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Banknotes residues and thermoplastic starch as sustainable reinforcements for LDPE-based agricultural composites

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Abstract

This study examines the development and characterization of composites comprising low-density polyethylene (LDPE), thermoplastic starch (TPS), and cellulose fibers sourced from recycled banknotes (BR). The composites were fabricated using extrusion and injection molding techniques, followed by an evaluation of their morphological, thermal, mechanical, and water absorption properties. The inclusion of BR fibers enhanced the mechanical performance of LDPE, notably improving tensile strength and elastic modulus, while the hydrophobic treatment of the fibers ensured minimal water absorption. The incorporation of TPS increased the composites' biodegradability potential but reduced tensile strength and increased water absorption due to its hydrophilic nature. Scanning electron microscopy revealed strong interfacial adhesion between the fibers and matrix and confirmed the complete dispersion of starch in TPS-containing samples. Thermogravimetric analysis highlighted the thermal stability of the composites and identified distinct degradation stages corresponding to the matrix, TPS, and fibers. These results indicate that the developed composites offer a viable solution for agricultural applications, balancing mechanical performance and environmental sustainability.

Keywords: LDPE composites, Recycled banknote fibers, Thermoplastic starch, Sustainable materials, Polymer reinforcement.

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Contents

Contribution of this paper to the literature

This study uniquely integrates recycled banknote fibers into LDPE composites, combining hydrophobic fiber treatment with thermoplastic starch to enhance mechanical properties and biodegradability. Unlike previous works, it explores the interplay of these components, demonstrating the feasibility of upcycling cellulose waste while achieving a balance between performance and environmental sustainability.

1. Introduction

Synthetic polymers are widely used across industries due to their versatile and desirable properties. Low-density polyethylene (LDPE) is widely used in agriculture for various applications such as mulching films and packages for fertilizers due to its flexibility, durability, and resistance to moisture and chemicals [1, 2]. However, these polymers are derived from non-renewable sources, which are both limited and environmentally harmful due to improper disposal and long degradation times [2, 3].

To reduce the environmental impact associated with synthetic polymers in agriculture, biodegradable natural materials are increasingly being explored [1, 4-6]. Starch stands out as a promising candidate due to its low cost and large-scale production. However, despite being a promising biodegradable material, starch has several limitations that drive its incorporation into other polymers like LDPE to improve performance. Those limitations include poor mechanical properties, high moisture absorption and low thermal stability [7]. To be compatible with LDPE, starch must undergo a destructuring process, transforming its granular structure into an amorphous material called thermoplastic starch (TPS) [8, 9].

Despite the potential of combining LDPE and TPS, poor compatibility between the materials leads to reduced mechanical performance. To improve the properties of this mixture, compatibilizing agents, typically organic acids, are often employed [10-12]. Since the main objective of this paper is to seek more sustainable alternatives, we proposed the use of banknotes residues (BR) from bills unfit for circulation. Such waste was made available by the Central Bank of Brazil, which states that approximately 800 tons of banknotes waste were discarded in 2017 [13]. Banknotes are composed of high-quality cellulose fibers, among other components, which guarantee properties such as mechanical and water resistance, which are essential for the blend of LDPE and TPS.

In a previous study Gil, et al. [13] BR were incorporated on LDPE matrix at concentrations between 1-20% resulting on physical interactions between the residues and polymer matrix, improving mechanical properties. These improvements include increased tensile strength and reduced elongation percentage, which are valuable for agricultural applications where durability and strength are required. Considering these promising outcomes, the addition of TPS into a LDPE/BR composite is intended to enhance the biodegradability, aiming to minimize the environmental impact.

In this paper, we developed a composite of LDPE, TPS, and BR, with the goal of creating a sustainable alternative to conventional agricultural polymers. This composite material not only demonstrates performance comparable to synthetic polymers but also incorporates renewable and recycled resources, making it a viable, eco-friendly substitute in agricultural settings.

2. Materials and Methods

The LDPE, code EI-1630, was supplied in pellet form by Quattor.Low-density. The corn starch with 70% amylose, and pure glycerol were used to produce thermoplastic starch (TPS). The banknote residue samples were provided by the Central Bank of Brazil (Banco Central do Brasil).

The preparation of the composite material using recycled banknote waste as reinforcement involved several steps. First, the thermoplastic starch (TPS) was produced from a mixture of corn starch, glycerol, and water in a ratio of 60:24:14% by weight. This mixture was stirred at 60°C for 30 minutes. Next, the banknote waste was shredded into small fragments, which were then mixed with the LDPE to form the primary matrix material. This mixture underwent two passes through a single-screw extruder to ensure sample homogeneity. TPS was then added to this mixture, followed by a third extrusion, according to the formulation specified for each test specimen as outlined in Table 1.

Following the mixing and extrusion steps, samples were injected into a mold with dimensions according to American Society for Testing and Materials (ASTM) D 638 – 03 standards. The produced materials were subsequently characterized to determine the composite's final properties and to evaluate the influence of fiber and TPS addition on the polymer matrix.

Table 1. Composites composition.

Sample	LDPE (%w/w)	Banknote residues (%w/w)	TPS (%w/w)
LDPE	100	0	0
LDPE/BR	85	15	0
LDPE/BR/TPS10	76.5	13.5	10
LDPE/BR/TPS20	68	12	20
LDPE/BR/TPS30	59.5	10.5	30

2.1. Mechanical Testing

The samples were characterized by tensile tests according to ASTM D638 standards. Testing was performed on a universal testing machine (EMIC DL 3000) using a 2 kN load cell. Results were analyzed through one-way analysis of variance (ANOVA) followed by Tukey's multiple comparison test. Statistical significance was set at $P < 0.05$. All analyses were conducted using PAST software (version 2.17c, 1999–2013).

2.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis curves were recorded on a Seiko - SII Nanotechnology Inc. Exstar 7200 instrument under nitrogen with a heating rate of 10 °C/min over a temperature range of 20 to 800 °C. Nitrogen was used as the purge gas at a flow rate of 30 mL/min.

2.3. Morphological Analysis

The morphological analyses of the composites were conducted using images obtained with a scanning electron microscope (SEM) (ZEISS, LEO, EVO 40) equipped with Extended Variable Pressure (XVP). Samples were mounted on carbon tape with the cross-sectional area positioned upward. All samples were coated with gold by sputtering.

2.4. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis in the 4000 to 650 cm^{-1} range was performed using a Nicolet 8700 spectrometer equipped with Fourier Transform and an ATR accessory. ZnSe crystal was used with 84 scans at a resolution of 4 cm^{-1}.

2.5. Water Absorption Test

The water absorption test was conducted in accordance with ASTM D570. Prior to immersion, samples were dried in an oven at 60°C for 48 hours to determine the initial mass. Specimens were then immersed in water at room temperature (23 ± 1°C). After 48 hours, the samples were removed from the water, quickly dried with paper, and weighed. This process was repeated until the mass stabilized. At the end of the test, a water absorption curve (%) versus immersion time (hours) was obtained as per ASTM D570 – 98. The percentage of water absorption in the composites was calculated using Equation 1:

$$\Delta M(\%) = \frac{M_f - M_i}{M_i} x100 \qquad (1)$$

Where ΔM is the water absorption percentage, and Mi and Mf represent the sample mass before and after immersion, respectively.

3. Results and Discussion

The tensile properties of composites and pure LDPE are shown in Table 2. As previously shown by Gil, et al. [13] the incorporation of banknote fibers into LDPE matrix introduces desirable reinforcing characteristics without the need for additional compatibilizing agents. Similarly, in this study, the LDPE/BR sample demonstrated a comparable performance, as shown in Table 2, with higher elastic modulus, lower tensile strain, and increased tensile strength compared to pure LDPE and samples containing TPS. As expected, the addition of cellulose fibers increased the elastic modulus of LDPE. Studies indicate that enhanced strength between the fiber and polymer matrix signifies good adhesion in the composite, which aligns with findings from other authors [13, 14].

The behavior of the samples with the addition of TPS showed, based on the analysis of Table 2, that the addition of starch reduces the maximum stress supported by the material. It results in an increase in the elastic modulus and a reduction in the percentage of deformation. The incorporation of starch in the composite, as expected, causes embrittlement, due to the replacement of a resistant matrix with a fragile material [15].

Table 2. Mechanical properties (Young's modulus, tensile strength and elongation at break) of LDPE and LDPE composites.

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
LDPE	47.7 ± 6.6^{a}	9.85 ± 0.22^{a}	133 ± 4^{a}
LDPE/BR	73.8 ± 6.7^{b}	10.8 ± 0.15^{b}	19.7 ± 1.9^{b}
LDPE/BR/TPS10	66.2 ± 8.4^{b}	8.16 ± 0.14^{c}	28.1 ± 3.3^{c}
LDPE/BR/TPS20	62.4 ± 8.4^{b}	8.25 ± 0.59^{c}	$31.0 \pm 11^{c.d}$
LDPE/BR/TPS30	65.2 ± 10.4^{b}	8.35 ± 0.29^{c}	24.0 ± 3^{d}

Note: Identical letters indicate statistically similar means (within the same column) according to Tukey's test at a 5% significance level.

Thermal analysis of the samples can be observed in Figure 1. For the banknotes residues a minor weight loss can be observed at temperatures below 100°C due to moisture present in the material. In the range of 200 to 370°C, a more significant weight loss in the BR was observed, primarily due to the degradation of hemicellulose and cellulose, resulting in approximately 64% mass loss at 305°C. Beyond this range, the weight continues to decrease, attributed to the degradation of lignin and subsequent decomposition of the BR components. After reaching 600°C, the BR retained a significant percentage of its weight compared to the other samples, which can be attributed to the hydrophobic components added to banknotes, providing greater resistance to high temperatures. The thermal characteristics of the BR align with findings reported in other studies [13, 16].

In LDPE, a substantial weight loss is noted between 340 and 510°C, occurring in a single decomposition step. The LDPE/BR sample, however, displays two mass-loss intervals: the first between 270 and 370°C, and the second between 400 and 510°C, corresponding to BR and LDPE degradation, respectively. As noted in previous studies, compared to LDPE the thermal stability of the composite decreased, due to the decomposition temperature of hemicellulose, cellulose, and lignin present in the BR [13].

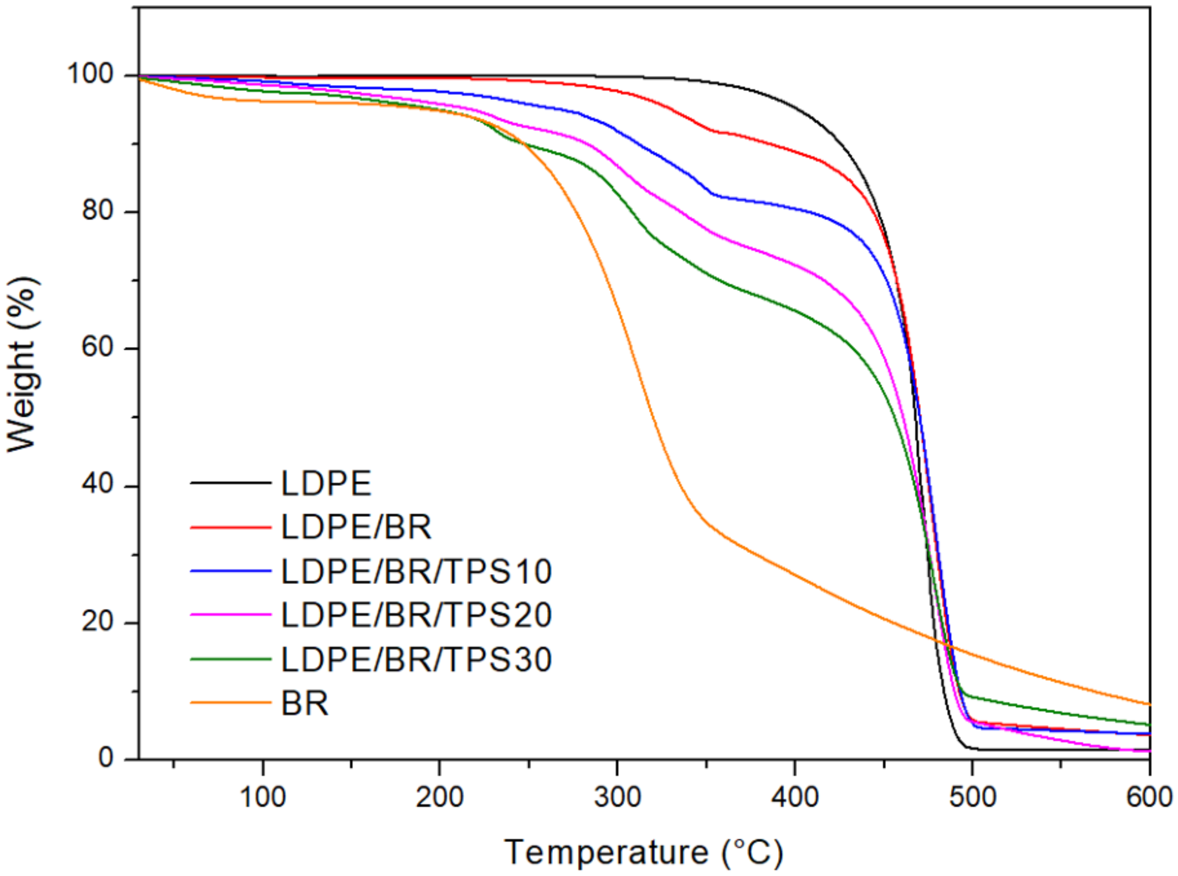

Figure 1. TGA of LDPE and LDPE composites.

The TGA curve for thermoplastic starch presents three stages of mass loss. The first, between 25 and 125°C, occurs due to water loss; the second, between 290 and 384°C, is considered as the main degradation stage; and the third stage, above 480°C, refers to the decomposition of residual matter [17].

The samples containing TPS present mass loss in the intervals of 200 to 270 °C, 270 to 370 °C and 370 to 510 °C, as shown in Table 3, which suggests the influence of fibers, TPS and LDPE, respectively. Studies have shown that the higher the starch content, the higher the storage modulus of LDPE/TPS blend [15]. This can be attributed to the rigid character of starch compared to the LDPE structure.

Table 3. Percentage of weight loss.

Sample	30-200°C	200-270°C	270-370°C	370-510°C	residues at 510°C
LDPE/BR	0.29	0.81	7.67	85.86	5.37
LDPE/BR/TPS10	2.24	2.78	13.07	77.3	4.61
LDPE/BR/TPS20	4.06	4.6	16.09	70.27	4.98
LDPE/BR/TPS30	4.97	6.7	19.62	60.05	8.66

Figure 2 presents the FTIR analysis data. In the BR spectrum, absorption bands are observed between 3334 and 3274 cm^{-1}, corresponding to the hydroxyl groups present in cellulose and hemicellulose; between 2916 and 2848 cm^{-1}, associated with the stretching vibrations of methylene groups; and at 1032 cm^{-1}, linked to C–O stretching. The pronounced peak at 1032 cm^{-1} indicates the significant presence of C–O stretching, consistent with findings in related literature, a characteristic of both hemicellulose and cellulose fibers [16]. In the LDPE spectrum, distinct peaks appear at 2914, 2846, 1463, and 719 cm^{-1}, which correspond to asymmetric CH_2 stretching, symmetric CH_2 stretching, bending deformation, and rocking deformation, respectively [13].

In the LDPE/BR samples, the absorption bands characteristic of pure LDPE was predominantly observed, with no clear indication of BR presence in the spectrum. This can be attributed to the low fiber content relative to the percentage of LDPE, which results in absorption bands of LDPE being intense enough to mask the characteristic bands of the fiber [13].

Figure 2 also shows the FTIR spectra of samples containing LDPE/BR/TPS. Mendes et al. analyzed the FTIR spectrum of TPS and identified absorption bands characteristic of starch and glycerol at 920, 1022, and 1140 cm^{-1} due to C–O stretching; at 1648 cm^{-1}, related to ester group formation; at 3277 and 2914 cm^{-1}, associated with O–H and C–H stretching, respectively; and at 1423 cm^{-1} due to glycerol [17]. The presence of ester bonding at regions around 1642 cm^{-1} and 1000 to 1200 cm^{-1} indicates an anhydride ring opening and bonding between starch and LDPE. Some of these TPS characteristic bands are present in the spectra of the samples, as highlighted in Figure 2, confirming the presence of TPS. Additionally, these bands are more pronounced in the spectra with higher TPS content, specifically in the LDPE/BR/TPS20 and LDPE/BR/TPS30, compared to the LDPE/BR/TPS10 sample.

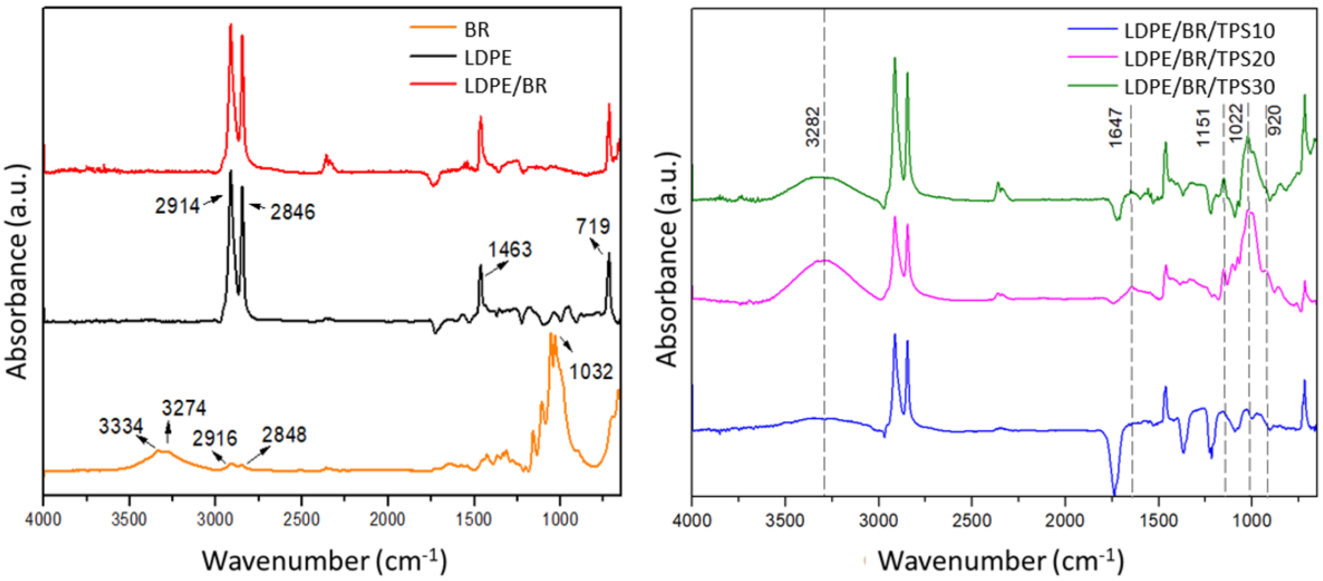

Figure 2. FTIR spectra of the banknotes residues, pure LDPE, and LDPE composites.

Water absorption over time for the samples is shown in Figure 3. As observed, pure LDPE does not absorb water (absent blue bar on graph), maintaining a stable weight throughout the process due to its hydrophobic nature [18]. The addition of fiber resulted in a quick absorption of 0.82%, with the weight stabilizing after the first measurement, indicating a fast yet minimal uptake by the composite. Although fibers are generally hydrophilic, banknote fibers contain components that provide hydrophobic properties (water resistance) compared to other cellulose fibers, explaining the low absorption observed [13]. With the addition of TPS, which has hydrophilic properties, an increase in water absorption over time was noted [18]. The sample showing the greatest mass variation throughout the experiment was LDPE/BR/TPS20.

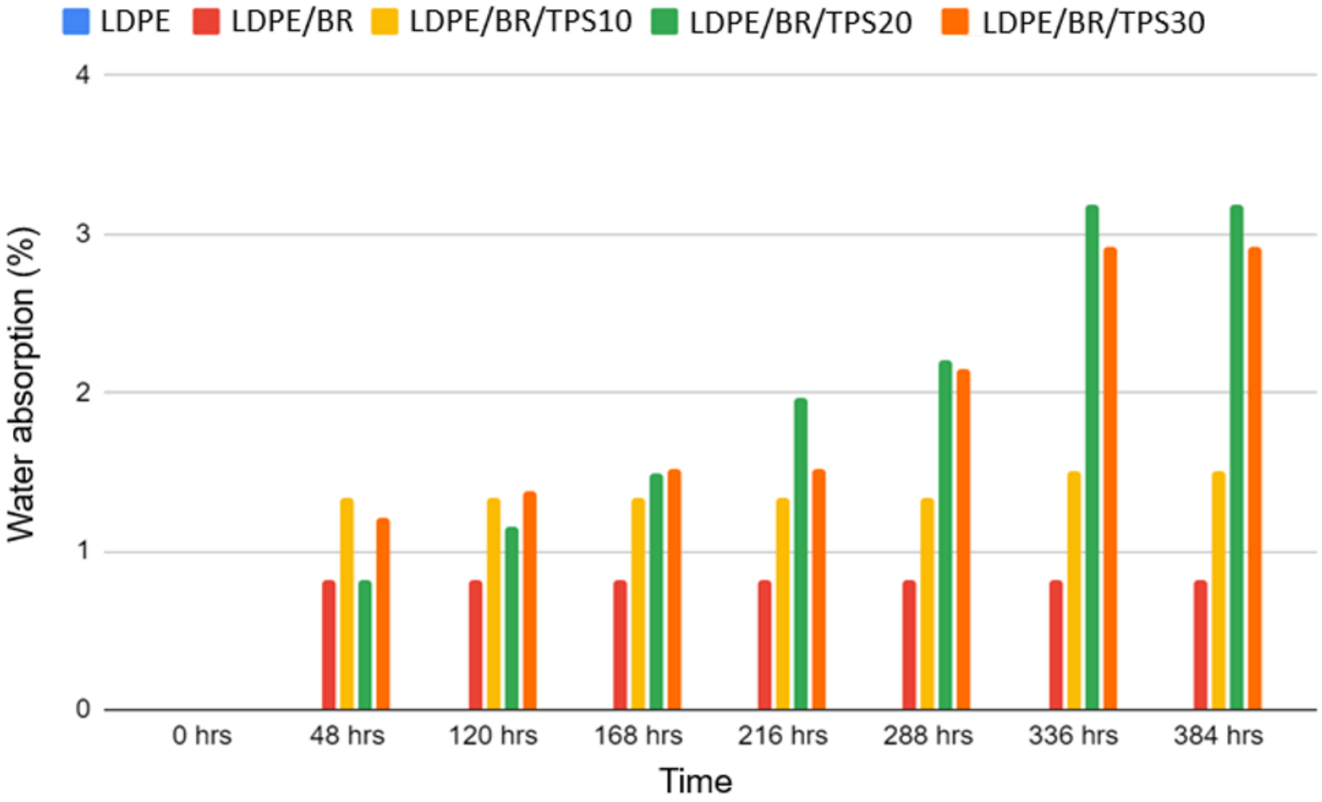

Figure 3. Percentage of water absorption as a function of time.

The morphology of the produced samples was examined using SEM, as shown in Figure 4. For comparison, images of the pure LDPE matrix and the fiber were also obtained (Figures 4 a-b). In polymeric materials, this analysis is crucial, as the physical-mechanical properties of the composites are directly influenced by the morphology of their constituents and their interfacial interactions. The images of the fibers (Figure 4a) show loose fibers and also fibers bound together by the resin that forms the banknotes. As observed in Figure 4b, the SEM image of pure LDPE displays a smooth and homogeneous surface, characteristic of its amorphous structure. The absence of significant microstructural features, such as fibers or particles, highlights its uniform composition. The LDPE/BR samples, on the other hand, demonstrate a notable difference in morphology, with fibers embedded within the polymer matrix (Figure 4 c). Unlike the smooth surface of pure LDPE, the composite samples exhibit a more fibrous and heterogeneous appearance, indicative of the incorporation of the fiber component. As already analyzed by Gil et al., the LDPE/BR samples show an absence of removed or empty fibers, suggesting a certain degree of interfacial bonding between the fiber and the LDPE matrix [13].

Furthermore, when TPS is added to the composite, as seen in Figures 4 d-f, the fracture surface becomes even more irregular and heterogeneous. Studies have previously revealed low interfacial adhesion between LDPE and TPS [14] however, the introduction of fibers appears to significantly enhance these interactions. Another critical observation is the absence of starch granules in the SEM images, indicating the complete destruction of the original corn starch structure during TPS preparation [19]. The differences in morphology between the pure

LDPE and the composite samples underscore the successful incorporation of fibers and TPS, as well as the potential for these modifications to influence the material's mechanical properties.

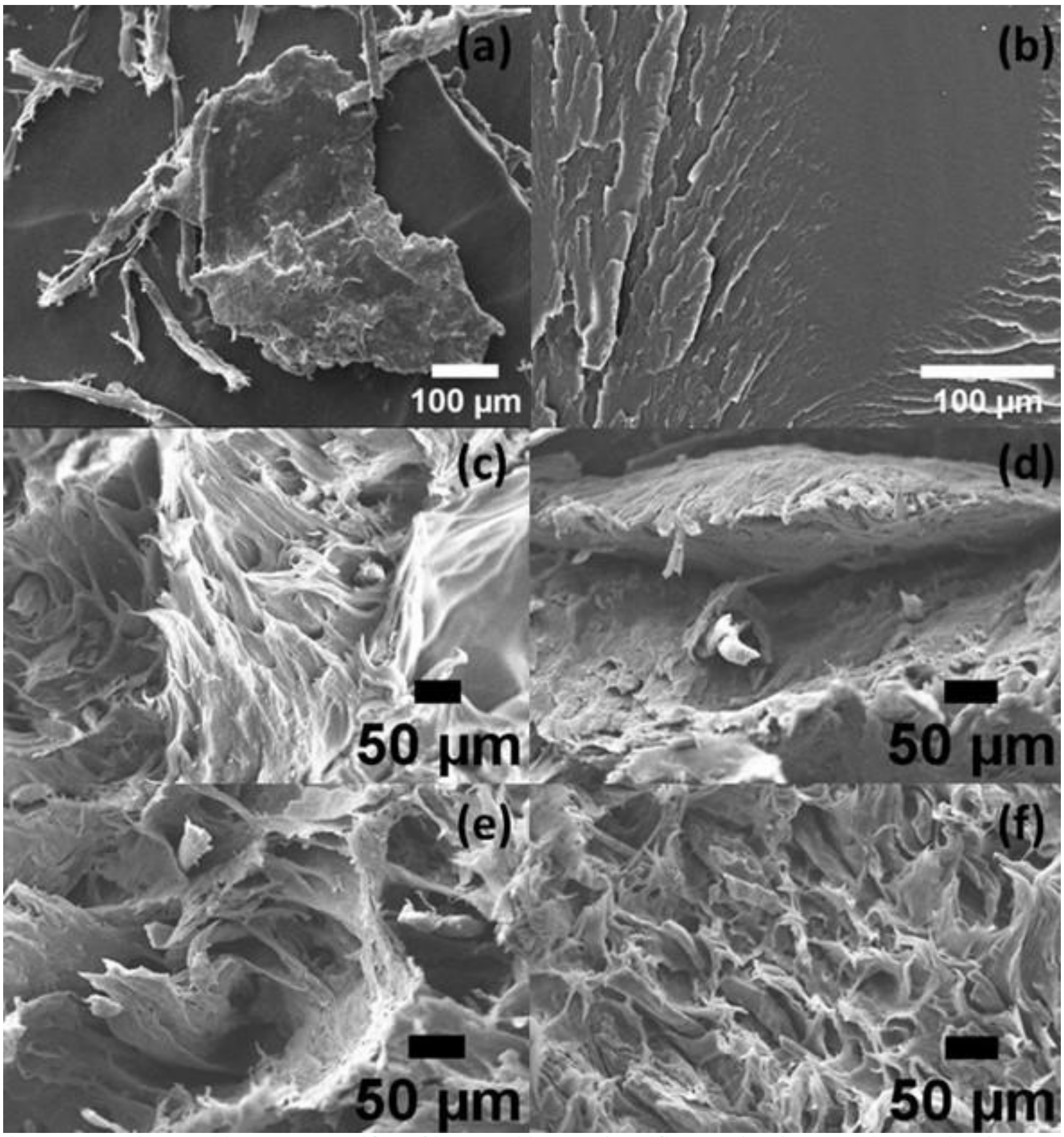

Figure 4. SEM images: (a) Banknotes residues, (b) LDPE, (c) LDPE/BR, (d) LDPE/BR/TPS10, (e) LDPE/BR/TPS20 and (f) LDPE/BR/TPS30.

4. Conclusion

This study successfully demonstrated the potential of developing composites using LDPE, cellulose fibers from recycled banknotes, and TPS for agricultural applications. The inclusion of cellulose fibers notably enhanced the mechanical properties of the polymer matrix, improving its tensile strength and stiffness without the need for compatibilizing agents. These findings highlight the efficiency of reusing cellulose-rich materials like banknotes as reinforcement in polymer composites.

The addition of TPS introduced a biodegradable component into the material, but also brought challenges such as increased water absorption and reduced mechanical strength due to its hydrophilic nature. Despite this, the proper dispersion of TPS, evidenced by the absence of starch granules in the SEM images, reflects the effectiveness of the processing method used.

Thermal analysis confirmed the distinct decomposition stages for the matrix, fibers, and TPS, emphasizing the complex interactions within the composite. The stability and interfacial bonding observed are promising indicators of the material's suitability for practical applications, especially in environments where moderate mechanical demands and sustainability are key factors.

The findings underscore the feasibility of developing eco-friendly composites with balanced mechanical and environmental properties. Future work could explore alternative fiber treatments or compatibilization strategies to further enhance the integration of TPS and fibers, aiming to expand the usability of these materials in diverse sectors.

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