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Enhancement of Polylactic Acid Packaging Sheet by Adding Three Bio-composites and Evaluating Them as Bioplastic

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THE food packaging industry is searching biodegradable alternatives to traditional plastics, with Polylactic Acid (PLA), starch (S), and cellulose (C) emerging as eco-friendly options. However, PLA faces challenges such as brittleness, rigidity, and low elasticity, limiting its use. This study examined the effect of cassava starch (CS), Polyhydroxybutyrate (PHB), and amorphous cellulose (AC) as copolymers to improve PLA properties. Results showed that incorporation of 8% AC was the most effective treatment, increased tensile strength by 16.8% and Young's modulus by 20.1%, while elongation at break was improved by 58.57%. Barrier properties: AC reduced oxygen permeability of PLA–film from 2.24 to 1.73 and water vapor permeability from 0.22 to 0.17 $cm^3.cm/m^2.d.kpa$. Thermal properties: The addition of AC increased PLA's crystallinity from 1.7% to 13.3%, and thereby improving mechanical strength. Annealing treatment of PLA/AC composite film at 80°C for 20 min increased crystallinity to 42%. Biodegradability: AC enhanced the water solubility of the composite, promoting biodegradability. In conclusion, presence of amorphous cellulose (AC) improves the mechanical, barrier, and biodegradability properties of PLA–films, making it a promising material for sustainable food packaging.

Keywords: Poly lactic acid, Starch, PHB. Composites poly hydroxy butyrate blends. Bioplastic

Introduction

Petrochemical-based polymers are becoming more and more used in packaging due to their low cost and high mechanical performance. As a result, thousands of tons of products manufactured from plastic materials end up in landfills, making the issue of disposing of municipal waste more pressing each year (Ncube et al., 2021). Because they can replace plastic materials derived from fossil fuels and solve the issue of waste disposal, biopolymers have drawn a lot of attention due to their biodegradability (Nonni et al., 2022). Biopolymers can be made by a variety of methods, including microbiological (PHB) and agricultural resource fermentation (PLA, for example), (Gan and Chow, 2018). Biocompatibility, effective thermal processing techniques, renewability, and low energy usage are some of PLA's attractive qualities (Paul et al., 2021). The Food and drug Administration (FDA) approved it for use in packaging fresh food or items with a short shelf life due to these qualities, (Wayman and Niemann, 2021). PLA has a lot of economic promises, but certain of its characteristics like brittleness, low heat temperature, low melt viscosity, and poor barrier qualities may limit it use in food packaging (Thanki et al., 2006). By choosing the right fillers and processing conditions, PLA's mechanical and physical qualities can be enhanced and customized for certain applications (Arrieta et al., 2014). Flax, starch, microcrystalline cellulose and lignin are components of this mixed fiber, together with cellulose, which are renewable

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and biocompatible, (Muller et al., 2017). Depending on their availability, suitable food contact qualities and affordable price, PLA and starch can be used in place of non-biodegradable petrochemical Polymers (Muller et al., 2017). However, PLA-films should be modified to overcome their disadvantages, (brittleness, low elasticity and mechanical resistance as well as their low resistance to O_2 - permeation), to meet the requirements of food packaging. Due to their complimentary qualities, their combination as mix films may offer qualities that are better suited for packaging purposes in terms of transparency, flavor and odor. Starch has physical properties that are comparable to those of traditional packaging plastic (Thanki et al., 2006; Wang et al., 2020). Cellulose consists of anhydro glucose chains that are stabilized by intramolecular hydrogen bonds (Frone et al., 2013). In recent years, a micro and nano cellulose crystal, as a type of biodegradable filler, has been added to PLA matrix and polymer composites as bio-nuclei for enhancement of crystallization and reinforcement of the composite films. PLA-nanocellulose composite films may exhibit good thermal and mechanical properties (Frone et al., 2013; Gan and chow, 2018). Usually, nanocellulose is found as a powder with particle size of 20 to 80 µm and its quantity added to the chosen polymer (PLA, starch and chitosan films) determine how well the optical qualities of the polymer/nano cellulose bio-composites can be achieved to meet certain packaging specifications (Paul et al., 2021). Amorphous cellulose (AC) was fabricated as a new reinforced material for PLA - bio composites by modifying cellulose structure via milling (Wang et al., 2020). Hydrolytic degradation of PLA-composite films was improved, because AC facilitates the water absorption of PLA (Paul et al., 2021). Polyhydroxy butyrate (PHB) is thermoplastic bio-based polyester that shows great promise for uses in packaging applications requiring short lifespans. It has melting point close to that of PLA (173-180°C) and crystallizes fast, which enables the physical blending in the melt state. Addition of PHB reduces wettability but it significantly improves the oxygen barrier and mechanical properties (Frone et al., 2013). Melt blinding, as a unit operation of film making, is a simple, easy to use, and affordable processing technique that greatly improves the addition of plasticizers to the formula of film production, lead to increase ductility (elongation at break), reduce tensile strength and glass transition temperature of the obtained films (Wan et al., 2020; Paul et al., 2021). Acetyls tributyl citrate (ATBC) has similar solubility parameters to those of biopolymers and it is wildly used as a plasticizer with high plasticizing efficiency in film production rather than other plasticizer (Polyethylene glycol, for example). It increases ductility and flexibility required for the obtained PLA-films (Muller et al., 2017). The aim of the present work was to evaluate the use of biodegradable additives (CS, PHB and AC) together with ATBC as plasticizer in preparation of PLA-composite films and to study their effects on mechanical, barrier qualities and thermal stability of the obtained films.

Materials and Methods

Materials

Poly lactic acid (PLA) pellets, code IN GEO ID. Nature Works. Poly hydroxy butyrate, (PHB), and cellulose fiber were purchased from Middle East chemicals company, Al Manial, Egypt. Cassava starch granules (CS) and Acetyl tributyl citrate (ATBC) were purchased from Sigma - Aldrich (Madrid- Spain).

Methods

Preparation of Amorphous Cellulose (AC)

Amorphous cellulose was prepared as follows: 150 g of cellulose fiber were mixed with the predetermined amount of distilled water in a beaker under magnetic stirring at room temperature (Paajanen et al., 2021). For hydrolysis, 90 mL of concentrated sulfuric acid solution was gradually added, while cooling the beaker (with content) in an ice-water bath and stirring for 60 min. The beaker content was poured out into 3-fold volume of deionized cold water and stirring until flocs of amorphous cellulose (AC), has been obtained. Centrifugation at 5000 xg for 10-15 min was used to separate flocs of amorphous cellulose (AC) from mother solution.

Preparation of PLA-Bio Composite Films

PLA pellets and the bio composite samples were dried in a vacuum oven at 80 °C for nine hours followed by 24 h at 30 °C, respectively. Dried PLA pellets were mixed with the corresponding bio-composite material (CS or PHB or AC) using a Brabender mixer (Polymix, Brabender, Duisburg, Germany) at 165 °C for 10 minutes and 27/22 rpm. Plasticizer (ATBC) was added to each composite after 3 minutes of mixing. Films were formed using a fully automated two - roll laboratory Brabender press at 180 °C and applying 5 bar pressure for 5 min followed by 10 bar pressure for further 5 min. The resulting 0.2 mm thickness films were immediately cooled by quenching in liquid N_2 until they reach room temperature. Unfilled PLA-films were prepared by melting and formation under the same conditions.

Annealing of PLA-Composite films:

The obtained (amorphous) sheets were annealed between 2 stainless steel hot press at 80 °C under 5 bar pressure for 1, 2, 3, 4, 5, 10, 20 and 60 min. The obtained film samples were tested for their crystallinity according to DSC- test as follows. Beside pure (neat) PLA-films, three bio composite film samples were prepared as follows:

1- PLA/CS (75:25 wt ratio)
2- PLA/PHB (75:25 wt ratio), and
3- PLA/ AC (92: 8 wt ratio)

Analysis and measurements

Mechanical characterization

An Instron 3365 universal materials testing machine was used to measure the samples' tensile properties. In order to calculate the strain at break, a caliper was used to measure the specimen gauge length (span) of approximately 25 mm for each sample after it was gripped. The crosshead speed was then set at 1 mm/min. The specimen's dimensions were 0.5 mm thick, 4 mm width, and 40 mm long. The force's maximum value, measured in N/m2, indicates the maximum material resistance to tensile extension and tensile strength (TS). The distance in %, calculated on the X-axis from the zero point to the first vertical drop of the curve (point of failure), represents the fracture percentage of elongation, i.e., the capacity of the material to stretch without breaking (Young, s modulus E), representing the material toughness. The ASTM D638 (2022) universal testing method was used to conduct the mechanical strength analysis.

Barrier properties (O_2, CO_2 and WV permeability)

The apparatus used is GBPI, China and applying standard method ASTM D3985 (2017). The amount of oxygen gas (cm^3) passing through a unit area of 1 m^2 during 24h was defined as follows:

$$\mathrm{OTR} = \mathrm{cm}^3\ \mathrm{O}_2 / (\mathrm{m}^2 \times 24\mathrm{h}) \quad \ldots\ldots\ldots\ 1$$

The permeability is obtained through multiplying the OTR by the film thickness (cm) and dividing by the difference of partial pressure (bar) present in the two chambers.

$$\text{Permeability} = \text{OTR} \times (\text{thickness}/\Delta P) = \mathrm{cm}^3\ \mathrm{O}_2.\mathrm{cm}/\mathrm{m}^2.\mathrm{d.bar} \quad 2$$

For CO_2 transmission, the following parameters and condition were used: Surface of the film 50 cm^2 (fixed by the dimension of the sample place in the equipment), a time of 24 hr for the experiment, precise relative humidity condition RH=0% and temperature at 23 °C. Transmission of H_2O was measured by using WPT-304 Siachen instrument and follow standard method ASTM D1653 (2021). The permeability is obtained by multiplying the transmission rate by the film thickness (cm) and dividing throw the difference of partial pressure (bar) present in the two chambers as mentioned in equation (2), but with replacing O_2 by H_2O.

Thermal characterization

A thermogravimetric analyzer made by Mettler Toledo (model STDA 851e and DSC 882e, respectively) was used to examine the thermal stability and thermal history of the PLA and the blends. To assess the raw materials' thermal stability under processing conditions, they were heated (isothermal mode) for 25 minutes at 180 °C with air flowing at a rate of 50 milliliters per minute. The thermogravimetric analysis (TGA) was carried out under a nitrogen atmosphere from room temperature to 600 °C, (50 mL N_2/min). Sample masses in both instances ranged from 5 to 7 g. For differential scanning calorimetry (DSC), film samples (6-12 mg) were placed in aluminum pans and sealed with a press (TA-Instruments). Every test consists of an initial heating phase that goes from -50 °C to 180 °C at 10 °C/min, a cooling phase that reaches -50 °C at the instrument's maximum rate, and a subsequent heating phase that reaches 200 °C at 10 °C/min. Glass transition (Tg), cold–crystallization (Tcc) and melting temp., (Tm) were determined during the second heating scan. The degree of crystallinity (Xc) was calculated by using Eq 3: (Nam et al., 2003).

$$\mathrm{X_c} = 100\, X\, \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^c}\, X\, \frac{1}{W} \quad \ldots\ldots\ldots\ldots\ldots\ 3$$

where, ΔH_m is the melting enthalpy, ΔH_{cc} is the cold crystallization enthalpy, $\Delta H^c m$ is the melting heat associated to pure crystalline PLA, reported to be 93 J/g and W is the weight fraction of PLA in the sample.

Film transparency and color

A COLOR FLEX DIFF 245% Hunter lab colorimeter (Hunter Associate laboratory Inc., Reston, VI, USA) was used to assess these properties. A white standard tile was used to calibrate the device, and the average value of five measurements taken at random locations across the sample's surface (20x20 mm^2) was computed. The color coordinates, L (lightness), a*= red: green, b*=yellow: blue, Chroma $C = \sqrt{a^2 + b^2}$ and $Hue^\circ = \tan^{-1}\frac{b}{a}$ were used to determine the color specifications and YI: Yellowness index was used to evaluate the color change from clear to yellow.

Total soluble matter (TSM)

TSM was applied to the PLA bio-composites in accordance with ASTM D570 (2022). Water absorption was calculated as the dry basis percentage of each sample that was dissolved in distilled water after a 24 hr period. The sample was cut to a 20 x 20 mm size and dried for 24 hours at 100 °C in an oven. After the sample was weighed, water was added. The sample was taken out, dried, and weighed the following day. The following formula was used to get the percentage of water absorption was calculated as follows:

$$\%\ \text{water absorption} = \left(\frac{M_0 - M_1}{M_o}\right) \times 100 \quad .....4$$

where, M_1 and M_0 are the wet weight and initial dry weight of the sample, respectively. Three films of each sample were tested, and the average value was determined as the water absorption ratio. In the hydrolytic degradation test, the sample was cut into the dimension of 30x15x0.3 mm, weighed and placed into capped flasks filled with 20 mL of distilled water at room temperature. After 48 h, the specimen was removed and dried in an oven for 24hr at 100 ℃ (Arrieta et al., 2014). The weight loss was calculated as follows:

$$\%\ \text{weight loss} = \left(\frac{W_0 - W_1}{W_o}\right) \times 100 \quad ....5$$

Where, W_1 is its initial dry weight of the sample before the hydrolytic degradation test, and W_0 is the weight of the sample after the hydrolytic degradation test.

Statistical analysis

The statistical analysis was carried out using Two-Way ANOVA using SPSS, ver. 27 (IBM Corp. Released 2013). Data were treated as a complete randomization design according to Steel et al. (1997). Multiple comparisons were carried out applying Duncan test the significance level was set at < 0.05

Results and Discussion

Mechanical properties of PLA-Composites

Assessing mechanical properties of packaging films is essential for estimating their suitability for processability through packaging machines, handling and distribution, where they are subjected to different types of stresses, forces and strains. Fig (1a) shows that tensile strength of pure PLA–films was 59.0 MPa, which agree with the values reported by Muller et al. (2017) and Wang et al. (2020) (17-74 MPa). The wide range depends on the molecular weight, orientation and crystallinity of the obtained PLA-film. Inclusion of 8% AC significantly increased the strength of the composite film to the level of 68.90 MPa (16.8% increase), while incorporation of PHB in the PLA-film slightly increased the tensile strength to the level of 61.78 MPa. On contrary, incorporation of CS decreased the tensile strength value of PLA-films by 23.80%. The improvement in tensile strength of PLA-film through incorporation of AC could be referred as reported by Fu et al. (2008); Lu et al. (2014) and Dawin et al. (2018) to good chemical interaction (hydrogen bonds), good adhesion, shape and size, similar crystallinity and melting properties with PLA. The relatively low tensile value of the PLA /CS bio – composite may be attributed to the hydrophilic character of starch, from one side, and to the thick weak interaction and adhesion between PLA and CS, from other side, which led to inefficiency of CS for load bearing (Bax and Mussig, 2008). The slight increase in TS of PLA/PHB films could be referred to the homogenous distribution of PHB molecules in PLA matrix (Haafiz et al., 2013).

Figure 1b illustrates the values of Young's modulus, which expresses the stress necessary for each unit change in deformation (elongation) of the tested material. Its value is also a measure for elasticity or stiffness of the material. As seen, the Young's modulus of neat PLA-films was 3.53 GPa, which gives a strain value lower than 3% and agree with the results reported by Salaberria et al. (2017); Yu et al. (2020) and Ludwiczk et al. (2021). This means that PLA -films are rigid (high tensile strength values) and brittle (low strain values) in comparison to high density polyethylene films, which have average tensile strength value of 12.3 to 28 MPa but a strain value of 55% to 240% (Wu & Wang, 2020). Incorporation of CS or PHB in the matrix of PLA-films decreased the Young's modulus values by 15% to the level of 2.99 to 3.10 GPa and largely decreased the stiffness of the PLA materials.

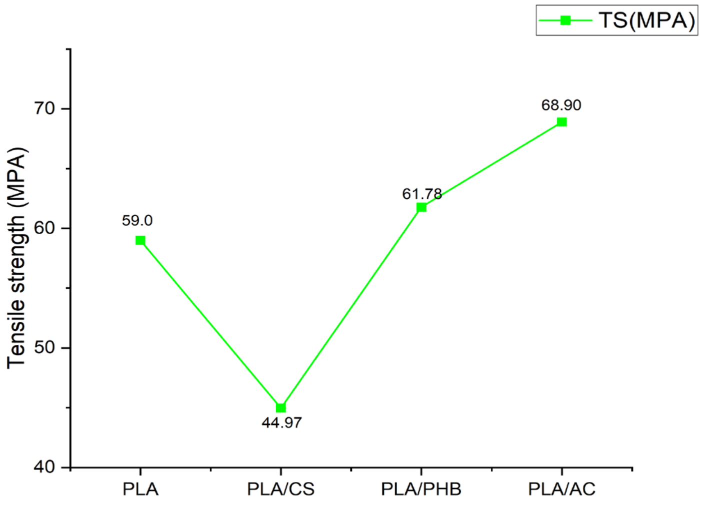

Fig. (1.a) TS for PLA and PLA bio-composite.

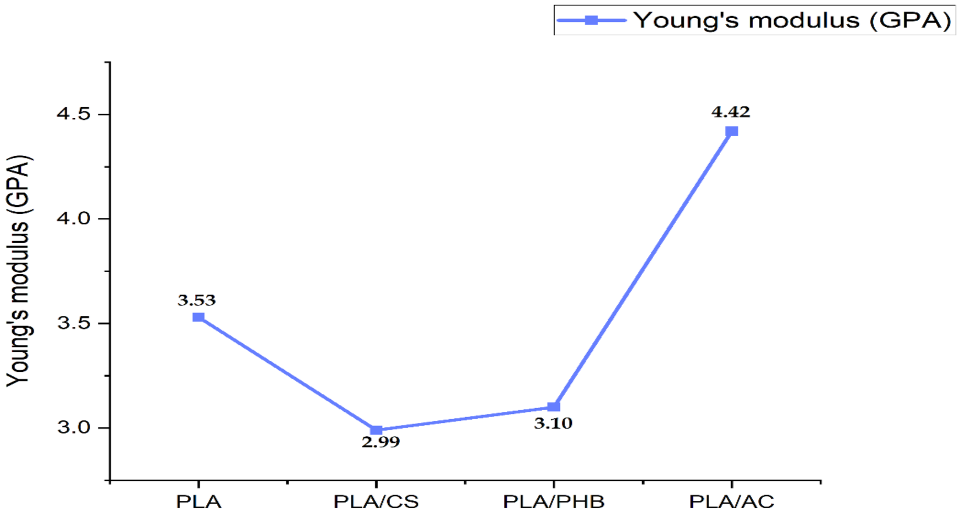

Fig. (1.b) Youngs modulus for PLA and PLA bio-composites.

The corresponding elongation values (Fig (1c)) of neat PLA–films and those containing CS or PHB were very low in the range of 2.8% to 3.06%. However, incorporation of AC in the matrix of PLA–films did increase the Young's modulus to the level of 4.42 GPa, and the obtained films were less brittle and showed elongation value of 4.44%, being almost 15% higher than those of other tested samples. This improvement could be explained by the diminished rigidity of their structure, creating a fine network structure and slowing down the fracture development of the PLA matrix during deformation (Aksman et al., 2003; Suryanegara et al., 2010). The obtained mechanical properties of pure (neat) PLA film and its composites are also comparable to those of polyethylene-terephthalate (PET films) reported by Valentas et al. (1997) and Vasylius et al. (2023), where PET has tensile strength values between 48.3 and 72.3 MPa, Young's modulus of 3.45 GPa and strain – elongation values between 5 to 6%.

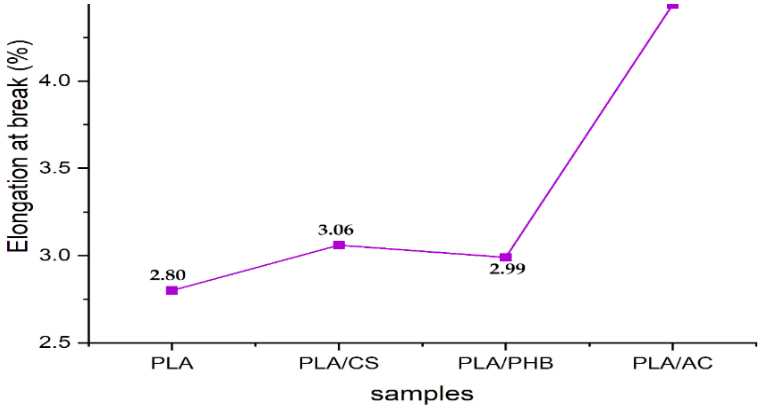

Fig. (1.c) E% for PLA and PLA Bio-composites .

Barrier properties of PLA-films and composites

Permeability characteristics of PLA-films for gases and vapors are essential for their possible use in food and modified atmosphere packaging and in assessing stability and shelf life of the product. Table 1 shows the permeability values of PLA-films for O_2, CO_2 and water vapors (WV). As seen, the permeability values of neat (pure) PLA for O_2 and CO_2 were 2.24 and 8.06 cm^3.cm/m^2.d.bar, respectively, while WV- permeability recorded 0.22 g H_2O cm/m^2.d.bar, which indicate the suitability of PLA-films as good barriers in food packaging. The obtained barrier properties of neat (pure) PLA-films agree with those reported by Duan and Thomas (2014) Carosio et al. (2014); Halasz, (2015); Beltran et al. (2021); Wang et al. (2021) and Mehan (2022). They reported PLA-permeability values for O_2 and WV in the range of 0.73 to 2.24 cm^3 O_2 .cm/m^2.d.bar and in the range of 0.44 to 0.95 gH_2O .cm/m^2.d.bar for water vapors. The observed barrier properties of PLA- films are comparable to those of industrial plastic films of HDPE, poly propylene and PET, which have O_2 and WV permeability in the range of 0.24 to 4.5 cm^3. cm/m^2.d.bar and 0.16 to 0.86 g H_2O.cm/m^2.d.bar, respectively (Valentas, 1997; Guzman et al., 2016). So, PLA-films could be successfully replacing the industrial Plastic films, if their elasticity and strain has been improved. Table 2 shows that the permeability of PLA-films for CO_2 was in the range of 8.06 cm^3.cm / m^2.d. bar, being about 4- folds higher than that of O_2, which agree with Siracusa et al. (2017), who indicated that permeability of PLA-films for CO_2 is almost 2-folds that of O_2 despite the larger size of CO_2 -molecule. The WV-permeability of PLA-films reports in the present work are much lower than those of other biodegradable composite films prepared from whey protein concentrate (mixed with pectin and alginate), which showed H_2O permeability of 1.92 cm^3. cm/m^2.d.bar, may be due to the hydrophobic character of PLA (Chakravartula et al., 2019). Addition of CS (25%wt) or PHB to the formula of PLA-films decreased the O_2–permeability by 19% and 10% respectively, while the reduction in CO_2 –permeability was only in the range of 11% and 9%, respectively, compared with those of pure PLA -films. On other side, the addition of only 8% AC led to about 22.76 and 21.1% reduction in O2 and CO2-permeability of the composite PLA-films. The reduction in gas permeability for the PLA -films could be referred to the change in crystallinity and free volume of the polymer, which affect the adsorption and solubility of the gases on the surface of the film as well as the path and diffusion through the matrix of the polymer film to the lower pressure side of the corresponding gas creating a tortuous path. On contrary, incorporation of CS or PHB in PLA-films did increase the values of WV-permeability by 9.1 and 4.5%, respectively probably due to the hydrophilic nature of starch and butyrate, while incorporation of AC successfully decreased the WV- permeability of the PLA–composite films by 22.7% beside its effect on reducing O_2 and CO_2 permeability. It seems that the presence of cellulose in PLA-films has a certain barrier effect through slowing down the diffusion through the polymer film (Marra et al., 2016). The reducing effect of cellulose fibers on the barrier properties of PLA – films has been confirmed by the works of Halasz et al. (2015); Guzman et al. (2016) and Faraj et al. (2022), who reported that incorporation of cellulose nano crystals has reduced the WV-permeability of PLA-films by 28%. Also, Marra et al. (2016) observed an increase in the permeation of the polar gas molecules (Water Vapors) compared with non-polar gases permeability (O_2 and CO_2). They referred this phenomenon of the composite films of PLA to the modification of free volume at the interface of the composite film leading to increase in permeability for polar water vapors.

Transparency and colorimetric properties

Optical clarity, opacity, transparency and surface color of PLA-films are important features for their possible application in food packaging. CIE- LAB space was used to identify the color parameters necessary for the evaluation of surface appearance for a packaging material. The obtained color coordinates (lightness-L-, redness-a -and yellowness-b) of the tested PLA- films are given in Table (2). As seen, neat PLA–films are characterized by high lightness (brightness), light green color shade and fade yellowness, since L, a and b coordinates recorded values of 94, -1.2 and 1.4, respectively. On other side, the used plasticizing material (ATBC) showed lower lightness (L= 82.3), fade redness (a=1.08) and strong yellowness color parameter (b=21.47). Chroma (C-values) of neat PLA-film and ATBC were 1.84 and 21.60, respectively, which reflect the color saturation degree of the plasticizer (ATBC). Correspondingly, the color type (Hue) of the neat PLA- film was 130.60° (light greenish shade) and 87.40° (pure yellow) for the ATBC material. Yellowness index (YI) of neat PLA and ATBC was 3.6 and 44.2, respectively. Addition of the plasticizer ATBC to PLA material during production of PLA- films induced major changes in the color parameters and appearance of the obtained films. The almost colorless neat PLA-films becomes yellowish in color with decrease in lightness (L= 91.6), fade greenish color shade (a= -0.8) and remarkable yellow color tone (b= 1.7). The color saturation (C–value) was increased to 1.87, while Hue-value was moved towards the yellow shade and recorded 115.20°, being lower than that of neat of PLA- film (130.60°). The yellowness index (YI) of the plasticizer containing PLA-film was slightly changed to the level of 4.4. Incorporation of AC, CS and PHB in the plasticized PLA-films did not change the lightness of the films (L = 90.2 to 90.8) but did pronounce the greenish color shade (a= -1.5 to -1.8) and strengthened the yellow- amber color appearance of the obtained films, since b- values were in the range of 9.6 to 10.8. The composite PLA/ films were more color saturated (C=9.7 to 10.9) and showed Hue values of yellow/ greenish type in the range of 97.9° to 100.6°. Correspondingly, the composite films showed -YI – values in the range of 18.5 to 21.15. The obtained results agree with those of Molinaro et al (2013), who reported L, a and b – values for neat PLA-films in the range of 93.7, -0.6 and 4 for L, a and b- values, respectively.

Thermal behavior of PLA-films

Thermal behavior of food packaging film is essential to assess thermal, dimension and chemical stability of the films during mechanical formation, handling and storage under different environmental conditions. It is also important for assessing the melting behavior of the packaging material to optimize the sealing temperature. Testing thermal behavior of packaging material include testing the change in weight of spicemen subjected to a range of high temperature under controlled heating regime (gravimetrical thermal analysis) as well as gathering of exo-and endo-thermal energy values during programmed heating of the packaging material (DSC-analysis), which is important for getting information about the internal structure of the packaging material.

TABLE 1. Permeability of PLA – composite films for gases and vapors (mean±SE).

Treatment	O_2 [$cm^3/(24\ h \times m^2)$] x (cm/ bar)	CO_2 [$cm^3/(24\ h \times m^2)$] x (cm/ bar)	WVP [$cm^3/(24\ h \times m^2)$] x(cm/ bar)
PLA	2.22 ± 0.01^a	8.06 ± 0.01^a	0.22 ± 0.01^a
PLA/CS	1.82 ± 0.01^c	7.17 ± 0.01^c	0.23 ± 0.01^a
PLA/PHB	2.02 ± 0.01^b	7.31 ± 0.01^b	0.23 ± 0.01^a
PLA/AC	1.72 ± 0.01^d	6.35 ± 0.01^d	0.17 ± 0.01^b

a, b & c: There is no significant difference (P>0.05) between any two means, within the same column have the same superscript letter.

TABLE 2. CIE-LAB Color Parameter and yellow index (YI) for PLA-film formulations.

Treatments	L*	a*	b*	C	Hue$^{\circ}$	YI
PLA	94.13 ±0.09^{a}	-1.23 ±0.02^{c}	1.42 ±0.01^{f}	1.84 ±0.01^{f}	130.63 ±0.02^{a}	3.65 ±0.02^{f}
ATBC	82.27 ±0.09^{e}	1.08 ±0.04^{a}	21.47 ±0.09^{a}	21.63 ±0.02^{a}	84.42 ±2.99^{d}	44.24 ±0.02^{a}
PLA-ATBC	91.37 ±0.15^{b}	-0.83 ±0.02^{b}	1.72 ±0.01^{e}	1.87 ±0.01^{e}	115.25 ±0.03^{b}	4.43 ±0.02^{e}
PLA-AC-ATBC	90.60 ±0.12^{c}	-1.52 ±0.01^{d}	10.67 ±0.09^{b}	10.92 ±0.01^{b}	97.93 ±0.01^{c}	21.15 ±0.03^{b}
PLA-CS-ATBC	90.27 ±0.09^{d}	-1.72 ±0.01^{e}	9.88 ±0.04^{c}	10.06 ±0.01^{c}	99.76 ±0.01^{c}	19.75 ±0.03^{c}
PLA-AHB-ATBC	90.30 ±0.06^{d}	-1.84 ±0.02^{f}	9.65 ±0.03^{d}	9.77 ±0.01^{d}	100.64 ±0.02^{c}	18.55 ±0.03^{d}

a, b & c: There is no significant difference (P>0.05) between any two means, within the same column have the same superscript letter.

Thermogravimetric analysis (TGA)

Figure 2 shows the change in weight (decomposition) of different PLA- films subjected to gradual heating regime up to 500 °C. No considerable decomposition and loss in weight have been appeared until 200 °C unless loss in the negligible water content at t= 100 °C and change of the film to the partially molten phase without weight loss. The onset temperature for starting degradation of pure (neat) PLA-films was 285 °C, which is slightly lower than those reported by Patwa et al. (2018) and Wang et al. (2021), who reported an onset temperature of 307°C for PLA-films. The end-temperature for the degradation (decomposition) of PLA -film was 380 °C, slightly lower than those reported by the aforementioned authors (398.7 °C). This shift in temperature range could be referred to the molecular weight and casting method of PLA-film. The $t_{50\%}$, (the temperature for achieving 50% decomposition) is 295 °C, which shows the narrow temperature range for decomposition of PLA-film. The residual mass of PLA-film after complete decomposition was lower than 3%. Incorporation of CS, PHB and AC in the matrix of PLA-film slightly decreased the onset temperature by 2-3°C, which indicates that these materials showed negligible effect on the thermal stability of PLA-films and on the residual final mass. The obtained results agree also with those of Fu et al. (2008), who found also that onset temperature for modified PLA-films was lower than those of pure film.

Differential Scanning Calorimetry (DSC) of PLA-films

DSC-analysis was performed on PLA-films in the range of 0 to 200°C to assess the endo- and exothermic phase changes occur in the film matrix. This temperature range (0°C -200 °C) is the important temperature range for processing, filling, sealing and storage of PLA-packages used in foods. The important parameters in this temperature range are the temperature for glass state transition of the film (Tg), temperature at which the molten film crystalizes (Tcc), melting temperature of the film (Tm) as well as the enthalpy flow associated with these phase changes. The PLA-film samples were subjected to two cycles of heating with a rapid cooling cycle in-between. DSC-data of the polymer samples were taken from the second heating cycle to avoid heat stresses history during casting or extrusion of the PLA-plates. Fig 3 (a-b) depicts the thermograms obtained during the first and second heating cycles. As seen, the course of the two thermograms (a and b) is different, because the effect of thermal stress history of the samples on the data obtained from first heating cycles and the DSC- behavior of the tested PLA-samples was evaluated from the data obtained from the second heating cycle (Fig 3b). As seen, the glass transition temperature of neat (pure) PLA –films were 62°C, which agree to a great extent with the values reported by Halasz et al. (2015); Marra et al. (2016); Ludwiczk (2021) and Wang et al. (2021). Tg of pure (neat)

PLA was 60°C in the first heating cycles and it was shifted to 62°C in the second heating cycle with a difference of 2°C between the two-heating cycle. According to Sharma et al., (2019), a shift of up to 5 could be observed for Tg of PLA– films during the two heating cycles, because rapid cooling after the first heating cycle affects the Tg of PLA. Tg is important to compare compatibility of different packaging films. Industrial plastic films such as PP and HDPE have much lower Tg temperatures between -20 to 100 °C (Valentas, 1997). PLA – films showed negligible crystallization at temperature of 116 °C with almost absence of exothermal heat flow during first and second heating cycle, which agree with the observation of Yu et al. (2020). Pure PLA- films showed a melting temperature at 150.4 °C with a very small endothermic heat flow and low crystallinity of 1.7 % (Table (3), which agree with Tm-values reported by Sharma et al. (2019). PLA – composite films containing CS, PHB and AC showed lower Tg (57.8 to 59.7 °C) than that of pure PLA-film (60 °C) during the first heating cycle, while Tg remained almost constant (62 °C) during second heating cycle for pure PLA – film and its composites. Temperature of cold crystallization (Tcc) of composite PLA-films was slightly different and was in the range of 111.4° to 112.3°C during the first heating cycle and moved to the range of 116.3 to 117.7 °C during the second heating cycle, which agree with the values reported by Molinaro et al., (2013); Halasz et al., (2015) and Beltran et al. (2021). A small shift of 1.3°C (decrease) in melting temperature has been observed for PLA-composite films. As seen in Fig. 3, exothermic heat flow at crystallization points and endo-thermic heat flow at melting points was increased for the PLA-films composites indicating the presence of higher ratios of crystallinity in the PLA-films composite. The crystallinity percent (Xc%) was increased in the film composite to the level of 11.2 to 13.5%. The presence of a single peak at melting point of the PLA-film composite proves the complete integrity of CS, PHB and AC in the matrix of PLA-films. Also, incorporation of CS, PHB and AC in the matrix of PLA-films acted as nucleus for crystallization and increased the crystallinity of the obtained films. The slight reduction in Tg in the first heating cycle of PLA -AC composite could be correlated with the increase in elongation ratio observed in Fig (1C). On other side, the differences in crystallization temperature (Tcc) of pure and composite PLA-films is correlated, according to Suryanegara et al. (2010), with perfectness of the formed crystals.

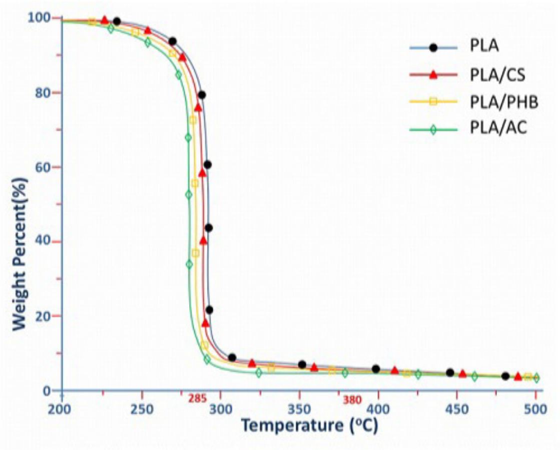

Fig. 2. TGA curves for PLA and PLA bio-composite samples.

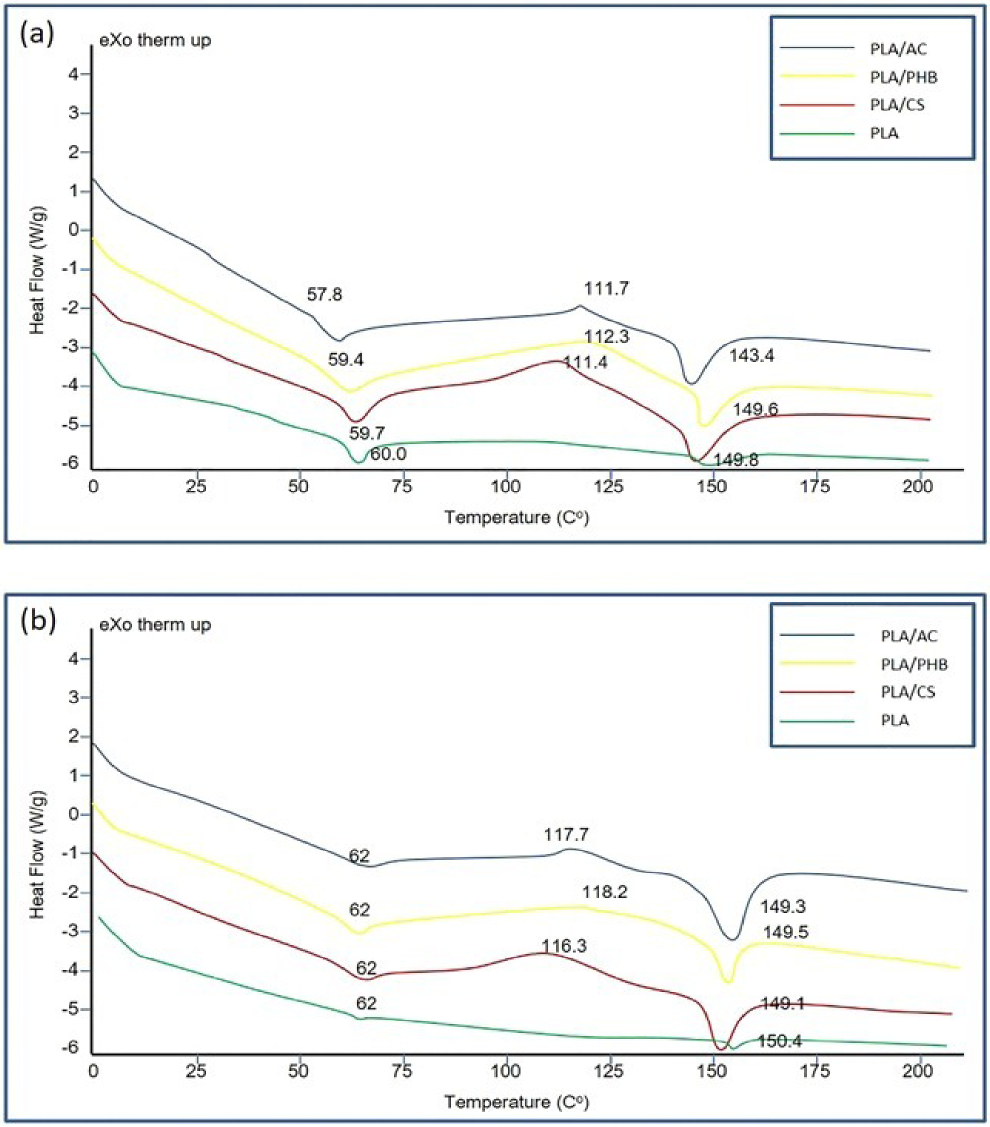

Fig. 3. DSC (a) first heating & (b) second heating of thermogravimetric for PLA and PLA biocomposites.

TABLE 3. Thermal characteristics and the degree of PLA crystallinity and its Bio-composites.

Treatment	Tg°C		Tcc°C		Tm°C	
	First	Second	First	Second	First	Second
PLA	60.00 ±0.00^{aB}	62.00 ±0.00^{aA}	-	-	150.20 ±0.06^{aB}	150.37 ±0.09^{aA}
PLA/HB	59.70 ±0.06^{bB}	62.00 ±0.00^{aA}	111.30 ±0.06^{cB}	116.40 ±0.06^{cA}	148.70 ±0.06^{cB}	149.13 ±0.09^{cA}
PLA/CS	59.30 ±0.06^{cB}	62.00 ±0.00^{aA}	112.27 ±0.09^{aB}	118.23 ±0.09^{aA}	149.43 ±0.09^{bA}	149.47 ±0.09^{bA}
PLA/AC	57.70 ±0.06^{dB}	62.00 ±0.00^{aA}	111.53 ±0.09^{bB}	117.53 ±0.09^{bA}	143.37 ±0.09^{dB}	149.33 ±0.09^{bA}

a, b & c: There is no significant difference (P>0.05) between any two means, within the same column have the same superscript letter;
A, B & C: There is no significant difference (P>0.05) between any two means, within the same row have the same superscript letter.

Annealing of PLA-Composite films

Annealing and crystallinity of PLA-films are important for their packaging applications. Results of DSC-analysis of PLA-films (Fig 3a & b) showed that presences of CS, PHB, AC and plasticizer ATBC in the matrix of PLA did accelerate the crystallization process of the bio-composite films. Fig. 4 shows the effect of annealing time on crystallinity % of PLA-films and its composites. As seen, annealing of neat PLA-film for 5 min did not increase the crystallinity of the film, may be due to low nucleation of PLA-molecules. Increasing annealing time to 10 min, did increase the crystallinity of neat PLA-film to the level of 25% and after 20 min, it reached the level of 40%. Extending annealing time to 60 min did remarkably not increase crystallinity ratio (41%). On contrary, annealing PLA-composite films for 5 min did rapidly increase the crystallinity % to the level of 28% to 32% with PLA-AC composite films showing the highest crystallinity value (32%). Increasing annealing time to 20 min slightly increased the crystallinity ratio to the level of 42 to 43%. The accelerated crystallinity of composite PLA-films could be referred to the increased nucleation of PLA-molecules induced by the presence of CS, PHB and AC molecules. As seen from Fig 4 and Fig 1, the presence of 8% AC in the matrix of PLA increased crystallinity level of the obtained composite film and improved the mechanical properties of the film (tensile, strength, Young's modules and strain at break). The obtained results agree with those of Barkhad etal. (2020); Bross et al. (2023) and Wang et al. (2023), who stated that annealing of PLA-film and its composites at 100 -140°C for 10 min was sufficient to achieve high crystallinity up to 40%

Water absorption and solubility of PLA-films

Water uptake is essential to evaluate the biodegradability and application possibility of PLA-bio composite films (Arrieta et al., 2014). Therefore, water uptake tests were carried out to determine the resistance of PLA-films for water (weight) gain. Fig. 5 depicts the course of water uptake by PLA-films in relation to contact time. As seen, the water uptake of pure (neat) PLA-film did not exceed 0.4% after 16 h contact time. The low water absorbency of PLA could be referred to its hydrophobic character. On other side, incorporation of PHB slightly increased the water level to 0.55%, may be due to the presence of ester groups which show hydrophilic nature. On contrary, incorporation of AC and CS substantially increased the water uptake to 1.17% and 1.5%, respectively probably due to the increased hydrogen bonds formation with water molecules and the hydrophilic nature of AC and CS (Tsuboi et al., 2021). It is worthy to mention that CS molecules are randomly distributed in the matrix of PLA, which facilitates water diffusion through the film thickness. The relatively low absorption capacity of PLA-AC film could be referred to the arranged structure and high crystallinity of AC, which limits diffusion of water molecules. The obtained results agree with those Mat Uzir et al. (2015).

Solubility is an important factor for estimating the biodegradability of films, which expresses the resistance to water and it depends on water diffusion through the matrix of the film (Shakaur et al., 2021). Fig 6 shows the weight loss of PLA-films over 16 days of contact with water. As seen, all tested films were stable during the first 2 days and showed no weight losses, may be because of the hydrophobic character of PLA and the slow diffusion of water molecules through the matrix of the films. Pure (neat) PLA and PLA- PHB composite showed 0.38 to 0.4 % weight loss after 16 days and exhibited trends similar to that of water absorption (Fig. 5). On contrary, PLA-CS composite showed the highest solubility ratio (0.65%) followed by its AC-composite (0.49%). This could be referred as reported by Khazraji and Robert (2013) to the randomly arranged structure of these two composites and to the poor adhesion (low cohesiveness) between the incorporated materials and PLA, which facilitated the penetrations of water for hydrolysis.

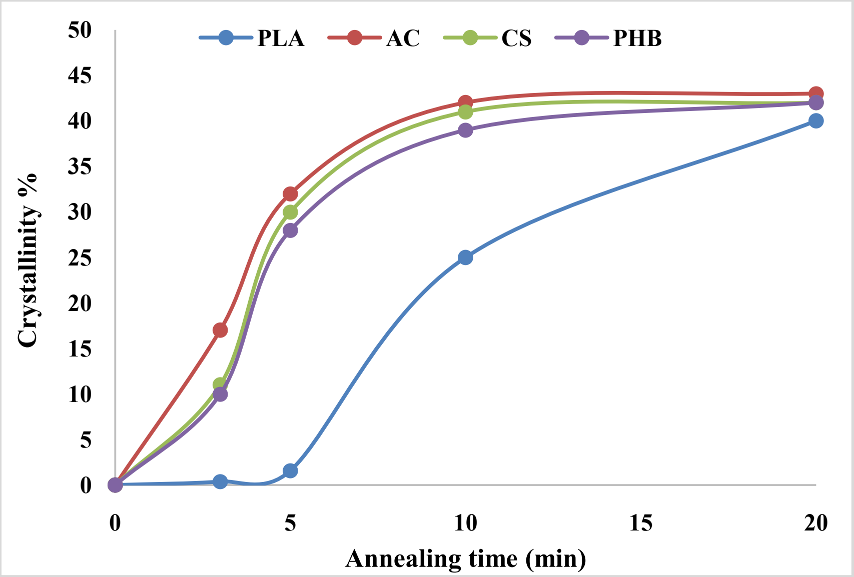

Fig. 4. Degree of crystallinity of PLA and PLA bio-composites with different annealing times.

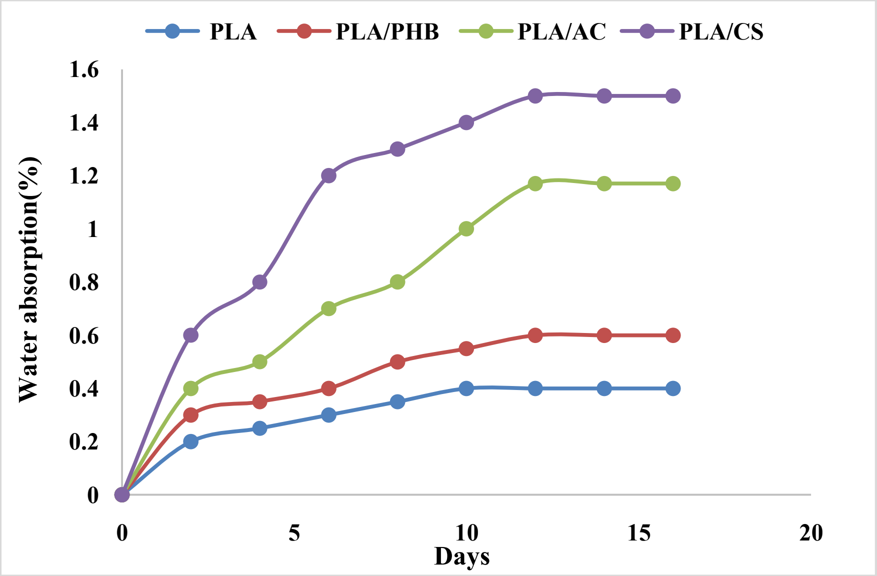

Fig. 5. Course of water uptake by PLA-films.

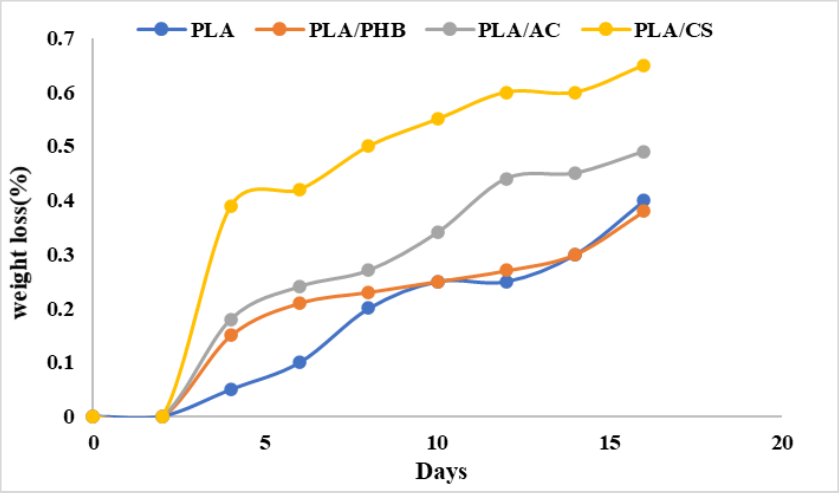

Fig. 6. Weight loss of PLA-films in contact with water.

Conclusions

Bio-composites from bioplastics are of great interest for packaging materials. This study was done to evaluate and compare three bio composites; PHB, CS and AC as reinforcement for PLA. These fillers improved the barrier and mechanical properties of PLA matrix. Also, thermogravimetric analysis (TGA) and calorimetric measurements (DSC) showed that PLA -composite exhibited an enhancement in the thermal stability, degradation and accelerated the crystallization process of all three bio composites compared to neat PLA. Confirming this finding, the water absorption test demonstrated a more significant increase in the hydrolytic degradation of the bio composites. Concerning color of the three composites films, there are slight amber color due to the ATBC addition (Plasticizer), but still mostly transparent. Incorporating AC gave a preferable bio-composites film and yield extraordinary performance in terms of the studied mechanical properties than that of CS and PHB. The improved properties of cellulose bio-composites could be attributed to the unique properties of its loosely ordered for arrangement and circular shape, and also was attributed to the compatibility of the matrix. Therefore, bioplastic film containing 8 wt % amorphous cellulose exhibited superior properties than pure PLA film, also than PLA/PHB & PLA/CS films. These improved properties suggest PLA- AC bioplastic film for several packaging applications including food in addition to drugs and other goods packaging. Finally, in these study results revealed that a new green composite of PLA/AC, which more successfully appreciated than PLA/PHB and PLA/CS and giving a preferable bio-composite film more preferable than neat PLA.

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