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Effect of Basalt Fibres on Thermal and Mechanical Properties of Recycled Multi-Material Packaging

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Abstract: The low-density polyethylene (LDPE)/aluminium mix obtained after the recovery of cellulose from multilayer aseptic packaging used in the food and beverage industry is generally destined for energy recovery. In this work we propose it as a matrix for value-added composite materials. A commercially available material (EcoAllene) obtained from multilayer packaging recycling was reinforced with short natural basalt fibres up to 30 wt.% by twin screw extrusion, aiming at improving the mechanical profile of such material and widening its applications. Thermal characterizations by thermogravimetric analysis and differential scanning calorimetry showed that the material is indeed a complex mixture of LDPE, HDPE, PP, and aluminium. Basalt fibres did not modify the melting and crystallization profile as well as the global degradation behaviour. Composites were then subjected to tensile, bending, Charpy impact tests and the fracture surfaces were investigated by scanning electron microscopy. Results highlighted a beneficial effect of basalt fibres to stiffness and strength in both loading conditions, with improvements by 107% and 162% for tensile and bending strength, respectively, which were linked also to a 45% enhancement of impact strength. This increased mechanical performance is promising for their use in automotive interiors and outdoor decking applications.

Keywords: polymer matrix composites; multi-material packaging; basalt fibres; mechanical properties; thermal properties; polymers and aluminium (PolyAl); recycling



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1. Introduction

Our world is currently tackling serious environmental challenges requiring actions that cannot be postponed any longer. In this regard, pollution generated by waste materials at the end of their life represents a significant concern. Packaging, in particular, is a part of our daily life, enabling the protection of food and beverages while securing their transport and limiting their wastage. But packaging is also the source of a huge waste generation all over the world. According to the recent statistics provided by Eurostat [1], which collect the developments during the period 2009–2019 on packaging waste for all EU Member States, the total amount of generated packaging materials increased by 20.1% from 2009 to 2019, with an average of 177.4 kg per inhabitant in the European Union (EU). In 2019, paper and cardboard (40.6%), plastic (19.4%), glass (19.2%), wood (15.6%) and metal (5.0%) were the most common types of packaging waste in EU. Not only waste generation increased, but also the recycling and recovery rates over this 10-year period. Nevertheless, these figures are impressive, and pose serious concerns about the environmental sustainability of our current packaging solutions and their disposal at the end of life.

Additional problems can be expected when multilayer polymer-coated paperboards are considered, i.e., beverage cartons, which display complex architectures depending on the specific type of food/beverage to preserve. In very general terms, for instance the well-known Tetra Pak[®] packaging, it shows a 6-layer structure which is made from

75 wt.% paperboard, 20 wt.% LDPE (low density polyethylene) and 5 wt.% thin (~6.5 µm) aluminium foil [2]. Each layer has a specific role: the paperboard endows the package with the required rigidity, LDPE is a sealable layer, acts as a barrier to prevent moisture getting in or out and to keep contents fresh and allows the paperboard to stick to the aluminium foil, while aluminium provides a barrier against oxygen and light. As reported by the Alliance for Beverage Cartons and the Environment, in 2019 the recycling rate for beverage cartons in Europe (EU-28) was around 51% [3]. These cartons are widespread because they allow products a long shelf life without the need of preservatives and with no deterioration of the content, but the development of recycling strategies represents an interesting challenge. In this framework, several recycling methodologies have been proposed and industrially implemented over the years, which have been recently reviewed by Robertson [4]. These approaches can be broadly divided in two families: a first family includes those that reprocess cartons as a mixture (incineration, gasification, pyrolysis) for energy recovery [5] or for manufacturing construction boards by hot compression [6–8], while the second one involves the removal of the cellulosic part in a previous step. In this case, which is the most common recycling strategy at an industrial level, the removal of cellulosic fraction is accomplished by hydropulping in paper mills thanks to centrifugal forces and water. The recovered fibre pulp is then used for producing new materials, such as corrugated cardboard or tissue paper. Once the cellulosic fibres have been removed by hydropulping, the material left over is mainly a mixture of polyethylene and aluminium, known as PolyAl or PE-AL, with additions of other impurities coming from caps and closures present in the beverage cartons. The PolyAl can be processed in several ways, which can be of mechanical, thermal [9], or chemical [2] nature. In the mechanical approach, the most exploited at industrial scale, PolyAl, depending on the technology, cleaning, and separation processes involved, can be used directly for end-market applications in injection moulding and extrusion. Such recovered materials have been characterized over the years. Lopes et al. [10] used PolyAl to create blends with PET (poly(ethylene terephthalate)), which showed elongation at break and impact resistance similar to PET/LDPE (virgin) blends but with increased Young's modulus. In [11], authors compared PolyAl with virgin LDPE, and the former displayed higher thermo-oxidative stability, crystallinity and tensile strength, but lower impact resistance. By using a patented production process granted by the Swiss company REPLAN Global Sgl, the Italian company Ecoplasteam S.p.a. commercialized a value-added product under the trade name EcoAllene® AA00 [12]. These polymer pellets can be injected, extruded, blended, and compounded like any other polymer, but also in this case, the resulting mechanical properties are poor and most suited for low-cost housing materials.

In an attempt to investigate how the industrial value of these recycled products can be maximized, Cravero and Frache [13] have recently studied the flammability and combustion behaviour of EcoAllene, proposing two different approaches: an intumescent system made of ammonium polyphosphate and pentaerythritol, and magnesium hydroxide. They reported an increase in the flammability rating, namely V2 for intumescent and V0 for magnesium hydroxide, and a reduced fire hazard (Fire Performance Index of 0.15 and 0.55; Flame Retardancy Index of 2.6 and 10.0), highlighting a full morphological compatibility only for the PolyAl–magnesium hydroxide formulations. A strategy for improving the mechanical properties involved the compounding of PolyAl with natural fibres. Hidalgo-Salazar et al. [14] incorporated fique fibres in PolyAl up to 30% by volume by compression moulding. The presence of fique mats improved tensile (strength in the range 13–20 MPa), flexural (strength in the range 21–27 MPa) and impact properties. A poor interfacial adhesion was noted, an issue that was addressed by Ayrilmis et al. [15], who compounded waste flour (rice husk and beech sawdust) and PolyAl with a coupling agent (maleic anhydride-grafted polyethylene). The flexural and tensile stiffness of PolyAl was significantly enhanced with increasing levels of the filler content, but the flexural strength of the resulting composites decreased when filler content reached 60 wt.%.

To broaden the value-added applications of such recycled materials, an in-depth testing of their thermal and mechanical properties is necessary, aiming at defining the best fit end markets. This is particularly true for EcoAllene, which, as a commercially available product, shows the most important characteristics of an industrial material, i.e., consistency and uniformity of supply, not being subject to the frequent adjustments typical of recycled materials sourced from heterogeneous plastics. No such studies are available in the literature; and to bridge this gap, the present work provides a comprehensive thermal and mechanical characterization of EcoAllene-based composites reinforced, for the first time, with natural fibers of mineral origin (basalt). Tensile, flexural and impact properties have been supplemented with differential scanning calorimetry, thermogravimetry and dynamic mechanical analysis to delineate the effect of basalt fibres and coupling agent on thermal stability, crystallization and glass transition behavior of the resulting composites. The results can pave the way for a more detailed and informed exploitation of this innovative ecological product while enhancing the recycling of products which would be disposed in incinerators and landfills at best.

2. Materials and Methods

2.1. Raw Materials

Chopped basalt fibres (BAS) were supplied by Mafic (Kells, Ireland) with a nominal length and diameter equal to 3.2 mm and 13 μm , respectively. These fibres were covered with a sizing compatible with polypropylene. The polymer matrix (EcoAllene[®] AA00) was supplied in pellets by Ecoplasteam S.p.a. (Alessandria, Italy). This is a polyethylene and aluminum waste obtained from the treatment of post-consumer packaging waste. To improve the interfacial adhesion between basalt fibres and polymer matrix, a commercially available coupling agent (CA) was used in some composite formulations. In particular, a maleic anhydride modified high density polyethylene (MA-g-PE) (Polybond[®] 3009) supplied by Addivant Corporation (Danbury, CT, USA) was used, which features a high maleic anhydride content in the range of 0.8–1.2%.

2.2. Processing

A two-step process was used to manufacture the specimens for the thermal and mechanical characterizations. At first the composites were compounded in a parallel co-rotating twin screw extruder (Thermo Scientific Process 11, Thermo Fisher Scientific, Waltham, MA, USA) with the following temperature profile ($^{\circ}\text{C}$, eight zones) from hopper to die: 160-160-170-180-180-180-175-175. Once compounded, the molten mass was transferred to an injection moulding machine (Haake MiniJet II Pro, Thermo Fisher Scientific), whose mould was kept at 50 $^{\circ}\text{C}$ and the loading cylinder at 175 $^{\circ}\text{C}$. During injection, a first step at a pressure of 600 bar for 10 s was followed by a post-injection step at 60 bar for an additional 10 s. Table 1 summarizes all the composite formulations.

Table 1. List of all EcoAllene-based composites.

Specimen ID	EcoAllene (wt.%)	Basalt Fibres (wt.%)	CA (wt.%)
EcoAl_neat	100	-	-
EcoAl_10BAS	90	10	-
EcoAl_10BAS+CA	85	10	5
EcoAl_30BAS	70	30	-
EcoAl_30BAS+CA	65	30	5

2.3. Mechanical Characterization of Composites

Composites were subjected to quasi-static tensile and three-point bending tests according to ISO 527-2 and ISO 178, respectively. Tensile tests were performed on a universal testing machine Z010 equipped with a 10 kN load cell (Zwick/Roell, Ulm, Germany) in displacement control. A cross-head speed of 10 mm/min with type 1BA samples (gauge

length = 30 mm) was used, while the strain was measured with a contacting extensometer. The same equipment was used for the bending tests, but with a cross-head speed of 5 mm/min, a support span length of 64 mm and a pre-load of 2 N. Strain was accurately measured with a displacement transducer in contact with the samples.

Dynamic Charpy impact tests were performed according to ISO 179-2 in an edgewise mode. Specimens of 80 × 10 × 4 mm size featured a notch type A and a span of 62 mm was used. Tests were conducted with a CEAST/Instron 9340 (Pianezza, Italy) instrumented drop weight tower by using an impact velocity of 2.90 m/s. For all mechanical tests, the results are the average of at least five replicates.

2.4. Thermal Characterization of Composites

The thermal stability of composites (~45 mg) was investigated by thermogravimetric analysis (TGA) in the temperature range from 25 °C to 800 °C in a nitrogen atmosphere by using a Setsys Evolution system by Setaram (Caluire, France).

The crystallization and melting behaviour of the different formulations was studied by differential scanning calorimetry (DSC). Specimens (~9.5 mg) were placed in a concavus aluminium crucible with pierced lid and analysed in a DSC 214 Polyma by Netzsch GmbH (Selb, Germany), according to the following thermal program in a nitrogen flow: heating from −40 °C to 220 °C (5 min hold), cooling to −40 °C (10 min hold), and heating to 220 °C, all steps conducted with a rate of 10 °C/min.

Dynamic mechanical analysis (DMA) was conducted in a three-point bending mode by using a DMA 242 E Artemis by Netzsch GmbH. Samples with size 60 × 10 × 4 mm were subjected to a heating rate of 2 °C/min from −160 °C up to 70 °C at a frequency of 1 Hz.

For all thermal characterizations, the results are the average of three replicates.

2.5. Morphological Characterization

The fracture surfaces of samples after tensile and Charpy impact tests were imaged by a field-emission scanning electron microscope (FE-SEM) Mira3 by Tescan (Brno, Czech Republic) equipped with an Octane Elect EDS System by EDAX (AMETEK GmbH, Unterschleissheim, Germany). Samples were sputter coated with gold prior to analysis.

3. Results

3.1. Thermal Characterization of Composites

The polymer matrix was obtained from recycling of post-consumer aseptic packaging, therefore it was necessary to assess its thermal stability and the effects induced by basalt fibres. In this regard, three specific temperatures were considered, namely $T_{5\%}$ and $T_{10\%}$, which represent the temperatures corresponding to a weight loss of 5% and 10%, respectively, and T_{max} which is the temperature of maximum degradation (peak of the derivative of weight over time curve). The values, summarized in Table 2, were calculated from representative TGA curves shown in Figure 1.

Table 2. $T_{5\%}$, $T_{10\%}$, and T_{max} for EcoAllene-based formulations obtained from TGA analysis.

Specimen ID	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)
EcoAl_neat	438.5 ± 0.6	452.5 ± 1.1	484.6 ± 0.8
EcoAl_10BAS	398.6 ± 0.9	430.2 ± 1.2	479.3 ± 0.9
EcoAl_10BAS+CA	395.6 ± 0.8	434.3 ± 1.2	481.8 ± 0.9
EcoAl_30BAS	403.1 ± 1.0	437.8 ± 1.1	481.3 ± 1.0
EcoAl_30BAS+CA	395.8 ± 0.9	435.0 ± 0.9	480.7 ± 1.1

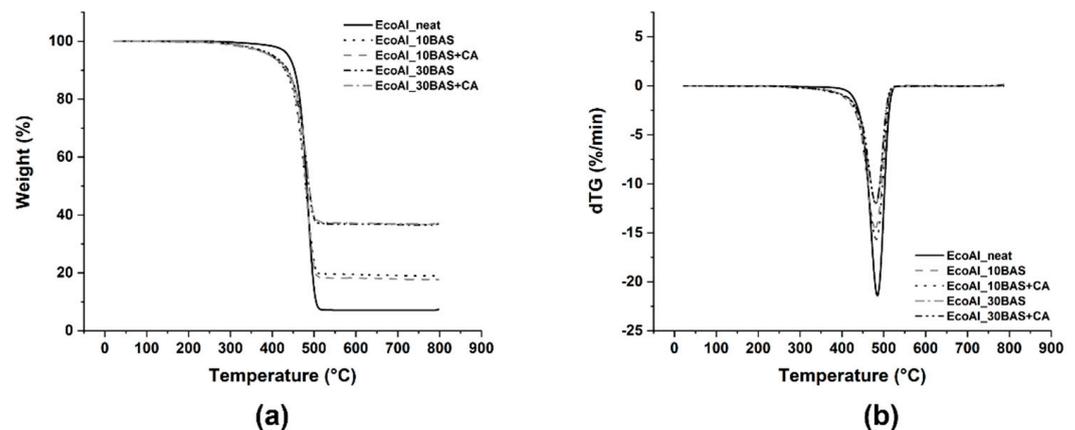


Figure 1. (a) TG and (b) derivative (dTG) curves for all EcoAllene-based formulations.

Neat EcoAllene displayed a single-step degradation behaviour, with a maximum degradation temperature of about 485 °C, which is in agreement with what reported in [13]. This degradation step can be ascribed to LDPE, while the residue is indicative of the aluminium content which is expected to show no sign of weight loss. In fact, Cravero and Frache [13] included in their study the thermograms of a pure LDPE which exhibited a maximum degradation temperature around 474 °C. In the work authored by Hidalgo-Salazar et al. [14], the authors reported a maximum degradation temperature around 470 °C. Recently, Georgiopoulou et al. [2] reported, for a LDPE/aluminium by-product recovered by a selective dissolution/precipitation process, a maximum degradation temperature of 482 °C, with an onset degradation temperature ($T_{5\%}$) of 429 °C, which are in close agreement with the values in Table 2. It is reasonable to assume the presence of impurities in the EcoAllene polymer that eventually shifted the maximum degradation temperature to slightly higher values. Another difference is the amount of aluminium, which was found to be around 7.5 wt.%, in contrast to more common amounts in the range 15–25 wt.% [2,13,14]. This might be ascribed to the patented process by Ecoplasteam which tends to reduce the content of aluminium in the final LDPE-Al mixture [13].

The addition of basalt fibres did not modify the global degradation behaviour, even though composites featured a lower thermal stability than neat EcoAllene, with a decrease in the temperatures of interest (Table 2). The residues were found to be equal to 18 wt.% and 38 wt.% for composites reinforced with 10 and 30 wt.%, respectively, thus confirming that the correct amount of basalt fibres was homogeneously dispersed in the matrix, because basalt fibres are thermally stable in the investigated temperature range [16]. It is worth mentioning the negative effect of basalt fibres on the thermal stability of EcoAllene, irrespective of fibre content. Despite the high thermal stability of inorganic basalt fibres, it is reasonable to assume that their incorporation in the polymer matrix increased the thermal diffusivity of the resulting composites, thus leading to a more favourable temperature distribution and a faster degradation, as also observed by Barczewski et al. [17] for polypropylene reinforced with basalt powder.

DSC analysis confirmed the presence of other polymer impurities in the neat EcoAllene in addition to LDPE and aluminium. Figure 2 shows the cooling and second heating curves for all EcoAllene-based composite formulations, while Table 3 summarizes the relevant thermal parameters.

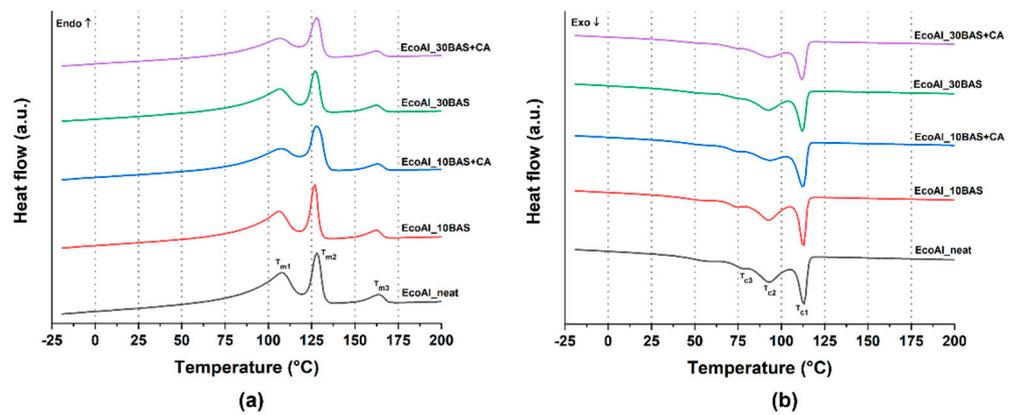


Figure 2. DSC 2nd heating scan (a) and cooling scan (b) for EcoAllene-based composites.

Table 3. Thermal properties of composites obtained from differential scanning calorimetry (DSC) analysis (T_m = melting temperature; T_c = crystallization temperature. Numbers 1 to 3 refer to the temperatures labeled in Figure 2).

Specimen ID	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°C)	T_{c1} (°C)	T_{c2} (°C)	T_{c3} (°C)
EcoAl_neat	108.5 ± 0.2	128.0 ± 0.1	163.8 ± 0.1	112.7 ± 0.01	92.6 ± 0.3	76.6 ± 0.3
EcoAl_10BAS	106.1 ± 0.1	126.7 ± 0.1	162.3 ± 0.1	112.7 ± 0.1	92.7 ± 0.1	75.3 ± 0.2
EcoAl_10BAS+CA	107.4 ± 0.1	127.6 ± 0.1	163.2 ± 0.2	112.5 ± 0.2	93.55 ± 0.2	74.2 ± 0.4
EcoAl_30BAS	106.7 ± 0.1	127.0 ± 0.1	162.4 ± 0.3	112.2 ± 0.1	92.55 ± 0.2	73.7 ± 0.1
EcoAl_30BAS+CA	107.1 ± 0.2	128.5 ± 0.4	162.7 ± 0.3	111.6 ± 0.4	92.6 ± 0.5	73.1 ± 0.5

During the heating scan (Figure 2a), three endothermic events were recorded, labelled as T_{m1} , T_{m2} and T_{m3} . In neat EcoAllene, these peaks were centred at ~ 108 , 128 and 164 °C, respectively. These events represent melting points that can be ascribed to LDPE ($T_m \sim 108$ °C [18]), HDPE (high density polyethylene, $T_m \sim 125$ °C [18]), and PP (polypropylene, $T_m \sim 168$ °C [19]), respectively. The exothermic peaks (labelled as T_{c1} , T_{c2} , and T_{c3} in Figure 2b) describe crystallization events. In this case, the correspondence with polymer species is less clear, but the lower temperature events, i.e., T_{c2} and T_{c3} , can be ascribed to LDPE [18], which is characterized by a broad melting range and low peak shape as a result of long branches and wider molecular weight distribution [20]. The sharper peak T_{c1} represents the crystallization of HDPE overlapped with that of the PP impurity, whose crystallization occurs in the temperature range ~ 110 – 115 °C [18,19,21,22].

Melting and crystallization temperatures were not significantly modified by the addition of basalt fibres, and no nucleating effect can be predicted by formation of transcrystallinity, which is dependent on a number of factors, such as fibre roughness, surface energy, and polymer chemical composition [23,24].

3.2. Thermo-Mechanical Characterization of Composites

Quasi-static mechanical characterization of composites was performed in tensile and three-point bending, whose representative stress vs. strain curves are shown in Figure 3 while the relevant mechanical properties are summarized in Table 4.

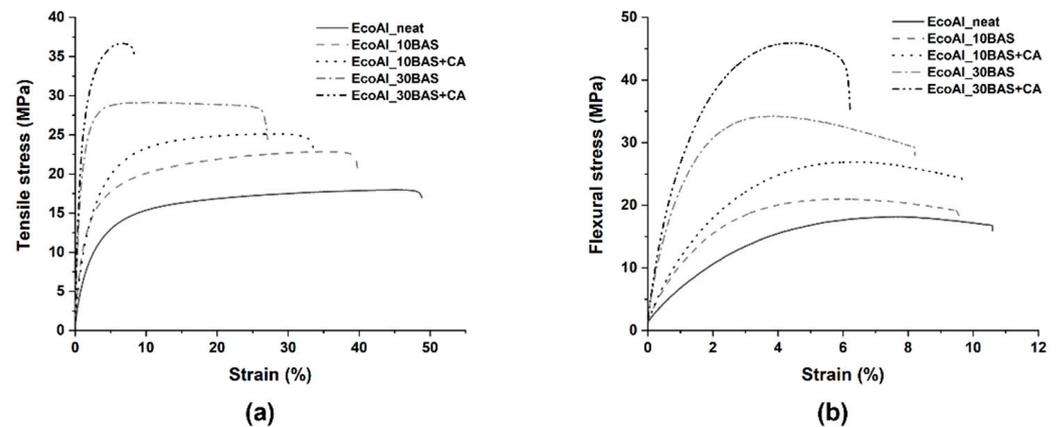


Figure 3. Representative (a) tensile and (b) three-point bending curves of EcoAllene-based composites.

Table 4. Tensile and flexural properties of EcoAllene-based composites.

Specimen ID	Tensile Modulus (MPa)	Tensile Strength (MPa)	Strain at Maximum Stress (%)	Flexural Modulus (MPa)	Flexural Strength (MPa)	Strain at Maximum Stress (%)
EcoAl_neat	338 ± 23	17.7 ± 0.9	45.6 ± 7.6	493 ± 6	18.1 ± 0.2	7.8 ± 0.1
EcoAl_10BAS	897 ± 42	22.4 ± 0.5	33.6 ± 3.0	904 ± 57	20.8 ± 0.2	6.1 ± 0.2
EcoAl_10BAS+CA	1150 ± 83	26.0 ± 0.2	14.7 ± 0.4	1130 ± 71	26.7 ± 0.6	6.6 ± 0.3
EcoAl_30BAS	2890 ± 44	29.6 ± 1.2	12.4 ± 1.8	2930 ± 179	34.5 ± 0.6	3.8 ± 0.3
EcoAl_30BAS+CA	3750 ± 142	36.6 ± 0.6	6.3 ± 0.5	3630 ± 85	47.4 ± 2.4	4.6 ± 0.2

Unreinforced EcoAllene featured poor mechanical properties, in terms of stiffness and strength, which are mostly ascribed to the low-density polyethylene. These results are in line with other studies [14,15], though the stiffness appears to be lower in the present case, likely due to a reduced amount of aluminium flakes which do not restrict to a great extent the polymer chains' mobility. As previously mentioned, aluminium content was found to be around 7.5 wt.%, lower than the usual amount of 15–20 wt.%. These poor mechanical properties were significantly improved by increasing the amount of basalt fibres, both in tensile and flexural loading. The tensile modulus increased by 165% and 755% as the basalt fibre content passed from 10 wt.% to 30 wt.% compared to unfilled EcoAllene, respectively, while the tensile strength improved by 27% and 67%. No decreasing trend with an increasing amount of basalt fibres was detected, at least in the range investigated in the present study. Ayrimis et al. [15] reported a reduction in tensile and flexural strength when moving from 40 wt.% to 60 wt.% of sawdust or rice husk flour. The significant improvements in mechanical properties reveal an efficient stress transfer at the basalt fibre/matrix interface, as confirmed by SEM observations reported in Figures 4 and 5. Unfilled EcoAllene showed a ductile failure (Figure 4) and few aluminium flakes were found to be well embedded in the polymer matrix (Figure 4e,f). When basalt fibres were added, a reduction in macro-ductility was noted (Figure 3a), even if at the micro scale (Figure 5c,d), ductile failure was still observed. Pull-out phenomena are present, but the length of pulled-out basalt fibres is limited with evidence of matrix sticking on basalt fibre surface (Figure 5b), thus confirming a good fibre/matrix interfacial adhesion promoted by the basalt sizing designed for polyolefins. Sizing application does not produce a homogeneous coverage on fibres, thus leaving room for further improvements. In this regard, the addition of the coupling agent resulted not only in a significant reduction in ductility (Figure 6), but also in a stronger interfacial adhesion (Figure 6c,d), as the matrix is well adhered to the fibres which in turn appear to be mostly broken on the same fracture plane with very limited pull-out. This behaviour is due to the ester linkages created by

hydrophilic OH groups reacting with acid anhydride groups from coupling agent. It is interesting to note that in bending, at the same level of basalt fibre content, the presence of the coupling agent is not detrimental to the strain at maximum stress. The coupling agent usually enables a better dispersion of fibres in the matrix, thus reducing the possibility of fibre clusters that can act as stress intensifier. The lack of stress amplification is especially important in bending, where the state of stress is complex including tensile, compression and shear.

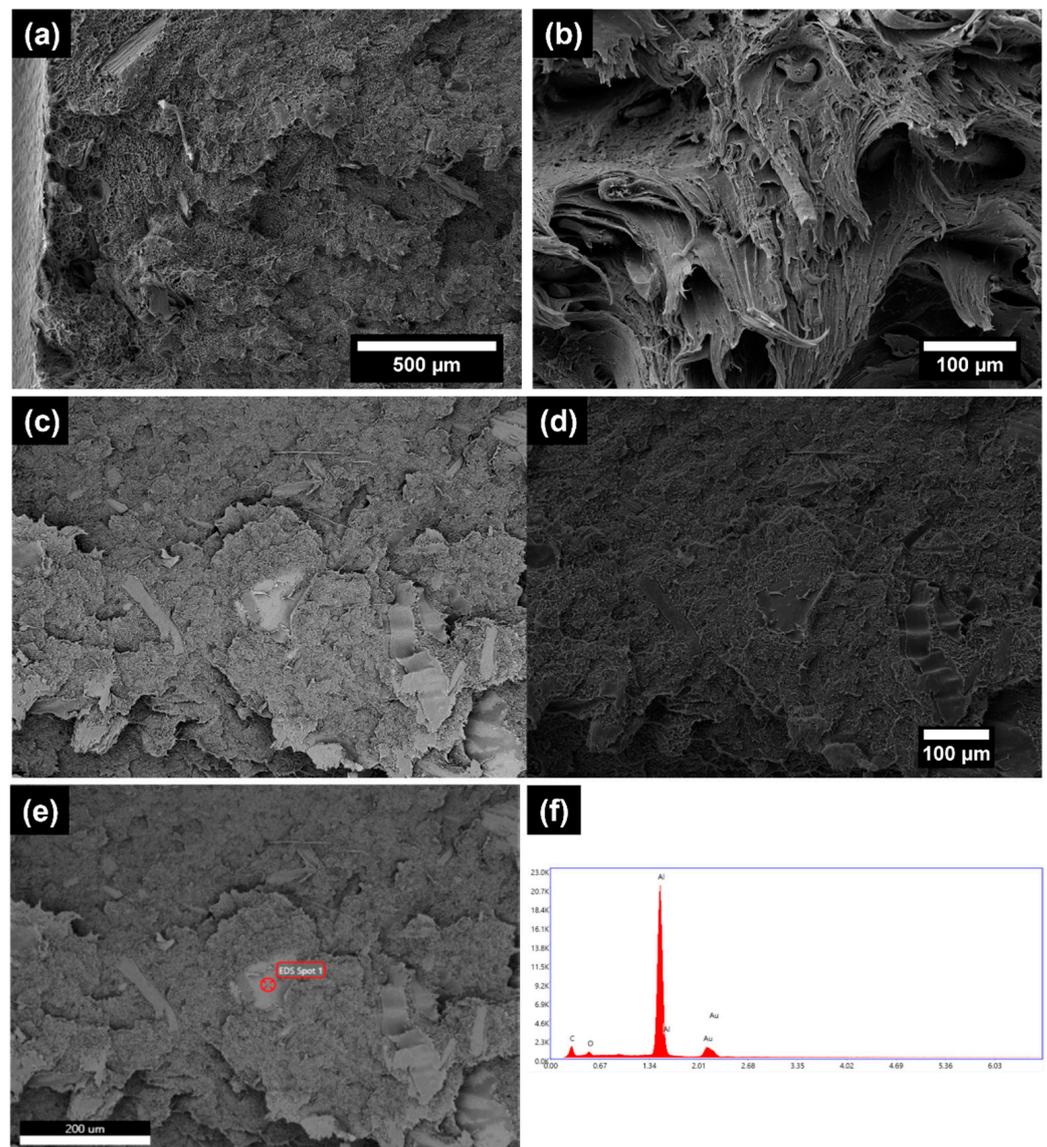


Figure 4. SEM micrographs of unfilled EcoAllene: (a,b) after Charpy impact test; (c,d) after tensile test. (c) shows the backscattered signal, while (d) the secondary signal; (e) after tensile test in backscattered signal and (f) EDS (Energy Dispersive X-ray Spectroscopy) spectrum.

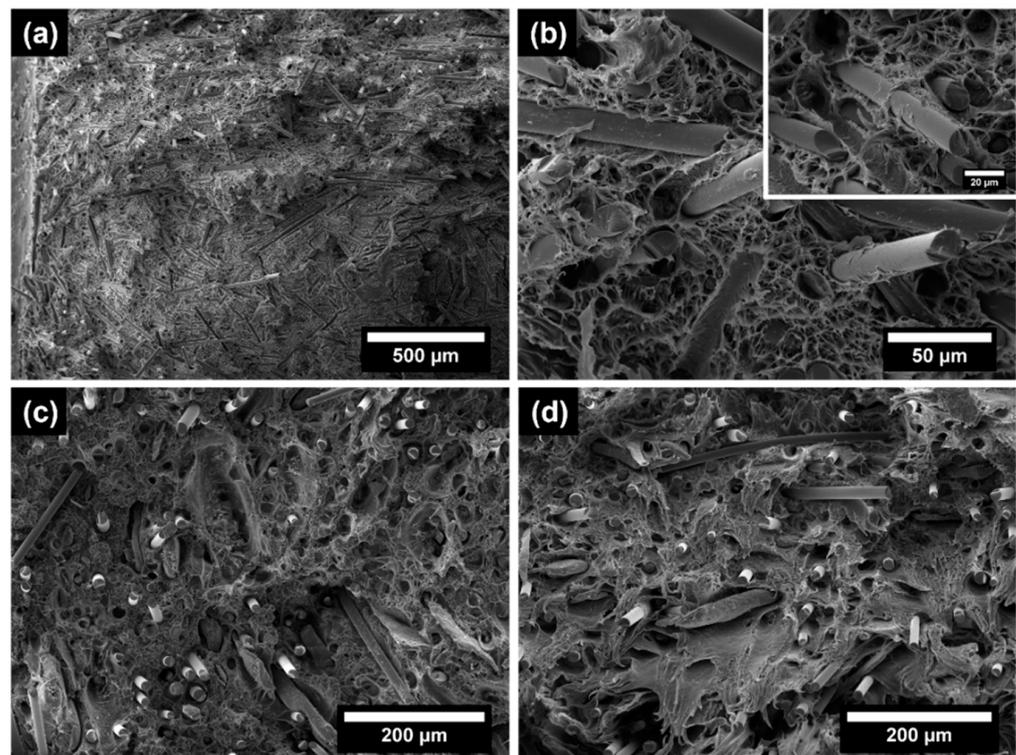


Figure 5. SEM micrographs of EcoAl_30BAS: (a,b) after Charpy impact test; (c,d) after tensile test.

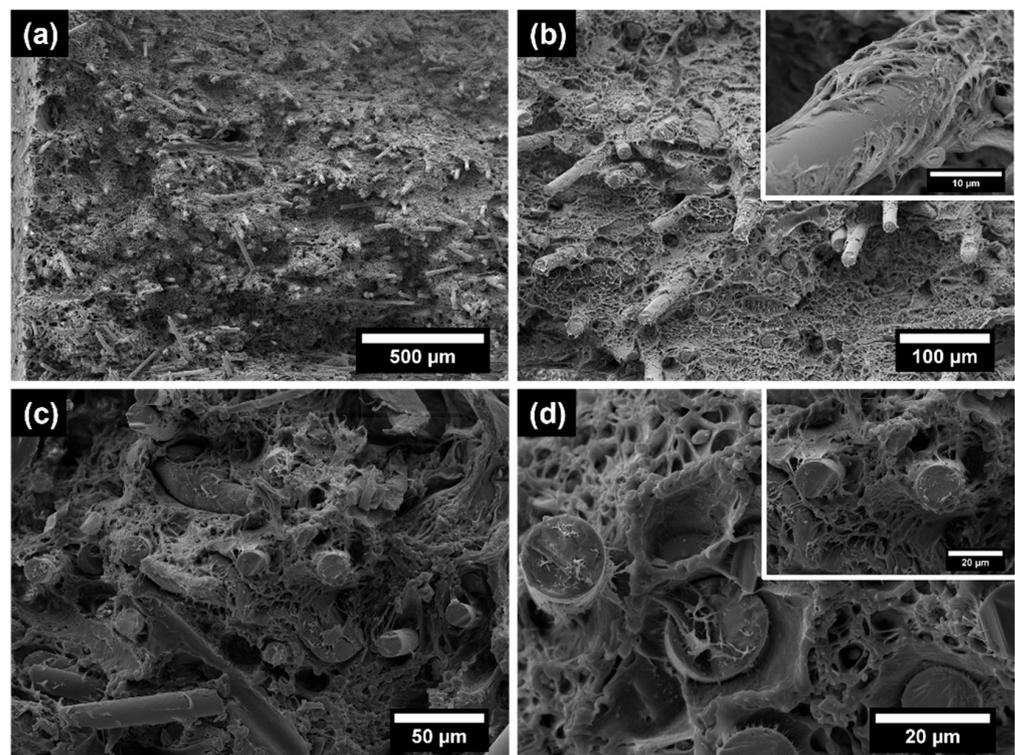


Figure 6. SEM micrographs of EcoAl_30BAS+CA: (a,b) after Charpy impact test; (c,d) after tensile test.

Dynamic properties were investigated by performing Charpy impact tests on notched samples, whose results are summarized in Figure 7 in terms of impact strength and peak force. The morphology of fracture surfaces is included in Figures 4a,b, 5a,b, and 6a,b for unfilled EcoAllene, EcoAl_30BAS and EcoAl_30BAS+CA, respectively. The notch is

visible on the left side of the corresponding micrographs at lower magnification. The poor impact strength of neat EcoAllene was increased by the addition of basalt fibres, reaching a maximum improvement at 30 wt.% of basalt fibres equal to 11% and 45% for formulations without and with the coupling agent, respectively.

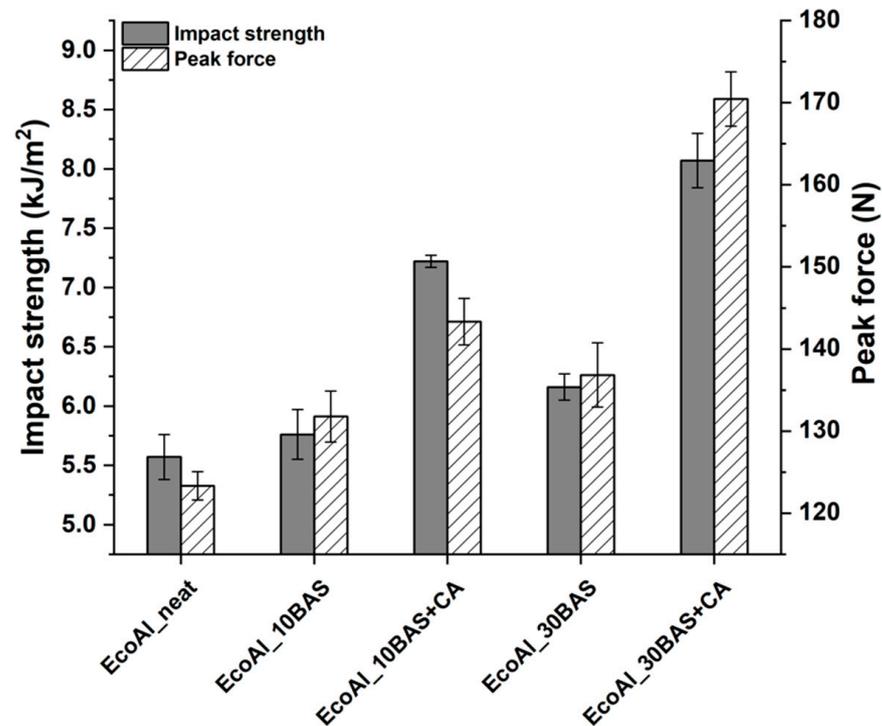


Figure 7. Charpy impact test results of EcoAllene-based composites.

The resistance of basalt fibres led to higher impact peak forces, with modified formulations featuring even higher impact strength and peak force. The strong fibre/matrix adhesion increased the work of fracture of the interphase that hindered crack propagation, thus confirming the effectiveness of MA-g-PE [25]. To validate the positive results obtained, in Table 5 the mechanical properties have been compared with those from other studies on polymer matrices reinforced with basalt and plant fibres (i.e., hemp and flax). Composites developed in the present study display mechanical properties close to those based on virgin HDPE, thus confirming the potential of a matrix coming from recycled materials to be used in outdoor applications, such as for instance as polyolefin-based plastic lumber decking boards.

The dynamic mechanical analysis (DMA) was conducted for detailing the effect of basalt fibres on the resulting EcoAllene-based composites' mechanical properties. Representative curves are included in Figure 8. The increase in storage modulus over the whole temperature range with the content of basalt fibres confirms tensile and bending tests' results, which pointed out a stiffening of composites compared to unfilled EcoAllene. DMA also provided important information about the glass transition temperature (T_g) and the damping properties of the composites, as expressed by the position and magnitude of $\tan\delta$, respectively [34].

Table 5. Summary of mechanical properties of polymer matrix composites reinforced with basalt and plant fibres.

Matrix Type	Fibre Type	Coupling Agent	Tensile Modulus (GPa)	Tensile Strength (MPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Charpy Impact Strength (kJ/m ²)	Fibre Content (wt%)	Reference
PP	Basalt	yes	4.7	68	73	3.3	5.6	20	[26]
HDPE	Basalt	yes	5.2	52	-	-	-	30	[21]
HDPE	Hemp	yes	3.8	36	-	-	-	30	[21]
HDPE	Basalt	no	6.46	47.87	81.4	6.05	-	40	[27]
HDPE	Flax	no	4.63	21.64	43.6	5.14	-	40	[27]
PLA	Basalt	no	7.8	72.14	130	6.7	-	15	[28]
Virgin HDPE	Basalt	no	4.2	41.6	52.4	4.1	-	30	[29]
Recycled HDPE	Basalt	no	4.2	40.6	45.6	3.6	-	30	[29]
PBS	Basalt	no	1.3	46	71	3.8	-	15 _{vol}	[30]
PA6	Basalt	no	7.79	120	170.8	6.06	12.7	30	[31]
Recycled PET	Basalt	no	4.07	57.38	103.80	4.53	4.83	30	[32]
Recycled PET	Basalt	no	8.65	112.9	-	7.74	8.1	30	[33]

PP = Polypropylene; HDPE = High density polyethylene; PLA = Polylactic acid; PBS = Polybutylene succinate; PA6 = Polyamide 6; PET = Polyethylene terephthalate.

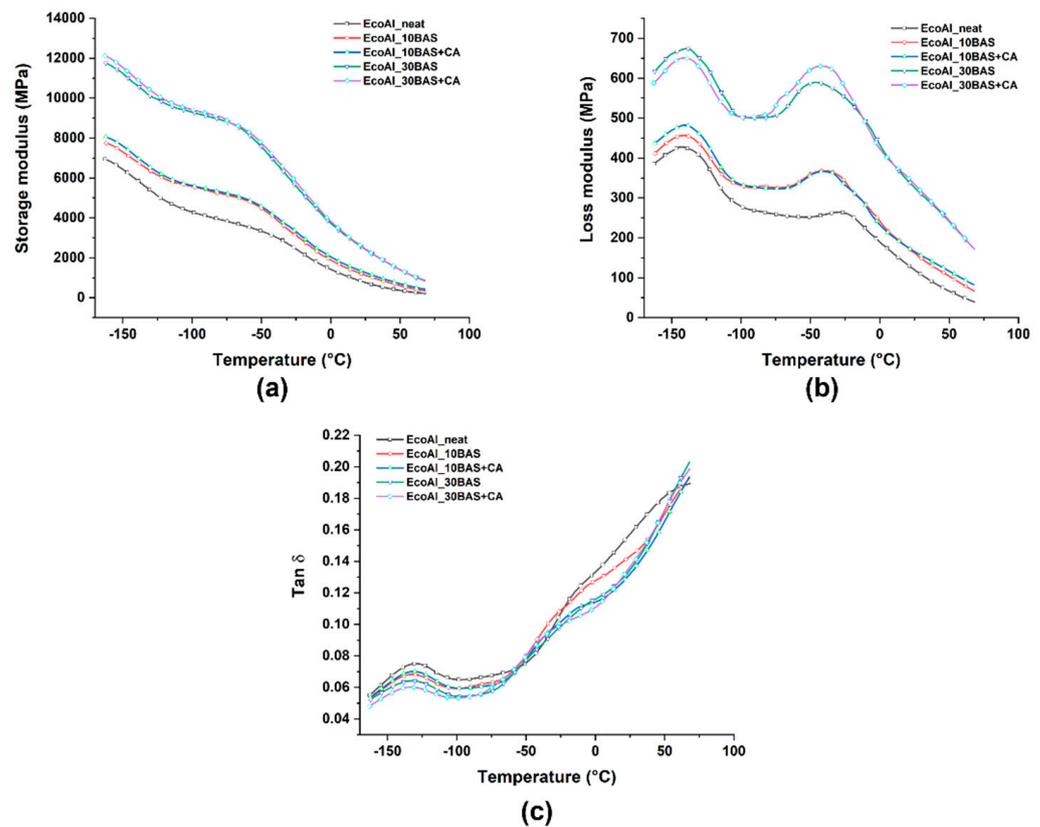


Figure 8. (a) Storage modulus, (b) loss modulus and (c) $\tan\delta$ curves as a function of temperature for all EcoAllene-based composites.

Glass transition temperature values, linked to changes in the mobility of small segments of polymer chains, did not show any significant shift with increasing content of basalt fibres, but the magnitude of $\tan\delta$, related to the energy dissipation ability of composites, dropped to lower values. A drop in $\tan\delta$ peak value is usually associated with improved interfacial adhesion and reduced polymer chain mobility [35], thus confirming results from quasi-static tests and SEM analysis. The dynamic loss modulus (Figure 8b), a measure of the energy absorbed due to relaxation phenomena, showed two main transitions: one located around -140 °C and another one around -40 °C, the so-called γ and β relaxations, respectively. The β relaxation is usually more intense in LDPE compared to HDPE and can be ascribed to the motion of branches in the amorphous matrix, while the γ relaxation is mostly confined to the bulk amorphous phase involving the motion of short segments in addition to some reorientation of loose chain ends inside the crystalline and amorphous fractions [36]. These relaxations support the predominant role played by low-density polyethylene in the EcoAllene matrix.

4. Conclusions

In the present work, post-consumer aseptic multilayer packaging consisting mainly of LDPE and aluminium was successfully proposed as a matrix for short fibre composites. In particular, basalt fibres were homogeneously dispersed by twin-screw extrusion in the matrix up to a content of 30 wt.%. Tensile and bending tests highlighted an increasing trend in stiffness and strength with basalt fibre content, which was improved further by the addition of a maleated coupling agent. The stronger interfacial adhesion, confirmed by SEM morphological observations, led to increases by 107% and 162% for tensile and bending strength, respectively, which were also linked to a 45% enhancement of impact strength. Thermal analysis of the commercially available recycled product showed that the matrix is

a complex mixture of LDPE, HDPE with traces of PP, but the addition of basalt fibres did not change the melting and crystallization temperatures. Indeed, basalt fibres reduced the thermal stability of EcoAllene-based composites as evaluated by TGA, likely due to the increased thermal diffusivity of the composites. DMA analysis revealed a better mechanical performance from $-160\text{ }^{\circ}\text{C}$ to $70\text{ }^{\circ}\text{C}$ due to the presence of basalt fibres. Results from the present study show that these low-cost reinforced thermoplastic composites show potential in automotive interiors and outdoor decking applications as exterior residential decking boards. In fact, the mechanical properties of the developed composites compare quite favourably with the minimum requirements stated by the ASTM D 6662 standard. Other applications, once fire resistance is suitably addressed, might include electrical components (such as electrical ducts), components for public transportation (such as seats, overhead bin), and furnishing and accessories, as this polymer can be easily coloured with a nice aesthetic finish.

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