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Biodegradable Package Films Of Poly(L-Lactic) Acid/Extracted Gelatin Blend From White Leather Fibers

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IN food packaging area, the substantial utilization of synthetic plastics has a huge environmental impact and there is necessitate really for more biodegradable packaging materials. Blending of poly (lactic acid) (PLA) and extracted gelatin (EG) was investigated as prospective replacements for non-degradable petrochemical polymers. EG is a biopolymer extracted from white leather fibers wastes in the leather industry after alkaline hydrolysis. Both polymers need modification for food packaging requirements. PLA films are very brittle and gelatin is sensitive to water and the properties of its films are reliant on the moisture content with low mechanical strength. An investigation on the blending of PLA and EG films gives better properties more suitable for packaging depending on their paired characteristics. The resulting biodegradable films were characterized using by FTIR, SEM, TGA/DTA, and simulated soil burial respirometric testing. The properties of some characteristics of PLA and EG blends in terms of mechanical and thermal properties have been discussed as biodegradable packaging films. It was found that the addition of 30 wt % of EG offering blended films with good thermal processability, transparency and flexibility, as well as films with good mechanical.

Keywords: Gelatin, PLA, biodegradable package filmsز

Introduction

Leather industry is responsible for a huge amounts of wastes during the hide tanning process producing leather as a stock for shoes, automotive and furniture markets [1-3]. The process of making leather produces enormous quantities of solid and liquid wastes. The production of one ton of rawhide yields an average 250 kg of tanned leather, 250 kg tanned leather waste, 250 kg of untanned waste, besides almost 60,000 kg of waste water. The skin trimmings, keratin, fleshing, chrome shaving and buffing wastes are the generated solid wastes in leather production process in where protein is the principal constituent of all wastes[4-8].

The problem has admittedly received more attention because it has been mostly disposed until now to the landfill. If protein solid wastes are not used, processed or properly treated, they may cause serious environmental problems that threaten the sustainability of the leather industry. Many clean treatment methods designed to reduce solid and liquid wastes have showed and confirmed to be economically and environmentally valuable [9-14]. White leather shavings fibers (WLSF) signify the main by-product wastes of the leather industry which treated into a combination of useful products such as glue and gelatin for industrial applications [7].Gelatin was studied for mixing with polymeric materials with confident results.

There is increasing consideration in the extraction process of gelatin and its derivatives due to the growing tendency to use gelatin to substitute synthetic agents in various industrial processes, which results in a greater support

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of the by-products from animal slaughter. Gelatin's characteristics depend on the raw material and the extraction conditions, which subsequently determine its application. Gelatin has a widespread variety of applications in the food, pharmaceutical, cosmetic and packaging industries, among others [7].

Nowadays in packaging technology, synthetic polymers are sources of many problems because of their partial recycling potential. A huge amounts of packages are disposed of by a landfill or incineration must be performed at elevated temperatures to avoid the forming of degradation products with unfavorable (regularly carcinogenic) properties which have a detrimental effect on disposal costs. Hundreds of years are the elongated degradation time of synthetic polymers in landfills [15-21].

Poly(ethylene terephthalate) (PET), polystyrene (PS), polypropylene (PP), polyethylene (PE) and polyamide (PA) are petroleum plastics usually utilized for packaging purposes. Plastic is highly successful in the packaging market because of the tremendous combination of strength, transparency, stability and flexibility which make it suitable for a permanent environmental issues as food packaging. On the other hand, in spite of their good properties, their using, collection and aggregation application involved dangerous environmental problems because of dependence on fossil fuels [16].The global plastics consumption are approaching 100 MT/Y so; it has now become an urgent concern to find an alternate to plastic, produced from renewable and recycling resources.

To overcome the increasing production of plastics wastes and pollution problems, researchers concentrated on the improvement of substitute packaging materials, obtained from renewable materials resources, which are biodegradable or compost. Biodegradable plastics and biodegradable packaging for products have already been invented such as cellulose, starch, protein. Biodegradable polymers in which consider the time required for degradation of germs, clamps or weather in landfills in an average of weeks or months, are represent a very attractive alternative in this area. In addition, these polymers come from natural sources of renewable raw materials (animal or plant proteins), are not poisonous. Biopolymers utilized to replace non-biodegradable plastics by a new natural and environmentally kindly materials, called bioplastic which decrease environmental influence and oil-dependence [22-23].

Bioplastics are derived from three main groups based on their source and biodegradable nature: the 1st biobased non-biodegradable bioplastics (PET, PA), the 2nd biobased biodegradable bioplastics (PLA), polyhydroxyalkanoates (PHA), starch or gelatins) and the 3rd fossil based biodegradable bioplastics (e.g., polycaprolactone (PCL). So, biobased categorized as those gained from biomass (PS and gelatin) or petrochemicals (e.g., PLA, PCL) according to European Bioplastics. Generally, for food requirements, the functional properties of biopolymer-based materials are essential to modified for their mechanical properties. These could be occurred through crosslinking (physical or chemical modifications) and blending with extra constituents (plasticizers or compatibilizers) [16]. Gelatin is amorphous while PLA is semicrystalline and crystallization degree of films rely on the source and the treatment environments, which significantly affects the mechanical performance of the material [24-27].

PLA is insoluble in polar protic solvents, but it is soluble in nonpolar solvents, which are toxic, but also soluble in polar aprotic solvents. Depending on stereochemistry and molecular weight of PLA, the degradation half-life time from 8 months to 2 years [28]. PLA has many features; it is biodegradable, renewable and biocompatible and it accepted by the Food and Drug Administration (FDA) for straight interaction with biological liquids, comparing to those of petroleum plastics such as PET. It is extremely transparent and has good water vapor barrier properties [29,30]. Because of increasing industrial construction technologies, PLA became very economical in price. However, PLA has inadequate gas barrier ability because of its hydrophobic in nature. Although it's hard resistance (its tensile strength from 20 to 70 MPa) [31, 32] it is very fragile, with a smaller amount 11% of elongation at break [33].

In case of PLA blending, Fortunati et al. [31] studied the addition of chitosan (C) to PLA by extrusion, both polymers are not compatible and because of the lack of (C) fusion during treatment, the polymer molecules were remained in the final films. Therefore, (C) did not affect the thermal behavior of polymer films or total crystallization of PLA with less intensity and elasticity, without any modification in the thermal properties of PLA. Similarly, the incorporation of chitosan into the higher permeability of water vapor than these PLA films is elegant with antimicrobial activity against the bacteria. Also, preparation of polymer blends of PLA, poly(butylene succinate-*co*-adipate) (PBSA) and poly(butylene adipate-*co*-terephthalate) (PBAT) was investigated with targets for application of puffed film extrusion method by Weraporn et al. [32] The morphological studies pointed out that PLA and PBSA showed an insufficient compatibility with phase separation. The PLA/PBSA polymer blends of 80/20 % by weight showed good distribution of the compounds after adding a range of 10-30 % of PBAT by weight and respectable mechanical properties with a higher stress strength of 41 Mpa and 27 J/m. Yuyue et al. [43] also developed the effect of biobased (PLA/PCL) blends films with a combination of changed cinnamaldehyde contents (4 - 8 wt %) on the physical and microbial quality of the *Agaricus bisporus* was stored at 5 ± 1 °C for 15 days. The results are recommended using PLA/PCL/C9 film with higher permeability to water vapor to maintain the quality of fresh mushrooms.

While in case of gelatin blending, Buğra [34] studied the addition of chitosan (C) to collagen hydrolysate extracted from leather (CH) to assess the possibility of polymer films suitable for applications as packaging material. The results showed that, the addition of (C) caused an increase in the thickness and tensile strength resulting in stronger films comparing with CH film but decreased the elongation at break % and solubility of films. FTIR and DSC provided total miscibility between polymers and SEM revealed that composite films CH/C showed a homogeneous structure. Isabell and Peter [35] studied the enhancement of water resistance in films based on collagen-and the effect of different crosslinking agents and cross-linkers concentration grads. The results revealed that thermal crosslinking leads to weaker bonds than the chemically crosslinking.

In packaging technology, films or foils gained from collagen hydrolysate are characterized by high efficiency of the barrier of O_2, CO_2 and aromatic substances. The hydrophilic character of protein films can be better controlled by increasing the density of the interconnections that attained through cross-reactions through specific aldehydes [23]. An appropriate degree of cross-linking allows controlling the rate of dissolving films and also the rate of releasing active components from such packages [24-26]. Biodegradable packaging materials from hydrolysate of gelatin leather waste applied to form high impact polymer films as eco-friendly packaging materials for numerous applications.

Blending of extracted gelatin (EG) with biodegradable polymer (PLA) being the scope of this research which explores the ability forming biodegradable films. The effect of gelatin addition on the biodegradation rate and composition of the films was achieved by respirometric test simulating soil burial experiments. Thermal and mechanical properties, besides to instrumental analysis as SEM morphology, FTIR were also characterized for biodegradable film samples.

Experimental part

Materials

L-lactic acid (98 %), p-toluenesulfonic acid (ACS reagent 98.5 %) and stannous octoate (92 %) were provided by Acros. The thermoplastic PLA/EG elastomer produced by blending of PLA and gelatin which extracted from white leather shavings fibers by alkaline hydrolysis. Extracted gelatin from white leather shavings fibers by alkaline hydrolysis was extracted and characterized (nitrogen content, moisture, ash content, fat content and average molecular weight) according to our previous research work [7]. Essential physically investigation of EG was presented in Table 1 where amino acid content was shown in Table 2.

TABLE 1. The properties of EG. (Mean ± SD, n = 3).

Properties	Value
pH	6.5- 7.2
Nitrogen Content %	13.2 ± 0.6
Moisture Content %	5.2 ± 0.4
Ash Content %	4.3 ± 0.5
Fat Content %	0.45 ± 0.05
Average molecular weight	20 K Dalton

All the percentage represented in a dry basis except for moisture.

Methods

Synthesis of PLA polymer

L-lactic acid (1.03 g) was polymerized by using p-toluenesulfonic acid and stannous octoate (0.6 wt %) as a catalyst were stirred for 12 h. at 150 °C. the prepared PLA was precipitated in acetone followed by filtration and drying under vacuum for 36 hours at 40 °C.

Amino acids of extracted gelatin at optimum condition

The amino acid compositions of the gelatin extracted from white leather shavings fibers (WLSF) were measured according to Elsayed et al., [7]. The experimental results showed that under the conventional acidic hydrolysis conditions, complete hydrolysis of the white leather shavings fibers (WLSF) was proceeded with yield of 16 amino acids as revealed in Table 2.

PLA prepared by dissolve 25 mg of the prepared polymer in 5 mL of acetone. Polymer solution was added to 10 ml of Millipore water drop wise. The mixture was stirred overnight to allow remove of acetone. Thermoplastic films were prepared by mixing the resultant solution ingredients containing PLA nanoparticles blended with different weight ratio 10 to 40 wt % of extracted gelatin (EG) where the content of EG in the blends of PLA/EG was variable from 10 and 40 wt % EG related to the total weight of blends as shown in Table 3. The symbols of the blends indicate the compositions. The mixture stirred for 60 min followed by film casting in Teflon petri dish and dried in vacuum oven at 30 °C overnight.

Analyses

The mean diameters investigation of dispersed samples was carried out with Dynamic laser scattering (DLS) instrument (PSS, Nicomp, USA), using the 632 nm HeNe laser with incident angel of light 170°, nanomaterial investigation lab., Central laboratory, national research Centre.

DSC was carried out in a TA Instruments Q100 to determine glass transitions (T_g), crystallization temperatures (T_c) and melting points (T_m). The thermal history was erased during the first run at a high heating rate up to 200 °C, followed by cooling cycle to -50 °C, after that, the heating rate was

TABLE 2. Amino acids composition (%) of the extracted gelatin. (Mean ± SD, n = 3).

Amino Acids	%	Amino Acids	%
Aspartic Acid	10.65	Leucine	6.52
Threonine	3.78	Isoleucine	2.74
Serine	6.26	Phenylalanine	5.44
Glutamic Acid	12.02	Tyrosine	2.34
Valine	3.75	Histidine	2.29
Methionine	0.42	Lysine	9.31
Proline	2.50	Arginine	25.03
NH_4^+	7.12		

Preparation of biodegradable packaging film

TABLE 3. Processing Behavior for Biodegradable Thermoplastic Composite Binary blends.

Films	Ingredient concentration (wt %)	
	PLA	EG
PLA	100	0
PLA/10EG	90	10
PLA/20EG	80	20
PLA/30EG	70	30
PLA/40EG	60	40

modulated ± 1.0 °C min^{-1} with heating rate 5.0°C to 200 °C min^{-1}. According to ASTM D 3418, T_g was calculated as the midpoint temperature.

GPC was used to determine the molecular weights by Waters equipment with differential refractometer as a detector and quaternary pump controller model 600. Two columns type Waters Styragel HT6E and HR4E were applied for the assignment of the molecular weights of prepared PLA samples. This system was operated at flow rates of 0.6 and 0.4 mL min^{-1}, as optimum column measurement conditions. Calibration curves prepared from polystyrene standards in tetrahydrofuran at 30 °C was used to calculate the molecular weights.

Fourier transform infrared spectroscopy (Nexus 670 FTIR, Nicolet, US) over range of 400–4000 cm^{-1} with KBr disk was used to investigate the composition of the blend.

Thermal analysis (TGA/DTA) of the polymer samples were applied through Perkin Elmer analyzer, rate = 10 °C/min, from room temperature to 600 °C at the National Research Centre of Egypt.

Dumbbell-shaped polymer specimens were used for the measurement of tensile strength and elongation at break (%) according to ASTM D638. These tests were carried out using Zwick/Roell (Z010) and cross-head speed of 50 mm/min at room temperature. The average value for each test was taken for three samples to confirm the results (mean ± SD, n = 3).

The biodegradation was completed in Erlenmeyer jars holding a multistate substrate having the accompanying structure: the base position of every flagon was loaded up with 20 g perlite (hygroscopic aluminosilicate) [36, 37]. Films and control were put in the center. Carbon dioxide delivered inside the hatching time from the test cups flushed with CO_2-air which was resolved as percent of hypothetical amount of CO_2 from the test material, reasoned by its carbon content, revised for the measures of CO_2 created in the spaces amid the brooding time. CO_2 delivered was dictated by adsorption in solution of potassium hydroxide (0.025 N) and retrotitration with 0.05 N HCl. Each test was completed for three examples and average value was considered to guarantee the outcomes (Mean ± S.D., n=3).

Results and Discussion

Dynamic light scattering (DLS)

DLS mentioned as one of the leading tool for understanding the dynamics of polymers models and verifying them in dilute solution. It allows monitoring the size and hydrodynamic polymer molecules radius in solution. As shown in Figure 1, the particle size distribution of PLA which dispersed in aqueous medium presence relative particle diameter measurement distribution over a narrow range from 30 - 110 nm with a percentage more than 90 % of particles by volume distribution.

Low dispersity, a narrow distribution of particle size, of PLA indicated to the homogenized distribution of blended film gelatin. These

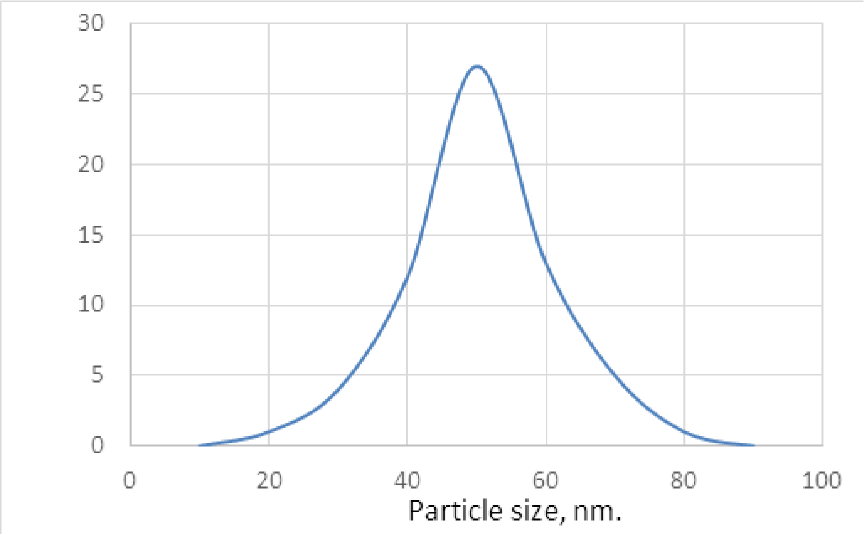

Fig. 1. Particle size distribution of PLA homopolymer dispersed in aqueous medium.

confirm continuous films with ± 45 µm and for PLA and ± 70 µm for PLA/EG films. Particle size behavior gives PLA and PLA/EG film a range of application from few µm as packaging films.

Gel permeation chromatography (GPC)

GPC used for investigation the molecular weight of the prepared polymers. GPC chromatograph was shown in Figure 2 as unimodel without humps or shoulder. This is indicated to smooth molar distribution of nano-PLA chains. Number average molecular weight (*Mn*) = 54 KDa, weight average molecular weight (*Mw*) = 156 KDa and molecular–weight dispersity (*ĐM*) is 2.8 as molar indices of PLA. Complete conversion polymerization can be indicated to relatively high weight average molecular weight than number average with related to molecular–weight dispersity (*ĐM)* index.

Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy was among the most powerful spectroscopic techniques for gelatin analysis used to study the changes in the functional groups as well as chemical composition and secondary structure of gelatin. Figure 3 and Table 4 shows a typical FTIR spectrum for EG, PLA and PLA/EG. It shows three major peak regions marked as 1st region (3600 - 2700 cm^{-1}), 2nd region (1900 - 900 cm^{-1}), and 3rd region (500 - 900 cm^{-1}). The regions area are set to the bonds and similar results were also detected by Zhang et al. 49 Self-assembly of collagen fibrillogenesis of the amide A and amide (I-III) peaks related to broadening, increasing in intensity and a small shift to lower wave number. The shifting, increasing in intensity and broadening are related to the increasing in intermolecular interactions by hydrogen bonding in gelatin [38].

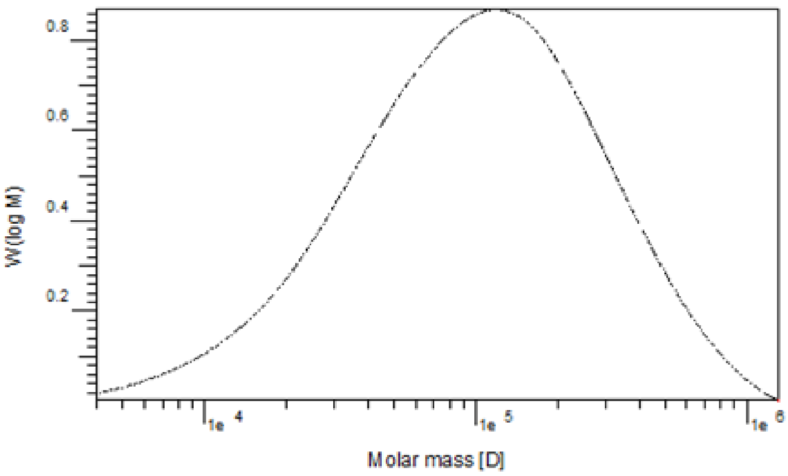

Fig. 2. Gel permission chromatography of PLA in THF.

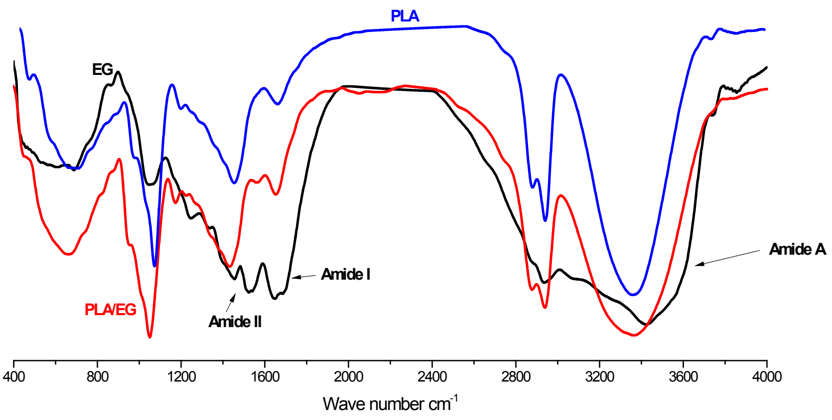

Fig. 3. FTIR Spectra for EG, PLA and PLA/10EG blended.

The FTIR spectrum show characteristic absorbance peaks of the chemical groups of the gelatin, PLA and PLA/10EG in Figure 3 and Table 4. The absorbance bands are recognized as follows: a strong and broadening overlap band in the range of 3600-3300 cm^{-1} allocated to NH bond in the peptide group and for the OH of carboxylic group of gelatin, the bands at 2938, 2877 cm^{-1} are from -CH$_3$ and -CH$_2$ stretching vibrations for the gelatin and PLA chain. The strong band at 1646,1652 cm^{-1} is related to C=O overlying between carbonyl groups of gelatin and the carbonyl groups of PLA stretching vibrations, the bands at 1335 cm^{-1} and 1433 cm^{-1} are related to – CH$_3$ and -CH$_2$ bending vibration. Also, the band at 1225 cm^{-1} was allocated to NH bending vibration of the amide group and the band at 1174, 1051 cm^{-1} is attributed to C-O-C of amide bond in gelatin and PLA stretching vibrations, the bands at 987 cm^{-1}, 969 cm^{-1}, 695 cm^{-1} are the skeletal stretch C-C- and CH out off plane [7,38].

The amide I, from 1600 to 1800 cm^{-1}, is the best valuable of IR spectroscopic analysis for the secondary structure of gelatins. Clarifying of the amide I band presented that the bands range consist of three components peaks, their location displayed in Figure 4 and Table 4.

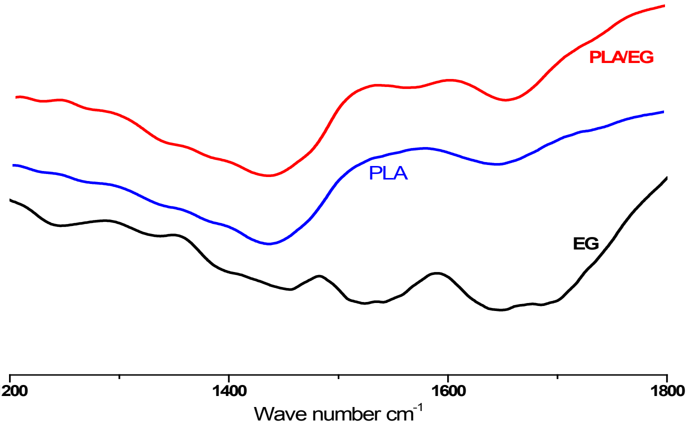

Fig. 4. Amide I and amide II band for EG, PLA and PLA/10EG blended.

TABLE 4. FTIR spectra and assignments for gelatin, PLA and PLA/10EG.

Region	Peak wave number cm $^{-1}$			Assignment
	EG	PLA	PLA/10EG	
Amide A	3500	--------	3500	NH stretch
	3422	3361	3363	OH stretch
	2936	2938	2938	CH$_2$ asymmetrical stretch
	2850	2877	2877	CH$_2$ symmetrical stretch
Amide I	1647	1646	1652	C=O stretch coupled with COO-
Amide II	1524	---------	1561	NH bend coupled C-N stretch
	1455	1435	1433	CH$_2$ bend
	1331	1382, 1362	1335	CH$_3$ bend, CH$_2$ wagging of proline
Amide III	1246	------	1225	NH bend
	1047	1051	1174,1051	C-O stretch
Amide IV	863	987	957	-C-C-, skeletal stretch
Amide V	687	678	877	CH out off plane, skeletal stretch
Amide VI	611	637, 542	748, 665	CH out off plane, skeletal stretch

Extracted gelatins also demonstrated the significant peaks at about 900 and 1100 cm^{-1}. Absorption peak related to C-O vibration due to PLA. PLA and gelatin are linked with glycation (non-enzymatic glycosylation) and required in the foundation of pentosidine crosslinks, in addition the peak corresponding to amide III was clearer in the case of gelatin [7].

Scanning electron microscope (SEM)

SEM is a precious technique for evaluating the morphology of the various treatments effects for PLA and PLA/EG. It used to study the surface topography, the shape, the features of gelatin blended with the polymer. Results of extracted gelatin, PLA and different blending of PLA/EG (10- 40 wt %) samples were shown in Figure 5.

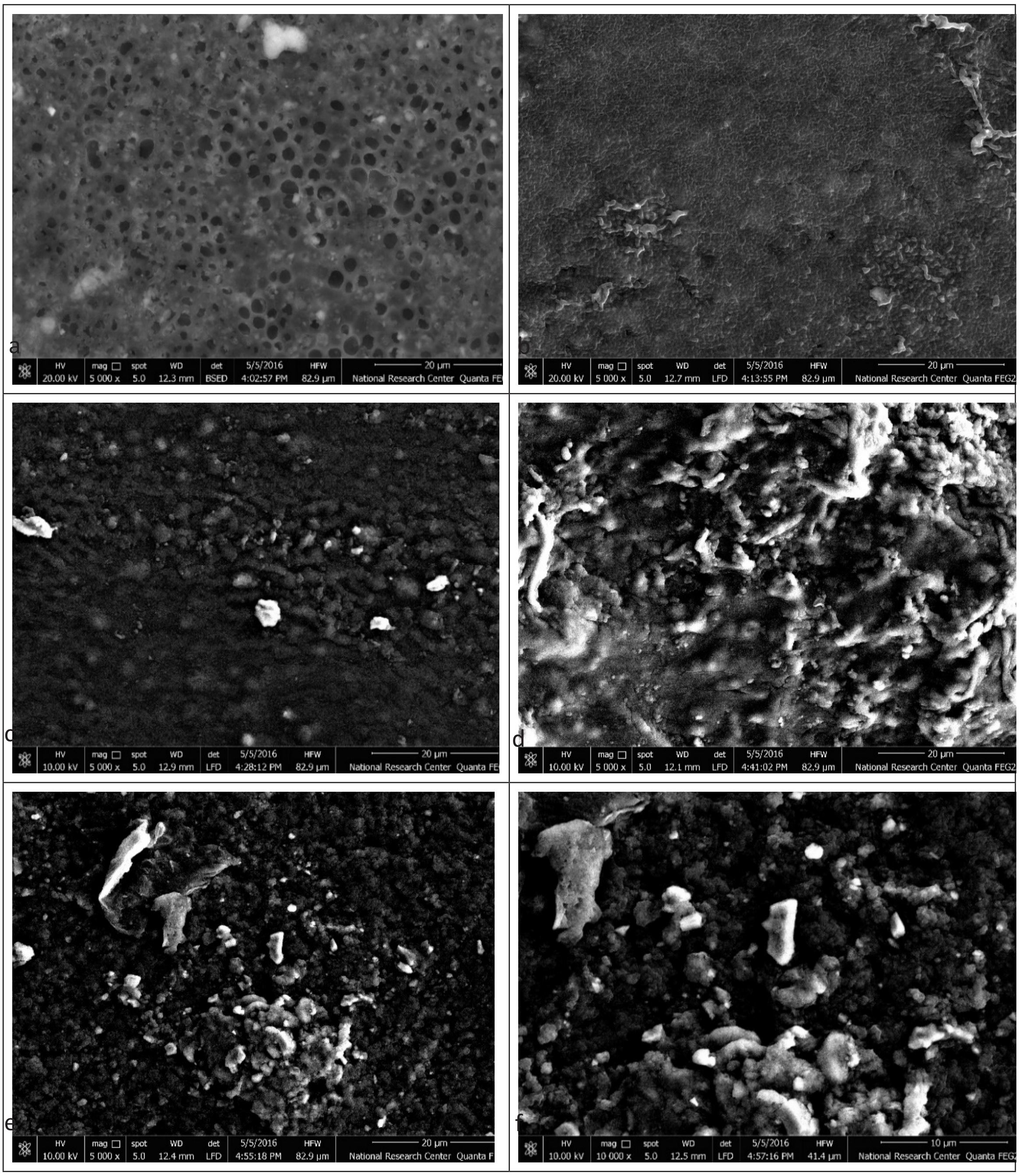

Fig. 5. SEM microscope images of the pristine PLA, PLA blended with different percent of gelatin a) PLA, b) PLA/10EG, c) PLA/20EG, d) PLA/30EG and e) & f) PLA/40EG.

The morphology of PLA before and after combining with EG could be identified by means of SEM, as presented in Figure 5. Topographic images were found that PLA was a kind of homogenous morphology. The roughness of the film surface was increased with increasing gelatin percentage in PLA/EG films. This indicated that the interaction between the EG with PLA polymer was mostly homogenized [37-42].

SEM measurements were used to study the dependence of the properties of combined polymer films on both structures and the surfaces morphology of the fractured impact specimens as presented in Figure 5. As shown in Figure 5(a), it was clearly found that the fracture surface of raw PLA was clear, rather smooth and monotonous except for some holes, which resembled a typical brittle fracture mechanism for solvent evaporation. While the surface fracture of the PLA/EG was coarse and more elaborated surface features than did raw PLA (Figure 5(b)), and it was very interesting that there were many filaments on the fracture surface, which displayed the toughness part. Many rougher rupture surfaces and a larger number of dispersed phases were shown in the samples of gelatins (Figures 5(c) to (f)). With the increase of gelatin content in PLA matrix, the dispersion of gelatin became more and more homogeneous. When the mass fraction of gelatin was 30 wt %, a double continuous phase morphology consisting of the modified PLA and gelatin was obviously obtained in PLA/EG biodegradable film. However, when the mass fraction of gelatin was 40 wt %, the larger the aggregates of gelatin were observed in the combined PLA/EG blends, which could be the stress concentration and phase separation that led to the premature and brittle failure.

Differential scanning calorimetry (DSC)

A typical DSC thermogram of PLA is presented in Figure 6. The thermal transitions are presented as the glass transition temperature of PLA. It is in agreement with standard values of PLA homopolymer at this composition, T_g = 65 °C where the melting point T_m = 159 °C. Previous thermal parameters verified the suitability of PLA to apply as polymer coating for packaging materials sheets. Low melting temperature gives an opportunity to apply as melted coat through manufacture line or as soluble coat through film coater or spray techniques. These unique multi-coating techniques open the window of industrial applications in many fields to use PLA coat as antimicrobial film on many substrates according to desirable coating process.

Thermal gravimetric analysis (TGA)

TGA is a thermo-analytical technique function of temperature. The response to thermal treatment depends on the gelatin structure and its morphology at each step. Thermal behaviors extracted by NaOH from white shaving leather waste are presented in Figure 7. It was obvious that there are three main degradation stages. The 1st stage represents dehydration volatilization of

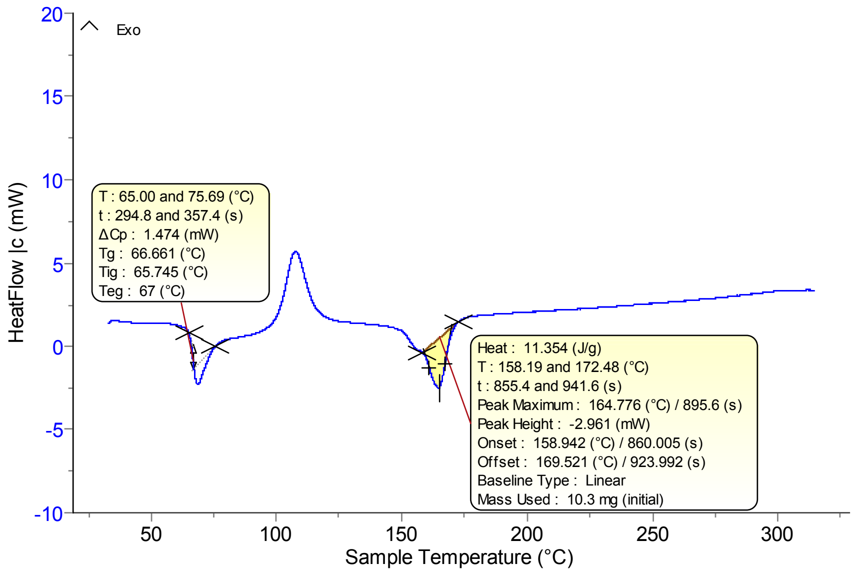

Fig. 6. Differential scanning calorimetry (DSC) thermograms of PLA

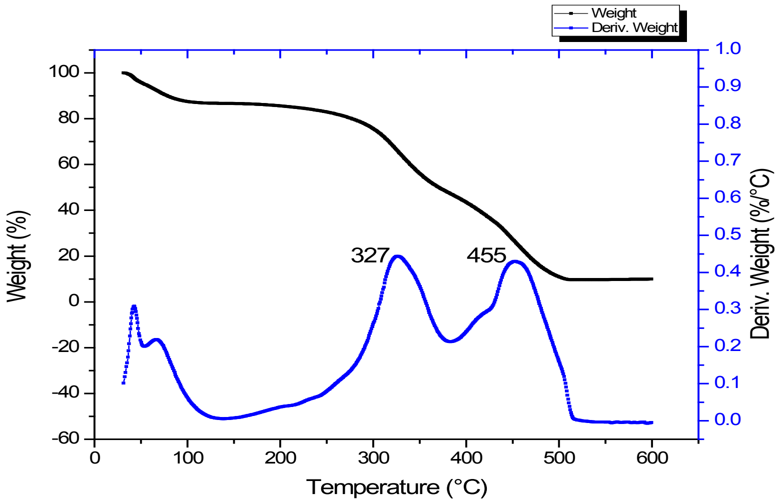

Fig. 7. TGA/DTG of extracted gelatin by NaOH.

few molecular weight substances. The 2nd stage is the main degradation stage and the 3rd stage is the carbonization stage [7].

The gelatin sample extracted by NaOH from white leather shavings fibers (WLSF) has an initial weight loss of about 12 % at a temperature between 50-120 °C due to the evaporation of water included in gelatin. There is a gradually decreased in the weight loss of the gelatin which reaches 60 % at a temperature between 130- 440 °C due to the degradation of gelatin chain. The third peak at 400-600 °C involved the degradation of the rest of gelatin with a weight loss of 19 %. After 600 °C, the ash formed with about 9 % of the initial weight [43-45].

PLA Thermogram was exhibit three decomposition stages in ranges as shown in Figure 8. The first stage, start from room temperature until 210 °C with an initial weight loss of 17 %. This stage based on water loss and any trapped solvent with some mobility of the PLA chains. The second stage (Tmax$_1$) laid in rage from 250 °C to 360 °C followed by third decomposition stage from 360 °C to 400 °C (Tmax$_2$) with total of weight loss of 59 %.

Figure 9 shows the thermo-gravimetric curve of PLA that blended with different contents of gelatin which applied under thermal behavior testing from room temperature to 600 °C to study the decomposition stages of certain blend ratios. As a presence in Figure 9, the decomposition of PLA was affected by the addition of gelatin from 10 to 40 wt %. As the addition of gelatin increased, the degradation temperature increased reaching to the highest degradation in case of PLA/30EG as shown in Table 5. This effect related to the strong interaction and good compatibility and blending of the gelatin and the nanoparticles of PLA. Four stages of PLA/EG as unique behavior for biodegradable blend than parent sample of PLA are illustrated with expanded of first stage from 150 °C until 170 °C. This is could be due to trapping of water molecules in gelatin matrices. That is following with three decompositions stages (chain mobility, cracking and decomposed). The second stage (Tmax$_1$) laid in rage from 230 °C to 300 °C followed by third decomposition stage from 350 °C to 440 °C (Tmax$_2$) with total of weight loss of 85 %. The ash formed with 15 - 20 % of the initial weight loss which presence complete dissociations until 600 °C.

In Table 5, the thermal decay of PLA was affected by addition of gelatin from 10 to 40 wt %. In which PLA/30EG reaches to the highest thermal decomposition temperature of Tmax$_1$ reaching to 275 °C and Tmax$_2$ expanded to 440 °C as the effect of gelatin flexible chain related to hard chain polymer of PLA.

Mechanical properties

The mechanical features contain measuring of the tensile strength at rupture and elongation at break % which approved by official methods and average values of at three tests were taken for each item. In the following stage, 10- 40 wt % of gelatin were incorporated in PLA matrix to prepare blended films by solvent casting. As the addition of gelatin increased from 10 to 40 wt %, the tensile

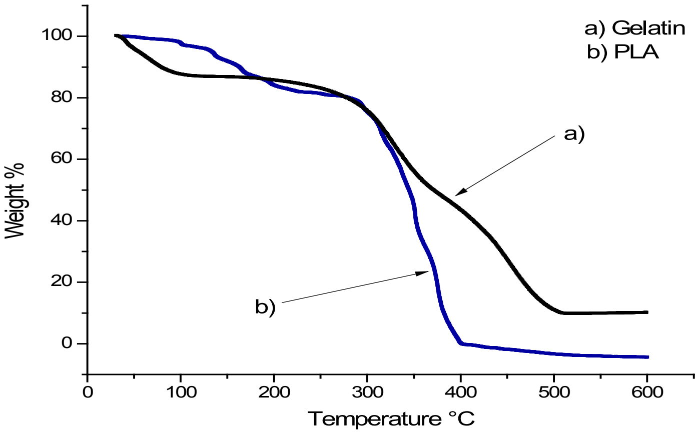

Fig. 8. TGA of a) extracted gelatin and b) PLA.

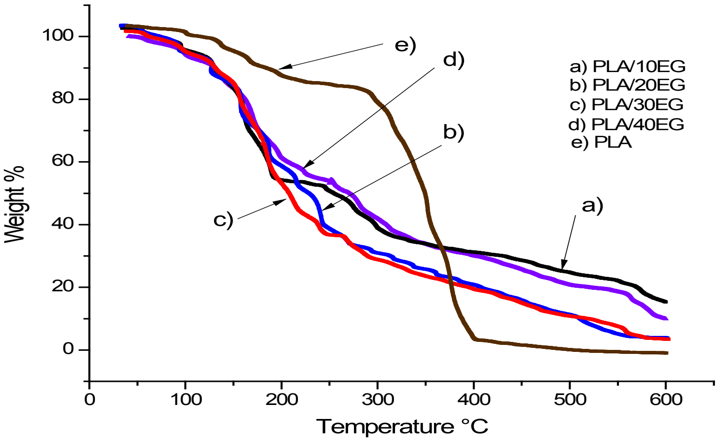

Fig. 9. TGA of PLA blended with different amount of gelatin a) PLA/10EG, b) PLA/20EG, PLA/30EG, PLA/40EG and e) pure PLA.

TABLE 5. Thermal data of PLA/ EG (10-40 wt %) blended films

Formulation	**1st Degradation T_i (°C)**	**2nd Degradation T_{max1} (°C)**	**3rd Degradation T_{max2} (°C)**	**Char content at 600 °C , %**
PLA/10EG	150	232	404	15
PLA/20EG	155	237	400	17
PLA/30EG	170	275	440	12
PLA/40EG	170	252	427	17.5
PLA	210	345	375	0
EG	75	327	455	9

strength MPa decreased while the elongation at break % increased. The strength of PLA/EG blended films interconnected matrix decreased with addition of gelatin to the thermoplastic films because of the incorporation of the microstructure of blended films leads to reduction in the mechanical properties of thermoplastic films. So, the best improvement observed in the case of 20 and 30 wt % gelatin films for elongation at break % wherever increased by 344 % and 250 %, respectively as matched to PLA neat films.

These improvements in elongation at break % are related to the increased interaction flexibility between gelatin and PLA matrix by increase sliding coefficient between polymer chains. Maximum mechanical properties were at the presence in the blended sample with 20 wt % gelatin. Higher than this percentage, high flexibility of gelatin chains are affected on the high loading force applied during mechanical measurement. From the obtained results of PLA/20EG, the tensile strength decreased from 11.7 to 3.41 MPa and the elongation at break % increased significantly by 340 %. The rapid extension of the blended film cannot give the chance for huge elongation before sample cutting. This relative relationship between applied force and measured tensile strength and elongation at break % of the blended sample can be pointed to prospected applications for prepared polymer film as biodegradable packaging films.

Biodegradation of PLA/EG blended films

Biodegradation respirometric trials were accomplished by a simulated soil burial test to achieve the investigation of biocompatible treating blends. Biodegradable films including different amounts of EG (10 - 40 wt %) showed different biodegradation ranges exceeded 70 % of mineralization afterward 30 days of incubation, while pure EG film showed about 80 % biodegradation rate within the same time in Figure 10. The results obtained by increasing amounts of EG, clearly indicates a positive effect of EG on the rate of biodegradation and the amount of blended PLA/EG films. In considering of the modulating

TABLE 6. Physico-mechanical properties of PLA and PLA/EG blends with different ratios.

Sample	Stress, MPa	Tensile, MPa	Elongation at break %	Elasticity
PLA	11.70	13.40	4	Hard
PLA/10EG	5.40	5.41	71	Semi elastic
PLA/20EG	3.41	3.44	344	High elastic
PLA/30EG	0.65	1.35	250	Elastic
PLA/40EG	0.66	1.47	210	Elastic

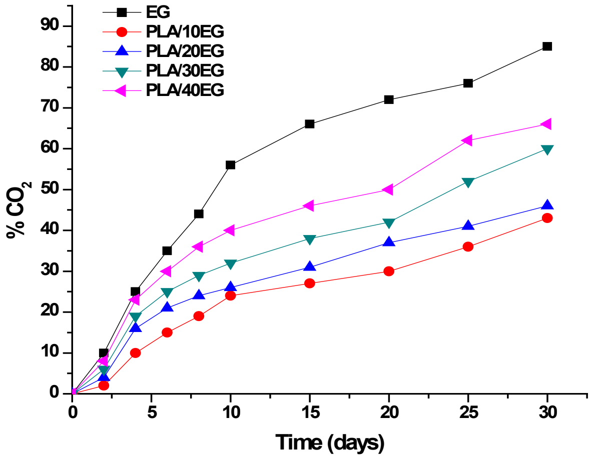

Fig. 10. Biodegradation curves of PLA/EG at different compositions of gelatin of biodegradable thermoplastic films at different time intervals.

possibilities at the environmental durations of the blended films without crosslinking agent were evaluated to discover better blending components for obtaining a reliable covering films. The increasing biodegradation rate with the extent of EG thermoplastic films caused by PLA addition which related to a chemical, physical entanglement doing by the PLA on the gelatin. Also, EG appears to increase the biological degradation of PLA/EG blends films compared to pure PLA film in existence of soil microorganisms which detected by the current results verified by films containing different amounts of EG, such as PLA/10-40EG films. Higher mineralization of PLA/EG blended films was achieved because of the strong interaction and the irreversible adsorption of the biodegradable polymer with gelatin extracted into the soil clay matrices [36].

Conclusions

The leather processing industry generates huge amounts of fiber wastes that have higher potential possibility of economic reuses through chemical hydrolysis recovery of WLSF. The extracted gelatin (EG) incorporated with the PLA matrix. The moderately molecular weight of EG permitted a good blending with PLA as described by SEM. Elongation at break % of PLA/EG thermoplastic films increased with increasing the extent of EG reaching 30 wt % while the stress decreases with any significant effect for applications in the packaging sector. By studying the thermal, mechanical and morphology properties of the prepared biodegradable films PLA/ EG, it was found that the addition of 30 wt % of EG offering blended films with good thermal processability, transparency and flexibility, as well as films with good mechanical properties. The thermal decay of PLA was affected by addition of gelatin from 10 to 40 wt %. In which PLA/30EG reaches to the highest thermal decomposition temperature of $Tmax_1$ reaching to 275 °C and $Tmax_2$ expanded to 440 °C as the effect of gelatin flexible chain related to hard chain polymer of PLA. The best improvement observed in the case of 30 wt % gelatin films for elongation at break % wherever increased by 344 % and 250 %, respectively as matched to PLA neat films. Also, EG appears to increase the biological degradation of PLA/EG blends films compared to pure PLA film in existence of soil microorganisms which detected by the current results verified by films containing different amounts of EG, such as PLA/30EG films. It was cleared that the utilization of gelatin extracted from the leather industry for biodegradable films production appeared achievable and encouraging. The promising obtaining results allow for low-cost biodegradable packaging films preparation.

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Competing interests. The authors have declared no conflict of interest

Compliance with Ethics Requirements This article does not contain any studies with human or animal subjects.

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Research Ethics. We are not required to complete an ethical assessment prior to conducting your research.

Animal ethics: we are not required to complete an ethical assessment prior to conducting your research.

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صناعه الجلود ينشا عنها كميات هائلة من المخلفات الصلبة التي في حالة إعادة استخدامها يكون لها مردود اقتصادي كبير من خلال التحليل الكيميائي للمخلفات البيضاء من صناعة الجلود. حيث أن الجيلاتين المستخرج من المخلفات البيضاء لصناعة الجلود يتم دمجه مع حمض اللاكتيك حيث يسمح الوزن الجزيئي للبولي لاكتيك بالمزج الجيد الذي يتضح باستخدام صور الميكروسكوب الالكتروني. وقد زادت نسبة الاستطالة بالنسبه للافلام كلما زادت نسبة إضافة الجيلاتين حتى يصل الى ٣٠ في المئة من الاصل في حين أن النقص في قوة الشد ليس لها تاثير كبير على التطبيقات في قطاع التغليف . و بدراسة الخواص الحرارية والميكانيكية والمورفولوجية للافلام القابلة للتحلل المحضرة وجد أن إضافة ٣٠ في المئة من الجيلاتين المستخلص تعطي أفلام لها خواص حرارية وميكانيكية جيدة وكذلك من حيث الشفافية والمورونة. وقد أتضح أن استخدام الجيلاتين المستخرج من صناعة الجلود لإنتاج الأفلام القابلة للتحلل يبدو مشجعا وقابلاً للتحقيق. كذلك تتيح النتائج الواعدة الحصول على أفلام تغليف منخفضة التكلفة قابلة للتحلل.