

Article

Utilization of Multilayered Polyethylene Terephthalate (PET)-Based Film Packaging Waste Using Reactive Compatibilizers and Impact Modifier

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Abstract: This research aimed to evaluate the material properties of reactive extrusion-modified blends containing PET multilayered foil waste. Three types of PET-based multilayer foil waste were used as the compound during the reprocessing of standard bottle-grade PET. Flakes used for this purpose were made from laminated foils: (A) PET/PE, (B) PET/EVOH/PE, and PET/PE/met. All types of the prepared materials were compounded with 30% of the waste foil flakes. Additionally, the blend was modified with an epoxy-based chain extender and polyolefin-based impact modifier. The prepared blends were processed using two methods; initially, the materials were prepared by injection molding, while cast-film samples were also prepared. All samples were subjected to full characterization using mechanical testing methods, thermal analysis, and structural observations. The study shows that the addition of multilayered foil waste is leading to significant deterioration of PET-based material properties. While, in most cases, the use of a chain extender led to some improvement in mechanical characteristics, the impact modifier addition strongly influenced most of the properties. It was also observed that the reactive extrusion procedure led to melt strength improvement, which greatly facilitates the film production process. Due to the limited possibility of separating the film components, the developed method of foil recycling might be useful for the utilization of multilayered packaging.

Keywords: polyethylene terephthalate (PET); recycling; post-consumer recycled (PCR); multilayer foil; reactive compatibilizers; impact modifier



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1. Introduction

Most of the currently produced plastics are based on a non-renewable raw material, which is crude oil. Currently, saving the main raw material in this case oil and avoiding environmental pollution are fundamental goals for the world economy. This target might be achieved through the use of renewable materials and post-consumer (PCR) waste recycling. These concepts are now not only an expression of good will, but also a statutory requirement in many countries [1–5].

Based on the current publication of the European Parliament “Plastic Waste and Recycling in the EU: Facts and Figures”, the production of plastics has increased in just a few decades—from 1.5 million tonnes in 1950 to 359 million tonnes in 2018, of which packaging production accounts for approx. 40%. As part of the Green Deal, 55% of plastic packaging waste should be recycled by 2030 [6].

However, it should be emphasized that in the last decade, the issue of recycling polymer products has begun to be treated more seriously by many packaging manufacturers.

Among all varieties of packaging materials, particularly effective recycling systems have been implemented for PET-based materials (polyethylene terephthalate) [7–10]. This is particularly the case due to the characteristics of PET used in the packaging industry, where transparent products with a very low content of fillers, dyes, or modifiers predominate. The issue of recycling polymer products started to be treated more seriously by many packaging manufacturers. An additional stimulus for increasing the share of recycled plastics is the legislative actions of governmental institutions, whose directives more and more often impose the requirement to use recycled plastics. However, the recycling of multi-material packaging is still a serious problem [11–13], where multilayer PET films account for a significant share of the market of this type of material [14,15]. In the case of PET film laminates, the most commonly used additive is the PE layer, which facilitates welding. The modification of this type of material is still a significant technological problem, especially in the context of storage stability, barrier properties and the ability to be welded [16–18]. Another type of additive is EVOH as a barrier layer or metalized layer, usually aluminum-based alloy. Often, additives of this type are used simultaneously.

Today, improved methods of processing multi-material packaging allow for a partial solution to the problem of their recycling, and additionally with the help of newly developed modifiers, which significantly improve the properties of products obtained from recyclates. Reactive extrusion with a chain extender and impact modifier can be used to improve the recycling of multi-material packaging, including PET packaging [19–21]. The concept presented in the work to improve the properties of polymer systems through the simultaneous use of a chain extender and an elastomer phase was already proved to be effective to many types of polyesters like PET [22], PBT [23] or PTT [24]. Initially, reactive additives were in the form of dicumyl peroxide (DCP) [25,26] or aromatic diisocyanate (MDI) [27,28]; however, due to large problems with effectiveness and thermal stability of these compounds, they are now replaced by epoxy functionalized oligomers [19,29], like the used styrene-acrylonitrile-glycidyl methacrylate copolymer. The dominant mechanism underlying the effectiveness of the extrusion technique using chain extenders is the grafting reaction of polymer chains through the formation of bonds with the functional groups of copolymers and sections of macromolecules of the modified polymer. Our previous work was aimed at determining the effectiveness of commercial-based compounds dedicated for PET resin recycling [9]; however, the results partly confirmed that besides the content of the used reactive compound, there are several other factors that influence the process efficiency, including temperature, time of the process, and material pretreatment.

Due to the experience of previous works, an additional modification using an elastomer phase was used for the presented works. This strategy, called rubber toughening, is used for many technical materials. In recent years, dedicated impact modifiers have been increasingly used [30,31], which is a significant improvement in comparison to the originally used materials, such as natural rubber, or its synthetic varieties, such as EPDM [32,33] or SEBS [34,35]. For our study, we decided to use the POE-g-GMA copolymer, where the presence of glycidyl methacrylate groups is additionally affecting the compatibilization of the elastomeric phase.

In this work, the task is focused on the technical aspect of the usage of multilayer recyclates blended with reactive chain extenders and impact modifiers, using recycled polymer blends in the reactive extrusion process in order to achieve better chemical and rheological properties. The recipe used allows for the implementation of various applications based on recycled material. It is possible to increase the amount of recyclates while maintaining the mechanical properties of the product.

2. Experimental Section

2.1. Materials

One type of PET recyclate was used in this research. They were rPET—PET flakes (bottle grade flakes) with MFI 85 g/10 min, density of 1.268 g/cm³, and intrinsic viscosity IV 0.604 dL/g. In addition, three types of PET flakes from the original multilayer films

were used: Foil 1 (PET/PE)—APET/PE flakes. The origin APET/PE (APET and LLDPE) film is produced by thermolamination process and Foil 2 (PET/EVOH/PE)—APET/PE flakes. The origin APET/PE (APET and LLDPE/EVOH/LLDPE) film is produced by the thermolamination process and Foil 3 (PET/MET)—APET MET flakes made from the origin APET metallized film. It is worth noting that the thickness of the single PE layer was 50 μm , which means that, depending on the material type, the formulation of the final material was different. For PET/PE flakes, the PE content was 10%. The PET/EVOH/PE foil consists of 20% PE and 2% EVOH. The thickness of the aluminum layer in PET metallized material (PET/MET) was around 10 nm, which translates into negligible weight content.

All of the processed materials, including bottle grade flakes and multilayer film waste, were supplied by Eurocast company (Strzebielino, Poland), and the material is post-production waste generated during the start-up of technological lines. Due to business confidentiality, information on the exact composition of individual materials has not been published. The appearance of the main blends ingredients are presented in Figure 1. It is worth noting that the PET/MET foil was characterized by intensive gold color, which is the result of yellow dye addition.

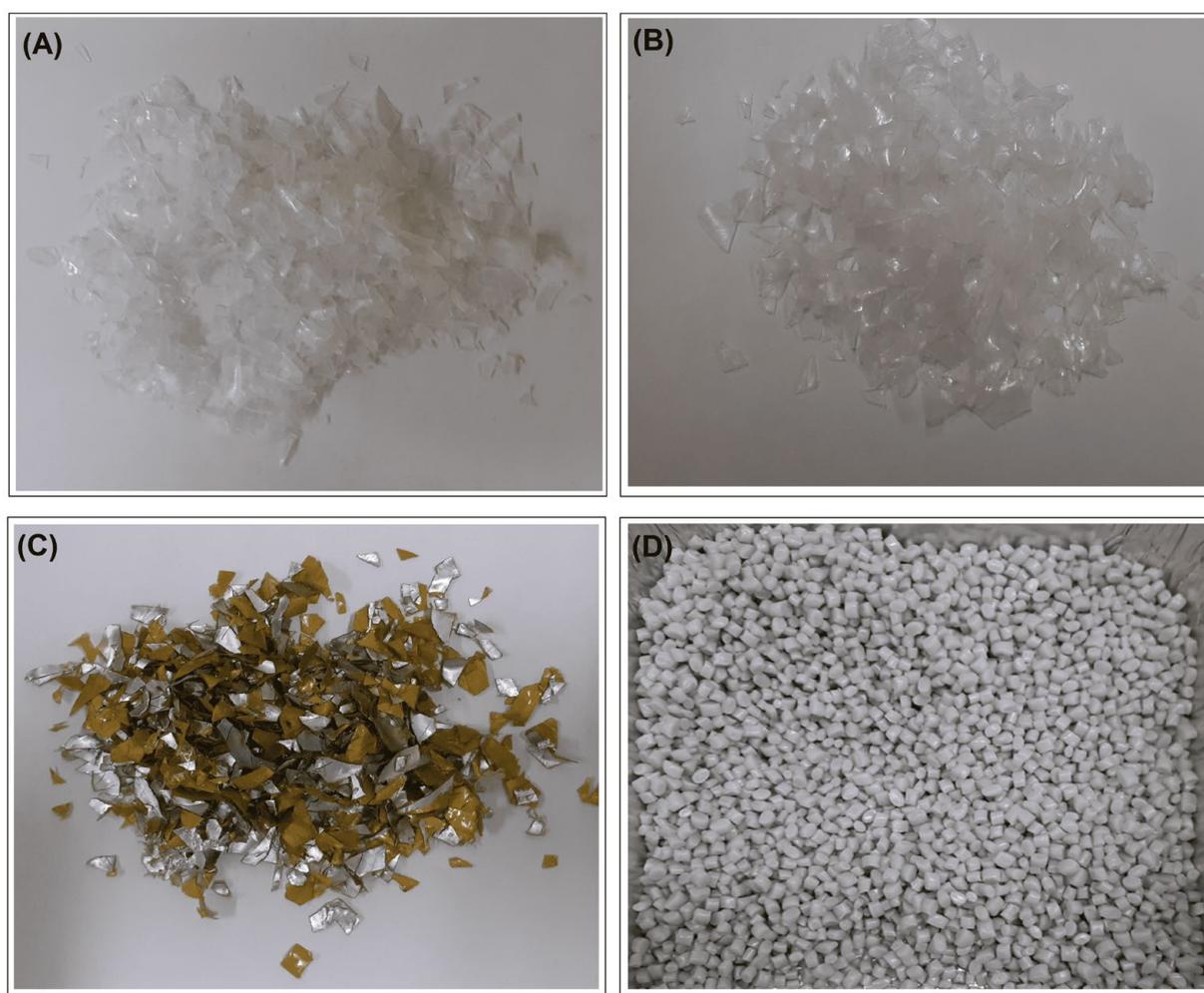


Figure 1. The appearance of the raw materials used for the blend preparation: (A) PET/PE flakes; (B) PET/EVOH/PE flakes; (C) PET/MET flakes; (D) rPET pellets.

As modifiers, two types of materials were used: chain extender (CE)—epoxy-based reactive compound consisting of styrene-acrylonitrile-glycidyl methacrylate ternary random copolymer, SAG-008 supplied by Fine-Blend Company and impact modifier (IM)—polyolefin-based elastomer grafted with glycidyl methacrylate groups (POE-g-GMA), the IM was supplied in the form of transparent pellets, and the used type was SOG-03, also from Fine-Blend company.

2.2. Sample Preparation

Material processing starts with the preparation of the foil samples. Recycled foil was supplied in the form of milled flakes. In order to obtain uniform properties, the flakes were melt-blended using a twin-screw extruder, model Zamak EH16.2D (Zamak Mercator, Skawina, Poland). For unmodified samples, the flakes were dosed directly into the machine hopper and extruded, while for the modified materials, flakes were mixed with rPET, CE, and IM granules. Before each processing stage, all pellets and flakes, were dried for a minimum of 4 h at 80 °C.

For this purpose, the extruder barrel was heated to 280 °C, and the pre-milled foil material was fed to the machine hopper. After melting and mixing, the material was cooled and pelletized. The prepared pellets were used as the input material for the preparation of the modified blends. The second stage of the extrusion process was conducted using the same twin-screw extruder; however, this time, all materials were in the pelletized form. All 9 types of blends were prepared at the same conditions, where barrel temperature was as follows: 255-255-280-280-280-280-270-270-260 °C. The screw speed was set to 120 rpm. We use the same belt conveyor for extrudate cooling and knife pelletized for granulate preparation. The prepared pellets were then used for the preparation of injection molded and extruder foil samples.

The injection molding process was conducted using the Engel Victory 50 hydraulic machine. The machine was equipped with a 25 mm screw and 500 kN molding press. The screw temperature was set to 265 °C; the mold temperature was 20 °C. The injection pressure was set to 1100 bar, while the holding pressure was 650 bar. The holding time was 10 s, and the cooling time was 30 s. During processing, the material was shaped into the form of dumbbell samples (1A—ISO 527 standard) [36] and sample bars (10 × 10 × 80 mm).

The foil samples were prepared using a single screw extruder, model Metalchem W25-30D (IMPiB, Torun, Poland). The machine was equipped with a flat die and chill-roll system. The extruder barrel was heated to 275 °C while the die temperature was set to 280 °C. During processing, the crew speed was set to 80 rpm for all materials. All foil samples were extruded at single draw speeds of 5 m/min. Chill-roll temperature was set to 60 °C. The full list of samples with formulations are listed in Table 1.

Table 1. List of samples together with formulation content.

Sample	rPET	Foil 1 (PET/PE)	Foil 2 (PET/EVOH/PE)	Foil 3 (PET/MET)	Chain Extender (CE)	Impact Modifier (IM)
rPET	100	-	-	-	-	-
PET/PE	70	30	-	-	-	-
PET/EVOH/PE	70	-	30	-	-	-
PET/MET	70	-	-	30	-	-
PET/PE(CE)	69	30	-	-	1.0	-
PET/EVOH/PE(CE)	69	-	30	-	1.0	-
PET/MET(CE)	69	-	-	30	1.0	-
PET/PE(CE-IM)	55	24	-	-	1.0	20
PET/EVOH/PE(CE-IM)	55	-	24	-	1.0	20
PET/MET(CE-IM)	55	-	-	24	1.0	20

2.3. Characterization Methods

Mechanical tests of injection molded and foil samples

For the mechanical properties evaluation, we use tensile testing for both molded samples and cast-extruded foils. Due to the different methodology of testing, we use separate procedures. The injection molded samples were measured using Zwick/Roell Machine model Z010 (Zwick/Roell GmbH, Ulm, Germany). Tests were performed at the cross-head speed of 10 mm/min. The foil samples were measured using Instron 2519-101 machine, equipped with a 2000 N load cell. Tests were conducted using 15 mm width samples, cross-head speed was set to 500 mm/min. All measurements were conducted according to ISO 527 standard [36].

Additional impact resistance measurements were performed using Zwick/Roell HIT 15 machine equipped with 5 J hammer. The tests were carried out using notched samples and Charpy method fixture (ISO 179 standard) [37].

The results of the mechanical tests, for both molded samples and foil specimens, were obtained from at least 5 repetitions.

Haze, transmission, and transparency testing of the foils

The optical properties of the foils were tested using the Haze-Gard Plus apparatus Model 4725.

Thermal analysis

Differential scanning calorimetry measurements (DSC) were performed using the standard heating/cooling/heating procedure. Tests were carried out from 20 to 300 °C at the heating/cooling rate of 10 °C/min. During the measurements, samples (≈ 5 mg) were placed inside the aluminum crucible; the oven chamber was purged with nitrogen (N_2 flow = 20 mL/min), and we used the pierced lid. Samples were cut from the injection-molded specimens. The used apparatus was DSC F1 Phoenix from Netzsch company (Selb, Germany).

Color changes

The determination of L^*a^*b chromatic parameters, according to the International Commission on Illumination (CIE), was used to evaluate the visible changes in the color of the prepared samples. The measurements were conducted using a portable spectrophotometer—NR145 Precision Colorimeter 3nh (Shenzhen, China) equipped with standard light illuminant D65 and aperture $\Phi 8$.

Structure analysis

The fractured surface of the Charpy impact sample was used for microscopic observations. Scanning electron microscope (SEM) type MIRA3 (Tescan, Brno, Czech Republic) was used for this purpose. Prior to scanning, the sample was coated with a thin layer of carbon (≈ 20 nm) using Jeol JEE 4B vacuum evaporator.

3. Results and Discussion

3.1. Mechanical Properties of Injection Molded and Foil Extruded Materials

The table below presents the results of the mechanical properties obtained for injection-molded samples. The tensile modulus, tensile strength and elongation at break were calculated during the static tensile measurements, while the impact strength values were obtained from the Charpy tests. Additionally, the load/strain curves recorded during the tensile test are presented in the Figure 2.

All the most important characteristics are presented in the form of mean value and standard deviation in Table 2. For clarity, all values are also presented in the form of plots (see Figure 3).

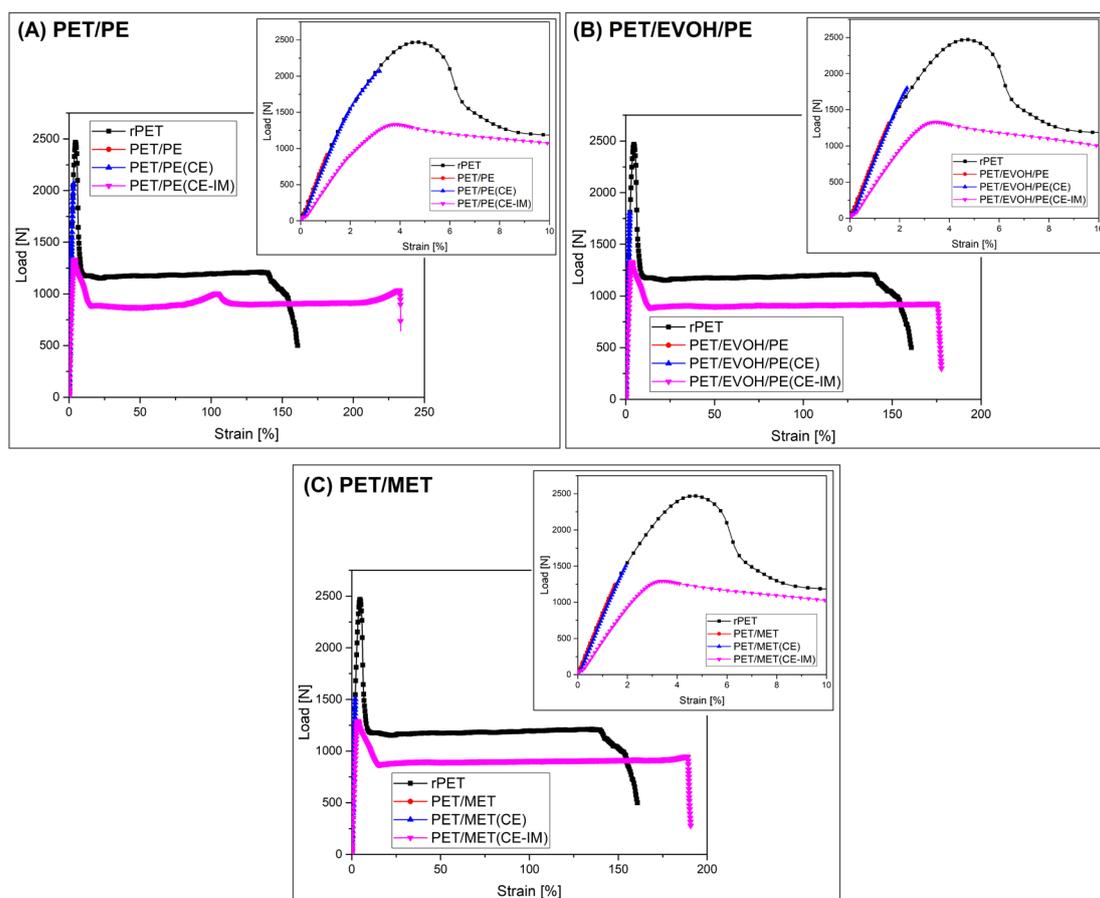


Figure 2. The results of the tensile test for molded samples: (A) PET/PE blends; (B) PET/EVOH/PE blends; (C) PET/MET samples.

Table 2. Mechanical properties recorded for the injection-molded samples.

Sample	Tensile Test						Charpy Test	
	Tensile Modulus [MPa]		Tensile Strength [Mpa]		Elongation at Break [%]		Impact Strength (Notched) [kJ/m ²]	
	Mean Value	SD *	Mean Value	SD *	Mean Value	SD *	Mean Value	SD *
rPET	2640	15.6	61.9	0.174	130	37	3.09	0.45
PET/PE	1780	172	25.6	3.6	1	0.11	1.27	0.37
PET/EVOH/PE	2230	101	30.9	2.12	1.2	0.09	1.28	0.97
PET/MET	2680	67.7	30.6	3.3	1.2	0.13	1.17	0.1
PET/PE(CE)	1400	18	48.3	3.58	2.2	0.3	2.04	0.4
PET/EVOH/PE(CE)	1370	23.7	44.1	2.93	2	0.34	1.3	0.11
PET/MET(CE)	1460	23.6	38.2	3.6	1.7	0.24	1.37	0.07
PET/PE(CE-IM)	1370	18.8	33.2	0.15	200	35	36.23	10.52
PET/EVOH/PE(CE-IM)	1360	57	33.3	0.129	170	56	18.33	1.72
PET/MET(CE-IM)	1420	28.1	32.2	0.193	150	25	15.35	1.17

* SD (standard deviation).

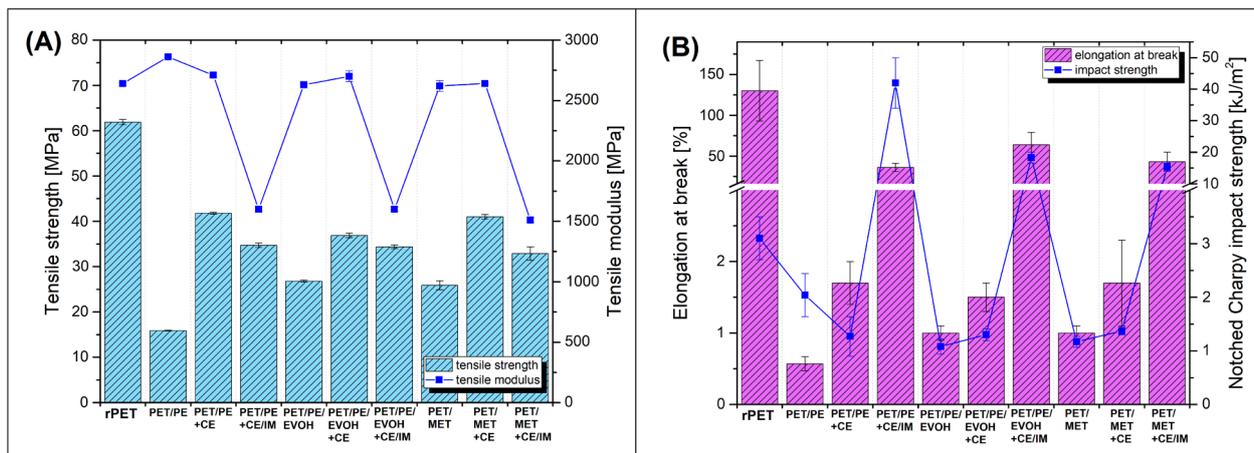


Figure 3. Mechanical properties recorded for the injection-molded samples: (A) tensile strength/modulus; (B) elongation at break/impact strength.

Based on the results presented in the table above, a significant effect of the CE and CE-IM additives on the mechanical properties of the samples obtained in the injection molding process can be observed. An increase in the tensile strength of samples with the addition of a chain extender was observed: from 25.6 MPa for PET/PE to 48.3 MPa for PET/PE (CE); from 30.9 MPa for PET/EVOH/PE to 44.1 MPa for PET/EVOH/PE (CE) and from 30.6 MPa for PET/MET up to 38.2 MPa for PET/MET (CE). After introducing the impact modifier, the tensile strength of the tested samples slightly decreased compared to materials with only the addition of a chain extender. The values were, respectively, 33.2 MPa for PET/PE (CE-IM); 33.3 MPa for PET/EVOH/PE (CE-IM), and 32.2 for PET/MET (CE-IM). Similarly, with the addition of a chain extender, the elongation at break increases from 1% to 2.2% for PET/PE (CE); from 1.2% to 2% for PET/EVOH/PE (CE); and from 1.2% to 1.7% for PET/MET (CE). After the addition of an impact modifier to the analyzed materials, a rapid increase in elongation is observed, corresponding to the following values: 200% PET/PE (CE-IM); 170% PET/EVOH/PE (CE-IM); and 150% PET/MET (CE-IM). So there is an increase over the starting materials of 20%, respectively, 17% and 15%.

When analyzing the results of the static tensile test, a significantly higher increase in the tensile strength value for samples with the addition of the CE chain extender can be observed in relation to the samples with the chain extender and CE-IM impact modifier, with the highest increase observed for PET/PE(CE) samples. An increase in tensile stress is quite a typical phenomenon for materials subjected to the reactive extrusion process, where the improved molecular weight results in more ductile behavior of the tested material, which consequently also improves the results of the strength factor. The obtained reduction of strength for materials with the addition of IM elastomer cannot be considered as a negative phenomenon since the content of the used elastomeric compound was relatively high (20 wt%). The decrease in the tensile strength value is not as pronounced for modified samples as the reduction in the tensile modulus value.

With the increase in elongation at break in each case, the most favorable are the samples with the addition of the impact modifier. The increase in the elongation value for CE-IM samples is definitely above 10 kJ. However, analyzing the results of the notched Charpy impact strength tests, the addition of the chain extender causes a slight increase in impact strength from 1.27 to 2.04 kJ/m² (PET/PE); 1.28–1.3 kJ/m² (PET/EVOH/PE); and 1.17–1.37 kJ/m² (PET/MET); however, after adding the impact modifier, the impact strength of the samples after modification increased to 36.23 kJ/m²; 18.33 kJ/m²; and 15.35 kJ/m² (sequence of materials as above). This is an increase of 28.5; 14.3; and 13.1 times, respectively.

Summarizing, the results of the above mechanical tests for injected materials, the values of elongation at break, and Charpy impact strength are higher for the CE-IM

modified samples compared to rPET. When the chain extender (CE) was used alone, the values for recycled rPET were not achieved. The results of the presented research do not differ from the results of the work carried out so far, including PET-based blends [21,38,39]. Apart from the impact modifiers used in other works, which are sometimes compounds based on styrene or acrylic copolymers [40,41], the convergence with the results obtained for the POE-g-GMA copolymer is still very high.

The Table 3 presents the results of mechanical properties obtained for extruded foil samples. As previously, the results are also presented in the form of plots (see Figure 4).

Table 3. Mechanical properties recorded for foil samples.

Sample	Tensile Strength [MPa]		Elongation at Break [%]	
	Mean Value	SD *	Mean Value	SD *
rPET	49	4.2	632	131
PET/PE	57	1.7	2	0.6
PET/EVOH/PE	32	2.8	4	1
PET/MET	22	0.6	76	21
PET/PE(CE)	37	1.4	3.3	0.8
PET/EVOH/PE(CE)	24.7	2.1	4.3	1.4
PET/MET(CE)	21	2.2	162	37
PET/PE(CE-IM)	43.2	4.2	5.6	0.7
PET/EVOH/PE(CE-IM)	40	2.3	4.6	0.9
PET/MET(CE-IM)	22	1.5	116	24

*SD (standard deviation).

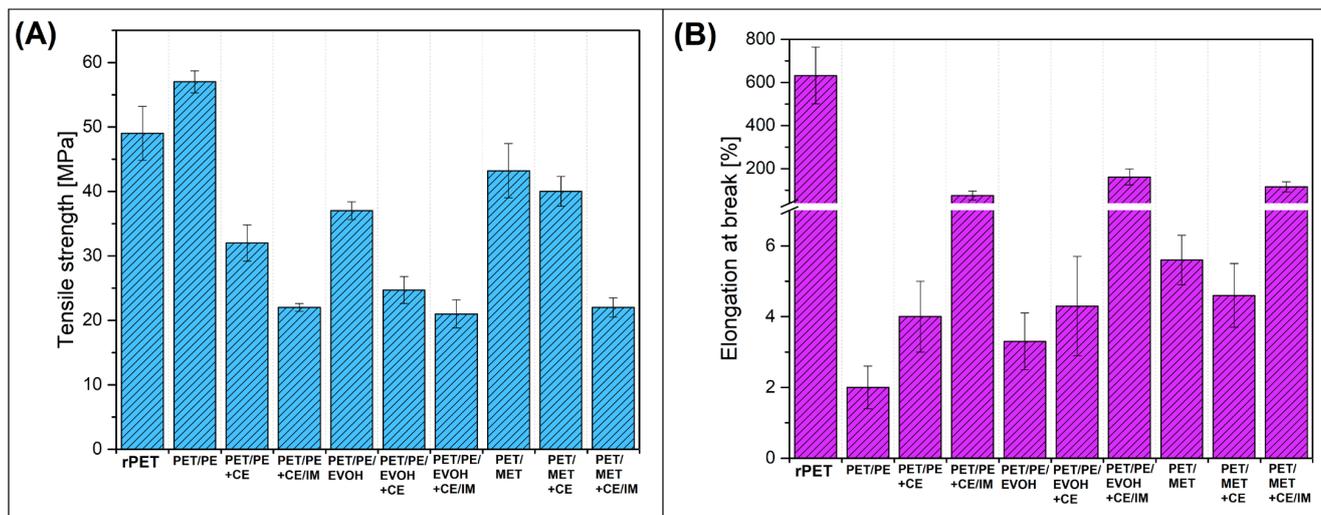


Figure 4. Mechanical properties recorded for foil samples: (A) tensile strength; (B) elongation at break.

As we can see, in the case of metallized films, the increase in elongation is more than twofold. After the addition of an impact modifier to the analyzed foils, a small increase in elongation is observed for PET/PE (CE-IM) from 4.3% to 5.6% and for PET/EVOH/PE(CE-IM) from 4% to 4.3% and a small decrease for PET/MET (CE-IM) from 162% to 116%.

The last result is surprising, as one would expect a further increase in elongation of the film with the addition of the impact modifier. This may be due to the fact that the addition of a chain extender to PET/MET films, which clearly improved the elongation of these films, exhausted all possible active bonds, and the further introduction of an impact modifier not only did not improve the elongation, but on the contrary acted as a retarder of the chain extender.

Summarizing the test results for extruded films, it is clear that the effect of adding modifiers in the form of a chain extender and an impact modifier has a different impact on improving the properties of extruded films. This may be due to the fact that in the laboratory single-screw extruder, the mixing of ingredients is not as good as in the case of laboratory tests using a twin-screw extruder and an injection molding machine in the process. In none of the analyzed cases, the obtained values of tensile strength and elongation at break did not reach the values for rPET foil.

3.2. Thermal Properties by Differential Scanning Calorimetry (DSC) Measurements

The differential scanning calorimetry tests were performed in order to calculate the basic thermal properties of the prepared materials. The most important characteristics like melting temperature (T_m), enthalpy (H_m), or crystallinity are collected in Table 4. The following figures present a comparison of the appearance of the DSC signals for unmodified (see Figure 5) and modified blends (see Figure 6).

Table 4. The thermal properties of the prepared materials obtained from the DSC measurements.

Sample	T_m Peak [°C]	T_{cc} Peak [°C]	T_c [°C]	H_{cc} [J/g]	H_m [J/g]	X_c [%]
rPET	253.6	130.0	194.1	22.6	42.2	14.0
PET/PE	254.9	122.6	203.8	30.2	51.5	15.2
PET/EVOH/PE	257.5	123.6	203.6	28.7	49.7	15.0
PET/MET	254.9	123.2	203.6	25.2	48.2	16.4
PET/PE(CE)	254.4	122.7	202.1	24.3	45.3	15.0
PET/EVOH/PE(CE)	254.6	121.6	202.6	26.5	48.2	15.5
PET/MET(CE)	254.0	123.1	202.0	23.9	45.4	14.3
PET/PE(CE-IM)	253.9	124.1	196.3	20.0	36.2	14.5
PET/EVOH/PE(CE-IM)	251.4	123.3	195.8	19.9	33.9	12.5
PET/MET(CE-IM)	252.8	123.7	194.7	18.4	34.8	14.6

The analysis of the table values shows only a small deviation of the crystallinity level, where the reference value for rPET of 14% was only slightly changed for most of the samples. The observed deviation of 2% cannot be treated as a significant shift, rather than the DSC method inaccuracy. Some visible trends are more pronounced when comparing the thermograms to the presented figures.

For all samples with the addition of foil waste, the cold crystallization peak (T_{cc}) was shifted to a lower temperature from the reference 130 °C for pure rPET resin. For example T_{cc} for the PET/PE material was 122.6, while for the rest of the specimens, the values ranged from 121 to 125 °C. That small change suggests a small nucleation effect that can be partly caused by a lower molecular weight of the recycled foil waste and/or the influence of the impurities for the waste-based blends.

Interestingly, for none of the prepared blends, the presence of polyethylene (PE) phase was not detected on the DSC plots. That kind of behavior can be explained by relatively small content of the PE, where for PET/PE, the content reached 3% and for PET/EVOH/PE, 6%. However, considering the higher melting enthalpy for the crystalline phase, the DSC signal should indicate the presence of the PE. A certain explanation may be the behavior of PE structures at high temperatures in PET processing, where in the case of such a small content of the PE phase it is possible to obtain a greater degree of gelation of the polymer structure and, consequently, the inability to form crystalline structures during the cooling stage.

The melting point for the analyzed materials was slightly above 250 °C, and its highest value was recorded for the PET/EVOH/PE material. The influence of sample structure modifications on this endothermic process is observed. CE-IM materials are characterized by the lowest melting temperatures in their respective groups. Compared to PET/PE, PET/EVOH, and PET/MET, rPET has the lowest T_m , which is 253.6 °C. The heat of fusion for rPET is 42.2 J/g, and it is the lowest value obtained for the tested, unmodified

materials. The value of this parameter decreases successively for the following samples: PET/PE, PET/EVOH/PE, PET/MET, and rPET. On the DSC thermograms, we can see the small additional melting peak at around 235 °C, which is the result of the appearance of secondary crystal structures with lower lamellae thickness. As reported by other studies, the chain extender addition induces the appearance of a double peak. Due to the increase in molecular weight, the formation of crystal structures is limited, hence the formation of not fully developed subsidiary crystals [21,38].

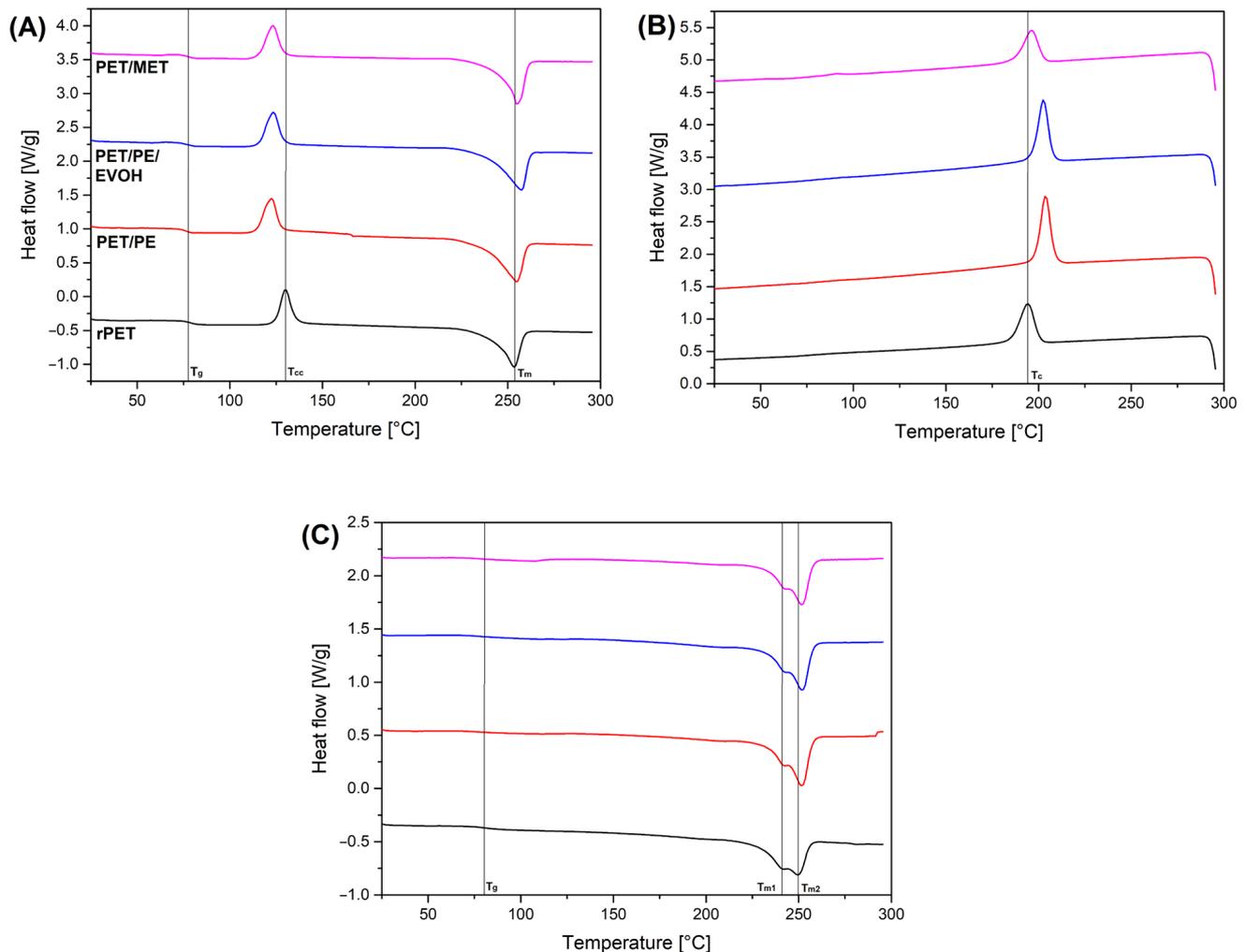


Figure 5. The DSC plots for reference rPET samples and unmodified blends with the addition of foil waste. (A) First heating, (B) cooling, (C) second heating stage of the measurements.

The rPET crystallization takes place at the lowest temperature among the tested samples. Also for this parameter, the influence of structure modification on the obtained results is observed. CE-IM materials, on the other hand, are characterized by the smallest T_c , which is still higher than for rPET. The cold crystallization temperature for rPET is slightly higher compared to the analyzed materials. Within each group of samples: PET/PE, PET/EVOH/PE, and PET/MET, similar values of this parameter were recorded. Based on the obtained results, it can be concluded that the amount of heat necessary for cold crystallization decreases with the modification of materials, while the improvement of mechanical properties affects this parameter more strongly than the branching of polymer chains. This trend is observed for each group of samples tested. The heat of cold crystallization for rPET is 22.6 J/g, and it is the lowest amount of energy among unmodified materials that is released during this exothermic process. The obtained contents of the crystalline phase range

from 12.5 to 16.4%. This range is typical for fast-cooled PET resin, which was confirmed by other studies [42–44]. The lowest X_c value was recorded for PET/EVOH/PE(CE-IM), and the highest for PET/MET. Among the unmodified, analyzed materials, comparable amounts of the crystalline phase were obtained for PET/PE and PET/EVOH/PE, while chain branching and improvement of mechanical properties significantly reduced the X_c value for the second of the discussed materials.

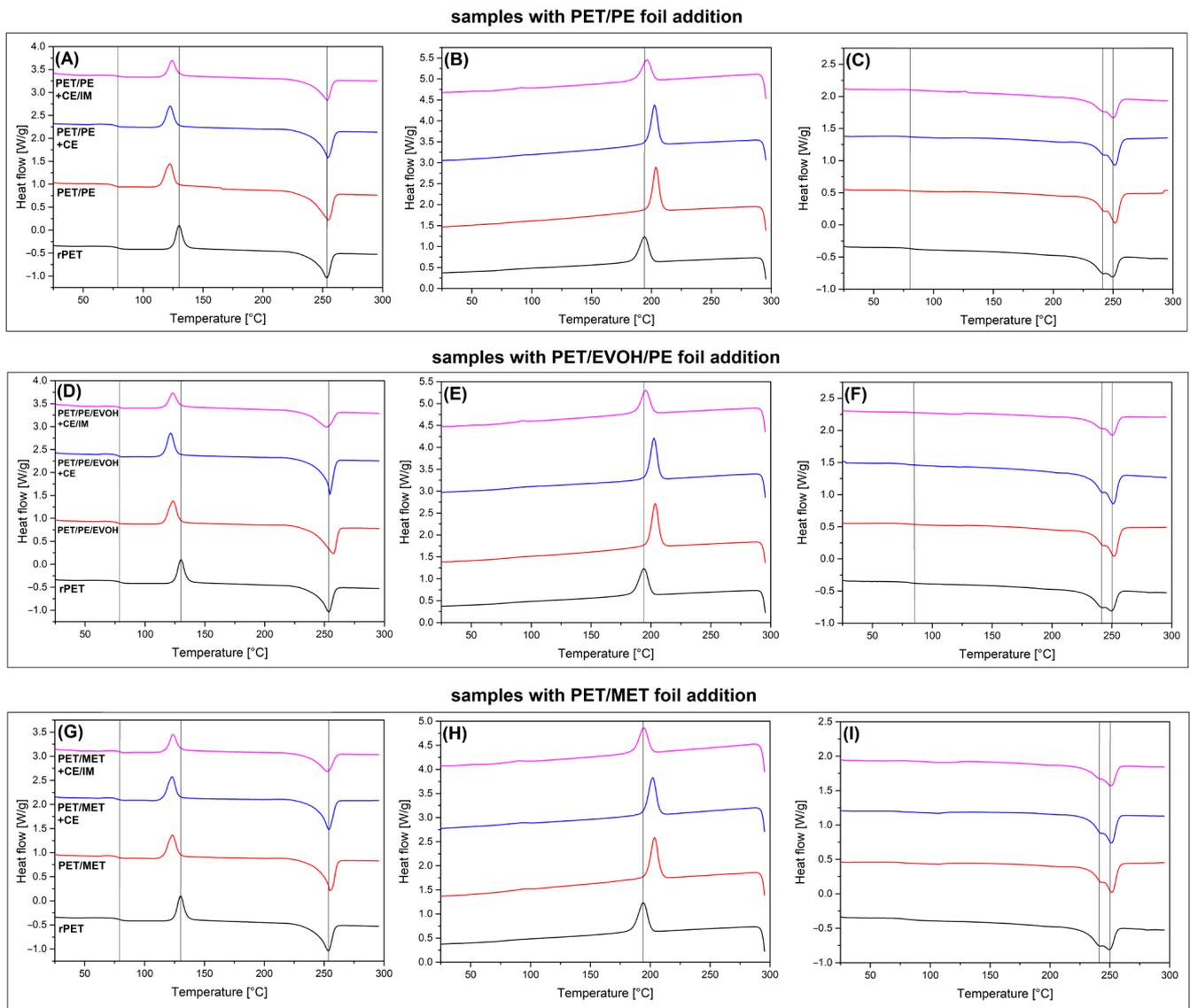


Figure 6. The compilation of the DSC plots for prepared blends. Charts present the 1st heating, cooling, and 2nd heating plot comparison. (A–C) PET/PE, (D–F) PET/EVOH/PE, (G–I) PET/MET samples.

3.3. Color and Sample Appearance

Table 5 presents the results of the color change measurements expressed by CIE $L^*a^*b^*$ coordinates. According to the previously described procedure, we also calculate the total color difference parameter ΔE [45,46]:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (1)$$

Table 5. The results of the color change measurements expressed by CIE L*a*b* coordinates for injection molded samples.

Sample	L (lightness)	a (−green/+red)	b (−blue/+yellow)	ΔE
rPET	60.13	−1.28	4.77	No change
PET/PE	38.50	3.41	13.45	4.11
PET/EVOH/PE	48.71	−0.99	5.14	0.30
PET/MET	43.83	−2.48	29.43	5.26
PET/PE(CE)	43.03	1.86	6.43	3.69
PET/EVOH/PE(CE)	49.19	−0.43	5.29	0.70
PET/MET(CE)	44.83	−3.38	28.91	5.33
PET/PE(CE-IM)	72.95	−2.57	−1.84	1.73
PET/EVOH/PE(CE-IM)	77.50	−2.98	−2.17	1.99
PET/MET(CE-IM)	67.74	−4.44	21.16	4.23

As can be seen from Table 5, the smallest total differences for color changes compared to recycled PET are found in PET/PE(CE) and PET/EVOH/PE(CE) samples ($\Delta E = 0.3$ and 0.7) with the addition of a chain extender followed by PET/MET and PET/MET(CE) samples ($\Delta E = 1.73$ and 1.99 , respectively). However, in the case of samples with the addition of metalized foil, we can clearly see in the photo (Figure 7) that their color has become green (for PET/MET samples), dark green (for PET/MET(CE) samples) and light green for samples with a chain extender and impact modifier (PET/MET (CE-IM)). The light green color was the consequence of using the addition of yellow colorant to metalized foil. When evaluating the color of the obtained samples by visual analysis, all the samples with the content of the impact modifier seem to be the brightest, which may be due to the high b^* value (meaning yellowness of the samples). As a result, the PET/EVOH/PE (CE-IM) sample appears to have the most favorable light color, followed by the PET/PE (CE-IM) sample and finally the rPET sample. Analyzing the measurements of lightness of samples made with a spectrophotometer, the lightness samples turned out to be PET/PE ($L^* = 38.5$) and PET/EVOH/PE ($L^* = 43$), followed by PET/PE (CE-IM) samples ($L^* = 44$) and PET/EVOH/PE (CE-IM) ($L^* = 45$). The darkest samples, however, are all samples with only the addition of a chain extender. Summing up the analysis of color changes of the produced samples, it should be stated that they are significant, but they do not eliminate the possibility of using the prepared blends for the production of foil with a 30% content of PET multilayer foil wastes. The most favorable and pure color is characterized by samples made of blends containing both a chain extender and an impact modifier. An interesting result also seems to be obtaining a bright green color for samples prepared with 30% addition of APET waste metalized film, chain extender, and impact modifier. All the resulting shades of green are a consequence of using a yellow dye in the PET/MET foil. In the case of the manufactured foil, the aim of this treatment was to give a gilding effect, which is achieved by reflecting light from the metalized layer. For the reprocessed materials, the yellow color changes to green. Such a change may be the result of limited thermal durability of the used dye.

As can be seen from the comparison of the delta E parameter in Table 6, the samples made of PET/MET foil differ the most in color, and for the rest of the samples there is basically no visible difference. This calculation effect is also confirmed by photos of all foils taken against the background of the logo of the Poznan University of Technology, shown in Figure 8, where the greatest haze of the logo is visible for all PET/MET foil samples, and then for foils made with the addition of an impact modifier (IM).

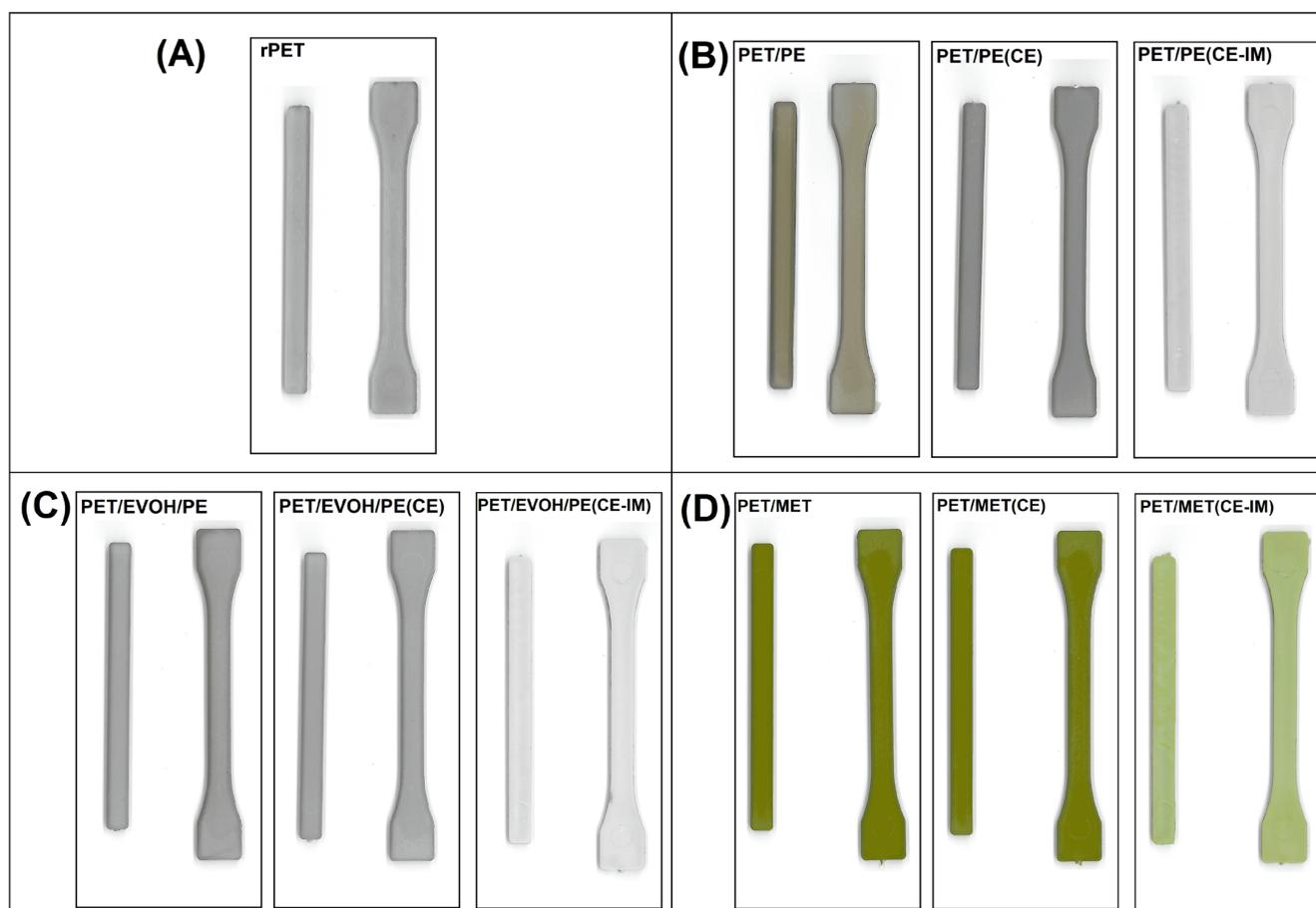


Figure 7. View of all tested types of injection molded samples. (A) reference rPET sample; (B) materials with PET/PE foil addition; (C) blends with PET/EVOH/PE addition; (D) blends with PET/MET addition.

Table 6. The results of the color change measurements expressed by CIE L*a*b* coordinates for foil samples.

Sample	L (lightness)	a (−green/+red)	b (−blue/+yellow)	ΔE
rPET	88.97	1.42	−2.37	No change
PET/PE	89.48	1.30	−2.34	0.08
PET/EVOH/PE	88.89	1.37	−2.17	0.09
PET/MET	84.35	−0.81	17.94	8.71
PET/PE(CE)	89.60	1.30	−2.42	0.09
PET/EVOH/PE(CE)	89.50	1.30	−2.48	0.10
PET/MET(CE)	86.87	0.16	12.78	6.45
PET/PE(CE-IM)	90.38	1.29	−1.59	0.34
PET/EVOH/PE(CE-IM)	90.43	1.34	−1.93	0.19
PET/MET(CE-IM)	85.85	−0.79	18.13	8.79

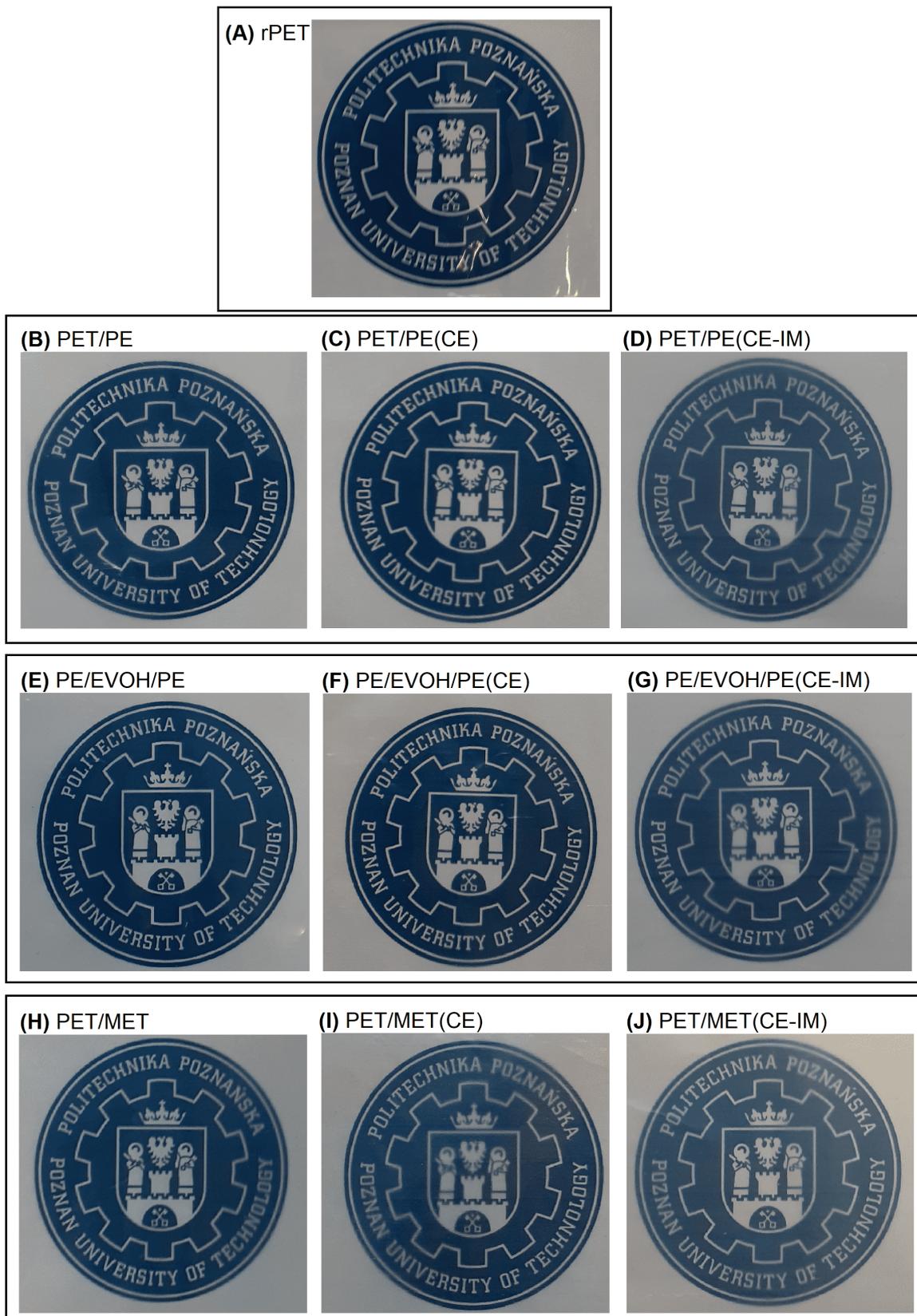


Figure 8. View of all tested types of film samples against the background of the logo of Poznan University of Technology (Politechnika Poznańska).

3.4. Structure of Modified Blends—Scanning Electron Microscopy Observations (SEM)

The structure of the prepared blends was investigated using SEM analysis. We used the fractured surface of the impact sample for this purpose. Images taken at $\times 200$ and $\times 5000$ magnification are collected in Figure 9.

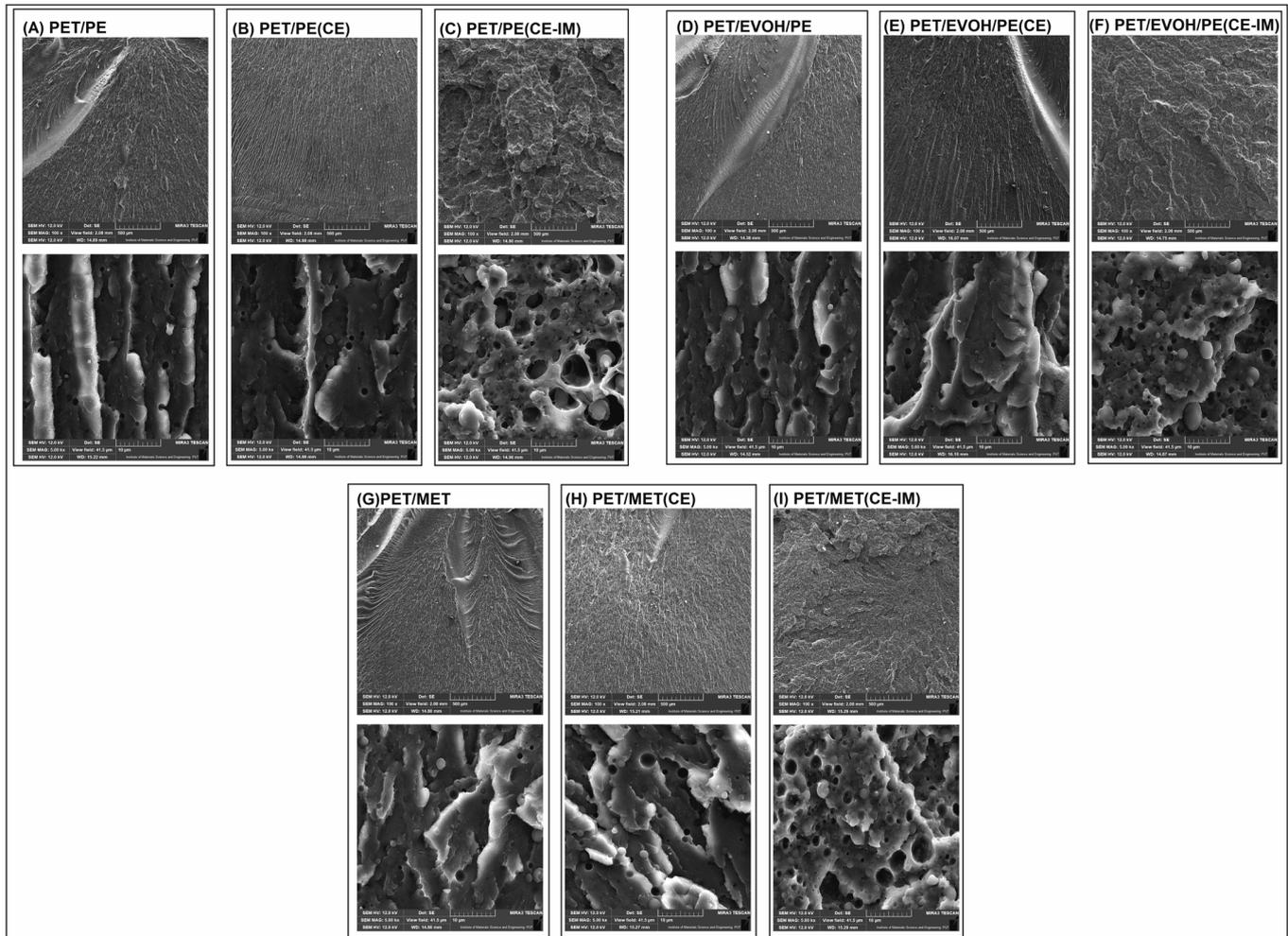


Figure 9. Surface of the fractured injection molded samples. Scanning electron microscopy observations.

As can be seen by comparing the overall comparative projection made at $\times 200$, there is no visible difference between the unmodified blend and chain extender (CE)-modified samples. The surface of the sample was quite smooth regardless of the addition of foil waste. Interestingly, when zoomed in, the structure of the material turns out to be two-phase. A large number of spherical inclusions is revealed, where the diameter of these particles ranges from 1 to 3 μm . The genesis of this type of inclusion is closely related to the presence of a PE layer in foil waste used during work. The PE content in the obtained blend is clearly lower than for the laminated foil, and does not exceed several percent, which is due to the significant addition of rPET in the composition. Of all the analyzed materials, significant structural changes concern primarily materials with the addition of IM. This is mainly due to the use of quite a large amount of POE-g-GMA modifier (20%). However, when observing the sample surfaces, apart from visible elastomer inclusions, the large number of spherical holes suggest an insufficient interface between the elastomeric phase and matrix PET. That kind of behavior suggests that the used compatibilization methodology did not bring the expected results. In the case of this type of materials, the expected behavior would be significant fragmentation of the structure, visible in the form of elastomer inclusions

with sizes not exceeding 1 μm . In the case in question, we are dealing with particles up to 5 μm in size, which indirectly suggests low efficiency of the reactive extrusion process.

4. Conclusions

In this work, the technical aspect of the usage of multilayer recyclates blended with reactive chain extender and impact modifier has been shown. The way of using the recycled polymer blends in the reactive extrusion process in order to achieve better chemical and rheological properties has been described, too. In most cases, the use of a chain extender led to some improvements in mechanical characteristics, but the impact modifier addition strongly improved most of the properties. It was also observed that the reactive extrusion procedure led to melt strength improvement, which greatly facilitates the film production process. Importantly, the observed changes in color and haze of the produced films (except for films made of PET/MET recyclates) are relatively small. The recipe used in the study allows for the implementation of various applications based on recycled material. We can conclude that it is possible to increase the amount of recyclates while maintaining the mechanical properties of the product. The research has also shown that reactive extrusion with chain extender and impact modifier can be used to improve the recycling of multi-material PET packaging. Due to the limited possibility of separating the film components, the developed method of foil recycling might be very useful for the utilization of multilayered packaging. The presented study proves that the utilization of the reactive extrusion method can be an effective method for compatibilization of the multilayered type of PET foil waste. The presented study can be treated as a preliminary study to further work where it is planned to achieve several fundamental goals:

- Production of a functional foil with a minimum content of the multilayer waste foil of 50%;
- Optimization of the material composition in order to limit the content of chain extenders and elastomeric impact modifiers, and utilization of the ANOVA method;
- Upscaling of the developed methodology from the lab to industry scale process.

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References

1. Antonopoulos, I.; Faraca, G.; Tonini, D. Recycling of Post-Consumer Plastic Packaging Waste in the EU: Recovery Rates, Material Flows, and Barriers. *Waste Manag.* **2021**, *126*, 694–705. [[CrossRef](#)] [[PubMed](#)]
2. Franz, R.; Welle, F. Recycling of Post-Consumer Packaging Materials into New Food Packaging Applications—Critical Review of the European Approach and Future Perspectives. *Sustainability* **2022**, *14*, 824. [[CrossRef](#)]
3. Hahladakis, J.N.; Iacovidou, E. An Overview of the Challenges and Trade-Offs in Closing the Loop of Post-Consumer Plastic Waste (PCPW): Focus on Recycling. *J. Hazard. Mater.* **2019**, *380*, 120887. [[CrossRef](#)] [[PubMed](#)]

4. Fei, X.; Wang, J.; Zhu, J.; Wang, X.; Liu, X. Biobased Poly(Ethylene 2,5-Furancoate): No Longer an Alternative, but an Irreplaceable Polyester in the Polymer Industry. *ACS Sustain. Chem. Eng.* **2020**, *8*, 8471–8485. [CrossRef]
5. Lee, T.-H.; Liu, H.; Forrester, M.J.; Shen, L.; Wang, T.; Yu, H.; He, J.-H.; Li, W.; Kraus, G.A.; Cochran, E.W. Next-Generation High-Performance Biobased Naphthalate-Modified PET for Sustainable Food Packaging Applications. *Macromolecules* **2022**, *55*, 7785–7797. [CrossRef]
6. European Parliament. *Plastic Waste and Recycling in the EU: Facts and Figures*; European Parliament: Strasbourg, France, 2018.
7. Luijsterburg, B.; Goossens, H. Assessment of Plastic Packaging Waste: Material Origin, Methods, Properties. *Resour. Conserv. Recycl.* **2014**, *85*, 88–97. [CrossRef]
8. de Jesus Pacheco, D.A.; ten Caten, C.S.; Jung, C.F.; Sassanelli, C.; Terzi, S. Overcoming Barriers towards Sustainable Product-Service Systems in Small and Medium-Sized Enterprises: State of the Art and a Novel Decision Matrix. *J. Clean. Prod.* **2019**, *222*, 903–921. [CrossRef]
9. Szymczak, P.; Dziadowiec, D.; Andrzejewski, J.; Szostak, M. The Efficiency Evaluation of the Reactive Extrusion Process for Polyethylene Terephthalate (PET). Monitoring of the Industrial Foil Manufacturing Process by In-Line Rheological Measurements. *Appl. Sci.* **2023**, *13*, 3434. [CrossRef]
10. Lee, T.; Forrester, M.; Wang, T.; Shen, L.; Liu, H.; Dileep, D.; Kuehl, B.; Li, W.; Kraus, G.; Cochran, E. Dihydroxyterephthalate—A Trojan Horse PET Coint for Facile Chemical Recycling. *Adv. Mater.* **2023**, *35*, 2210154. [CrossRef]
11. de Mello Soares, C.T.; Ek, M.; Östmark, E.; Gällstedt, M.; Karlsson, S. Recycling of Multi-Material Multilayer Plastic Packaging: Current Trends and Future Scenarios. *Resour. Conserv. Recycl.* **2022**, *176*, 105905. [CrossRef]
12. Sergi, C.; Tirillò, J.; Valente, T.; Sarasini, F. Effect of Basalt Fibres on Thermal and Mechanical Properties of Recycled Multi-Material Packaging. *J. Compos. Sci.* **2022**, *6*, 72. [CrossRef]
13. Bauer, A.-S.; Tacker, M.; Uysal-Unalan, I.; Cruz, R.M.S.; Varzakas, T.; Krauter, V. Recyclability and Redesign Challenges in Multilayer Flexible Food Packaging—A Review. *Foods* **2021**, *10*, 2702. [CrossRef] [PubMed]
14. Grant, A.; Lahme, V.; Connock, T.; Lugal, L. How Circular Is PET? A Report on the Circularity of PET Bottles, Using Europe as a Case Study. Eunomia/Zero Waste Europa 2022. Available online: <https://zerowasteurope.eu/library/how-circular-is-pet/> (accessed on 2 October 2023).
15. Howard, M.; Yan, X.; Mustafee, N.; Charnley, F.; Böhm, S.; Pascucci, S. Going beyond Waste Reduction: Exploring Tools and Methods for Circular Economy Adoption in Small-Medium Enterprises. *Resour. Conserv. Recycl.* **2022**, *182*, 106345. [CrossRef]
16. Kaiser, K.M.A.; Ginzinger, T. Production of a PET//LDPE Laminate Using a Reversibly Crosslinking Packaging Adhesive and Recycling in a Small-Scale Technical Plant. *Recycling* **2021**, *6*, 47. [CrossRef]
17. Boonthanakorn, J.; Daud, W.; Aontee, A.; Wongs-Aree, C. Quality Preservation of Fresh-Cut Durian Cv. ‘Monthong’ Using Micro-Perforated PET/PE Films. *Food Packag. Shelf Life* **2020**, *23*, 100452. [CrossRef]
18. Dziadowiec, D.; Matykiewicz, D.; Szostak, M.; Andrzejewski, J. Overview of the Cast Polyolefin Film Extrusion Technology for Multi-Layer Packaging Applications. *Materials* **2023**, *16*, 1071. [CrossRef]
19. Makkam, S.; Harnnarongchai, W. Rheological and Mechanical Properties of Recycled PET Modified by Reactive Extrusion. *Energy Procedia* **2014**, *56*, 547–553. [CrossRef]
20. Asensio, M.; Nuñez, K.; Guerrero, J.; Herrero, M.; Merino, J.C.; Pastor, J.M. Rheological Modification of Recycled Poly(Ethylene Terephthalate): Blending and Reactive Extrusion. *Polym. Degrad. Stab.* **2020**, *179*, 109258. [CrossRef]
21. Kiliaris, P.; Papispyrides, C.D.; Pfaendner, R. Reactive-Extrusion Route for the Closed-Loop Recycling of Poly(Ethylene Terephthalate). *J. Appl. Polym. Sci.* **2007**, *104*, 1671–1678. [CrossRef]
22. Zander, N.E.; Boelter, Z.R. Rubber Toughened Recycled Polyethylene Terephthalate for Material Extrusion Additive Manufacturing. *Polym. Int.* **2021**, *70*, 742–748. [CrossRef]
23. Hert, M. Tough Thermoplastic Polyesters by Reactive Extrusion with Epoxy-containing Copolymers. *Die Angew. Makromol. Chemie* **1992**, *196*, 89–99. [CrossRef]
24. Snowdon, M.R.; Mohanty, A.K.; Misra, M. Effect of Compatibilization on Biobased Rubber-Toughened Poly(Trimethylene Terephthalate): Miscibility, Morphology, and Mechanical Properties. *ACS Omega* **2018**, *3*, 7300–7309. [CrossRef] [PubMed]
25. Przybysz-Romatowska, M.; Haponiuk, J.; Formela, K. Reactive Extrusion of Biodegradable Aliphatic Polyesters in the Presence of Free-Radical-Initiators: A Review. *Polym. Degrad. Stab.* **2020**, *182*, 109383. [CrossRef]
26. Ebadi, H.; Yousefi, A.A.; Oromiehie, A. Reactive Extrusion and Barrier Properties of PP/PET Films. *Iran. Polym. J. (Engl. Ed.)* **2007**, *16*, 659–669.
27. Tang, X.; Guo, W.; Yin, G.; Li, B.; Wu, C. Reactive Extrusion of Recycled Poly(Ethylene Terephthalate) with Polycarbonate by Addition of Chain Extender. *J. Appl. Polym. Sci.* **2007**, *104*, 2602–2607. [CrossRef]
28. Jang, J.; Shin, H.; Seo, J. In-Situ Chain Extension of Polyethylene Terephthalate Flakes Using Reactive Extrusion as an Upcycling Approach. *Chem. Eng. Sci.* **2023**, *282*, 119289. [CrossRef]
29. Candal, M.V.; Safari, M.; Fernández, M.; Otaegi, I.; Múgica, A.; Zubitur, M.; Gericca-Echevarria, G.; Sebastián, V.; Irusta, S.; Loaeza, D.; et al. Structure and Properties of Reactively Extruded Opaque Post-Consumer Recycled PET. *Polymers* **2021**, *13*, 3531. [CrossRef]
30. Nagarajan, V.; Zhang, K.; Misra, M.; Mohanty, A.K. Overcoming the Fundamental Challenges in Improving the Impact Strength and Crystallinity of PLA Biocomposites: Influence of Nucleating Agent and Mold Temperature. *ACS Appl. Mater. Interfaces* **2015**, *7*, 11203–11214. [CrossRef]

31. Mohanty, A.K.; Misra, M.; Behazin, E.; Rodriguez-Uribe, A. Toughened Polyolefin and Biocarbon Based Light-Weight Biocomposites and Method of Making the Same. US 2018/0066087 A1, 8 March 2018.
32. Bartczak, Z.; Argon, A.S.; Cohen, R.E.; Weinberg, M. Toughness Mechanism in Semi-Crystalline Polymer Blends: I. High-Density Polyethylene Toughened with Rubbers. *Polymer* **1999**, *40*, 2331–2346. [[CrossRef](#)]
33. Pesetski, S.S.; Filimonov, O.V.; Koval, V.N.; Golubovich, V.V. Structural Features and Relaxation Properties of PET/PC Blends Containing Impact Strength Modifier and Chain Extender. *Express Polym. Lett.* **2009**, *3*, 606–614. [[CrossRef](#)]
34. Torrado, A.R.; Shemelya, C.M.; English, J.D.; Lin, Y.; Wicker, R.B.; Roberson, D.A. Characterizing the Effect of Additives to ABS on the Mechanical Property Anisotropy of Specimens Fabricated by Material Extrusion 3D Printing. *Addit. Manuf.* **2015**, *6*, 16–29. [[CrossRef](#)]
35. Li, J.; Wang, X.; Yang, C.; Yang, J.; Wang, Y.; Zhang, J. Toughening Modification of Polycarbonate/Poly(Butylene Terephthalate) Blends Achieved by Simultaneous Addition of Elastomer Particles and Carbon Nanotubes. *Compos. Part A Appl. Sci. Manuf.* **2016**, *90*, 200–210. [[CrossRef](#)]
36. *ISO 527-1*; Determination of Tensile Properties. ISO: Geneva, Switzerland, 2012.
37. *ISO 179-1*; Determination of Charpy Impact Properties. ISO: Geneva, Switzerland, 2010.
38. Montava-Jorda, S.; Lascano, D.; Quiles-Carrillo, L.; Montanes, N.; Boronat, T.; Martinez-Sanz, A.V.; Ferrandiz-Bou, S.; Torres-Giner, S. Mechanical Recycling of Partially Bio-Based and Recycled Polyethylene Terephthalate Blends by Reactive Extrusion with Poly(Styrene-Co-Glycidyl Methacrylate). *Polymers* **2020**, *12*, 174. [[CrossRef](#)] [[PubMed](#)]
39. Dal Lago, E.; Boaretti, C.; Piovesan, F.; Roso, M.; Lorenzetti, A.; Modesti, M. The Effect of Different Compatibilizers on the Properties of a Post-Industrial PC/PET Blend. *Materials* **2018**, *12*, 49. [[CrossRef](#)] [[PubMed](#)]
40. Pracella, M.; Chionna, D.; Pawlak, A.; Galeski, A. Reactive Mixing of PET and PET/PP Blends with Glycidyl Methacrylate-Modified Styrene-*b*-(Ethylene-Co-Olefin) Block Copolymers. *J. Appl. Polym. Sci.* **2005**, *98*, 2201–2211. [[CrossRef](#)]
41. Tahmasebi, F.; Jafari, S.H.; Farnia, S.M.F. SbB-g-GMA Copolymer as a Dual Functional Reactive Compatibilizer and Impact Modifier for Potential Recycling of PET and PS via Melt Blending Approach. *J. Polym. Environ.* **2023**, *31*, 3106–3119. [[CrossRef](#)]
42. Torres, N.; Robin, J.J.; Boutevin, B. Study of Thermal and Mechanical Properties of Virgin and Recycled Poly(Ethylene Terephthalate) before and after Injection Molding. *Eur. Polym. J.* **2000**, *36*, 2075–2080. [[CrossRef](#)]
43. Negoro, T.; Thodsaratpreeyakul, W.; Takada, Y.; Thumsorn, S.; Inoya, H.; Hamada, H. Role of Crystallinity on Moisture Absorption and Mechanical Performance of Recycled PET Compounds. *Energy Procedia* **2016**, *89*, 323–327. [[CrossRef](#)]
44. Elamri, A.; Zdiri, K.; Harzallah, O.; Lammam, A. Progress in Polyethylene Terephthalate Recycling. In *Polyethylene Terephthalate: Uses, Properties and Degradation*; Nova Science Publishers: New York, NY, USA, 2017.
45. Aniśko, J.; Barczewski, M. Uniaxial Rotational Molding of Bio-Based Low-Density Polyethylene Filled with Black Tea Waste. *Materials* **2023**, *16*, 3641. [[CrossRef](#)]
46. Bociaga, E.; Trzaskalska, M. Influence of Polymer Processing Parameters and Coloring Agents on Gloss and Color of Acrylonitrile-Butadiene-Styrene Terpolymer Moldings. *Polimery* **2016**, *61*, 544–550. [[CrossRef](#)]

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