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Performance, durability and recycling of thermoplastic biocomposites reinforced with coriander straw

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ABSTRACT

In this study, coriander straw fiber was effectively incorporated as a reinforcing filler in polypropylene and biobased low-density polyethylene composite materials through twin-screw extrusion compounding and injection molding. Maleic anhydride-grafted copolymers were added as a coupling agent and effectively provided fiber/matrix compatibilization. With a significant reinforcing effect, resulting in a 50% increase in the flexural and tensile strength (from 19 to 28 MPa and from 12 to 17 MPa, respectively, for polypropylene composites) as compared to the native polymer, coriander straw allowed the production of 40% filled thermoplastic biocomposites with adequate mechanical properties comparable to those of commercial wood fibers, excellent durability in terms of UV and hygrothermal weathering and high potential for recycling. At the same time, such coriander biocomposites show a favorable cost structure, with 28% reduction of the granule cost as compared to wood fiber composites.

1. Introduction

In recent years, society has been marked by increasing environmental awareness and a critical pressure on government and industry towards the implementation of renewable resources, sustainable processing and efficient waste management. One of the major industries that is currently undergoing a radical transformation, with important achievements in green technology, is the materials industry. Here, the use of renewable raw materials such as plant fibers and biobased polymers has become widespread as a viable alternative to traditional petroleum-based materials, as well as for the development of novel applications. In this regard, natural fiber composites have become well-established in the automotive and the construction industry [1,2]. The advantages of natural fibers include a low cost and abundant availability, as well as a low density and satisfactory specific performance properties with a good reinforcing efficiency comparable to traditional fillers such as glass fiber [3].

However, adequate fiber dispersion in the polymer matrix can be particularly challenging for natural fiber composites, while it is a crucial factor determining the mechanical performance of the composite material. The excellent mixing efficiency and flexibility inherent to twin-screw extruders may be a key advantage and several studies have reported superior material properties when using twin-screw extrusion for compounding, as compared to an internal mixer or a single-screw extruder [4–6]. While the fibers act as reinforcing fillers inside the biocomposites, the matrix material largely dictates the appearance and overall durability of the product and effectively transfers mechanical stress to the fibers. Polypropylene (PP) and polyethylene (PE) present the most widely applied thermoplastics for biocomposites, partly owing to the fact that their melting temperature is below 200 °C, which allows processing without thermal degradation of the fibers [1,7]. Therefore, these thermoplastic polymers were chosen as the matrix material for the biocomposites produced in this study. They further show wide applications that do not require very high strength properties, in contrast to e.g. carbon fiber-reinforced composites, and are thus suitable as a matrix for sustainable, renewable fiber composites. Polypropylene has been widely applied in the automotive industry and for food packaging, while low-density polyethylene is primarily used for plastic films (e.g. shopping bags).

Both these matrices are petroleum-based polymers, which, to date, still dominate the market for plastic materials. However, finite petroleum resources and environmental concerns have led to important

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research efforts in the search for and the evaluation of more sustainable, biobased alternatives and in the past decade, biobased plastics have experienced fast growth. Biopolyethylene (BioPE) can be produced from renewable resources via ethylene obtained from the dehydration of bioethanol, in turn originating from fermentable sugars mainly from sugarcane [8]. While PP and PE are non-biodegradable materials, reports have shown that mechanical recycling of plastic waste is often preferable over composting in terms of economics and environmental impact [9,10]. Multiple reprocessing cycles inevitably bring about a certain degree of mechanical and thermal degradation of the polymer matrix as well as the fiber reinforcement and repeated mechanical recycling could be detrimental to the mechanical properties of the composites [11]. However, several studies have shown that the mechanical performance of composites reinforced with natural fibers is significantly better maintained throughout reprocessing cycles than those reinforced with glass fibers, owing to the inherent flexibility of the former and the ability to withstand external mechanical forces [11,12]. As such, these biocomposites show better property retention through recycling, resulting in substantial advantages in terms of life cycle impact and efficient waste management strategies.

Recently, the vegetable oil of coriander (*Coriandrum sativum* L.) fruits has gained great interest from the food and cosmetic industry [13]. It has been approved as a novel food ingredient (NFI) and can be obtained in high quality through twin-screw extrusion pressing [14,15]. The global production of coriander fruits is estimated around 600,000 tons/year, while 60–80% of the crop yield is represented by coriander straw and is considered a crop residue [16,17]. Given the increasing trend of the market for coriander oil, by-products from the pressing process and coriander straw will become increasingly available. Previous studies have demonstrated the effective use of the press cake as a natural binder in fiberboard materials [18–20]. This study aims to valorize the coriander straw fraction through its incorporation in thermoplastic biocomposites, at the same time producing more sustainable alternatives to current commercial wood-plastic composites and contributing to the setup of an efficient coriander biorefinery system. Coriander fiber-reinforced PP and BioPE composites were manufactured and their mechanical performance, durability, and recycling potential was evaluated. Further, to evaluate their competitiveness with current commercial composite materials, a critical analysis of the feasibility of coriander fibers as a reinforcement in plastic materials was made and compared with two types of commercial grade wood fibers.

2. Materials and methods

2.1. Materials

Coriander straw of French origin (GSN maintenaire variety) was supplied by GSN Semences (Le Houga, France). Prior to its use, it was milled with an Electra F3 (Electra SAS, Poudenas, France) hammer mill through three successive passages with the application of a screen of, respectively, 12 mm, 2 mm, and 1 mm. The density of the coriander straw fibers was determined through pycnometry using ethanol and was 1.32 ± 0.09 g/cm^3. Its cellulose, hemicelluloses, and lignins contents were determined by the use of the acid detergent fiber-neutral detergent fiber (ADF-NDF) method of Van Soest and Wine [21,22] and were 52.5 ± 0.1%, 21.2 ± 0.5%, and 9.8 ± 0.2%, respectively. The commercial wood fiber samples consisted of Jeluxyl WEHO 800 s (softwood) and Jeluxyl HAHO 150/30 (hardwood) from JELU-WERK (Rosenberg, Germany). The polypropylene used in this study, type Hifax EP3080, was obtained from LyondellBasell (Rotterdam, Netherlands). Biobased low-density polyethylene, type SPB608, was purchased from Braskem (São Paulo, Brazil). The physical, mechanical and thermal properties of the raw polymer materials are listed in Table 1. The coupling agents, Licocene PP MA 6452 fine grain (MAPP, density 0.91 g/cm^3, viscosity 1100 MPa·s at 170 °C) and Licocene PE MA 4351 fine grain (MAPE, density 0.99 g/cm^3, viscosity 300 MPa·s at 140 °C), were obtained from Clariant (Muttenz, Switzerland). An overview of the global manufacturing process of the PP and BioPE biocomposite materials is presented in Fig. 1.

Table 1
Physical, thermal and mechanical properties of the raw polymer materials.

	PP (Basell Hifax EP3080)	BioPE (Braskem SPB608)
Density (g/cm^3)	0.9	0.915
Melt flow rate (g/10 min)	7.5 (230 °C, 2.16 kg)	30 (190 °C, 2.16 kg)
Vicat softening temperature (°C)	130	79
Tensile stress at break (MPa)	13	8
Tensile strain at break (%)	> 100	390
Flexural modulus (MPa)	900	450

2.2. Compounding

Coriander straw was dried overnight at 80 °C using a ventilated oven to a moisture content of 3–4% prior to compounding. PP and BioPE composite blends were produced by means of twin-screw extrusion compounding, using a Clextral Evolum 25 (Clextral, Firminy, France) co-rotating twin-screw extruder. The extruder barrel, with a length of 1 m and an L/D of 40, consisted of 10 successive modules. Three blocks of kneading elements (bilobe paddles) were incorporated in the screw profile near modules 6–8 in order to ensure adequate dispersion of the fibers in the polymer matrix. Dispersion was further improved by means of reverse screw elements, positioned immediately after the second kneading block. The temperature profile of the consecutive modules was the following: 60 °C/170 °C/180 °C/190 °C/180 °C/180 °C/170 °C/165 °C/160 °C/155 °C/155 °C (die). The screw speed (S_S, rpm) was set at 150 rpm and the total feed rate (Q, kg/h) was 10 kg/h. The feeding rates of the matrix material, the fibers and the coupling agent were adjusted according to the produced formulation and as such, a constant filling coefficient of 0.067 kg/h rpm was maintained.

2.3. Molding

PP and BioPE composites were formed through injection molding using a Negro Bossi (Cologno Monzese, Italy) VE 160–720 injection press with a clamping force of 160 ton. The temperature profile along the plasticizing screw was 150 °C/170 °C/180 °C/130 °C (nozzle). Shot building occurred over a length of 25 mm, with a screw speed of 150 rpm and a counter pressure of 5 bar. The injection speed was 100 mm/s with a pressure of 2000 bar. A clamping force of 1600 kN was applied and the mold temperature was kept at 20 °C through water cooling. The cooling time was 15 s. Continuous production of composite testing specimens was possible for all PP and BioPE formulations.

2.4. Accelerated aging

The durability of PP and BioPE biocomposites was assessed by subjecting the materials to laboratory artificial weathering conditions, including exposure to UV irradiation and/or hygrothermal aging according to ISO 4892-2:2013 [23] and ISO 9142:2003 [24], respectively, with an exposure time of 3 weeks. UV aging was carried out by the use of an Atlas SUNTEST CPS + benchtop xenon lamp unit (Amtek Industries, Ajman, United Arab Emirates) of 1500 W, with a simulation of solar radiation through irradiation at 300–800 nm. Hygrothermal aging was conducted through cyclic climatic aging involving humidity, cold and heat where once cycle was 24 h and consisted of the following temperature/relative humidity profile: 40 °C/90% (15 h); 40 to −20 °C/90% (1 h); −20 °C/90% (2 h); −20 to 70 °C/90 to 50% (1 h);

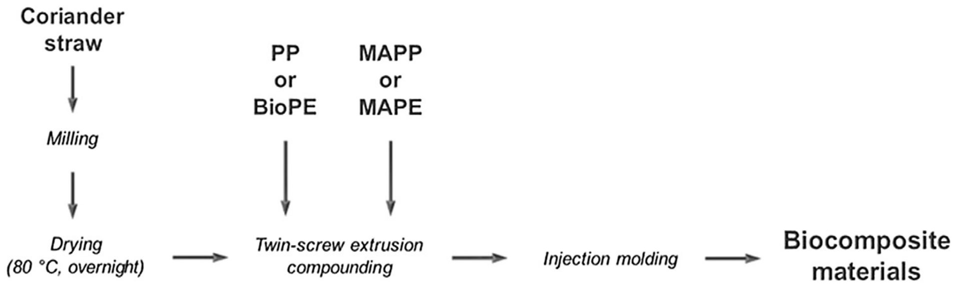

Fig. 1. Scheme of the complete manufacturing process for the coriander fiber-reinforced thermoplastic composites.

70 °C/50% (4 h); 70 to 40 °C/50 to 90% (1 h).

2.5. Scanning electron microscopy

The morphology and structural organization of coriander fiber-reinforced PP and BioPE composites was studied by the use of scanning electron microscopy (SEM). For this, a ZEISS EVO HD 15 LS scanning electron microscope (Carl Zeiss Microscopy GmbH, Jena, Germany) was used with a 10 kV acceleration voltage, a probe current of 120 pA, an applied pressure of 30 Pa and a 10 mm working distance.

2.6. Colorimetry

The color characteristics of the native and recycled PP and BioPE composites were measured with a Konica Minolta CR-410 (Tokyo, Japan) colorimeter, equipped with a pulsed xenon lamp and six silicon photocells. Results were expressed according to the CIE $L^*a^*b^*$ color space [25], where L^* represents lightness and ranges between 0 (black) and 100 (white), a^* represents hue on the green (negative) to red (positive) axis and b^* represents hue on the blue (negative) to yellow (positive) axis. The color difference ΔE^* was calculated according to CIE76, with $\Delta E^* = [(L_O{}^* - L^*)^2 + (a_O{}^* - a^*)^2 + (b_O{}^* - b^*)^2]^{1/2}$. All determinations were carried out in triplicate.

2.7. Thermogravimetric analysis

The thermal stability of the PP and BioPE composites was determined by thermogravimetric analysis (TGA) using a Shimadzu TGA-50 (Shimadzu Corporation, Kyoto, Japan) thermogravimetric analyzer. Analyses were conducted under air from 25 to 750 °C, with a heating rate of 10 °C/min.

2.8. Mechanical analysis

Tensile and flexural tests were conducted according to ISO 527-4:1997 [26] and ISO 178:2010 [27], respectively, using an Instron 33R 4204 (Norwood, MA, USA) universal testing system equipped with a load cell of 5000 N for tensile tests and 500 N for flexural tests. For tensile tests, a testing speed of 3 mm/min was applied, while determination of the Young's modulus was conducted with increased sensitivity by the use of an extensometer with a crosshead speed of 1 mm/min. Three-point flexural tests were carried with a grip separation 40 mm and a testing speed of 2 mm/min. All tests were conducted through six repetitions. Charpy impact properties were determined according to ISO 179-1:2010 [28] with a Testwell Wolpert (Gennevilliers, France) 0–40 daN cm Charpy testing apparatus. Tests were conducted at 20 °C with a 25 mm distance between the anvils. All analyses comprised eight repetitions.

2.9. Data analysis

Experimental data from twin-screw extrusion and density and mechanical analyses are expressed as the mean ± the standard deviation. Differences in means were detected by the use of a one-way analysis of variance (ANOVA) with the GLM procedure of SAS data analysis software (Cary, NC, USA). Post hoc comparison between different individual means was performed by the use of Duncan's multiple range test at a 5% probability level.

3. Results and discussion

Coriander straw constitutes a crop residue in the cultivation of coriander fruits representing up to 80% of the crop yield, and will become increasingly available owing to the recent surge of interest in coriander vegetable oil from the food and cosmetic industry. With a view to the development of a sustainable coriander biorefinery, coriander straw fibers (CF) were applied as a reinforcement in thermoplastic composites with polypropylene (PP) or biobased low-density polyethylene (BioPE) as the matrix material. As a strategy to overcome fiber/matrix incompatibility, leading to poor mechanical properties and low durability of the composite materials, maleic anhydride-grafted copolymers, in particular maleic anhydride-grafted polypropylene (MAPP) and maleic anhydride-grafted polyethylene (MAPE), were added to the biocomposites as a coupling agent. A preliminary study (non-published results) served to evaluate the effectiveness of the maleated coupling agent inside the coriander fiber-reinforced biocomposites and showed that an addition of 10% of MAPP or MAPE relative to the coriander fiber weight was sufficient to attain good interfacial cohesion and was thus applied during the course of this study.

Aiming at the production of high-quality composite materials with good performance whilst ensuring the industrial relevance of the obtained results, the biocomposites were manufactured through twin-screw extrusion compounding and subsequent injection molding of the composite granules, with both processes operating in a continuous mode (Fig. 1). The thermal decomposition of the biocomposites was determined through thermogravimetric (TGA) analysis and is presented in Fig. 2. This reveals that the addition of coriander straw fibers results in a slight decrease of the temperature at which the biocomposites starts to degrade (from 260 to 220 °C for PP and from 280 to 260 °C for BioPE, with the addition of 40% of coriander fibers). However, this involves a minor difference and no degradation occurs before 200 °C, thus allowing their production through extrusion compounding and injection molding at 180 °C without the risk for degradation.

3.1. Morphological characteristics

The morphology and structural characteristics of the biocomposites were studied through the observation of fracture surfaces by the use of scanning electron microscopy (SEM) of samples fractured by impact loading. Fig. 3 presents SEM images of PP (top) and BioPE (bottom) composites with 40% of coriander fibers, while the images on the right side involve a magnification of a fiber structure. For both polymers, the SEM analyses demonstrate the effective role of the coupling agent. This can be seen as a proper embedding of the fiber in the polymer matrix, while the magnified images further show a rupture of the fiber structure through impact fracturing, rather than a disintegration of the fiber/

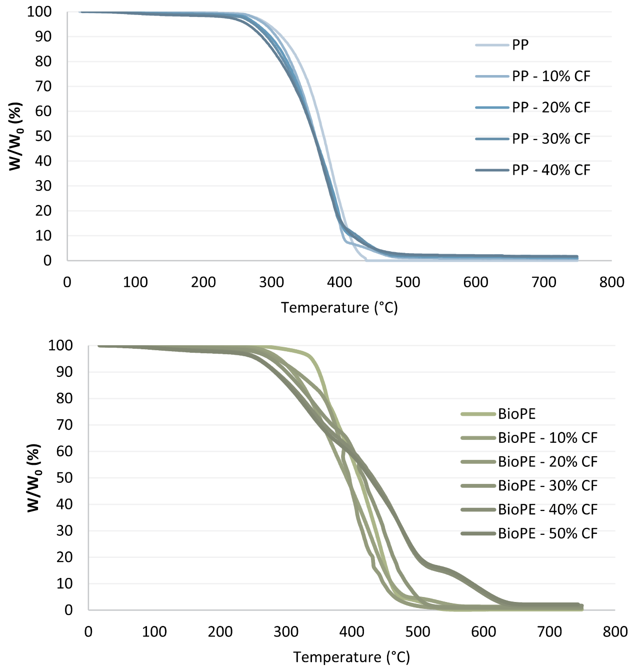

Fig. 2. Thermal degradation curves of coriander fiber-reinforced PP composites (top) and coriander fiber-reinforced BioPE composites (bottom). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

matrix interface, revealing the efficient stress transfer from the matrix to the fiber during impact loading.

3.2. Mechanical characteristics

Firstly, in terms of density of the composite materials, a progressive increase of the PP and the BioPE biocomposites is observed with an increased fiber loading, from 843 kg/m^3 for native PP to 939 kg/m^3 for PP with 30% of coriander fibers and up to 984 kg/m3 with 40% of coriander fibers, while BioPE composites showed a density of 854 kg/m^3 for the native polymer and 952 kg/m^3, 988 kg/m^3 and 1033 kg/m^3 for a fiber loading of 30, 40 and 50%, respectively. This increase in material density directly results from the higher density of the coriander straw fiber (1320 kg/m^3) as compared to the density of the PP (843 kg/m^3) or the BioPE (854 kg/m^3) polymer matrix.

Then, the mechanical performance of the coriander fiber-reinforced PP and BioPE composites was evaluated through their flexural, tensile, and impact properties (Fig. 4). When comparing the PP and BioPE polymer matrices, it is clear that PP renders more brittle composite materials as compared to BioPE, which is a low-density PE and imparts ductility to the composites. Next to this, for the native PP polymer and for all biocomposites, a difference between the flexural and tensile strengths was observed, the latter being consistently lower than the former. This may be explained through the fact that during tensile tests, the entire board specimen is subjected to the tensile stress and rupture proceeds through propagation of the largest defect of the sample. This is in contrast to flexural tests, where the maximal stress on the material sample is located at the opposite face of the area perpendicular to the central support. If the largest defect in the sample is not located at this central section, its influence on rupture and thus on the flexural strength of the material will be minimal. Therefore, the maximal stresses at break in tension will be lower as compared to those in flexion.

Regarding the tensile properties of the biocomposites, an increasing

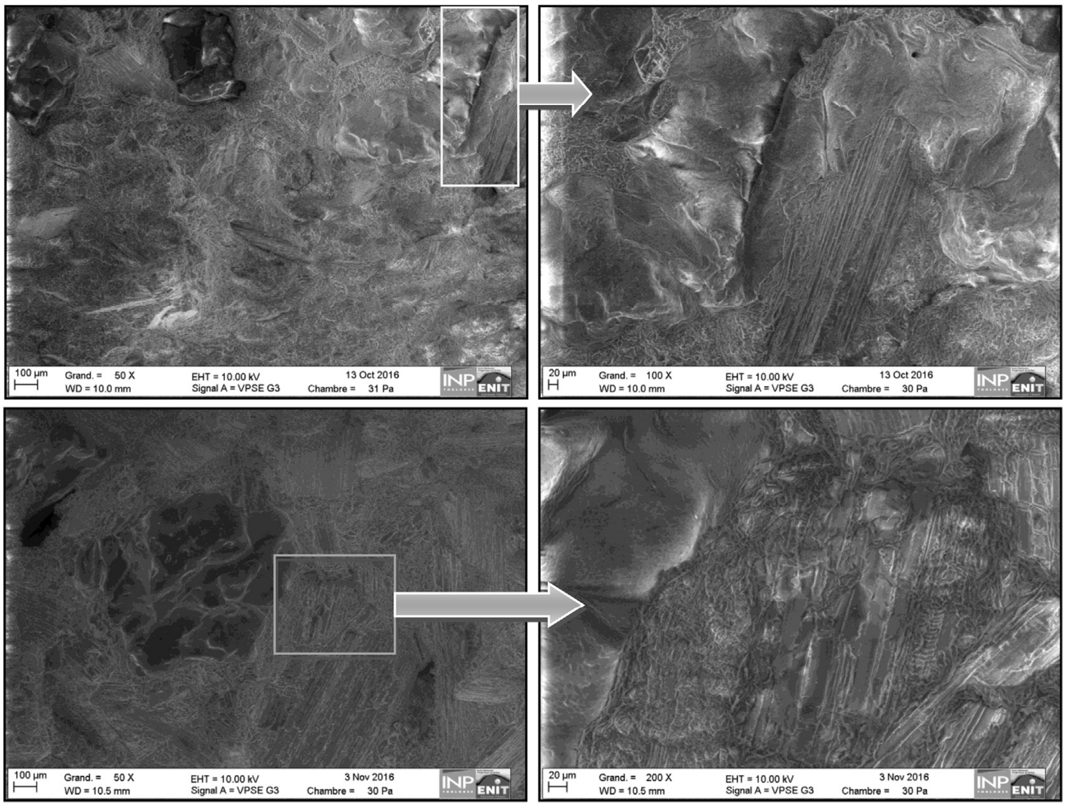

Fig. 3. SEM image (50 ×) and zoom (100 ×) of the fracture surface of a PP (top) and a BioPE (bottom) biocomposite with 40% of coriander fiber.

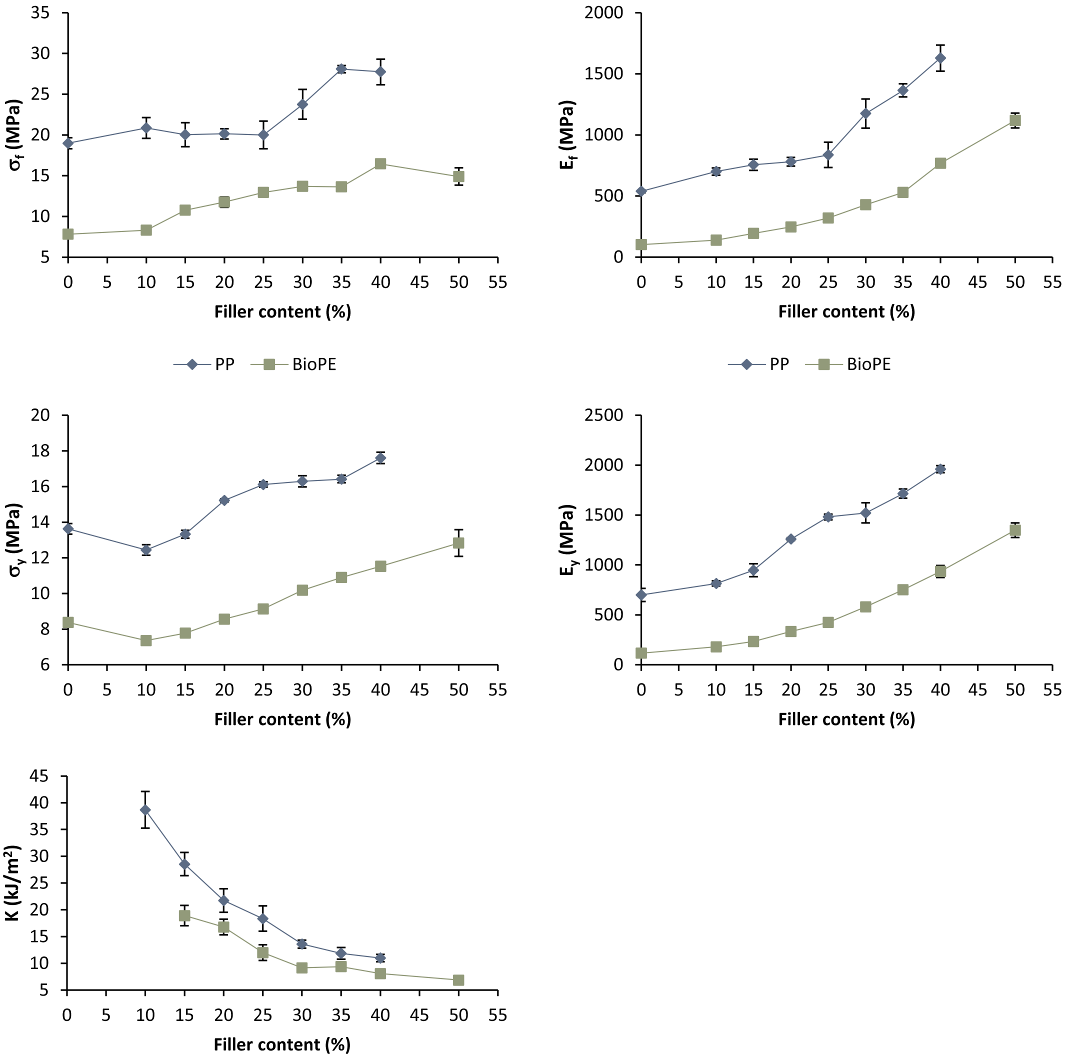

Fig. 4. Mechanical properties of coriander fiber-reinforced PP and BioPE composites as a function of the filler content. σ_f, flexural strength (MPa); E_f, modulus of elasticity (MPa); σ_y, tensile strength (MPa); E_y, Young's modulus (MPa); K, impact resilience (kJ/m^2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

amount of coriander fiber leads to an increased tensile strength and Young's modulus for both polymer matrices and thus to more rigid materials with an improved resistance to tensile stress. This trend holds for high fiber contents of up to 40% for PP and up to 50% for BioPE, resulting in a net increase of the tensile strength of 47 and 56%, respectively, and a 3- and 12-fold increase of the Young's modulus, respectively, which demonstrates the effectiveness of the maleated coupling agent (Fig. 4). The latter ensures a strong fiber/matrix interaction and as such, prevents the agglomeration of fiber particles in the case of high fiber loadings which would otherwise create weak spots within the material sensitive to fracture. The reinforcing effect of the coriander fibers further manifests in the flexural properties of the biocomposites. An increasing material stiffness, represented by an increasing flexural modulus, is observed for both polymer matrices with an increasing fiber content. However, regarding the flexural strength, this property seems to reach a maximum value around a fiber content of 40%, resulting in a strength of 27.7 and 16.5 MPa for a PP and a BioPE matrix, respectively, and representing a 46 and 112% increase as compared to the native polymer matrix.

For the purpose of comparison, materials from a PP biocomposite formulation with 25% of coriander fibers, but without the addition of the coupling agent (PP(75)/CF(25)), were tested for their mechanical properties and displayed a flexural strength (σ_f) of 15.5 ± 0.8 MPa and a tensile strength (σ_y) of 6.1 ± 1.4 MPa. These values are significantly lower than the ones for the PP composite materials including the coupling agent (20 and 16 MPa for σ_f and σ_y, respectively; Fig. 4) and even for the native PP polymer materials (19 and 12 MPa for σ_f and σ_y, respectively; Fig. 4), thus illustrating the importance of the coupling agent and its role in interfacial bonding. While natural fiber reinforcements improve the flexural and tensile properties of thermoplastic composites, they typically lead to a reduced impact strength, which is commonly reported as one of the major disadvantages of natural fibers as compared to synthetic reinforcements [1]. This negative effect on the impact resistance was also observed for the coriander fiber-reinforced PP and BioPE composites from this study, where the incorporation of 30% of coriander straw fibers results in a decrease of the impact resilience (K) of 83% for PP composites, as compared to the neat matrix. As such, the PP and BioPE biocomposites show a relatively moderate impact resistance ranging between 22 and 11 kJ/m^2 (PP) and between 17 and 7 kJ/m^2 (BioPE) when at least 20% of fibers are added. Depending on the anticipated application, a careful balancing may be made between the flexural and tensile properties and the impact properties through a variation of the reinforcing fiber content.

Aiming at the evaluation of coriander straw fiber as a reinforcement in thermoplastic composite materials while excluding the interfering factor of the quality of the native polymer matrix, an extensive

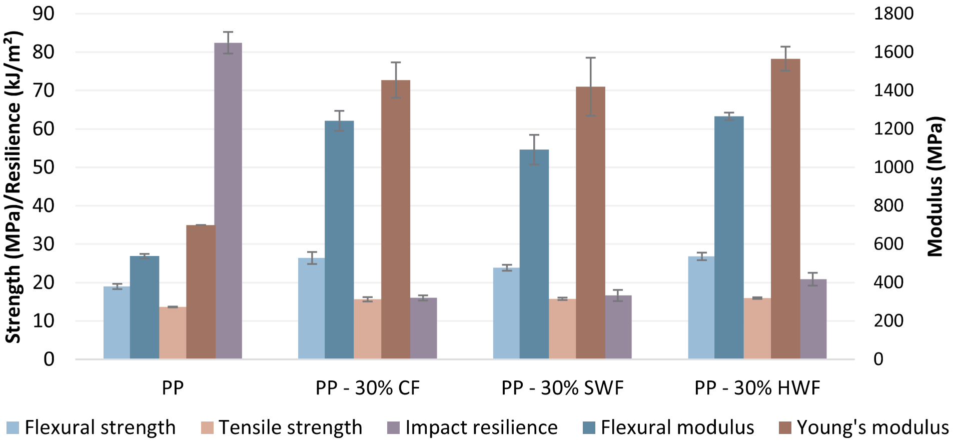

Fig. 5. Comparison of the mechanical properties of PP composites reinforced with coriander straw, softwood, and hardwood fibers. CF, coriander straw fiber; SWF, softwood fiber; HWF, hardwood fiber. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

comparison of coriander fiber and two types of commercial wood fibers was made through the production and characterization of 30% fiber-reinforced PP biocomposites using the same matrix materials and manufacturing processes, including both twin-screw extrusion and injection molding. Furthermore, as the wood fibers consisted of commercial grades and thus showed a specific particle size distribution, the coriander straw fibers were screened in order to near the particle size of the wood fibers and as such, minimize the impact of fiber size on the composites' performance. Then, a true evaluation of the industrial feasibility of the use of coriander straw in biocomposites was possible. The mechanical properties of the native PP matrix and the manufactured biocomposites are presented in Fig. 5. From this, it can be stated that the PP composite materials containing coriander fibers compare well to those containing wood fibers in terms of mechanical properties, with a tensile strength around 16 MPa and bending strengths ranging between 24 and 28 MPa. In terms of the impact strength, however, hardwood fibers tend to outperform coriander fibers (19 vs. 15 kJ/m^2), which is owing to their inherent structural characteristics and high cellulose content [29,30].

3.3. Durability

Durability presents a material characteristic of key importance as it largely dictates the service life of the product. The durability of the coriander fiber-reinforced thermoplastic composite materials from this study and the impact of the presence of coriander straw fibers was assessed through accelerated UV and hygrothermal aging. This consisted of exposing the materials for 3 weeks to UV irradiation and/or cyclic aging comprising heat, cold and humidity. The mechanical performance after different accelerated ageing conditions of the PP and BioPE composites, including the native matrix materials and 30% fiber-filled biocomposites, are shown in Fig. 6.

Hygrothermal and/or UV exposure exerted a minor impact on the material density. This effect was mainly observed for the native polymer materials, with PP and BioPE showing an increase of 3 and 5% to 856 ± 6 and 898 ± 8 kg/m^3, respectively, after hygrothermal and UV aging. This could result from oxidation reactions of the polymer, occurring through free radicals and catalyzed by UV radiation and heat [31]. The increase in density for the fiber-filled composites was negligible, which further reveals that moisture absorption by the lignocellulosic fibers was insignificant. When considering the flexural properties, a reinforcing effect is seen after aging for the 30% filled biocomposites, while this effect was much less important (BioPE) or even absent (PP) for the native matrix materials (Fig. 6). The flexural strength of 30% PP biocomposites increased significantly by 36%, reaching 32 MPa, after UV exposure, while the native matrix polymer showed a decreased (−25%) flexural strength of 14 MPa. At the same time, the flexural modulus was found to increase after climatic aging of the biocomposites, illustrating rigidification of the composites. This phenomenon has also been reported for date palm fiber/PP composites and may be explained through photo- and/or thermo-oxidation of the PP/PE polymer, resulting in chain scissions and thus, a reduced molecular weight, and in the formation of carbonyl groups [31,32]. While the reduced chain length results in slightly more rigid materials, it is detrimental in terms of mechanical strength. However, as interfacial adhesion plays a crucial role in mechanical performance, the reinforcing effect of aging may be attributed to a stronger fiber/matrix interaction owing to the newly formed carbonyl groups. Furthermore, crosslinking reactions between the reactive matrix polymer and the lignin fraction may occur, contributing to a strong adhesion and an improvement of the mechanical strength properties [7,31].

Regarding the tensile properties, it is important to take into account the different regions of the composite materials affected by flexural and tensile testing. While flexural properties are mainly dictated by the surface properties of the tested materials, tensile properties are dominated by their inner core [33]. At the same time, UV radiation mainly impacts the outer surface of the composites and thus, the flexural properties. Extensive crosslinking reactions between the fiber and the matrix may in that case not occur in the inner core of the biocomposites, and a relatively minor aging effect is observed for the tensile strength of the fiber-reinforced composites (Fig. 6). Nevertheless, when compared to the neat matrix material, the presence of the coriander fibers exerts a positive influence on this account, which might result from different factors. Firstly, the incorporation of fibers leads to substantial darkening of the materials, which could provide protection against UV irradiation. Next to this, certain compounds from the lignocellulosic straw material, e.g. lignins, may act as natural antioxidants, thereby limiting oxidation processes through radical scavenging [1].

In terms of the Young's modulus, important negative effects of −23 to −31% and −13 to −27% may be observed from aging for the 30% fiber-filled PP and BioPE composites, respectively. Even though this increase in ductility seems to result in large part from the presence of the fibers, it must be kept in mind that these reinforced biocomposites already show much greater rigidity as compared to the native polymer matrices. While the rigidifying effect of polymer chain scissions will be much less important in the inner core of the material, the fibers might have further reduced this effect by limiting oxidation. Finally, the impact resistance was found to decrease by 13% through combined hygrothermal and UV aging for 30% PP biocomposites, while it increased by 15% in the case of BioPE biocomposites. Here, again, the competing effects of polymer degradation and enhanced fiber/matrix interactions

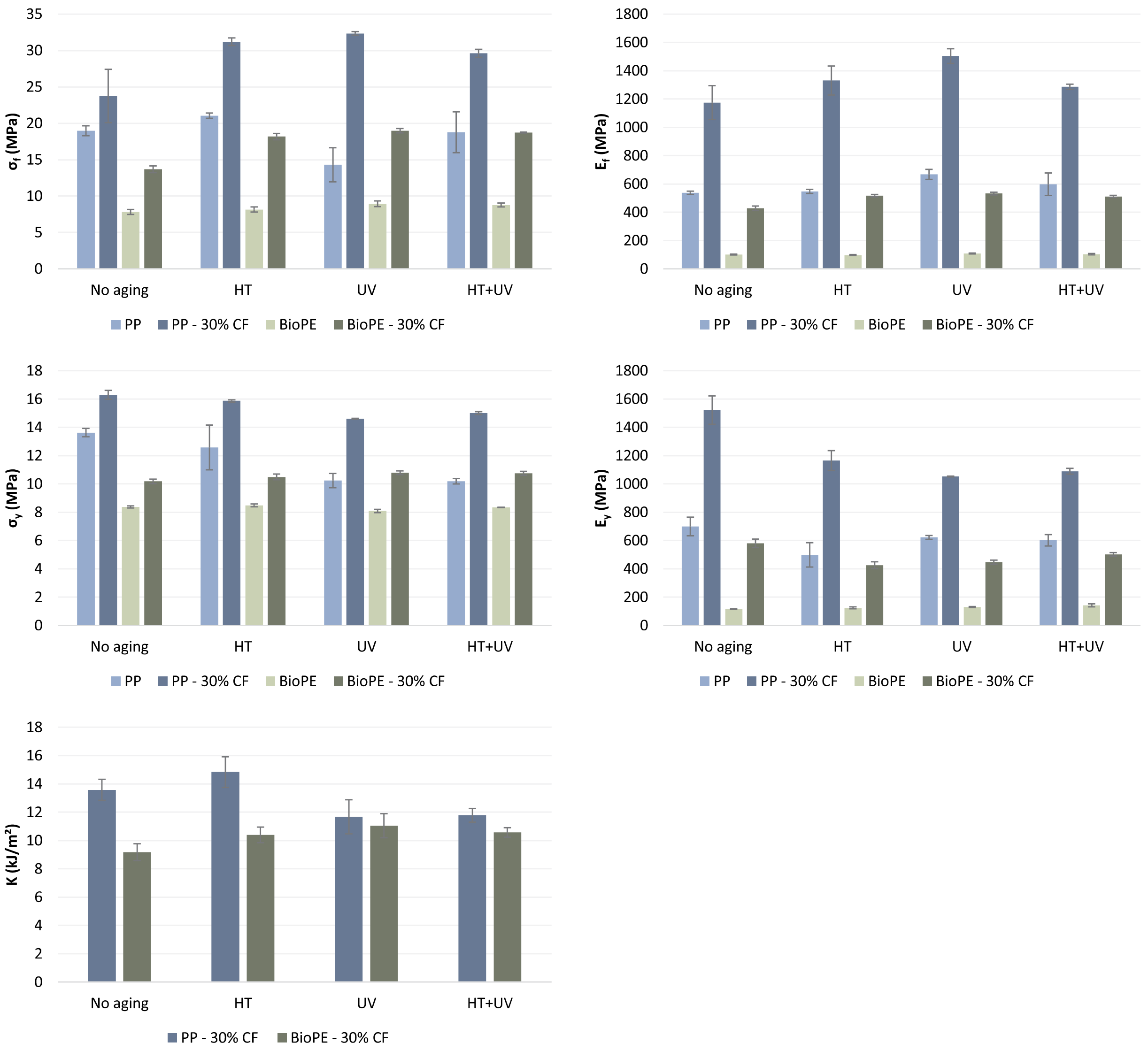

Fig. 6. Mechanical properties of coriander fiber-reinforced PP and BioPE composites after hygrothermal and/or UV exposure. σ_f, flexural strength (MPa); E_f, modulus of elasticity (MPa); σ_y, tensile strength (MPa); E_y, Young's modulus (MPa); K, impact resilience (kJ/m2). HT, hygrothermal exposure; UV, UV radiation exposure; HT + UV, combined hygrothermal and UV radiation exposure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

may determine the net resulting influence of aging on the impact resilience of the biocomposite materials.

3.4. Recycling potential

Efficient waste management strategies have become of major importance as the widespread use of plastics is deeply entrenched in society, and environmental concerns on plastic accumulation and the depletion of fossil resources are dominating current political agendas. In this regard, recycling could present a key solution for the end of life phase of plastic materials and has been shown highly beneficial in terms of sustainability and economics [9]. Nevertheless, recycling inevitably brings about a certain degree of thermomechanical degradation of both the matrix and the reinforcing fiber material through consecutive reprocessing cycles [11]. Therefore, the impact of 5 successive cycles of grinding and injection molding, was evaluated on the mechanical performance of the native PP/BioPE matrix materials and the corresponding 40% coriander fiber-reinforced biocomposites (Fig. 7).

Several different phenomena affecting the structural integrity of the composites occur during reprocessing. This includes a decrease in fiber length and, consequently, the fiber aspect ratio (i.e. the ratio of the fiber length to the fiber width), due to the breakage of fibers under the high shearing and elongation forces associated with high temperature and pressure injection molding [12]. Also, degradation of the maleated coupling agent and the polymer matrix occurs, resulting in a significant decrease in molecular weight caused by random chain scissions in the polymer backbone [34]. The latter is clearly demonstrated in Fig. 7 by the flexural and tensile properties of the virgin PP and BioPE matrix materials, showing a significant decline with additional reprocessing cycles, except for the tensile properties of the PP matrix, whose changes were negligible. As an example, the flexural strength of virgin BioPE decreased by 5%, from 7.8 to 7.4 MPa, after 2 cycles and by more than 10%, to 7 MPa, after 5 consecutive cycles.

Regarding the 40% fiber-reinforced composites, the results are less straightforward. The tensile and flexural properties of the reinforced composites seem to show an increasing trend within a limited number of cycles, after which they tend to decrease. This phenomenon has been reported by several studies and can be explained by the simultaneous occurrence of fiber fibrillation and an enhanced dispersion of the shorter fibers in the polymer matrix, on the one hand, and degradation

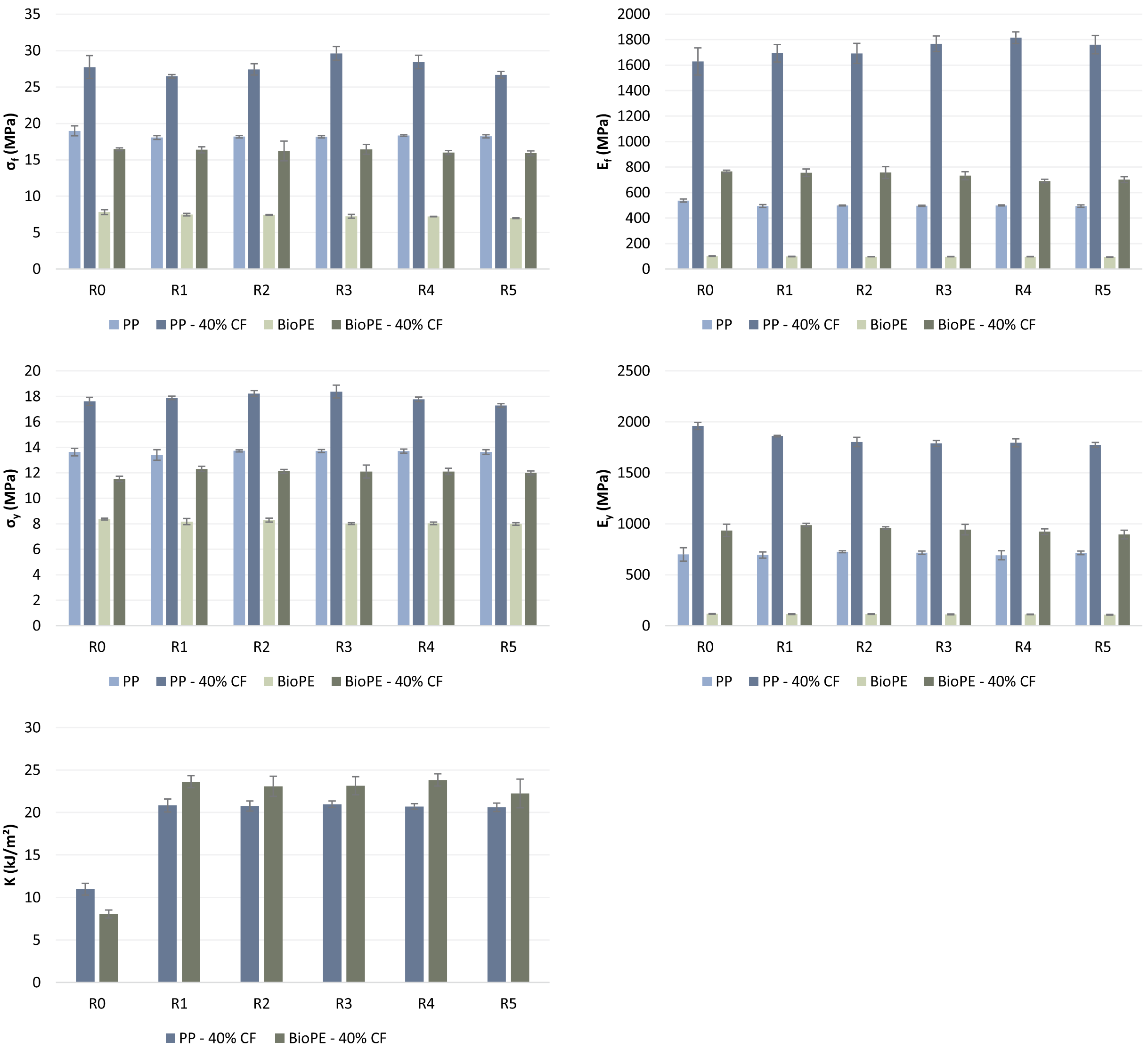

Fig. 7. Mechanical properties of recycled coriander fiber-reinforced PP and BioPE composites. σ_f, flexural strength (MPa); E_f, modulus of elasticity (MPa); σ_y, tensile strength (MPa); E_y, Young's modulus (MPa); K, impact resilience (kJ/m2). R0 to R5 represents the reprocessing cycle, with R0 the original composite materials. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of the fiber and the matrix, on the other hand [34,35]. While the former seems to show an overriding influence within a low extent of reprocessing, the latter becomes predominant with an increasing number of cycles. In general, however, the changes in tensile and flexural strength are rather unimportant, never representing more than 4%, and the coriander fiber-reinforced thermoplastic biocomposites show good retention of mechanical performance throughout at least 5 reprocessing cycles, indicating their satisfactory potential for recycling.

Regarding the impact resilience of the coriander fiber-reinforced composites, a considerable increase is observed immediately after the first reprocessing and persists for up to 5 cycles. For the PP biocomposites, an increase of around 90% is observed, attaining a resilience of 21 kJ/m^2, while for BioPE biocomposites, the impact resilience increased by almost 200% and reached values over 23 kJ/m^2 (Fig. 7). An increase in impact strength with recycling has been reported in previous studies, albeit to a lesser extent, and was attributed to the reduction of the fiber length, rendering the materials more ductile, and to the degradation of the maleated coupling agent [11,36,37]. The former is confirmed by a decrease in the Young's modulus (Fig. 7), while in terms of the latter, Bourmaud et al. [36] argue that due to deterioration of the interfacial bonding between the fiber and the matrix, caused by the degradation of MAPP, the shortened fibers easily debond from the matrix material under loading, inducing an increase in the energy that can be absorbed by the composite at failure.

Physical appearance presents an important factor for consumer materials and off-colors or color inconsistencies could lead to issues with their marketability. This should be taken into account when considering the use of recycled composites in certain applications. The color characteristics of the recycled biocomposites were determined by colorimetry and expressed in the CIELAB color space. Firstly, these analyses revealed the distinctly darker color of the 40% fiber-filled composites, as compared to the native matrices, by a substantially lower L^* value (38.6 ± 0.6 vs. 80.6 ± 0.1 for PP and 37.1 ± 0.5 vs. 72.5 ± 0.1 for BioPE). Further, reprocessing was shown to result in darkening of the materials and this effect is observed for both the fiber-reinforced biocomposites and the virgin matrices. In the case of the PP composites, the L^* value decreased to 78.2 ± 0.1 and to 32.5 ± 0.4 after 5 reprocessing cycles for the native PP matrix and the 40% filled composites, respectively. Similar results were found for the BioPE composites, with 5 reprocessing cycles resulting in an L^* value of 70.3 ± 0.1 and 32.3 ± 0.1 for the native BioPE and the 40% filled composite material, respectively. This was most likely caused by thermal degradation of the lignocellulosic fibers as well as the thermoplastic matrices, resulting in the formation of dark oxidation

Table 2
Cost structure of coriander fiber- or wood fiber-reinforced PP and BioPE composite granules.

	Granule cost (€/kg)	Matrix cost fraction (%)	Fiber cost fraction (%)	Coupling agent cost fraction (%)
PP(1 0 0)	1.27	98.7	–	–
PP(95)/MAPP(5)	1.34	92.5	–	6.2
PP(89)/MAPP(1)/CF(10)	1.22	91.1	0.7	6.8
PP(83.5)/MAPP (1.5)/CF(15)	1.20	87.1	1.1	10.5
PP(78)/MAPP(2)/CF(20)	1.18	82.9	1.5	14.2
PP(72.5)/MAPP(2.5)/CF(25)	1.15	78.6	2.0	18.1
PP(67)/MAPP(3)/CF(30)	1.13	74.0	2.4	22.1
PP(61.5)/MAPP(3.5)/CF(35)	1.11	69.3	2.8	26.4
PP(56)/MAPP(4)/CF(40)	1.09	64.5	3.3	30.8
BioPE(1 0 0)	2.51	99.6	–	–
BioPE(95)/MAPP(5)	2.56	96.8	–	2.8
BioPE(89)/MAPE(1)/CF(10)	2.32	96.0	0.4	3.1
BioPE(83.5)/MAPE(1.5)/CF(15)	2.22	94.0	0.6	4.9
BioPE(78)/MAPE(2)/CF(20)	2.12	91.9	0.9	6.8
BioPE(72.5)/MAPE(2.5)/CF(25)	2.03	89.5	1.1	9.0
BioPE(67)/MAPE(3)/CF(30)	1.93	86.8	1.4	11.3
BioPE(61.5)/MAPE(3.5)/CF(35)	1.83	83.9	1.7	13.9
BioPE(56)/MAPE(4)/CF(40)	1.74	80.6	2.1	16.7
BioPE(45)/MAPE(5)/CF(50)	1.54	72.9	2.9	23.5
PP(68.5)/MAPP(1.5)/CF(30)	1.03	83.4	2.6	12.2
PP(68.5)/MAPP(1.5)/WF(30)	1.44	64.0	25.2	9.4
PP(68.5)/MAPP(1.5)/WF(30)[a]	1.29	72.4	10.6	15.4

[a] Reduced cost of wood fiber at high purchasing volumes (> 6 tonnes).

products [7,38]. The discoloration was more extensive in the case of the 40% fiber composites than for the native matrices and may further be quantified by the use of ΔE^*. Mahy et al. [39] have proposed a JND (just noticeable difference) of 2.3 ΔE^* units, which would represent a color difference that is distinctively visible by the naked eye. As such, the 40% fiber-reinforced PP and BioPE biocomposites would be visibly different in terms of color after 2 reprocessing cycles, showing an L^* value of 35.0 ± 0.1 and 34.9 ± 0.2, respectively, leading to a ΔE^* of 4.6 and 3.4 units, respectively, which should be kept in mind when considering different applications, e.g. consumer packaging.

3.5. Cost structure

One of the main drivers for the use of natural fibers, as opposed to synthetic alternatives, consists of the associated cost reductions. The incorporation of coriander fibers, costing only 0.09 €/kg, could provide significant economic benefits as compared to synthetic reinforcements, e.g. E-glass fibers which cost around 2.65 €/kg [40]. The cost structure of the PP and BioPE composite granules with varying fiber content is presented in Table 2. The energy consumption of the compounding process was always relatively low (between 200 and 213 kWh/kg for PP composites and between 119 and 136 kWh/kg for BioPE composites), leading to a low production cost and a fraction of the total cost (excluding transportation and personnel costs) represented by extrusion compounding of below 1.5% for PP and below 0.7% for BioPE composites.

When incorporating 40% of coriander fiber, the total cost of the granules decreases by 14% (from 1.27 to 1.09 €/kg) for PP biocomposites and by 31% (from 2.51 to 1.74 €/kg) for BioPE. In the case of BioPE, the production of biocomposites with 50% of coriander fiber was possible and these materials show an attractive granule cost of only 1.54 €/kg. As an interesting side note, this cost approaches the cost of petroleum derived LDPE (1.3–1.5 €/kg) [41]. Thus, while the relatively high price of biobased PE is one of its main disadvantages and limits its wide industrial implementation, the addition of coriander straw to produce fully biobased (except for MAPE) “green composites” not only provides substantial reinforcement, but also results in a more favorable cost structure of the product.

The relatively modest cost reduction of the biocomposites, especially in the case of PP, can be attributed to the addition of the maleated coupling agent, which is the most expensive component of the composites (8.35 €/kg and 7.25 €/kg for MAPP and MAPE, respectively). As such, it presents an important cost factor, even if it is added in relatively small amounts. Indeed, when looking at Table 2, the coupling agent represents more than 30% of the total cost of the 40% coriander fiber-reinforced PP composites. Therefore, in the interests of economic feasibility, 30% fiber-filled PP biocomposites with 5% of MAPP (wt% relative to the fiber content), rather than 10%, were produced and evaluated. Regarding the mechanical performance properties of the composite materials, Fig. 5 shows that these are well maintained with a reduction of the amount of MAPP, except for a slight decrease in the bending modulus, which reveals that 5% of MAPP is sufficient to ensure adequate fiber/matrix adhesion. This adaptation resulted in a significant cost reduction of 9% of the produced composite granules, from 1.13 to 1.03 €/kg (Table 2).

The use of coriander straw (0.09 €/kg) rather than softwood or hardwood fibers (1.12 €/kg) would entail a 28% decrease in the cost of PP biocomposite granules with 30% of fibers. Even with a reduced cost of the wood fibers of 0.61 €/kg, rather than 1.12 €/kg, which holds for large purchasing volumes of over 6 tonnes, replacing the wood fibers with coriander fibers would still bring a 20% cost saving, from 1.29 to 1.03 €/kg (Table 2). Replacing wood fibers with coriander straw as a reinforcement in thermoplastic composites could thus be interesting from an economic point of view. Furthermore, it could bring substantial environmental benefits given the fact that coriander straw constitutes a crop residue, thus avoiding deforestation and the competition for agricultural land use with food production, which often presents an issue for fiber crops such as jute or flax. The coriander fiber-reinforced thermoplastic composite materials could then present a more sustainable and cost-effective solution for applications in the automotive industry, in the construction industry as non-structural materials, e.g. for door and window frames, or for sports equipment. Alternatively, they could serve for the production of materials with a core-shell structure, where the coriander-based biocomposites would make up the inner core and a synthetic fiber-reinforced composite would form a strong shell with specific target properties, e.g. as a moisture barrier, resulting in a fine-tuned material with reduced cost.

4. Conclusion

This study aimed to evaluate coriander straw fibers as a reinforcement in thermoplastic composites. Polypropylene (PP) and biobased low-density polyethylene (BioPE) biocomposites with fiber contents up to 40 and 50%, respectively, were successfully produced in a continuous mode through twin-screw extrusion compounding and injection molding. The resulting materials showed adequate mechanical performance, with a flexural strength of 28 and 16 MPa and a tensile strength of 17 and 12 MPa for PP and BioPE composites, respectively, with 40% of coriander fiber. As compared to the native polymer matrix, the addition of coriander straw fibers significantly reinforced the materials, with a 50% increase in flexural and tensile properties with a 40% fiber loading, while the flexural strength of the BioPE biocomposites increased more than twofold in that case. However, the impact resistance was found to decrease with an increasing fiber content. Careful balancing of the desired material properties, depending on the intended application, may thus be carried out through varying the amount of coriander fiber reinforcement. Furthermore, the reinforcing capacity of the coriander straw was shown comparable to that of commercial grade softwood and hardwood fibers. The manufactured biocomposites also showed excellent durability through good retention of their mechanical performance after accelerated UV and/or hygrothermal aging. Additionally, their recycling potential was confirmed by the limited loss in mechanical properties, below 10%, throughout five successive reprocessing cycles, while the impact strength was substantially enhanced by almost 90% (PP) or 200% (BioPE). As an increasingly abundant crop residue, coriander straw and the reinforced thermoplastic composites show a favorable cost structure, leading to a 28% reduction in the 30% filled composite granule cost as compared to commercial wood fibers. Therefore, coriander straw fiber shows significant industrial potential as a replacement for synthetic or wood based reinforcements in thermoplastic composites, while providing important recycling possibilities. As such, it could provide notable environmental and economic benefits, which are of key significance in the current pursuit for sustainability.

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