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A New Approach Using Multi-Layer Films from Food Waste as a Shrink Film

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Abstract: Multi-layer films are one of the most challenging classes of polymer waste for recycling, as they consist of a mixture of constituent materials like polyethylene (PE), polyamide 6 (PA6), and ethylene vinyl alcohol (EVOH). This study investigates the characterization, washing, and mechanical properties of recycled blends derived from such multi-layer films. Raman spectroscopy and Differential Scanning Calorimetry (DSC) were used to characterize the individual components in single- and multi-layer films, and distinct properties of LDPE, LLDPE, PA6, and EVOH were observed. Mechanical properties enhanced by proper shredding, washing procedures, and multiple combinations of polyethylene blends were investigated to optimize the mechanical characteristics of the recycled materials, especially strain at break. Additionally, the shrinkage behavior of the recycled films was compared to commercial shrink films, demonstrating their potential for use in industry packaging applications. These results highlight a more sustainable possibility for multi-layer packaging applications.

Keywords: multi-layer films; mechanical recycling; industrial application; PA6; PE; EVOH

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1. Introduction

Plastic multi-layer packaging can be found in every industry nowadays. Its low cost, high versatility, and easy processing have led to its integration into food processing. Combining different polymers enables packaging to achieve desired properties such as barrier performance, sealability, abrasion resistance, mechanical strength, and printability [1]. Furthermore, multi-layered materials allowed for a decrease in the thickness of packaging and, therefore, reduced the polymer used in packaging. When recycling plastics, special attention must be paid to polymer systems with a short cycle time. The different application areas usually have very different service lives. If packaging is only used for a few days to months before it reaches the end of its service life, products from the construction industry can remain in use for up to 20 years and longer. The sector with the shortest lifespan—namely packaging—accounts for around 40% of the quantity on the market. In Europe, 17.8 Mt of used packaging was collected in 2018—but only 7.5 Mt was recycled [2]. This results in an average material recycling rate of 42% [3]. The remaining packaging waste was sent for thermal recovery (7 Mt) or untreated landfill (3.3 Mt) [3].

There are currently many recycling options: from mechanical recycling (where the macromolecules remain in their original form) to feedstock or chemical recycling (macromolecules are broken down into smaller molecules and subsequently used) and thermal recycling (only the energy content is used) [2]. Current research work in mechanical recycling is moving toward processing material flows. For example, research is being

conducted into multi-sensor-based sorting systems with artificial intelligence or so-called tracing systems [4,5]. This research aims to generate unmixed material streams so that they can then be returned to the cycle via the conventional recycling route. However, these methods have one major disadvantage—they all fail with composite materials such as multi-layer films. The immiscibility of polymers such as low-density polyethylene (LDPE), polyamide 6 (PA6), and EVOH) poses significant challenges during mechanical recycling, often resulting in a complicated recyclability assessment.

Then again, mechanical recycling is regarded as the preferable treatment of plastic multi-layer packaging after waste avoidance and reuse, even though the fact that chemical recycling has the potential to recover all components without deteriorating their properties [6–8]. This preference arises because chemical recycling usually demands more energy than mechanical recycling and involves chemicals, which need additional treatment [9,10].

During mechanical recycling, the immiscible polymers in multi-layer packaging form a multi-phase system characterized by poor interfacial adhesion, adversely affecting the recycled material's mechanical properties [11]. Numerous compatibilizers were studied to improve the adhesion of two immiscible polymers [1,12–18]. The compatibilizers enhance minor phase dispersion, reduce particle size, and increase interfacial adhesion, thereby improving mechanical properties compared to un-compatibilized blends. While most studies focus on binary polymer blends, multi-material systems present additional challenges. Identifying a single compatibilizer capable of addressing all components in a blend is a complex problem. For instance, Wang et al. [18] successfully used a multi-phase compatibilizer, PP-g-(MAH-co-St), to improve the compatibility of a PP-PS-PA6 blend, achieving reduced minor phase particle sizes and improved interfacial adhesion.

Furthermore, particle dispersion and size can be further optimized by adjusting the blend's material ratios and processing conditions [19,20]. Although this approach does not directly enhance interfacial adhesion, it can improve mechanical properties, particularly elongation at break and impact strength. Despite extensive research on polymer compatibilization and multi-layer packaging recycling, few studies focus on industrial applications and practical implementation.

This paper explores the mechanical recycling of industrial multi-layer plastic waste composed of PEs, PA6, and EVOH. Compatibilizers based on acrylic acid and oxazolines were selected based on their effectiveness in binary polymer blends and tested on this complex waste stream [21,22]. The study evaluates different approaches to mechanical recycling, both with and without compatibilizers, and describes the recycling process, including applying recycled material.

2. Materials and Methods

2.1. Materials

Polymer waste was provided by PrimAs Tiefkühlprodukte GmbH (Oberhofen, Austria) and consisted of various plastic films. The films were analyzed by Raman spectroscopy (Horiba JY Lab RAM HR 800 by HORIBA Jobin Yvon GmbH, Bensheim, Germany) with a 514 nm laser diode. Spectra were collected from the cross-section of the films with an exposure time of 3 s and accumulation number of 6 in a range of 400–3500 cm^{-1}. The spectra were processed using Spectragryph 1.2 software, applying adaptive baseline correction with a coarseness of 12%. Differential scanning calorimeter DSC1 by Mettler–Toledo AG (Schwerzenbach, Switzerland) was used to determine the melting temperatures of the films. The films were heated to 250 °C, cooled to 25 °C, and reheated to 250 °C. The heating and cooling rate was 10 °C min^{-1}. Melting temperatures were evaluated using STARe 16a Software from Mettler–Toledo AG (Schwerzenbach, Switzerland).

Two types of multi-layer films (MFs) and two types of single-layer films (SFs) were selected for recycling. The multi-layer films consist of LDPE, PA6, and EVOH in different ratios. Both MF types were in direct contact with food and contained paper labels. The SFs were used as shrink film (LDPE) and stretch film (LLDPE). While SFs did not contain food residues, they accumulated dirt as they served as top packaging layers. Additionally, labels were only sparsely present on SFs.

As the availability of films depended on the company's plastic waste composition, the goal was to maintain a recycling ratio similar to the waste film ratio found at the company. Previous waste analysis indicated that the ratio between MF1, MF2, and both SFs was approximately 32:10:35. The proportions of SF1 and SF2 fluctuated throughout the year but were mostly equal (1:1 ratio). Table 1 presents the composition of the analyzed films.

Table 1. Composition of plastic films in %.

	LDPE	LLDPE	PA6	EVOH
MF 1	59	0	29	12
MF 2	90	0	8	2
SF 1	100	0	0	0
SF 2	0	100	0	0

From these four films, different groups of blends were prepared.

1. Blends with different LDPE-PA6-EVOH ratios were created by mixing MF1, MF2 and SF1;
2. Blends with different amounts of LLDPE were prepared by maintaining the MF1 and MF2 constant while adjusting the amounts of SF1 and SF2;
3. Blends with different compatibilizers were based on a constant MF1:MF2:S1 ratio, with three different compatibilizers added in varying amounts (Table 2).

Table 3 shows the composition of the prepared blends. Blend LLDPE_0 was used as the default reference blend for varying LLDPE ratios and compatibilizers, as its composition matched the plastic waste profile of the company. The compatibilizers used in this study (Table 2) were selected based on previous research performed on PA6-LDPE blends [23–28]. Acrylic acid grafted polyethylene reduces the interfacial tension between LDPE and PA6, leading to smaller dispersed particle sizes [26,29].

Oxazoline-based compatibilizers were chosen for their reactivity with amide groups. It is suspected that oxazolines tend to migrate towards the interface and react there, which should improve the miscibility of polymers [22,23]. Additionally, oxazolines may improve the effectiveness of acrylic acid-based compatibilizers in LDPE-PA6 blends [30].

All three compatibilizers were used individually and combinations of PBO with 4% TPPE and BHOB with 4% TPPE were also tested.

Table 2. Used compatibilizers.

Name	Used Abbreviation
acrylic acid grafted polyethylene	TPPE
1,3-phenylene-bis-oxazoline	BHOB
2,2′-(1,4-phenylene)bis(2-oxazoline)	PBO

Table 3. Recycled blend compositions.

Blend's Name	MF1 (%)	MF2 (%)	SF1 (%)	SF2 (%)	TPPE (%)	BHOB (%)	PBO (%)
PE_PA 87:11	42	13	45	-	-	-	-
PE_PA 70:25	79	3	17	-	-	-	-
PE_PA 60:35	75	3	22	-	-	-	-
PE_PA 50:45	71	3	26	-	-	-	-
LLDPE_0	42	13	45	-	-	-	-
LLDPE_25	42	13	33.75	11.25	-	-	-
LLDPE_50	42	13	22.5	22.5	-	-	-
LLDPE_75	42	13	11.25	33.75	-	-	-
LLDPE_100	42	13	-	45	-	-	-
LLDPE_0	42	13	45	-	-	-	-
1 BHOB	42	13	44	-	-	1	-
2 BHOB	41	13	44	-	-	-	2
3 BHOB	41	13	43	-	-	3	-
4 BHOB	40	13	43	-	-	4	-
1 PBO	42	13	44	-	-	-	1
2 PBO	41	13	44	-	-	-	2
3 PBO	41	13	43	-	-	-	3
4 TPPE	40	13	43	-	4	-	-
0.4 TPPE + HBOB	40	13	43	-	4	0.4	-
0.7 TPPE + HBOB	40	12	43	-	4	0.7	-
0.4 TPPE + PBO	40	13	43	-	4	-	0.4
0.7 TPPE + PBO	40	12	43	-	4	-	0.7

2.2. Recycling

The recycling process was divided into several steps: shredding, washing, reprocessing (kneading or compounding), and film production.

2.2.1. Shredding

Several cutting techniques were examined for all the films. The SCHEER TYPE SGS-50-EL Strand pelletizer (Scheer, MAAG Group, Großostheim, Germany) was used to produce fine flakes (1 × 2 cm), while manual cutting yielded larger pieces (40 × 20 cm). The industrial single shaft shredder WS 11 by Wagner, The Shredder Company (Neuhaus am Klausenbach, Austria) was used to prepare flakes measuring 3 × 2 cm. During the cutting, paper labels were removed.

2.2.2. Washing

Several washing methods were tested:

1. Washing in cold water (15 °C) without detergent;
2. Washing in warm water (60 °C) without detergent;
3. Washing in cold water (15 °C) with detergent (dishwasher with <15% surfactants, 15 mL L^{-1});
4. Washing in warm water (60 °C) with detergent (dishwasher with <15% surfactants, 15 mL L^{-1});
5. Washing in 2% NaOH solution and rinsing with acetone.

To evaluate the impact of washing conditions, a custom washing device was built (Figure 1). The device consisted of a water container, a rotating cage with a lid, and a propeller. Plastic "stones" (polypropylene cylinders, 2 cm in diameter and 5 cm long) were

added to increase friction. The placement of films in the cage ensured that the films stayed under the water and that the films rotated in the water.

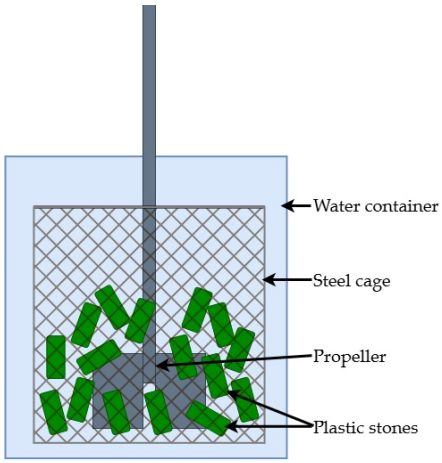


Figure 1. Drawing of washing device. The steel cage is filled with plastic stones and attached to the rotor, and it can be immersed in the water.

Different sizes of cut film were washed to assess the influence of film size on the quality of washing. The standard household washing machine (Indesit IWC 6145 by Whirlpool, Stuttgart, Germany) was used to wash films up to 2 kg with a water temperature of 60 °C and with 9 g dishwasher detergent (with <15% surfactants) per kg of plastic film. After washing, the films were dried in the Drying oven SF 110 by Memmert, Inc. (Schwabach, Germany) at 60 °C for at least 12 h.

2.2.3. Reprocessing

A Brabender mixer (Measuring mixer 350 EHT by Brabender GmbH & Co. KG, Duisburg, Germany) with a 38 mL chamber was used to prepare mixtures from waste films. Cut, washed, and dried films were kneaded at 230 °C with 80 rpm for 4.5 min. The mixed material was then removed and cooled at room temperature. Approximately 40 g of each blend from Table 3 was prepared.

For the pilot test, a twin-screw extruder (Leistritz ZSE 18 HP-48D by Leistritz Extrusionstechnik, Inc. Nuremberg, Germany) was used. The distance between screws was 15 mm. Screws with a diameter of 18 mm and with a screw length of 48D were used. Each film was compounded separately into granules, which were then mixed in desired ratios and compounded again. Table 4 lists the compounding conditions. Using this method, 25 kg of blends LLDPE_50 and LLDPE_100 were prepared.

Table 4. Used compounding conditions for SF, MF, and blends.

Material	Temperature Profile (°C)	Screw Speed
Single films	30-170-170-170-170-170-170-170-170-170-170-170-170	250 rpm
Multi-layer films and blends	30-170-250-260-270-270-270-270-270-270-270-270-270	350 rpm

2.2.4. Film Making

Films for tensile testing were prepared using a vacuum press (P 200 S by COLLIN Lab & Pilot Solutions GmbH, Maitenbeth, Germany). Approximately 10 g of the material was pressed at the maximum temperature of 230 °C and under a maximum pressure of 200 bar

for 20 min. Film thickness ranged between 200 and 600 µm; as a rule, blends with higher strain at break were thinner than the blends with smaller strain at break.

For the pilot test, thin films were manufactured at COLLIN Lab & Pilot Solutions GmbH (Maitenbeth, Germany) using Extruder LAB E 30 T with Flat Film Die BSD and horizontal Flat Film Line with 3 rolls. The maximum extruder temperature was 265 °C, and the winding speed was 17 m min^{-1}. The produced films were 35 cm wide and 16 µm thick.

2.3. Mechanical Testing

Tensile tests were performed according to DIN EN ISO 527-3 on 15 ×150 mm samples cut from pressed films. As the pressed films were isotropic, only one set of at least 5 samples per blend was tested.

Thin films were tested both in the machine direction and transverse to the machine direction. All samples were tested on the universal testing machine ZWICK Z001 (Zwick/Roell Gmbh & Co, Ulm, Germany) at a testing speed of 200 m ms^{-1} with a 50 mm clamp distance at room temperature.

2.4. Shrinkage Test

A shrinkage test was conducted in the Drying oven SF 110 by Memmert, Inc. (Schwabach, Germany) to simulate conditions during the packaging process. To assess shrinkage, thin film strips (20 cm in length) were cut in the longitudinal direction. Two reference marks were placed 10 cm apart on the bottom side of each strip.

The strips were suspended in the oven, which was heated to 180 °C for 10, 15, 20, 25, 30, 35 and 40 s. After removing the strips from the oven, the distance between the marks was measured, and shrinkage in the longitudinal direction was calculated based on the difference in length. The shrinkage behavior of the recycled films was compared to that of the conventional shrink film used by PrimAs Tiefkühlprodukte GmbH (Oberhofen, Austria).

3. Results and Discussion

3.1. Characterization of Films

SF1 and SF2 exhibited very similar Raman spectra (Figure 2). The most intense peaks that appeared at 2880 and 2846 cm^{-1} are assigned to $–CH_2$ asymmetric and symmetric stretching, respectively. Additionally, five characteristic polyethylene peaks were observed at 1437, 1415, 1294, 1127, and 1061 cm^{-1}, corresponding to CH_2 bending, CH, vibrations in orthorhombic unit cells, CH_2 twisting, C–C stretching, and C–C stretching, respectively [31,32].

Differences in the intensity of specific peaks suggest two different kinds of polyethylenes. In SF1, the peak at 2880 cm^{-1} was more intense than the peak at 2846 cm^{-1}, which is characteristic of LDPE. In contrast, LLDPE typically exhibits a lower intensity ratio in this region. These peaks indicate the amount of crystalline PE (1415 cm^{-1}) and amorphous PE (1440 cm^{-1}) [33]. The ratio of those peaks shows that SF2 has a higher amount of crystalline phase than SF1.

For MF1 and MF2, three distinct Raman spectra were recorded. Figure 2 displays the Raman spectra of MF1. MF1_a and MF2_a spectra closely resembled SF1 but included an additional peak at 1530 cm^{-1} and a broad low-intensity peak at 870 cm^{-1}, which were likely caused by a blue pigment present in the films.

The MF1_b spectrum displayed characteristic peaks of polyamide 6: 1636, 1466, 1281 cm^{-1} assigned to the C=O stretch of Amide I, C–N stretch, and N–H bend of Amide II and C–N stretch and N–H bend of Amide III, respectively. The peaks at 1127, 1082, and 1064 cm^{-1} are assigned to skeletal stretches of PA6. The spectrum also shows peaks of N–H stretching at 3301 cm^{-1}, CH stretching at 2928 cm^{-1}, CH_2 bending at 1443 cm^{-1}, CH_2

twisting at 1306 cm^{-1}, and CCO stretching at 993 cm^{-1} [34,35]. The MF2_b spectrum closely resembled the MF1_b spectrum, except for a slight shift in the C=O band to 1620 cm^{-1}, which could be attributed to minor compositional variations or partial laser excitation of adjacent layers due to the small thickness of the material.

The MF1_c spectrum shared many similarities with MF1_a, but exhibited a broad OH stretching peak at 3305 cm^{-1} and a peak at 2905 $cm-^{1}$, which were absent in polyethylene spectra but characteristic of EVOH [36]. The MF2_c spectrum displayed the same features as MF1_c.

DSC measurements of SF1 (Supplementary Figure S1) showed two melting peaks at 109 and 118 °C. The SF2 (Supplementary Figure S1) had a melting peak at 124 °C. These temperatures correspond to the melting temperatures of LDPE and LLDPE.

DSC measurements of MF1 (Supplementary Figure S2) showed the most prominent melting peaks at 112 °C and smaller ones at 160 °C and 216 °C, corresponding with melting temperatures of LDPE, EVOH, and PA6, respectively. The MF2 DSC curve (Supplementary Figure S2) had a melting peak at 122 °C, a very small melting peak at 172 °C, and a third peak at 215 °C. Again, these melting peaks correspond to the LDPE, EVOH, and PA6 melting peaks.

Based on Raman spectroscopy and DSC results, three materials—LDPE, PA6, and EVOH—were identified in the MF1 and MF2. The composition of each film (Table 1 was determined based on layer thickness measurements using light microscopy and Raman spectra collected at specific layers.

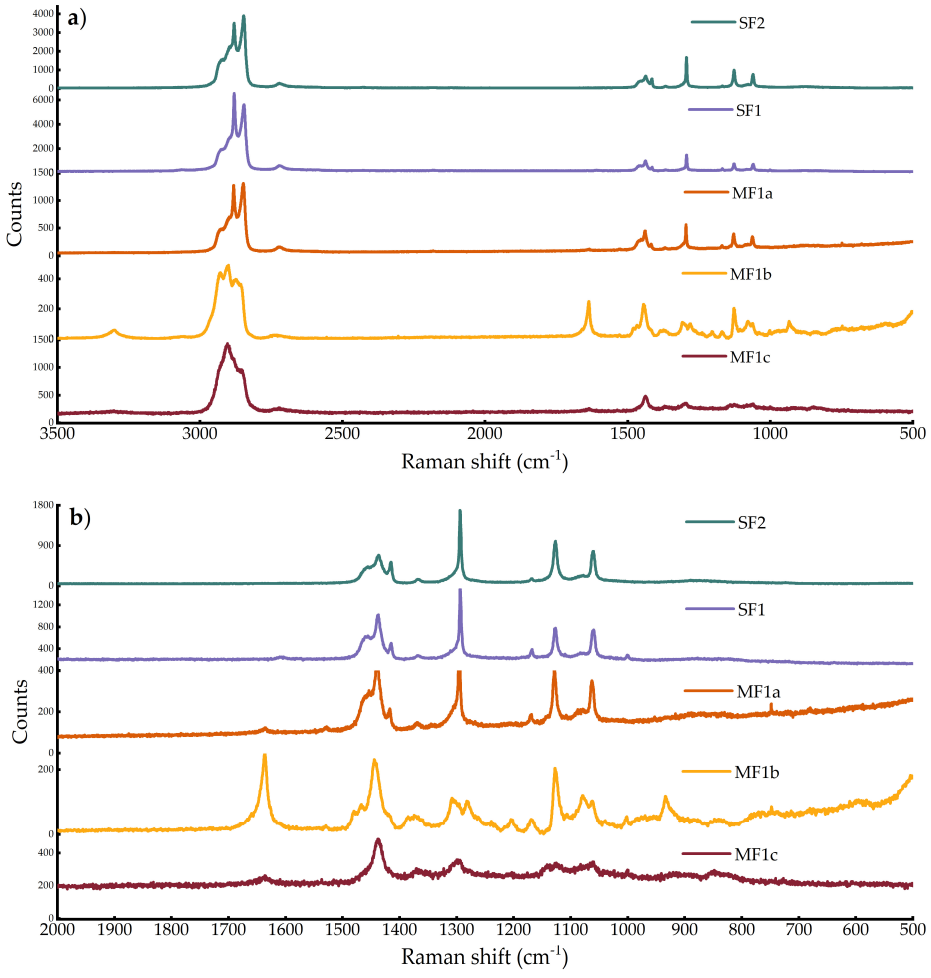


Figure 2. (**a**) The whole spectra of SF1, SF2, and MF1 are shown; and (**b**) shows only the range of 500–2000 cm^{-1}. Spectra are stacked for clarity.

3.2. Shredding

The initial step of cutting large plastic bags played a crucial role in subsequent processing, facilitating better washing efficiency and faster drying. Before cutting, factors such as drying, mixing, and compounding needed to be considered to ensure that the shredded material was suitable for further recycling steps.

A granulator was used to prepare fine flakes from the film. The use of shredders with opposing knives is well established in the waste industry, as their design prevents excessive film melting, ensuring that flakes remain easy to wash. This is particularly important for PE-based films, which tend to melt slightly when cut using high-speed blades, potentially clogging machines and sealing impurities within the material.

The shredder produced flakes measuring approximately 3 × 4 cm. Flake size significantly affected downstream processing, as smaller flakes might be too light to enter the feeder properly, whereas larger flakes might not fit between the blades of certain machines.

The industrial shredder required a large volume of films for efficient operation, making it suitable for processing pilot-scale blends but not small-scale trials, which did not meet the machine's minimum volume requirements.

Manual cutting provided the possibility to tailor the size and shape of the cut film precisely for the kneader and compounder, although it is more time-consuming than machine shredding. Films were cut into stripes 25–50 cm long, wide 15–20 cm, and narrowing towards one end, which enhanced washing efficiency and ease of handling during processing. In contrast, smaller pieces (5 × 5 cm) led to uneven feeding of the compounder, requiring manual pushing, which resulted in feeding delays, clogging, and inconsistent material production.

The cutting process also involved removing the paper labels. All of the processed films were void of paper labels before recycling.

3.3. Washing

Washing is a key step in recycling. Any contamination or food residues negatively affect the properties of recycled materials, often resulting in undesirable odors.

The quality of washing was evaluated subjectively, with clean films defined as those free from visible particles, stains, and odors.

In the first step, the size of the washed film was tested. The whole films, films cut into pieces approximately 20 × 20 cm and shredded flakes were washed. Mechanical washing of whole films was insufficient for removing food residues while washing cut or shredded films was more effective. The water-to-film ratio significantly influenced cleaning efficiency—flakes required more water for thorough cleaning, whereas larger pieces needed less. Smaller pieces also dried faster than larger ones.

Washing without detergent removed most food residues and dirt, but left fatty stains, especially in cold water. Warm water improved cleaning efficiency and the addition of detergent effectively eliminated fat residues and other contaminants. Using detergent required two steps process. where films were first washed for 50 min in detergent and then rinsed with clean water. Also, in this case, washing in warm water led to a cleaner film surface. The detergent helped to remove some of the fats from the film even in the cold water, but not all. The combination of warm water and the detergent removed all dirt and fat from the films.

An attempt to remove paper labels during washing was performed. The films with labels in the form of flakes and 20 × 20 cm pieces were washed in a solution of NaOH for 50 min. The solution's temperature was around 55 °C. After 50 min, the paper labels were separated from the films. Due to the different densities, the plastic films and paper labels created two separate layers. The bath was left to settle for an hour and then the

paper labels could be easily removed. The films were then rinsed with water and acetone to remove the glue, which stayed on the films after the labels were removed. This way of washing successfully removed all the food residues, fats, and also paper labels. It was more time-consuming than washing films with pre-removed labels. The demand for time would be higher with the bigger volumes of films, as the time needed for separation of the paper labels from the films would be prolonged with upscaling. Also, the film's size affects the washing process duration. The films shredded into flakes were washed faster and the paper labels were separated quickly from the plastic. However, the sedimentation process took longer. The 20 × 20 cm pieces needed longer to be washed and to separate paper labels from the plastic, but the sedimentation occurred faster than with shredded flakes. The wastewater from plastic recycling might need pre-treatment before being sent into the sewage network, even without using any chemicals [32]. The pre-treatment demands would be even higher after washing in NaOH. Due to the complexity and time required for NaOH treatment, this method was not used for large-scale recycling.

Specimens from unwashed and washed films were prepared for the tensile test to evaluate the influence of washing on the mechanical properties of recycled material. Multi-layer films were mixed with the single-layer films in ratios stated in Table 5. This material was pressed and cut into tensile test specimens.

The tensile test showed (Figure 3) that the recycled material prepared from washed films (in warm water with a detergent) has better tensile strength and strain at break than from unwashed films. This is also true for single-layer films, which are not in direct contact with the food and are significantly cleaner than multi-layer films.

Table 5. Composition of blends used for evaluating influence of washing.

Blend Name	Multi-Layer Films (%)	Single Layer Films (%)	Washed/Unwashed
M-S 80-20 uw	80	20	unwashed
M-S 80-20 w	80	20	washed
M-S 60-40 uw	60	40	unwashed
M-S 60-40 w	60	40	washed
M-S 40-60 uw	40	60	unwashed
M-S 40-60 w	40	60	washed
M-S 20-80 uw	20	80	unwashed
M-S 20-80 w	20	80	washed
M uw	100	0	unwashed
M w	100	0	washed
S uw	0	100	unwashed
S w	0	100	washed

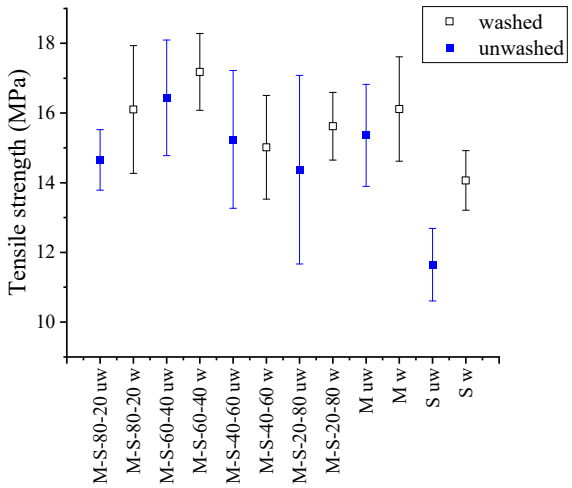


Figure 3. Tensile strength of washed and unwashed blends.

Therefore, all films were washed before kneading or compounding. As a default method, films were washed in warm water with dishwasher detergent using a household washing machine and then dried at 55 °C for at least 12 h before further processing.

3.4. Mechanical Properties

3.4.1. Tensile Test of Blends with Different LDPE-PA6-EVOH Ratios

The blend compositions were based on the company's make-up of plastic waste. Mechanical properties were compared across blends prepared using identical recycling steps. The tensile test specimens were prepared from kneaded material pressed in a vacuum press. Various PE, EVOH, and PA6 ratios were created by mixing MF1, MF2, and SF1 (Table 6).

Table 6. Composition of blends.

Blend	LDPE (%)	EVOH (%)	PA6 (%)
PE_PA 87:11	87	2	11
PE_PA 70:25	70	5	25
PE_PA 60:35	60	5	35
PE_PA 50:45	50	5	45

The strain at break results are shown in Figure 4. The highest strain at break shows blend PE_PA 87:11. This was expected as it has the highest LDPE content, and the strain at break of LDPE is orders of magnitude higher than either PA6 or EVOH. However, no rapid decrease in strain at break was observed when the LDPE content decreased in PE_PA 70:25 and PE_PA 60:35. The PE_PA 60:35 has an even slightly higher strain at break than PE_PA 70:25, likely due to impurities or inhomogeneities, as indicated by the deviation in strain at break for this blend. A significant drop in the strain at break is visible when the LDPE content drops to 50% in the PE_PA 50:45 blend.

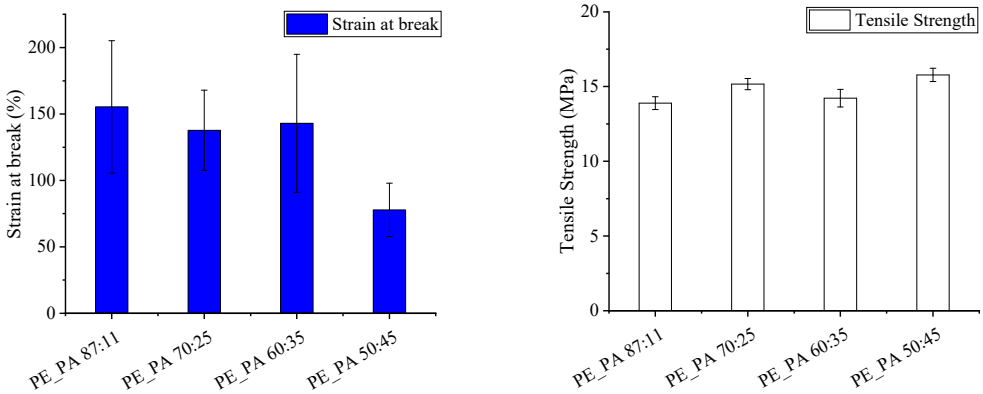


Figure 4. Strain at break and tensile strength of blends with different ratios of polymers.

Tensile strength ranged from 13.9 to 15.8 MPa, with PE_PA 87:11 having the lowest value and PE_PA 50:45 having the highest. Despite the increasing PA6 content, which has a much higher tensile strength than LDPE, no substantial improvement in tensile strength was observed. This suggests that PA6 and EVOH act primarily as fillers rather than contributors to material strength. Higher amounts of these minor phases influenced strain at break, as an increase in filler content typically leads to a reduction in strain at break [37]. Contrary to inorganic fillers, the size of PA6-EVOH phase particles is not constant. With an increasing PA6 content, the PA6-EVOH phase grows in size [19]. This supports the hypothesis that blends morphology transitions from finely dispersed PA6-EVOH particles to larger particles with increasing PA6 content. This observation aligns with the findings

of Nwanoneyi et al. [38], who noted that higher filler content increases composite tensile strength, but that bigger particle size diminishes the strengthening effect.

3.4.2. Tensile Test of Blends with Different LLDPE-LDPE Ratio

The tensile strength of the blends LLDPE_0–LLDPE_75 is within the range of 13.5–14.1 MPa. The LLDPE_100 blend, which contained only SF2, had a tensile strength of 15.1 MPa, which can be attributed to the inherently higher tensile strength of LLDPE compared to LDPE. However, this increase was too small to significantly impact the overall mechanical properties of the recycled material.

In contrast, strain at break (Figure 5) was more influenced by the LDPE-to-LLDPE ratio. The blend LLDPE_100 had strain at the break 345%, nearly double the value observed in the best-performing LDPE-based blend. When comparing blend LLDPE_0, LLDPE_50, and LLDPE_100, a clear trend emerged—strain at break increased with increasing LLDPE content. However, blends LLDPE_25 and LLDPE_75 deviated from this trend, showing lower strain at break than LLDPE_0. It might be expected that the increasing LLDPE content would increase strain at break, given LLDPE's higher strain at break compared to LDPE. The deviation from this trend in LLDPE_25 and LLDPE_75 might be caused by the different quality of film waste received from the company, as the blends were prepared over a longer span of time. The test with virgin LDPE and LLDPE combined with MF1 and MF2 was conducted and it showed the linear trend of increasing strain at the break with increasing volume of LLDPE.

By replacing 50% of SF1 with SF2, strain at break increased from 155% to 319%. When SF2 fully replaced SF1, strain at break reached 347%. These results demonstrate that LLDPE incorporation can marginally improve strain at the break of the recycled material, while the tensile strength remains largely unchanged.

The increase in strain at break was primarily due to the better strain at break of SF2, which was 2.6 times higher than that of SF1. However, the most significant increase in the strain at break was observed between blends LLDPE_0 and LLDPE_50. After replacing more than 50% of SF1 with SF2, the increase in strain at break slowed down. This borderline was given by the amount of the minor phase, which played the role of filler.

The blends LLDPE_50 and LLDPE_100 were selected for upscaling, as their strain at break exceeded 300%, which met the technical requirements of the packaging line.

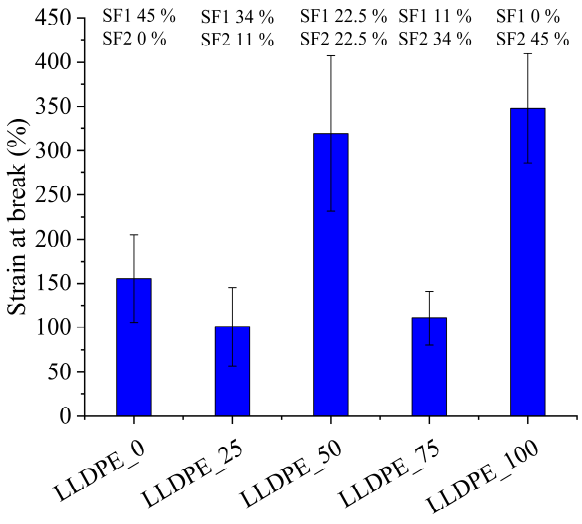


Figure 5. Strain at break of blends with different LLDPE content. The percentages of SF1 and SF2 used in each blend are stated above bars.

3.4.3. Tensile Test of Blends with Compatibilizers

The tensile strength was around 14.5 MPa. The lowest tensile strength was 13.9 MPa (LLDPE_0 without compatibilizer), while the highest was 15.3 MPa (4 BHOB blend). The almost unchanging tensile strength values were expected, as compatibilizers usually do not significantly improve tensile strength [18].

Figure 6 shows that only two blends exhibited higher strain at break than LLDPE_0: blend with 3% of BHOB and blend with 4% TPPE and 0.7% PBO. All other blends exhibited lower strain at break than the blend without any compatibilizers.

PBO reduced strain at break as its concentration increased, suggesting that it did not react in the blends and instead acted solely as a filler. Accumulation of PBO powder at the interface may have contributed to the rapid decline in strain at break.

Adding 3% BHOB improved strain at the break of the blend, but both lower or higher concentrations resulted in reduced strain at the break. The 3% of BHOB might be close to the critical amount needed for interfacial reaction, thereby improving blend miscibility.

The relatively short mixing time (4.5 min) may have limited compatibilizer migration and reaction, as previous studies [22] indicate that mixing times exceeding 10 min enhance compatibilizer performance. However, prolonging mixing time was avoided to minimize PE degradation. This may have prevented the compatibilizers from effectively dispersing and reacting, causing them to act as fillers instead.

TPPE alone did not improve the blend's strain at break, and its combination with BHOB further reduced performance. However, the combination of TPPE and PBO appeared to enhance strain at break in the LLDPE_0 blend. The blend with 4% TPPE and 0.7% PBO outperformed the strain at the break of the LLDPE_0.

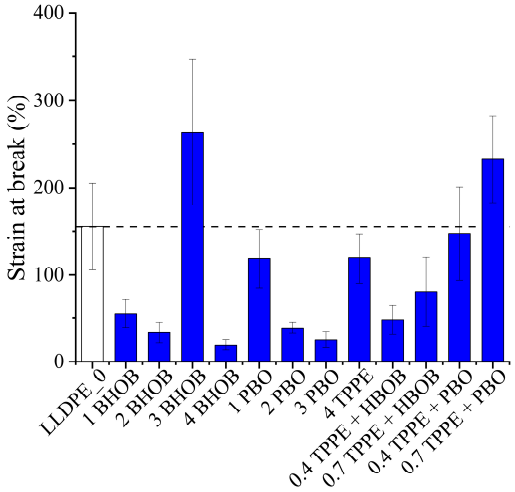


Figure 6. Strain at break of LLDPE_0 blends with different compatibilizers. The dashline represents strain at break of the LLDPE_0 that was used as a base for compatibilized blends.

A comparison between blends with different LLDPE ratios and with different compatibilizers indicated that LLDPE had greater potential to improve the properties of the LDPE-PA6-EVOH blends than any tested compatibilizer. The blends LLDPE_50 and LLDPE_100 exceeded 300% strain at break, whereas the best two blends with compatibilizers reached only 231% and 263%. Although the amount of LLDPE added was much higher than that of the compatibilizers, the improved mechanical properties could not be attributed to compatibilization effects. Instead, LLDPE's inherently higher strain at break contributed to the enhancement. Further studies are needed to understand if any other principle underlies improving blends' mechanical properties. Apart from the better strain

at break, LLDPE is a part of the plastic waste make-up as an SF2 and, therefore, brings no additional cost to recycling.

3.5. Shrinkage

The LLDPE_100 and LLDPE_50 blends were selected for pilot testing, and thin films prepared from these blends were tested for shrinkage in the longitudinal direction. The results were compared with a standard commercial shrink film.

Figure 7 compares the shrinkage behavior of the films over time. The commercial shrink film (Shrink film) reached 75% shrinkage after 40 s in the oven at 180 °C, whereas the maximal shrinkage of both recycled films was below 40%. The LLDPE_50 blend exhibited better shrinkage performance than LLDPE_100, likely due to its higher LDPE content, which is commonly used in shrink films. Recycled blends were unable to achieve full shrinkage of the PE matrix due to the presence of EVOH and PA6. The EVOH and PA6 form core–shell particles in the PE matrix [39], creating a physical barrier for PE chain movement and preventing full shrinkage.

However, the shrinkage performance of all three films was comparable during the initial heating phase (below 15 s) before the PE matrix achieved full shrinkage. After 10 s, the recycled films even showed slightly higher shrinkage than the commercial film. However, the shrinkage behavior changes most rapidly within the first few seconds of heating before stabilizing, making the difference between similar materials relatively small during this stage. From 15 s onward, differences between materials became apparent. After 20 s in the oven, the commercial shrink film had shrunk more than twice compared to the recycled blends. It is important to note that the time used for shrinkage during packaging is below 15 s. Moreover, although PA6 or EVOH hinder the full shrinkage of the films, their effects are negligible in practical application when in a short time.

Both recycled thin films were successfully tested in the packaging line of PrimAs company, and the results confirmed that the recycled films can function as shrink films with appropriate temperature adjustments in the packaging line.

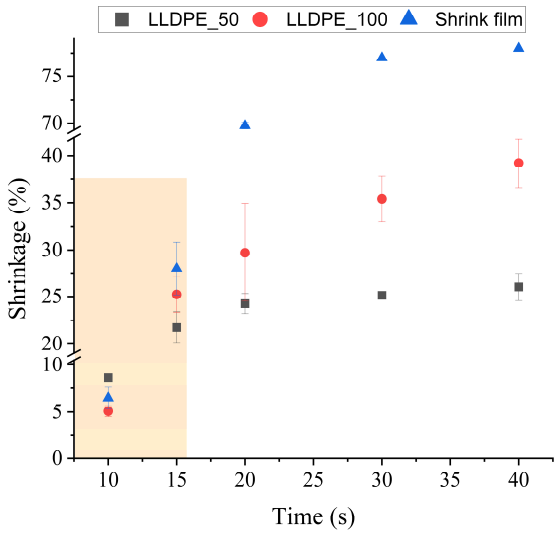


Figure 7. Shrinkage of the recycled material and the commercial shrink film in an oven at 180 °C.

4. Conclusions

This study highlights the importance of the washing step in the recycling process and emphasizes its significant influence on the mechanical properties of recycled materials. While the used compatibilizers did not improve the mechanical properties of the LDPE-EVOH-PA6 polymer blend, a notable enhancement was observed by substituting LDPE

with LLDPE. This replacement resulted in an increase of 205% and 222% in the strain at the break when 14% and 28% of LDPE in the blend were replaced, respectively.

Additionally, the successful preparation of recycled films, such as LLDPE_50 and LLDPE_100 blends, exhibited comparable shrinkage properties to conventional shrink film measured in hot air at 180 °C for 15 s. Moreover, the recycled film from the LLDPE_50 blend proved successful in the packaging line of a company, demonstrating the potential for incorporating recycled multi-layer plastic films back into the packaging and reducing dependence on virgin polymers in the industry.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/pr13020560/s1. Supplementary Figure S1 DSC curve of SF1 and SF2 measured from 20 °C to 200 °C with constant heating rate 10 °C/min. Curves are stacked for clarity. Supplementary Figure S2 DSC curve of MF1 and MF2 measured from 20 °C to 260 °C with constant heating rate 10 °C/min. Curves are stacked for clarity.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon request.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

LDPE	Low-Density Polyethylene
LLDPE	Linear Low-Density Polyethylene
PA6	Polyamide 6
EVOH	Ethylene Vinyl Alcohol Copolymer
MF	Multi-Layer Film
SF	Single-Layer Film
DSC	Differential Scanning Calorimetry
TPPE	Acrylic Acid Grafted Polyethylene
BHOB	2,2′-(1,3-Phenylene)bis(2-Oxazoline)
PBO	2,2′-(1,4-Phenylene)bis(2-Oxazoline)

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