yoksan, R. (2013). Preparation, characterization and antioxidant property of water-soluble ferulic acid grafted chitosan. *Carbohydrate Polymers, 96*(2), 495–502.

Yeh, J. T., Tsou, C. H., Huang, C. Y., Chen, K. N., Wu, C. S., & Chai, W. L. (2010). Compatible and crystallization properties of poly (lactic acid)/poly (butylene adipate-co-terephthalate) blends. *Journal of Applied Polymer Science, 116*(2), 680–687.

Zhang, L., Li, Y., Wang, H., Qiao, Y., Chen, J., & Cao, S. (2015). Strong and ductile poly (lactic acid) nanocomposite films reinforced with alkylated graphene nanosheets. *Chemical Engineering Journal, 264*, 538–546.