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FABRICATION OF LINEAR LOW-DENSITY POLYETHYLENE BASED BIODEGRADABLE COMPOSITE INCORPORATED LEATHER SHAVINGS

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ABSTRACT

The study was conducted to fabricate biodegradable composite films from leather shavings incorporated with LLDPE through blown film extrusion process. SEM and FTIR analyses were performed to observe and validate the surface morphology of the composites and the chemical bonding between leather shavings and LLDPE. The thermal stability of prepared composite films was analyzed through TGA and DSC tests. When compared to pure LLDPE film, the tensile strength of LS-LLDPE composite film was increased by 306.84% but the elongation at break was decreased dropped by 48.76%. The biodegradability of the composite films was justified through soil burial tests. Water absorption and OTR tests were conducted to investigate the water absorption rate and gas barrier properties of the fabricated composite film. The cost-effective and flexible composite film can be used as packaging materials as well as interior partitioning materials to reduce the environmental risks caused by leather shavings and buffing dust.

INTRODUCTION

The leather industry processes the by-product from the meat-processing industry and generates solid wastes in the form of fleshings, splits, shavings, buffing dusts and trimmings which contain mineral components and fats and liquid wastes in the form of waste water and sludge which are rich in organic compounds. (Rao et al., 2002; Sastry et al., 2005). Only a small portion of raw materials (20-25%) is converted to finished leather and 75–80% is released into the environment as solid waste, of which 56-60% is fleshing waste; 35-40% is leather shaving, split, and buffing dust; 5-7% is trimmings; and 2-5% is hair (Rajamani et al., 2009; Yorgancioglu et al., 2020). As, leather shavings constitute a large amount of solid waste, managing leather shavings is a pressing matter due to their negative impacts on the environment and human health (Menikpura et al., 2013). Leather shavings can be thermally treated to reduce the volume of waste to be disposed of but it created a high chance to convert nontoxic Cr(III) into carcinogenic Cr(IV) during thermal incineration at high temperatures. That's why, fabricating valuable products from leather shavings can be prominent solution of the problems generated due to the solid wastes from leather industry (Sekar et al., 2007).

With such motivation, considerable efforts are made on fabrication of composite materials from leather solid waste incorporated with different binders including latex, PVA, PCL, LLDPE, etc. Leather shavings was being used as fillers in producing composite which is potential, conducive and cost effective. They are being used as heat insulators, sound insulators, interior moldings for automobiles, soles and mid soles of shoes, packaging materials and so on (Sundar et al., 2011; Liu et al. 2014). It was also used to make composite leather boards for industrial purposes (Tahiri et al., 2003; Sundar et al., 2011; Selvaraj et al., 2019).

However, in the field of composite films, Linear low density polyethylene is emerging as a promising candidate due to their excellent performance to form composite films while most of other binders work for fabricating sheets (Ojeda et al., 2011; Oliveira et al., 2019). LLDPE is a copolymer of ethylene and alpha-olefin; butene, hexene, octene and 4- methyl–1-pentene and being widely used for producing blown films for packaging, wrapping and agricultural use. It has linear sequences and a certain amount of short chain branches which are responsible for its high crystallinity, better thermal properties and other superior properties like tensile strength, tear strength and puncture resistance, and therefore it has been used in modification of polymer composites (Rungswang et al., 2019).

Nowadays, repetitive research is conducted to convert waste material into valuable products. Latex reinforced waste buffing dust-jeans cotton composite materials were prepared which obtained a good properties as packaging materials but the TS and EB were poor (Islam et al., 2021). Composite film produced from protein hydrolysate incorporated with PVA, was used in different applications and compositing with protein hydrolysate modify the properties of the polymer (Yang et al., 2019). Biodegradable composite material was produced from leather solid waste incorporated with PVA and PCL which processed a poor mechanical properties (Ambone et al., 2016; Masilamani et al., 2017). Protein hydrolysate was blended easily and uniformly with mLLDPE and the obtained composite film retains good mechanical strength properties and also biodegradability behavior (Saha et al., 2003). LLDPE based active nanocomposite films with nanoclays impregnated with volatile compounds was fabricated for antimicrobial food packaging (Tornuk et al., 2018). LLDPE-Wood fiber and LLDPE-Lignin composite films were fabricated that had increased mechanical strength, thermal stability, and environmental safety (Guo, 2020; Chiappero et al., 2021).
In such phenomena, leather shavings was used to produce biodegradable composite film incorporated with linear low density polyethylene (LLDPE). Therefore, characterization of the resulting LS-LLDPE composite film was followed to ensure mechanical, chemical and thermal properties along with interfacial adhesion as well as convert tannery solid wastes into eco-friendly and valuable composite materials.

METHODOLOGY

MATERIALS

Laboratory grade LLDPE with density of 0.918 g/cm3 (at 23 °C) and Acetic acid were purchased from Sigma Aldrich in Bangladesh. Doha, Qatar (Qatofin Company Ltd.). Leather shavings (LS) was collected from the SAF Industries Ltd., Jashore, Bangladesh.

FABRICATION OF COMPOSITE FILMS

Moisture content from LS was removed by drying in an oven for 48 hours at 105°C. It was converted to fine powder through laboratory grinder (Pulversette 19). 0.5 M Acetic acid was used for the hydrolysis of the prepared sample at 70°C for 8 h through stirring. After that, the sample was filtered, the filter cake was dried and grinded again. After grinding, fine powder was obtained by filtering through a fine screener (0.2-1.5 mm). Collected LLDPE was dried for 12 hours at 80 °C. Composite film was prepared through RJ50 Ruitai Blown Film Molding Machine. The processing temperature was 200°C for the melting zone, 200°C for the die, 160°C for the feeding zone, and 160°C for the compression zone. The screw rotated at a rate of 25 times per minute. In order to fabricate the composite films, different percentages of LS were mixed with LLDPE. Table 1 represented the compositions of blended films.

Table 1. Composition of the films

Name	Composition
Control	100% LLDPE
LS-2.5	2.5% LS + 97.5% LLDPE
LS-5.0	5% LS + 95% LLDPE
LS-10	10% LS + 90% LLDPE

CHARACTERIZATION

Using the ASTM-D638 standard technique and an UTM machine, the mechanical characteristics of prepared LLDPE-based composite films, including TS and EB, were measured. For every sample, the test was run three times, and the average value was taken as the result. SEM was used to study the surface morphology of the composite films maintaining magnification between 10kx and 20kx, sample length at 2µm, and EHT at 20 kV. In order to justify the chemical bonding of the composite films,

Fourier Transform Infrared Spectroscopy (FTIR) was carried out using the Nicolet 6700 spectrometer from Thermo Scientific, USA, in the 4000 cm^{-1} to 400 cm^{-1} spectrum area with a resolution of 4 cm^{-1}. Additionally, TGA was carried out using High Resolution 2950 thermogravimetric analyzer in accordance with ASTM E1131 standard technique and DSC was carried out in accordance with ASTM F2625-10 (2016) utilizing DSC-60 plus series (Shimadzu, Japan). Oxygen transmission rate (OTR) was tested in accordance with ASTM D3985 to assess gas barrier properties. According to Chiappero et al., 2021, the biodegradability and water absorption of LS-LLDPE composite films were investigated.

RESULTS AND DISCUSSION

FOURIER TRANSFORM INFRARED SPECTROSCOPY

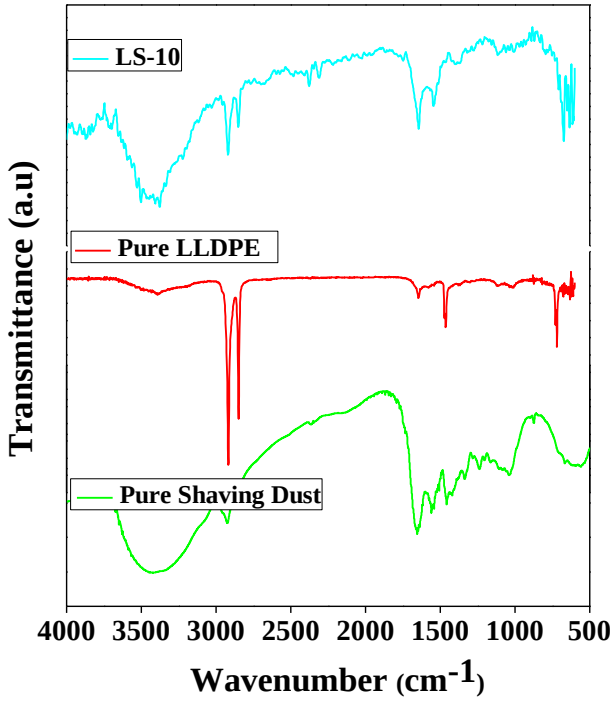

Figure 1. FTIR spectra of the LS, pure LLDPE film and LS-10 composite film

As shown in figure 1, FTIR test for LS, pure LLDPE film and LS-10 composite film was conducted. A strong peak at 2911 cm^{-1}, which exhibits C-H bonding, in LS that indicates the presence of collagen components, was used to support this claim. Denser peaks were seen at 1037, 1440, 1578, and 1657 cm^{-1} for LS (Zan et al., 2006; Tornuk et al., 2018; Prochon et al., 2020)). For pure LLDPE, the small peaks were found at 710, 1471, and 1641 cm^{-1}, respectively, and the sharp vibration was found at 2833 and 2927 cm^{-1}. For LS-10 composite films, the sharp peak between 3250 and 3500 cm^{-1} indicated C-H or O-H or N-H stretching of collagen contents present in the composite films, which may be from LS-10 (García et al., 2009). The CH_2=CH_2 (ethylene) bond, which was not damaged in the production of the composite films, was indicated by the peak found at 2927 cm^{-1} for the composite film. Due to thymol and C-H aromatic ring, a few faint peaks at 1377, 1515, 1657, and 1672 cm^{-1} were seen in composite film (Sanchez-Garcia et al., 2008; Krepker et al., 2018). These findings demonstrated that strong chemical bonding was obtained between LS and LLDPE in composite film.

THERMAL STUDY

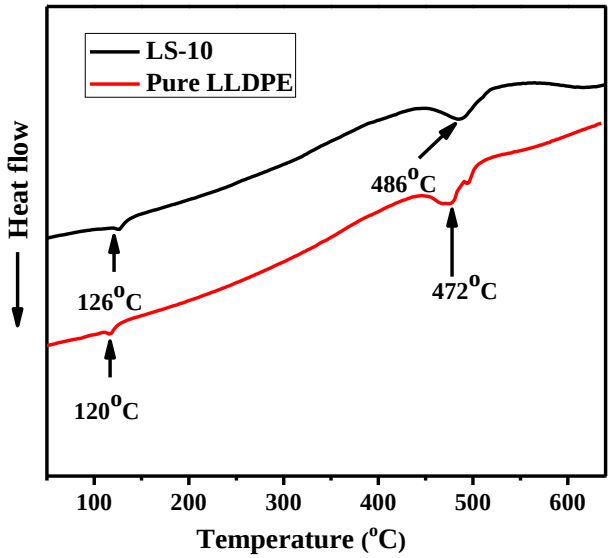

Figure 2. DSC studies of pure LLDPE film and LS-10 composite films

Figure 2 represents thermograms of pure LLDPE film, and LS-10 composite film from DSC analysis. There were two endothermic peaks in each of the three samples. A initial endothermic peak (Tm_1) and a second peak (Tm_2) are both present in pure LLDPE. While the second peak denotes the denature of the LLDPE molecule, the first peak may have been caused by a bonded water molecule. Tm_1 for the LS-10 composite film was recorded at 126 °C. It showed that Tm_1 was a little higher in composite film as compared to pure LLDPE film. When compared to pure LLDPE film, the second endothermic peaks of LS-10 composite films were at 486 °C. This resulted in a slight increase in Tm_2 for composite films containing LS-10. In earlier investigations, LLDPE-based composite films showed a similar thermal behavior (Tornuk et al., 2018). The DSC thermograms demonstrated that the produced composite film had a higher melting point than pure LLDPE film. It happened as a result of declining volatility and water molecule content in composite film (Joseph et. al, 2015; Ambone et al., 2016). Thermograms showed that composite film has greater thermal stability than pure LLDPE film. Table 2 represents the thermal analysis of pure LLDPE and LS-10 composite film. In TGA test, the samples were degraded in two phases. For pure LLDPE, the first peak was discovered at 407 °C. At this point, the weight decrease was 5.95%. The presence of moisture and volatile substances in the film may be the cause of the first deterioration (Senthil et al., 2015). At 519 °C, the pure LLDPE film was degraded completely. While the first degradation of the LS-10 composite film occurred at 415 °C, indicating that the first degradation temperature of composite film is higher than that of pure LLDPE film. It suggests that, the weight loss percentage for such composite film was lower than pure LLDPE film. Due to the hydrogen link formed by the C-H group of LLDPE and the peptide bond of the leather fiber, the initial temperature of degradation increased and the weight loss percentage decreased for composite film (Ray et al., 2002; Parisi et al., 2022). The total degradation of the LS-10 composite film was seen at 516 °C. The total degradation temperature of composite films was marginally lower than pure LLDPE film. Due to the ability to total degradation of leather fiber before pure LLDPE, the complete degradation temperatures of the composite films were decreased (Tornuk et Al., 2018; Selvaraj et al., 2019).

Table 2**.** Thermal properties of the films

Samples	DSC	TGA

	Tm_1 (°C)	Tm_2 (°C)	First degradation (°C)	Total degradation (°C)
Control (LLDPE)	120	472	407	519
LS-10 (LS-LLDPE)	126	486	415	516

SCANNING ELECTRON MICROSCOPE

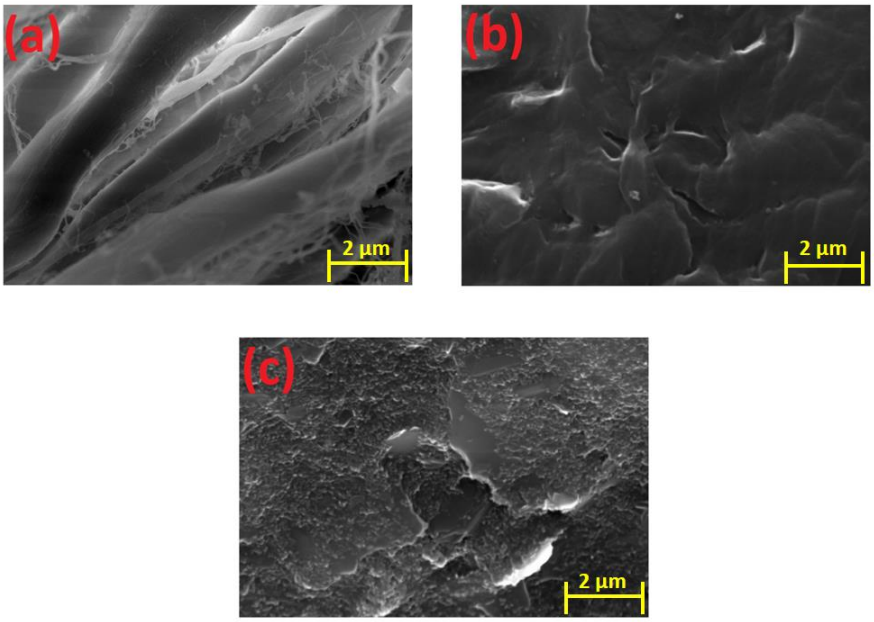

Figure 3. SEM studies of (a) LS, (b) LLDPE film, (c) LS-10 composite film

Figure 3 depicts the surface morphology of LS, pure LLDPE film, and LS-10 composite film. The leather fibers in figures (a) are clumped together, twisted, and cross-linked, indicating a strong hydrogen and ionic bonding between the LS own-fibers. The surface morphology of the pure LLDPE film, which is homogeneous and seems crack-free, is shown in figure (b). The morphology of the LS-10 composite in figure (c) showed a little rough but still good surface quality. For fiber-to-fiber interaction in LS and weak bonding between long fibers of LS and LLDPE, the LS-10 composite film's interface may be little rough (Sundar et al, 2011; Joseph et. al, 2015). Appropriate filler matrix ratio and other processing variables in the extrusion process, such as screw profiles, screw speed, and feeding rate, are crucial to prevent the agglomeration of fibers and obtain a uniform fiber/matrix interaction (Ščetar et al., 2013, Aldosari et al., 2021). The SEM study of the fabricated composite film represents uniformity with little crack of the surface and good interactions between LS and LLDPE.

SOIL BURIAL TEST

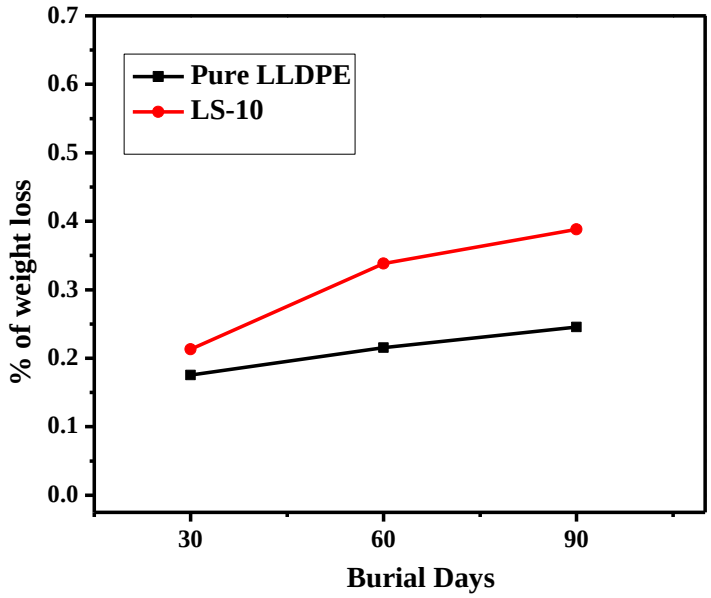

Figure 4. Soil burial test of the films

Figure 4 displays the weight loss percentages for LS-10, and pure LLDPE following soil burial testing. After 90 days of soil burial, weight loss was approximately five times greater for LS-10 compared to pure LLDPE film. The rapid biodegradability of collagen caused by enzymatic activity by various microorganisms is a significant factor in the increased biodegradability of prepared composite film (Guo, 2020; Chiappero et al., 2021).

GAS BARRIER PROPERTIES

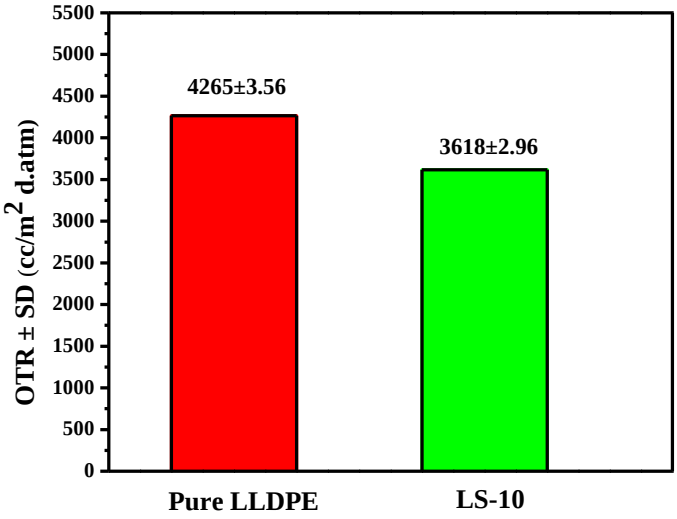

Figure 5. OTR of the films

Figure 5 shows the oxygen transmittance rates (OTR) for pure LLDPE film, and LS-10 composite films. Fibrous materials often have a high oxygen transfer rate. The oxygen transmission rate through the composite film is decreased with the addition of nano-fillers to the matrix. Pure LLDPE film had a higher OTR (4265±3.56 cc/m^2.d.atm) than LS-10 composite film (3618±2.96 cc/m^2.d.atm). It implied that when OTR fell, the gas barrier characteristics improved for the composite film. When compared to pure LLDPE film, the gas barrier characteristics of LS-10 composite was increased by 15.17%. The increased OTR of pure LLDPE was caused by its crystallinity, and the OTR was reduced following the

insertion of leather fibers as fillers (Tolinski, 2017). As a result, the fabricated composite films had much improved gas barrier qualities.

WATER ABSORPTION TEST

The ability to absorb water is a crucial quality both during and after its service life for a packaging film. To encourage biodegradable behavior, noble packaging materials should have a hydrophobic nature during their service lives and absorb water when they are no longer needed (Chiappero et al., 2021). Pure LLDPE absorbed about 1.45% of its weight in water. The percentage of water absorption for the fabricated composite film was increased with the inclusion of leather fiber. The percentage of water absorption for LS-2.5, LS-5, and LS-10 is 1.98, 2.74, and 3.68%, respectively. These are explained by the fact that collagen component in composite films has a higher polarity and is therefore more hydrophilic than pure LLDPE film. Other causes of water absorption include the cross-linked fiber structure of LS and the osmotic pressure of water (Liu et al., 2014). According to the results of the water absorption test, the water absorption behavior of composite film (LS-LLDPE) promotes both the service life and the biodegradability of the produced composite films at their end of life.

MECHANICAL TEST

The mechanical properties (TS and EB) of control and composite films were shown in table 3.

Table 3. TS and EB of pure LLDPE and LS-LLDPE composite films

Samples	Tensile Strength (MPa)	Elongation at Break (%)
Control	4.82±0.29	328.21±47.18
LS-2.5	11.06±2.21	267.25±21.84
LS-5	15.28±2.68	218.38±24.45
LS-10	19.61±3.19	168.16±23.52

Pure LLDPE exhibited tensile strength and elongation percentages of 4.82±0.29 MPa and 328.21±47.18%, respectively. The LS-10 composite film, which had a tensile strength of 19.61±3.19 MPa, 168.16±23.52% elongation at break, represents the highest tensile strength and the lowest percentage of elongation at break among the composite films made from LS and LLDPE. LS could provide fiber strength to the composite film which increased the tensile strength of composite films than pure LLDPE film (Sundar et al., 2011; Teklay et al., 2017). In earlier investigations, findings of a similar kind were discovered (Duan et al., 2012; Liu et al., 2014; Ugbaja et al., 2016; Islam et al., 2021). The results of mechanical tests were validated by the mentioned studies. Therefore, from all of the mentioned combinations, LS-10 composite film showed better tensile strength.

COMPARISON OF MECHANICAL STUDIES

Table 4 reports the comparative analysis of the mechanical characteristics of prepared composite film with previous investigations. In particular, prepared composite showed better tensile strength (TS) and elongation at break (EB) than some composite materials in earlier investigations. The prepared composite film had stronger tensile strength and a lower percentage of elongation in comparison to a recent work (Chiappero et al., 2021). In comparison to leather fiber/natural rubber and buffing/NBR based composites, the tensile strength was also found to be greater (Ravichandran et al., 2005; Hang et al., 2020; Islam et al., 2021). It could happen as a result of different fibers and matrices, changes in their ratio, and production techniques (Senthil et al., 2015; Parisi et al., 2022). However, the PLA and PVA-based leather composites outperformed LLDPE-based composite films in terms of tensile strength. PVA and PLA have intramolecular cross-linked structures, which was responsible for the creation of a network between their chains and improved mechanical properties (Liu et al., 2014; Masilamani et al., 2017). In respect of elongation at break, the fabricated composite film had a higher percentage of elongation than most of the mentioned composites in table 4. This may be happened because pure LLDPE has a superior crystal structure than those matrices. (Masilamani et al., 2017; Xu et al., 2022). The usage of leather fiber with LLDPE will create a new dimension for composite film

manufacturing, allowing for better tensile strength and optimum elongation percentage, as well as other properties.

Table 4. Comparison of mechanical properties with previous studies

Samples	Ratio	Tensile Strength (MPa)	Elongation at break (%)	Reference
LS-LLDPE	10:90	19.61±3.19	168.16±23.52	This study
Lignin-LLDPE	2.5:97.5	9.75±2.4	339.22±43.1	Chiappero et al., 2021
LB-Cotton-Latex	20:80	6.56±2.45	29.98±3.11	Islam et al., 2021
Gelatin-PVA	50:50	46.42±0.31	7.31±0.47	Masilamani et. al., 2017
LB-Natural Rubber	40:60	13.80	5.80	Ugbaja et al., 2016
LS-PLA	15:85	78	15	Duan et al., 2012
LS-PVA	5:95	60	340	Liu et al., 2014
LB-NBR	20:80	6.7	72.9	Hang et al., 2020
LF-Natural Rubber	50:50	5.73	210	Ravichandran et al., 2005

CONCLUSION

In conclusion, biodegradable composite films were fabricated along with higher tensile strength and optimum elongation at break. In comparison to pure LLDPE film, the tensile strength of LS-10 composite films was increased by 306.84%, while the elongation at break was reduced by 48.76%. Elongation at break, which results from the crystalline structure of LLDPE, ensures optimum bending and break-free shaping of packing material. The surface homogeneity and bond formation between leather fiber and LLDPE of LS-LLDPE were verified by SEM and FTIR, respectively. Improved thermal stability and degradation temperature of LS-LLDPE were observed by DSC and TGA studies. The LS-LLDPE composite film performed better results in OTR, soil burial, and water absorption tests than pure LLDPE film. Based on the characterization tests, these flexible and eco-friendly composite film could be a significant solution for leather solid waste management, as well as manufacturing packaging materials for commercial use. Further investigations should be ensured to enhance surface uniformity and create commercially viable composite film.

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