

Sustainable biocomposites based on Mater-Bi and grape pomace for a circular economy: Performance evaluation and degradation in soil

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ABSTRACT

Biodegradable polymers often exhibit inferior properties and higher cost compared to their fossil-derived counterparts. The addition of plant waste and by-products can improve their performances, providing in the meantime functional activity and reducing their cost. In this work, we summarize the preparation of different biocomposites (BioCs) incorporating two diverse amounts (10 % and 20 %) of grape pomace (GP) in a Mater-Bi (MB) sample. GP, MB as well as BioCs were fully characterized. The influence of addition of GP on the properties and degradation in soil of the biocomposites was evaluated in comparison with the neat MB. However, natural antioxidants and other active compounds from GP could be sensitive to temperature. Thus, GP and MB underwent heat treatment at 180 °C to simulate and induce possible degradation during BioCs processing. GP analysis (particle size 50 μm) showed only a slight decrease of antioxidant potency, despite the heat treatment simulating the BioCs processing. ¹H NMR of the MB soluble fraction in CDCl₃ displayed the presence of two polymeric components: polylactide (PLA) and poly(butylene adipate-co-butylene terephthalate) (PBAT). Introduction of GP in the polymer matrix induced a proportional increase of antioxidant property in the BioCs as well as in complex viscosity at low frequencies. Moreover, a slight increase in the elastic modulus was observed with increasing the crystallinity of the samples. Degradation rate in soil, monitored by weight loss, increased with filler content and time. Moreover, NMR showed that, in the recovered sample after 45 days, the composition of PBAT changed, with the terephthalic percentage increased.

1. Introduction

Every year, millions of tons of oil-derived plastics enter marine and terrestrial ecosystems, harming living organisms, polluting water sources, and contributing to the long-term accumulation of waste that takes years to degrade [1–4]. To tackle this environmental crisis, despite latest legislations on recyclability from the European community [5], in recent years there has been increasing interest in adopting more sustainable solutions, such as biodegradable polymers [6,7].

Nowadays, biodegradable polymers are a whole family of materials with different properties and applications [8]. They can be derived from

agro-sources, be synthesized by microorganisms or monomers, either bio-based or fossil-based [9]. When disposed in bioactive environments, under controlled conditions, biodegradable polymers are degraded by microorganisms, such as bacteria, fungi and algae, through the action of enzymes, and converted into biomass, CO₂ or CH₄, and water [10]. Nevertheless, the use of biodegradable polymers is often limited by their inferior properties and higher cost compared to their fossil-derived counterparts. Therefore, biodegradable polymer systems, such as composites and blends, in which the biodegradable polymeric matrix is associated with reinforcing fibers [11] and inorganic or organic [12] have gained more and more attention. In a similar way, plant waste and

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by-products can be useful to overcome the limits of biodegradable polymers, as they not only can improve performance, but also can provide in the meantime functional activity and reduce the overall cost of the material thus supplying cost-effective items.

Generally, degradation occurs to plastic materials during processing as well as the useful lifetime. Several environmental factors (e.g., sunlight UV radiation, oxygen, and heat) prompt and accelerate polymer degradation [13]. Additives, selected for a particular use and the predicted life prospect of the plastic items, limit or delay the degradation processes. Waste filler can provide “natural additives” and in the meantime increase the mechanical properties. However, they can also influence the polymer matrix biodegradability. In this scenario, grape pomace (GP) is increasingly attracting the interest of the scientific community both because it contains many plant constituents such as cellulose, hemicellulose, pectin and others [14,15], and because, according to recent reports, about 10–15 million tons of grape pomace are produced each year [16–18], leading to significant expenses for disposal and transportation. In addition, it is crucial to highlight that, if not managed properly, grape pomace can cause serious environmental damage and increase greenhouse gas emissions. Greenhouse gas emissions must be avoided in accordance with current legislation [19], to address growing environmental problems and promote sustainability.

Recently, the literature has reported several studies on the use of grape pomace in biodegradable polymer matrix. GP has been formulated with diverse biodegradable polymers and employed in different forms: as fillers after milling [20]; by using the solvent extract as a natural polyphenolic additive [21] or the solid residue after solvent extraction [22]. Growan et al. [23] improved the mechanical properties of bio-based poly(butylene succinate) (BioPBS) biocomposite containing 40 wt% grape pomaces. The addition of 3 wt% maleic anhydride-grafted BioPBS (MA-g-BioPBS) resulted in a significant increase in both flexural strength and impact strength. Bruna et al. [24] observed that the biocomposites (poly(lactic acid) (PLA)/GP) with the lowest GP content had better antimicrobial activity against *Escherichia coli* and *Listeria innocua*, while formulations with a high grape pomace content showed the highest antioxidant activity. However, a high temperature extrusion profile reduced the bioactivity of the materials due to GP degradation. Cerruti et al. [21] used an extract from winery waste as a natural additive for a Mater-Bi to improve its performance and tailor cost. They evaluated the effect of the extracted polyphenols on processability, mechanical properties, thermal stability and biodegradability. A decrease in melt viscosity in the modified Mater-Bi was showed. Tensile tests highlighted that the natural additive played a plasticizing effect on Mater-Bi. Moreover, the biodisintegration rate of loaded Mater-Bi decreased, thus suggesting that the polymer biodegradability was negatively influenced by the additive that acted as an antimicrobial agent. Ferri et al. [22] exploited extraction solid residues (between 5 and 20 % w/w) to prepare biocomposites based on a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) polymer. They found that the properties of the biocomposites until 20 % w/w were very similar to those of neat PHBV, thus allowing a reduction in the use of raw materials.

Although recent studies have explored the use of GP in biodegradable polymer matrix, to the best of our knowledge, no paper has investigated the antioxidant properties conferred on the material and the degradation of these biocomposites in soil, a crucial aspect for promoting a circular economy model.

Therefore, in this work, we summarize the preparation of different biocomposites (BioCs) incorporating two diverse amounts of GP, specifically 10 % and 20 %, within a Mater-Bi (MB) sample. Mater-Bi is one of the most common blends on the market. It is a family of polymers and blends partially based on TPS (Thermoplastic Starch) and is available in various chemical formulations depending on the components used [25–27]. However, with the aim of promoting a circular economy model and a closed-loop system, this paper examines how the addition of GP biowaste affects the properties of the biocomposites and their degradation process in soil, comparing the results with those obtained from

neat Mater-Bi. This study aims to evaluate the impact of GP on the characteristics and sustainability of the biocomposites, thus providing new insights into their environmental behavior and potential use into functional items, thereby minimizing environmental impact.

2. Experimental

2.1. Material

Mater-Bi® El51N0 (density: 1.23 g/cm³; melt flow index (MFI): 19 g/10 min (230 °C, 2.16 kg), melting temperature: 167 °C) was purchased by Novamont (NO, Italy), and GP, from cultivation on the Etna Mountain, were kindly provided by Al-Cantàra Srl (Randazzo, CT, Italy). All solvents and reagents were of high purity laboratory grade and used as received. Water and acetonitrile were acquired from Carlo Erba (MI, Italy), deuterated chloroform, caffeic acid, malvidin chloride, ellagic acid and quercetin from Sigma-Aldrich (MI, Italy), folin-ciocalteu reagent from Fluka (MI, Italy).

2.2. Preparation of grape pomace and biocomposites

The grape pomace was freeze-dried and milled. It was analyzed by scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Both the GP and MB samples underwent heat treatment at 180 °C (90 s in air) to simulate and induce possible degradation during BioCs processing. BioCs were prepared in a corotating twin-screw extruder (OMC, screw diameter = 19 mm, length/diameter ratio = 35 mm; temperature profile: 145–150–155–160–165–170–180 °C). Before the extrusion, MB was dried under vacuum at 60 °C for 4 h, while the filler at 80 °C overnight. The film samples were prepared by compression molding (180 °C, ~ 3 min).

2.3. Grape pomace and polyphenol analysis/screening

Dried and grinded grape pomace (~ 130 mg) and MB based biocomposites (~ 200 mg) were placed in a 10 mL vial and about 1 mL of a mixture 70–30 ETOH-H₂O was added. The suspension was kept overnight at room temperature, in the dark under vigorous and continuous stirring in the shaker (200 rpm). For each sample, it was considered an extractive duplicate. The resulting extract was then centrifuged at 3000 rpm (ALC PK 130 centrifuge, Milan Italy) for 10 min allowing recovering the supernatant solution. A small aliquot of this solution was filtered with PTFE filters (15 mm diameter, 0.45 μ pore size, Chemtek Analytica, Milan, Italy), put in a 2 mL amber vial, and freshly analyzed for the determination of the specialized secondary metabolites.

2.4. Characterization technique

2.4.1. Structural properties

Nuclear magnetic resonance experiments were performed at 27 °C in CDCl₃ containing 0.03 % v/v tetramethylsilane as an internal standard on an Agilent UNITYINOVA (Santa Clara, CA, USA) spectrometer operating at 500 MHz (¹H). Spectral width was 8012.8 Hz, acquisition time 4.089 s, delay between scans 4 s, number of points 65.536, and pulse width 45°. A gradient-enhanced COSY spectrum was acquired using the standard Agilent pulse sequence. FIDs were elaborated using the Mestre-Nova program (Mestrelab Research, Santiago de Compostela, Spain).

2.4.2. Rheological, mechanical and morphological properties

Viscosity was measured by An Ares G2 TA Instruments rotational rheometer with 25 mm plate and 1.5 mm gap. All the tests were performed at a temperature of 180 °C and in a frequency range of 0.1–100 rad/s with a strain 5 %. Tensile tests were carried out by an Instron universal testing machine mod. 3365 on rectangular specimens (length = 90 mm, width = 10 mm and thickness = 0.5 mm) according to ASTM

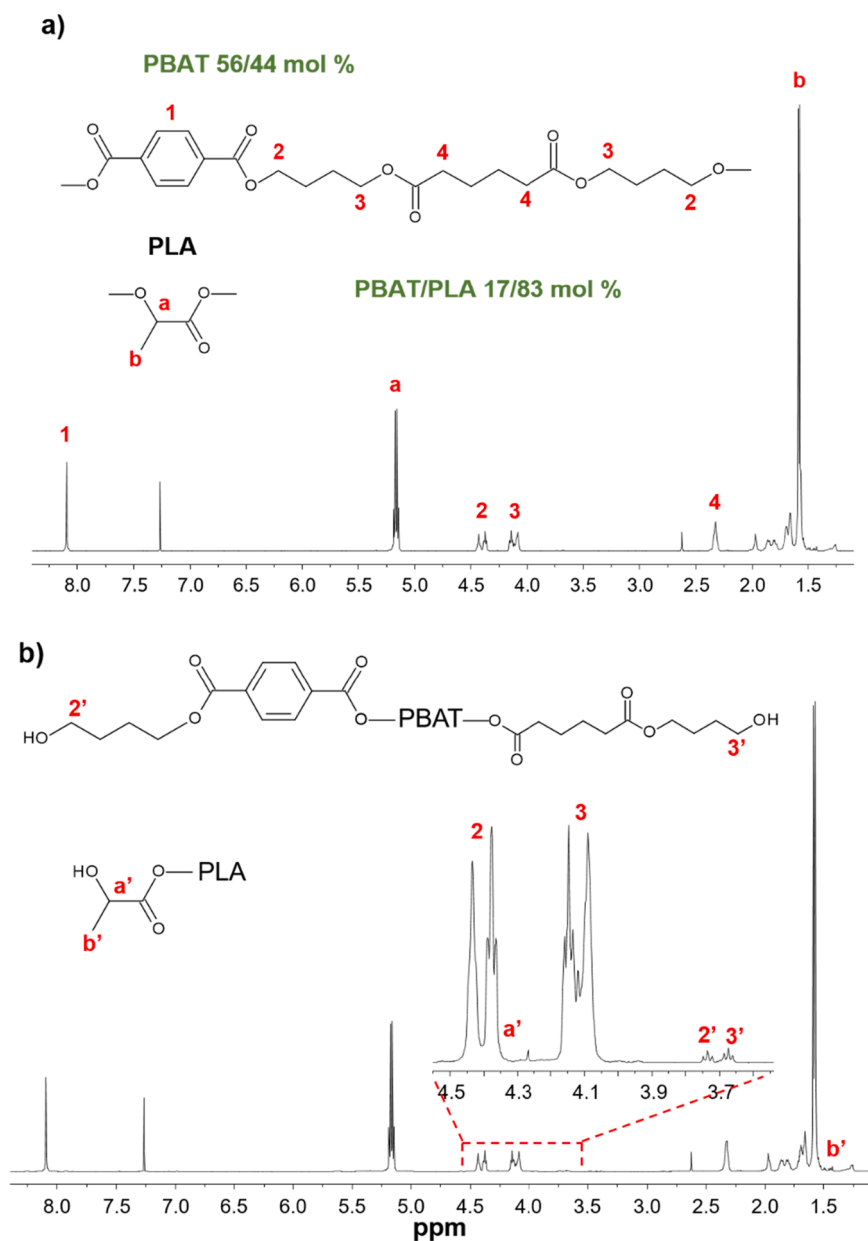


Fig. 1. (a) ¹H NMR spectrum of MB pellet sample and main peak assignments. (b) Expansion of ¹H NMR spectrum and assignments of end groups.

D638-14. The conditions of tests were rate = 1 mm/min until 3 % strain, then at 100 mm/min until failure. The tests were conducted on ten samples and the average values of 8 measurements with the respective standard deviations were then extrapolated. Dynamic mechanical thermal analysis (DMTA) was performed using a Metravib DMA 50 (Metravib, Limonest, France). Morphological analyses were carried out using a Quanta 200F scanning electron microscope (FEI Co., Hillsboro, OR, USA).

2.4.3. Thermal properties

Thermal analysis was carried out by differential scanning calorimetric (DSC) using a DSC-131 Setaram (Setaram, Hillsborough Township, NJ, USA). The amount of sample placed in the DSC aluminum pans was about 10 ± 2 mg, while the heating rate was 10 °C/min from 25 °C to 200 °C. The values were calculated as the average of four measurements. Thermogravimetric analyses (TGA) were performed using a thermogravimetric apparatus TGA Q500 (TA instruments, New Castle, DE, USA), using a platinum pan, under a nitrogen or air environment

(flow rate 60 ml/min), at a heating rate of 3 or 10 °C/min, from 50 °C to 700 °C. Sample weight was approximately 5 mg. The weight loss percentage and its derivate (DTG) were recorded as a function of temperature.

2.4.4. Identification and quantification of grape pomace biochemical markers via HPLC/DAD analyses

Chromatographic analyses were carried out on an Ultimate3000 UHPLC-focused instrument equipped with a binary high-pressure pump, a photodiode array detector, a thermostated column compartment and an automated sample injector (Thermo Fisher Scientific, Inc., Milan, Italy). Collected data were processed through a Chromeleon Chromatography Information Management System v. 6.80. Chromatographic runs were all carried out using a reverse-phase column (Gemini C18, 250×4.6 mm, 4.6 μm particle size, Phenomenex Italia s.r.l., Bologna, Italy) equipped with a guard column (Gemini C18 4×3.0 mm, 5 μm particle size, Phenomenex Italia s.r.l., Bologna, Italy). Components of the hydroalcoholic extracts of grape pomace were eluted using a gradient of B (2.5

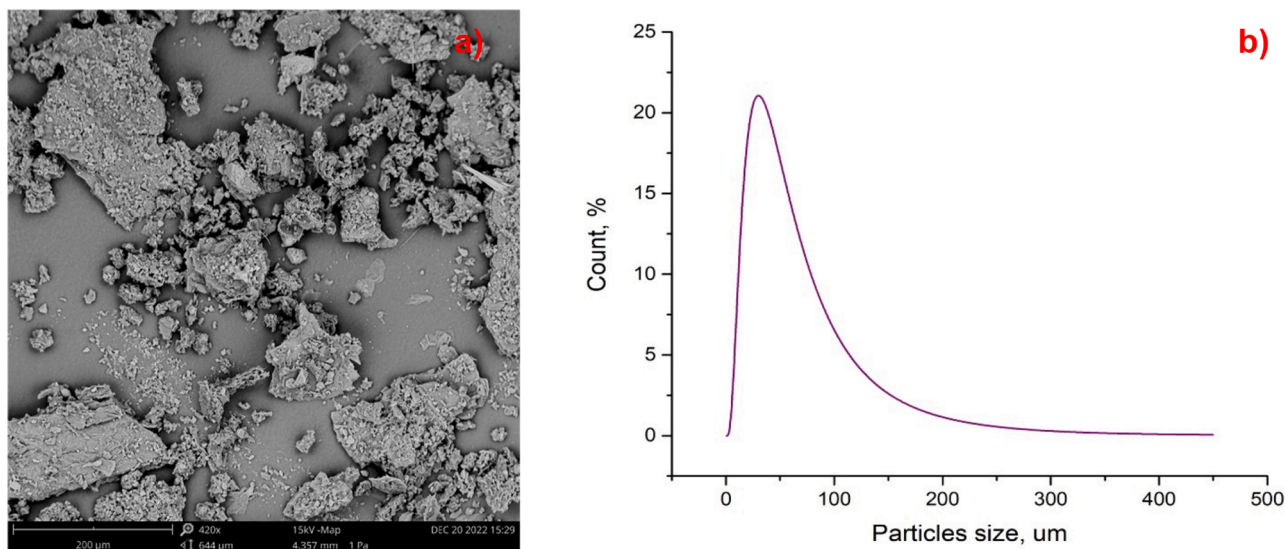


Fig. 2. (a) SEM images of grinded GP and (b) particle size distribution.

% formic acid in acetonitrile) in A (2.5 % formic acid in water): 0 min: 10 % B; 20 min: 35 % B; 25 min: 10 % B; then kept for other 7 min, 10 % B. The solvent flow rate was 1 mL/min, the temperature was kept at 25 °C, and the injector volume selected was 10 μL. The analysis was carried out at 280, 330, 350 and 520 nm, diagnostic wavelengths typically used for the identification of polyphenol metabolites. About 19 chromatographic peaks were detected belonging to the subclass of polyphenols flavonoids (F), hydroxycinnamic acids (HCA), anthocyanins (A) and ellagic acid derivatives (EAD). To quantify the metabolites, calibration curves were constructed using caffeic acid at 330 nm ($R^2 = 0.9999$), quercetin at 350 nm ($R^2 = 0.9992$), malvidin chloride at 520 nm ($R^2 = 0.9975$) and ellagic acid at 350 nm ($R^2 = 0.9745$).

2.4.5. Total polyphenols determination as tool to monitoring degradation of secondary metabolites after thermo-oxidative treatments

The Folin–Ciocalteu assay reported by Dewanto et al. [28] properly modified, was used to determine the total polyphenol content (TPC) of grape pomace and the 10 % and 20 % biocomposites MB-based. Briefly, 15 μL (40 mg/mL of vegetable matrix) of crude extract was added to 110 μL of water and 125 μL Folin–Ciocalteu reagent. After about five minutes, a 7 % sodium carbonate solution (1.25 mL) was added to this solution, obtaining 1.5 mL as total volume of incubation. After about 90 min of incubation in the shaker (170 rpm) at room temperature in the dark, the absorbance was measured at 765 nm using a UV-1601 PC UV–Visible spectrophotometer (Shimadzu, Milan, Italy). A calibration curve ($Y = 0.0583X + 0.0595$, $R^2 = 0.9785$) was constructed with gallic acid (stock solution concentration of 201 mM) by adding different aliquots (30, 40, 50, 75, and 120 μL). The results were expressed as mg of gallic acid equivalent/g of vegetable matrix (μg GAE/g of solid matrix).

2.4.6. Surface wettability

The surface wettability was measured at room temperature using a contact angle goniometer (OCA15EC, Dataphysics) on MB (thickness 290–390 μm) and BioCs (thickness 460–550 μm) before and after degradation in the soil. Static contact angle (SCA) values were determined by dropping 2 μL of water from a micro syringe onto the surfaces and analyzing the images taken by the connected video camera by software (SCA 20). To eliminate interference, the samples were previously equilibrated at 40 °C for 30 min and then SCA was measured. At least five measurements were carried out for each sample to ensure the repeatability of the experiments.

2.5. Evaluation of the degradability in soil

The soil burial test was carried out at 30.0 ± 0.1 °C, up to 45 days and degradation monitored through weight loss (WL). At least triplicate specimens of film samples were placed in darkened vessels containing a multi-layer substrate [29]. Filter paper was used as a positive control. Specimens with dimensions 2 cm × 2 cm were cut out of the prepared films (MB thickness 290–390 μm, BioCs thickness 460–550 μm, initial weight 150–200 mg, filter paper ~30 mg; PA114C Ohaus Pioneer Plus, $d = 0.1$ mg) and sandwiched between two layers of a mixture of milled perlite (70 g) and soil (200 g), moistened with 100 mL of distilled water. The bottom and top layers were filled with 60 g of perlite moistened with 120 mL of distilled water. Perlite was used for increasing the aeration of the soil and the amount of water retained. Samples were removed after regular intervals (15 days), brushed softly, washed with distilled water several times and dried under vacuum in the presence of P_2O_5 at room temperature, to constant weight [30]. The degree of degradation was evaluated by WL by using Eq. (1):

$$WL, \% = \frac{W_i - W_f}{W_i} \times 100 \quad (1)$$

where W_i is the initial weight of the sample and W_f is the weight after the established time.

3. Results and discussion

3.1. Mater-Bi and biowaste filler characterization

Structural and thermal characterization of MB pellet samples was carried out by NMR, DSC and TGA. 1H NMR of the soluble fraction in $CDCl_3$ showed the presence of two polymeric components: polylactide (PLA) and poly(butylene adipate-co-butylene terephthalate) (PBAT) (Fig. 1a). According to the literature [31], the methyl ($-CH_3$) and methenyl ($-CH=$) proton signals of PLA were found at $\delta = 1.58$ ppm and at $\delta = 5.17$ ppm. A gradient enhanced COSY spectrum allowed the assignment of the same moieties in the terminal lactic acid unit bearing the hydroxyl end group to the signals at $\delta = 1.49$ ppm and at $\delta = 4.35$ (Fig. 1b). According to Herrera et al. [32], PBAT was identified by the following resonances: at $\delta = 8.09$ ppm assigned to the aryl protons of PBAT; at $\delta = 4.40$ ppm assigned to the alpha protons of a butanediol monomer adjacent to a terephthalate monomer; at $\delta = 4.12$ ppm assigned to the alpha protons of a butanediol monomer adjacent to an adipate monomer; at $\delta = 2.33$ ppm assigned to the CH_2 linked to the

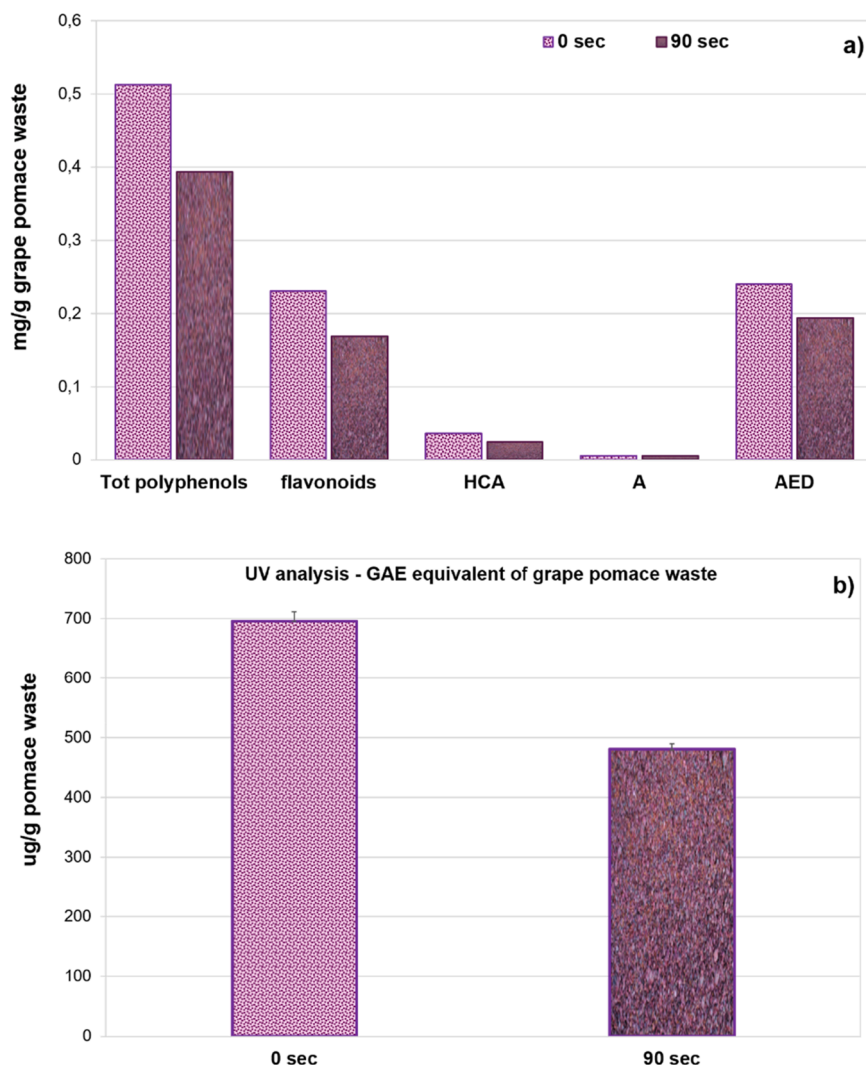


Fig. 3. (a) HPLC outcomes expressed as total content of polyphenols (line one) and divided by contribution of the subclass to which the metabolites belong (line two to five). (b) Total content of polyphenols in grape pomace determined by Folin-Ciocalteu assay and expressed by gallic acid equivalent.

carbonyl group in the adipate moiety. The signals between 2.00 and 1.62 ppm are due to the remaining protons of PBAT as detailed in Herrera et al. [32]. Finally, the small signals at $\delta = 3.74$ and 3.67 ppm were due to the alcoholic methylene protons of the terminal butanediol linked to the terephthalic and adipic moiety (Fig. 1b). The areas of peaks at $\delta = 4.40$ and 4.12 ppm were used to calculate the PBAT composition according to Eq. (2):

$$\text{Adipate mol, \%} = \frac{A_{4.12}}{A_{4.40} + A_{4.12}} \times 100 \quad (2)$$

where $A_{4.40}$ and $A_{4.12}$ are the area of signals at 4.40 and 4.12 ppm. The mol % composition of PBAT resulted to be 56 % adipate and 44 % terephthalate.

Eq. (3) was applied to calculate the mole percentage of PBAT and PLA in the soluble fraction of MB in CDCl_3 .

$$\text{PBAT, \% mol} = \frac{(A_2 + A_3)/4}{A_a + (A_2 + A_3)/4} \times 100 = 16.9 \quad (3)$$

where A_2 , A_3 , and A_a are the area of signals "2", "3", and "a" in the spectrum of Fig. 1a. The PBAT mol % in the PLA/PBAT mixture resulted to be 17 %, corresponding to 37 % in weight.

TGA and DTG recorded at 3 °C/min (Figure S1) highlighted several degradation steps, due to PLA and PBAT [33] and reasonably a small

amount of starch and an inorganic component.

Polyphenols and other active compounds from GP could be sensitive to temperature and undergo degradation during extrusion. Therefore, TGA in both air and nitrogen on GP, pretreated in oven at 90 °C, under vacuum for 1 h, was carried out. It showed good thermal stability and a starting degradation temperature at about 250 °C (Figure S2). The morphology and size distribution of the GP microparticles, freeze-dried and milled, were checked by SEM. The particles exhibit irregular shapes (Fig. 2a) and variable sizes ranging from a few microns to 200 μm (Fig. 2b). The biowaste filler is mainly composed of roundish aggregates, but platelet-like particles are also present showing a lack of homogeneity. Moreover, it is evident the presence of a rough surface that could improve the adhesion between the two phases.

Both MB and GP underwent heat treatment at 180 °C (90 s, in air) to simulate and induce possible degradation during BioCs processing. Hydroalcoholic soluble fractions extracted from GP heat treated (GP 90 s) and not (GP 0 s), employing EtOH-H₂O (70:30, v/v), were analyzed by HPLC-UV and UV. The crude hydroalcoholic extract from the grape pomace (0 s and 90 s), properly dried and grinded freshly, was analyzed by HPLC-UV to determine and quantify the secondary metabolites content in accordance with what has been previously reported in the literature by some of us [34]. For the detection of characteristic secondary metabolites, the analysis was carried out employing the wavelengths 280 nm for all UV active compounds, 330 nm for HCAs, 350 nm

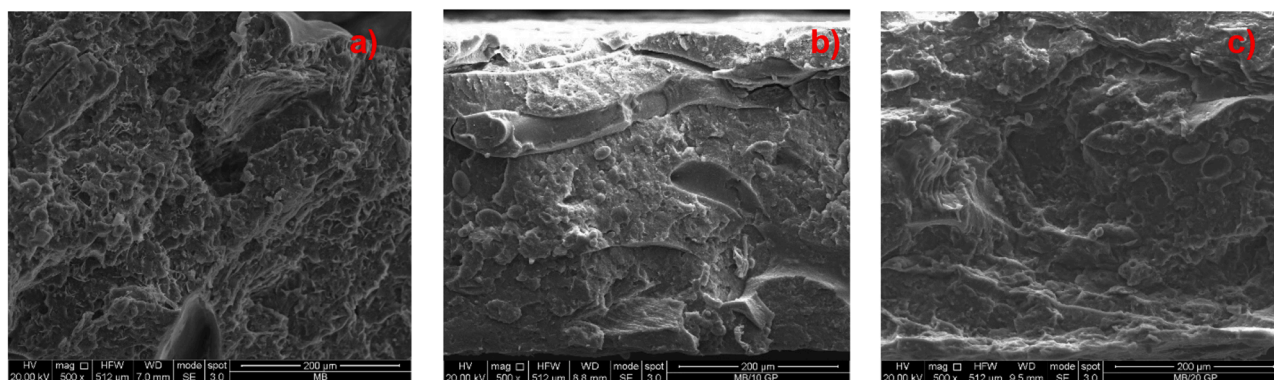


Fig. 4. SEM micrographs of fractured surface of (a) MB, and biocomposites with (b) 10 (MB 10 %) and (c) 20 % (MB 20 %) of GP.

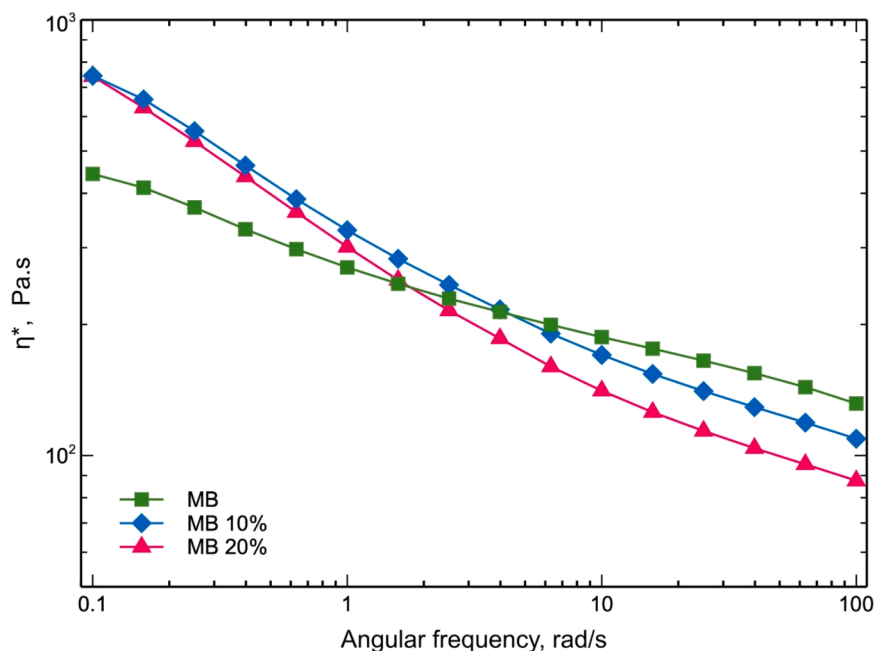


Fig. 5. Complex viscosity, η^* , curves as a function angular frequency of MaterBi and biocomposites.

for flavonoids and finally 520 nm for anthocyanins. The HPLC-UV analysis allowed us to detect nineteen chromatographic peaks as it is possible to observe in the chromatogram reported in **Figure S3** and in **Table S1** (see supporting).

The chromatographic analysis allowed us to distinguish about eight peaks (HCA1-HCA8) attributable to hydroxy cinnamic acids and five peaks (A1-A5) to the subclass of anthocyanins. To a quantitative point of view, flavonoids (F1-F5) and ellagic acid derivatives (r.t. = 10.92 min) are the most abundant compounds present in the extract (**Fig. 3a**). The content of secondary metabolites, such as quercetin and ellagic acid derivatives in grape pomace, allows us to predict that if present in the composition of a biocomposite material it could confer antioxidant properties to the polymer matrix and consequently could exert a protective activity on the material. This point was preliminary evaluated carrying out a thermic treatment on the grape pomace for 90 s. In this case, after the extraction of the grape pomace powder thermic treated, the Folin-Ciocalteu assay was employed as tool to monitoring the effect of high temperature on secondary metabolites in this matrix (**Fig. 3b**). As is possible to observe in the **Fig. 3**, although the effect of temperature causes a visible decrease in the total polyphenol content (GAE) estimated at around 30 %, the matrix shows a certain resistance to heat treatment that could maintained or improved when embedded in the

biocomposites.

3.2. Biocomposites characterization

Once the good thermal stability of the functional compounds in the GP was ascertained, biocomposites based on MB embedded with 10 % and 20 % of grape pomace were prepared. The SEM images of the fractured surfaces of the MB/GP composites show a good dispersion of the GP particles in the polymeric matrix (**Fig. 4**). Additionally, it is possible to distinguish the presence of the two polymer phases that constitute the MB, namely PBAT and PLA. In detail, PLA is the continuous phase, while PBAT is the dispersed phase, presents as droplets within the PLA matrix. This microdroplet morphology, characteristic of immiscible blends, highlights the different chemical nature and limited intrinsic compatibility of between the two components.

Fig. 5 shows the flow curves of MaterBi and biocomposite with 10 % and 20 % of filler. At low gradients, the addition of the biowaste filler leads to an increase in viscosity but, at higher frequency, a decrease compared to that of the matrix was recorded. Following the addition of the fillers, however, a much more accentuated non-Newtonian can be observed. The decrease in viscosity is greater as the filler content increases and, at higher gradients, viscosity of the biocomposite is lower

Table 1
Mechanical properties of MaterBi and biocomposites.

Sample code	E , MPa	TS , MPa	EB , %
MB	721 ± 32	12.4 ± 3.8	2.29 ± 0.52
MB 10 %	725 ± 37	10.3 ± 2.1	2.02 ± 0.38
MB 20 %	755 ± 44	10.7 ± 2.0	1.91 ± 0.29

than that of the matrix. This effect is probably due to a possible degradation effect of the polymers during the biocomposites preparation due to the presence of the filler. So, at low gradients the effect of the filler, which leads to an increase in viscosity, prevails but as the gradients increase the degradative phenomena probably cause a decrease in

molecular weight with a consequent decrease in viscosity. Preliminary tests on PLA and PBAT biocomposites highlighted just for PLA a considerable decrease in molecular weight with a consequent decrease in viscosity during processing with the GP (data not shown). It is noteworthy that this trend could be attributed to the contribution of polyphenols present in GP composition, with particular reference to hydroxycinnamic acids (HCA1 - HCA8) which could favor, under certain conditions, the hydrolysis of polyesters present in the material [35,36]. This effect is more pronounced with 20 % of fillers confirming that the grape pomace can induce and increase the degradation phenomena in the MB matrix. TGA and DTG showed a degradation temperature decrease for the first degradation step that could be related and

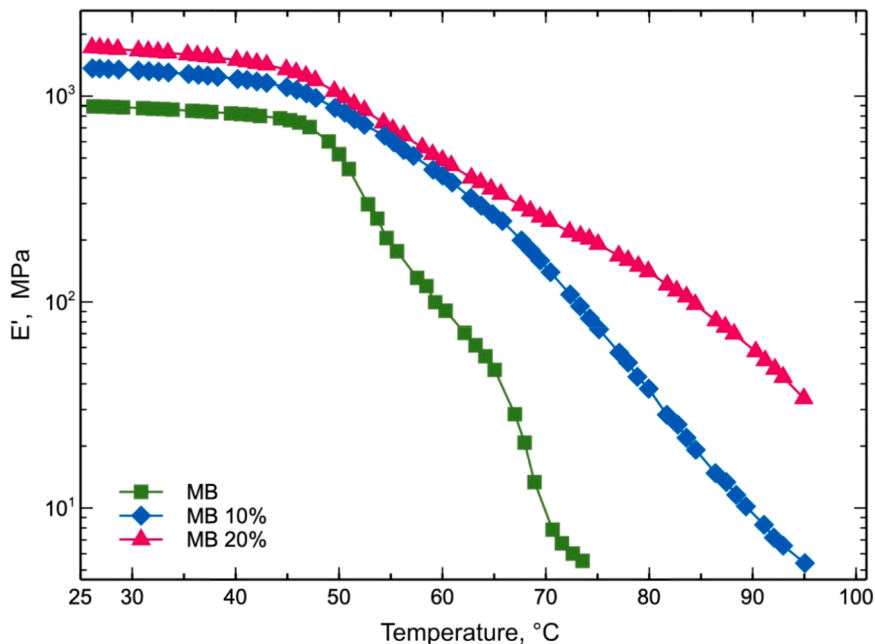


Fig. 6. Storage modulus curves, E' , as a function temperature of MaterBi and biocomposites.

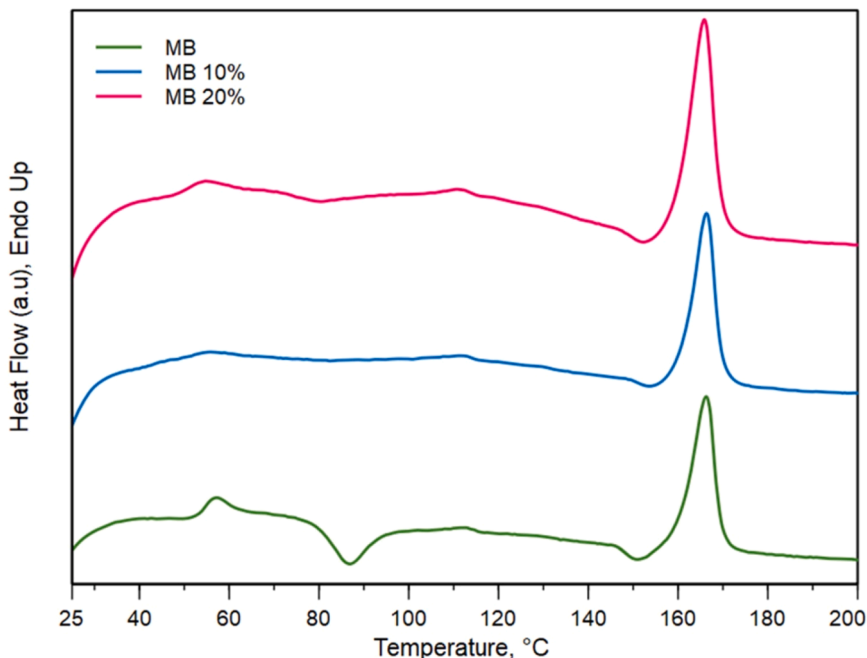


Fig. 7. DSC thermograms during the first heating scan of MaterBi and biocomposites.

Table 2

Glass transition temperature, T_g , melting temperature T_{melt} , cold, ΔH_{cc} , and melt, ΔH_{melt} , enthalpy values of MaterBi and biocomposites.

Sample code	T_g , °C	T_{melt} , °C	ΔH_{cc} , J/g	ΔH_{melt} , J/g	$\Delta H_{melt} - \Delta H_{cc}$, J/g
MB	56.1 ± 1.1	166.2 ± 0.9	11.4 ± 2.1	30.1 ± 0.9	18.7
	55.7 ± 0.8	166.3 ± 1.2	–	31.3 ± 1.2	31.3
MB 20 %	54.9 ± 0.6	166.8 ± 1.5	–	37.3 ± 1.8	37.3

confirmed a molecular weight decrease (Table S2).

Table 1 shows the principal mechanical properties of MaterBi and biocomposites. The addition of the filler leads to a slight increase in the value of elastic modulus (E) that is more pronounced with 20 % of grape pomace. Moreover, the filler introduction causes a slight decrease of tensile strength (TS) and elongation at break (EB), with a consequent embrittlement of the MB material, already brittle in its starting state.

The data recorded on the storage modulus (E') of MaterBi and biocomposites (Fig. 6) confirmed the results obtained with tensile test. The value of E' increases in the presence of the filler and this increase is more pronounced with 20 % of GP. The filler causes an increase in the stiffness of the materials as expected at a temperature of 25 °C. The storage modulus of the biocomposites remains higher at all temperatures investigated. It is observed that the decrease of the storage modulus E' for the biocomposites occurs at higher temperatures. This result highlights a higher thermal stability of the biocomposites as compared to the MB matrix.

Fig. 7 and Table 2 show the first scan thermograms and the average values of MB and biocomposites results obtained by DSC, respectively.

First, the thermograms curves display that the adding of grape pomace causes a slight shift of the melt temperature, suggesting that grape pomace is a nucleating agent for MB crystallization. This result has already been reported in the literature for a similar system that contains lignocellulosic fillers [37–39]. However, it is interesting to note that the value of melting enthalpy increases as grape pomace content increases. This result can be attributed to slight nucleating effect and, in general,

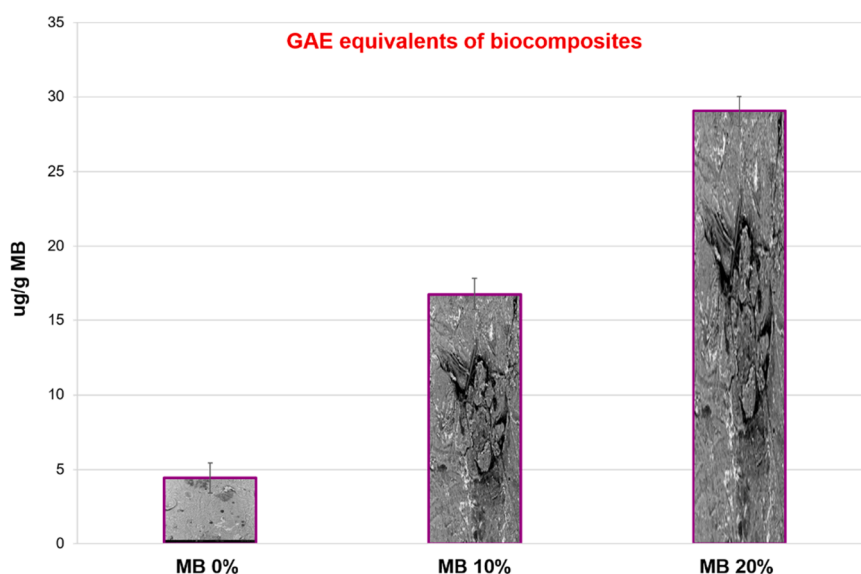


Fig. 8. Total content of polyphenols in Mater Bi and biocomposites, determined by Folin-Ciocalteu assay and expressed by gallic acid equivalent.

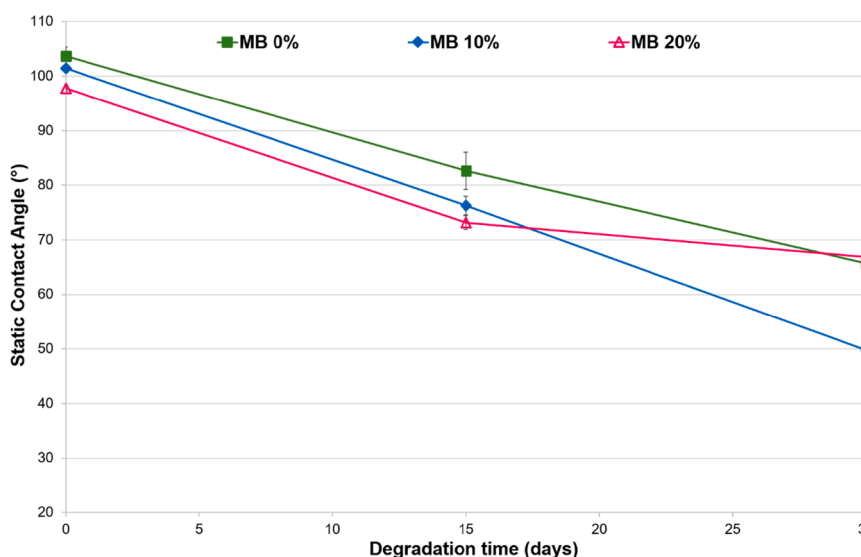


Fig. 9. Average static contact angle values for the MB and BioCs film samples vs degradation time in soil.

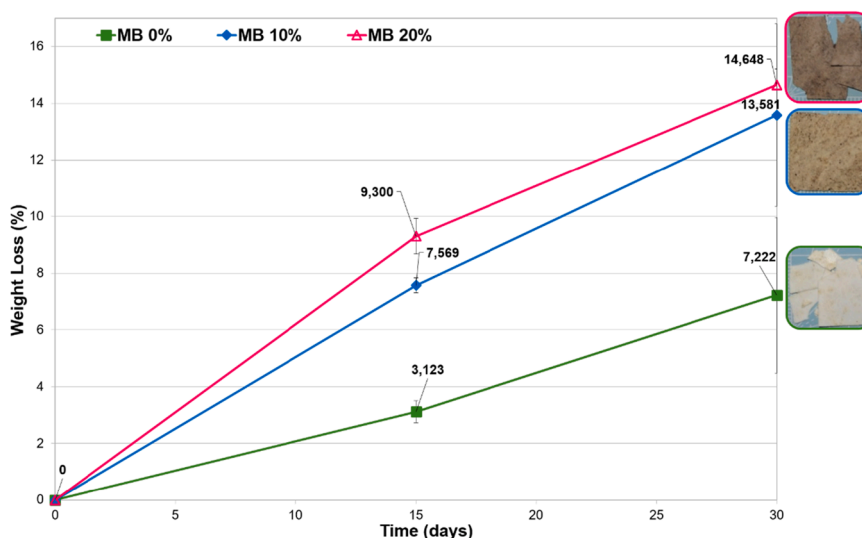


Fig. 10. Weight loss percentage vs. degradation time in soil of MB and BioCs and representative photographs of recovered film samples.

promotes a decrease in molecular weight that led to an increase of crystallinity (Table 2). As a result, the elastic modulus increase, observed during static and dynamic mechanical tests, can be attributed to the following behaviors.

Noteworthy, the introduction of the GP in the polymer matrix induced a proportional increase of antioxidant property in the BioCs (Fig. 8), relevant for thermo- and photo-oxidative stabilization during lifetime.

3.3. Evaluation of the degradability in soil

The degradation of plastic materials, traditional and biodegradable, involves different processes promoted by one or more environmental factors (e.g., temperature, light, microorganisms) or chemicals. Biodegradation is a multi-step process: in the first stage, macromolecular chains are depolymerized into monomers and oligomers; in the second one, the monomers and oligomers are taken up as biomass; and in the last step, the respiration of biomass consumes O_2 and produces CO_2 and H_2O (under aerobic conditions). Moreover, during the biodegradation process the growth of microorganisms and biofilms on the surface of the polymer sample can occur (biodeterioration), changing its mechanical and chemical-physical properties. All the standardized methods for determining biodegradation are addressed on the measurement of the conversion into carbon dioxide of the organic carbon initially present in the plastic by the oxygen. On the other hand, in the literature most of the papers concerning biodegradation of polymers and composites are based on weight loss that is accepted as a measurement of biodegradability of plastic films [10,40,41]. Every time WL is used to check the degradation of polymer matrices, only the first step of the biodegradation process is implicated, i.e., macromolecular chain depolymerization into oligomers that are gradually removed from the surface. In this work, we performed a soil burial test by using WL as a biodegradability index and monitored wettability and composition changes induced by degradation in soil. Soil burial degradation test was carried out up to 45 days sandwiching the polymer films between layers of a mixture of milled perlite and commercial soil to simulate soil degradation after the use lifetime. Perlite was used to increase the amount of water retained and accelerate degradation in soil ensuring a more favorable environment for the growth and the metabolic activities of microorganisms [29,42]. WL is related to biodegradability and allowed us to follow the changes induced by the biodegradation process over time. Thus, it was used as a parameter for evaluating biodegradability.

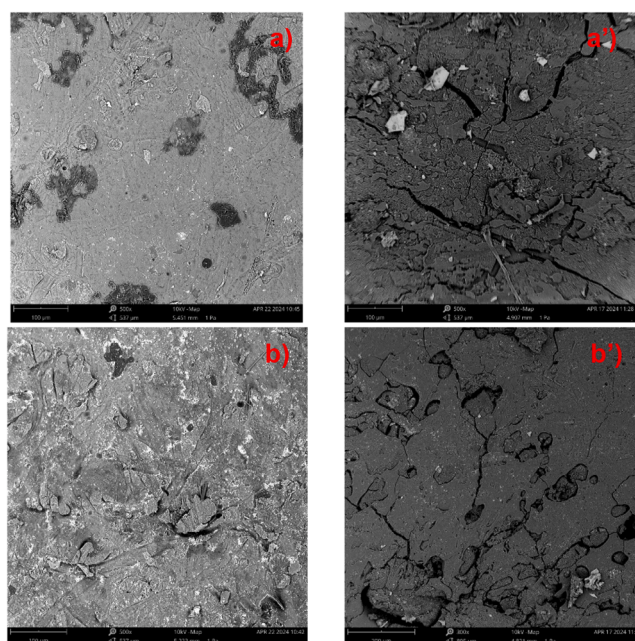


Fig. 11. SEM micrographs of the surface of (a) MB and (b) MB 20% film samples (a, b) before and (a', b') after 45 days.

Degradation in soil produced a contact angle decrease (Fig. 9), whereas WL increased with the filler content and degradation time (Fig. 10). Even though the test was carried out up to 45 days, data were reported in Figs. 9 and 10 up to a degradation time of 30 days. In fact, after 45 days, only fragments of the MB were recovered and did not allow SCA measurements to be performed and resulted in a high error in the WL. However, the complete data are reported in the SI (Figures S4 and S5). SCA measurements show lower values for BioCs that could be related to degradative phenomena during the processing and a relevant increase in wettability with the degradation time reasonably due to the formation of new hydrolytic chain ends. Chemical changes on the surface of the samples, induced by degradation in soil, increase wettability of films, highlighted by SCA decrease and, therefore, microbial susceptibility is encouraged with a lower degradation rate for the MB films although the lower thickness (Fig. 10). The increase in the degradation rate induced by the filler should be due to a decrease in molecular

Table 3

Changes in PBAT compositions and PBAT/PLA ratio in the recovered sample after 45 days of degradation in soil.

Sample code	Te/Ad	mol %		weight %	
		PBAT	PLA	PBAT	PLA
MB	44.1/55.9	16.9	83.1	37.1	62.9
MB after 45 days	48.0/52.0	15.4	84.6	34.6	65.4

weight during the processing and would require further inspections.

Despite evidence of a degradation process during processing, detected by several techniques and induced by biowaste filler, and a higher weight loss, degradation in soil of BioCs generated less fragments and microplastics than MB. The SEM images of the surfaces of the MB and the biocomposite with 20 % filler, both before and after 45 days of burial (Fig. 11), allow us to highlight the differences in the degradation process of the two samples, particularly focusing on the role of the grape pomace. It is evident that the neat MB shows more significant signs of degradation after 45 days of burial, with noticeable surface cracks. These signs are also present on the surface of the samples with grape pomace, but to a lesser extent (Fig. 11).

Moreover, NMR showed that, in the recovered sample after 45 days, the composition of PBAT was changed and the terephthalic percentage increased (Table 3), similarly with previous results displayed by ATR-FTIR analysis [43]. However, the percentage of PLA increases as well (Table 3), highlighting a preferential degradation and surface erosion of the aliphatic moiety of the PBAT fraction.

Finally, DSC analysis carried out on the recovered film samples highlighted an increase in the melting enthalpy, related to the crystallinity fraction (Fig. 12 and Table S3), observed in similar investigations. Moreover, melting temperature decreased and glass transition temperatures were no longer recorded [43]. In the recovered samples, crystallinity increases with the degradation time since the amorphous regions are faster and preferentially attacked by microorganisms and enzymes, as is well known in the literature [44,45].

4. Conclusion

Overall, the present study represents an example of a circular model approach with the reuse of biowaste to obtain functional biodegradable items, improving in the meanwhile the performance of the starting polymer matrix. From a circular economy point of view, the direct use of GP biowaste, which underwent simply a milling treatment, is worthy of significant attention. Actually, GP contains a relevant amount of natural remarkable functional compounds potentially useful for stabilizing polymer samples. No chemical and/or intensive energy treatments are mandatory. Therefore, from an environmental and cost-real approach, the direct use of GP not only fully exploits the agricultural biowaste, but also limits resource use. The thermal stability of GP during mixing with polymers can limit their usage. Interestingly, GP analysis by both UV and HPLC-UV showed only a slight decrease in antioxidant potency, despite the heat treatment simulating the BioCs processing. Additionally, SEM displayed that the filler was distributed homogeneously in the matrix. Noteworthy, the introduction of the GP in the MB polymer

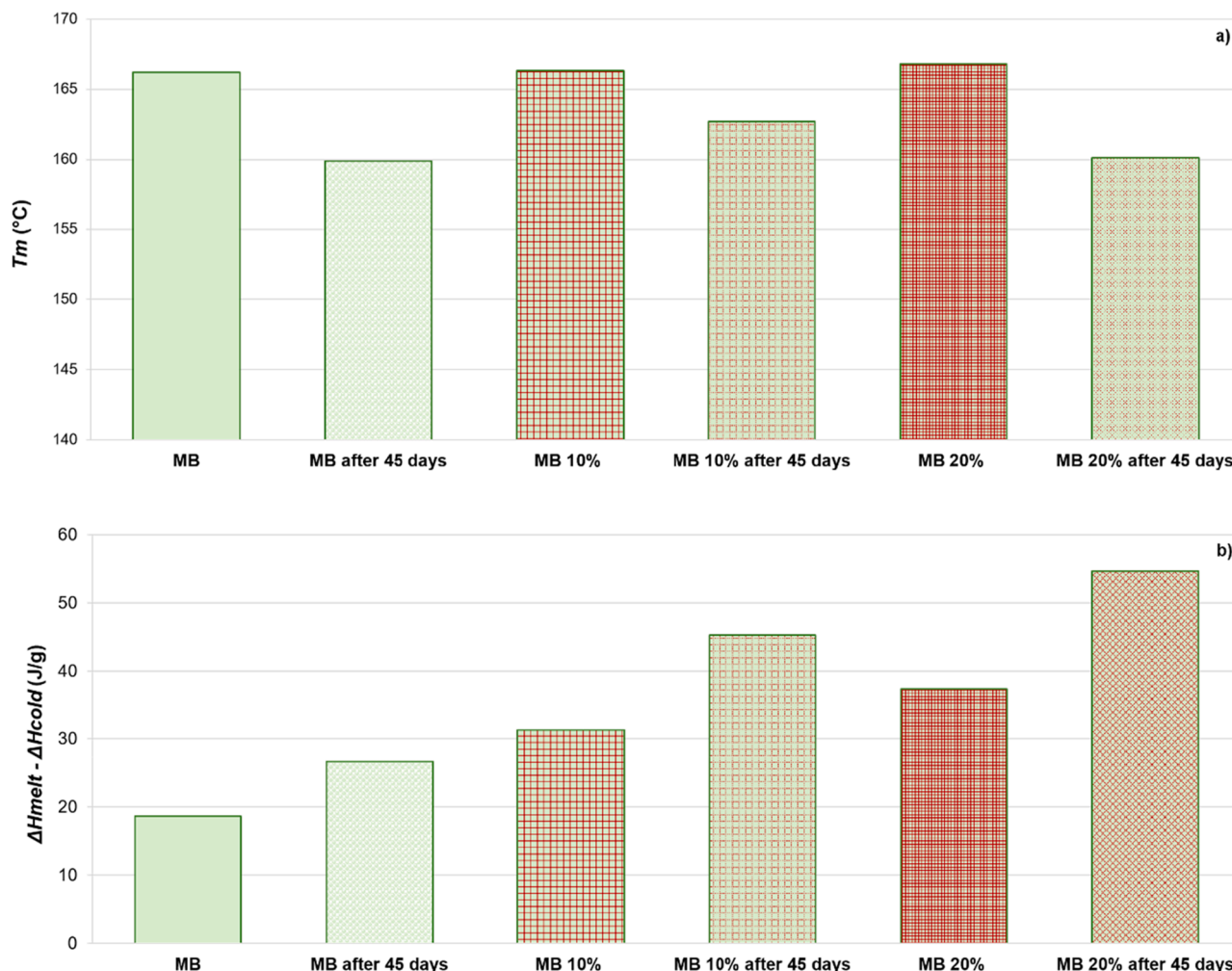


Fig. 12. Changes in melting (a) temperature (T_m) and (b) enthalpy of MB and biocomposites, before and after degradation (45 days).

matrix induced a proportional increase of antioxidant property in the BioCs. Surprisingly, rheological analysis highlighted that, at low gradients, the addition of the biowaste filler leads to an increase in viscosity but, at higher frequency, a slight decrease compared to that of the matrix was recorded. This behavior was attributed to a degradative effect caused probably by the filler during the processing, promoting a reduction of the molecular weight. Furthermore, the addition of GP accelerated the degradation rate in soil. Finally, NMR showed that, in the recovered sample after 45 days, the composition of PBAT was changed and the terephthalic percentage increased, similarly with previous results. This finding represents a second proof of a preferential erosion of the aliphatic moiety in PBAT film samples that could be amplified by the presence of the filler. These effects could be relevant in the commercial field since the PBAT is commonly used in biodegradable mulching films and other compostable commercial items.

CRedit authorship contribution statement

Vincenzo Titone: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Data curation. **Marco Rapisarda:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Data curation. **Luana Pulvirenti:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Data curation. **Edoardo Napoli:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Methodology, Data curation, Conceptualization. **Giuseppe Impallomeni:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Data curation. **Luigi Botta:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Methodology, Data curation. **Maria Chiara Mistretta:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization. **Paola Rizzarelli:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.polymdegradstab.2024.111091](https://doi.org/10.1016/j.polymdegradstab.2024.111091).

Data availability

Data will be made available on request.

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