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Effect of α-tocopherol on the processability, tensile properties, and structure of fully bio-based poly (butylene succinate)/Brewer's spent grain composites

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ABSTRACT

Renewable and biodegradable plastics are of interest to the scientific community as a solution to the environmental pollution caused by petroleum-based plastics. This aspect, combined with the need to dispose of enormous quantities of agri-food industrial waste (such as brewer's spent grains, or BSG), has led to the consideration of the direct use of polybutylene succinate (PBS, a bio-derived and biodegradable bioplastic) blended with BSG (at 25% by weight) to utilize "green" materials and recycle agri-food waste. Alpha-tocopherol (TOC) is added to the PBS/BSG biocomposite blend at 2–10% by weight. The blends' structure-property correlation was performed through chemical, physical, rheological, and tensile mechanical characterization. The results show that TOC performs the dual function of plasticizer and physical compatibilizer, due to the hydrogen bonding between PBS and BSG. This effect is attributed to the dual chemical structure of TOC (polar head and nonpolar tail), which should not exceed 4% by weight, as higher amounts reduce the crystallinity degree of PBS and destabilize its macromolecular structure, compromising its mechanical properties. Amounts lower than 4% by weight are insufficient for the compatibilizing/plasticizing effect. TOC at 4% by weight reduces the viscosity of the mixture (by ~2 orders of magnitude), mechanical stress during processing (-56%), improves deformability by 33%, and improves the toughness of the blend by 43%.

1. Introduction

Currently, fossil-based plastics are ubiquitous and widely employed due to their extraordinary versatility and high performance [1]. However, owing to their limited, if any, biodegradability, they accumulate in the environment, producing micro and nanoplastics, posing a serious hazard to life on Earth and the environment [2–4]. A possible remedy for this environmental issue is the switch to biodegradable plastics [5], which have gained increasing interest in recent years [6]. According to Eurobioplastics' latest report, biopolymer production is expected to reach 7.4 million tons by 2028 [7]. Among the most produced biopolymers, polybutylene succinate (PBS) is an interesting melt-processable (between 140 °C and 170 °C), semi-crystalline biodegradable thermoplastic polyester with good physical mechanical characteristics (TS (MPa) 37.0, E% 354 and E(MPa) 328) [8–11]. Several methods have been reported in the literature to modify the properties of PBS-based bioplastics, thereby broadening their range of applications including composite formulation, blending and co-polymerization with different monomers [12–15]. Blending of PBS with bio-fillers coming from agrifood waste is an effective strategy to reduce overall costs and increase feedstock availability, which are two major problems affecting bioplastics production [16]. Many different agrifood waste containing variable quantities of lignocellulose have been employed as bio-fillers for PBS biocomposites production, such as jute fibres [17,18],

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brewers' spent grain [16,19,20], grape pomace [21,22], almond shell flour [23], coffee grounds [22], potato peels [24], and wheat bran [25, 26]. Recently, it has been reported that beer spent grain (BSG) can be used to produce PBS/BSG biocomposites possessing higher physical and mechanical properties compared to any PBS/bio-filler composite described in the literature to date [16,27]. These interesting findings are ascribed to the elevated protein content of BSG (up to 20–25%), which are supposed to act as naturally occurring bio-compatibilizers [16,19]. Nonetheless, it is generally true that the presence of a bio-filler reduces physical mechanical characteristics compared to the virgin polymer due to reduced interfacial adhesion and crystallization degree [28]. Thus, this work aims to verify whether further addition of a plasticizer/compatibilizer could improve the overall characteristics of PBS/BSG blends. In particular, preliminary validation focused on the use of α-tocopherol (code for this paper: TOC) as an additive.

The α-Tocopherol or vitamin E is an oily liquid, clear or slightly yellow, and greasy to the touch [29]. It can be used as a natural biodegradable antioxidant with low toxicity both for the environment and humans [30,31], for food packaging applications [29–33], for biomedical grade Ultra High Molecular Weight Polyethylene, to enhance thermal stability and wear resistance [33–35]. The α-tocopherol has also been used in other renewable plastics, Azevedo et al. [36] encapsulated it in PLA nanoparticles and added it to LDPE to slow down oxidation reactions in food packaging. Jiang et al. prepared poly (lactic)-acid-poly(3-hydroxybutyrate-co-4-hydroxybutyrate) or PLA-PHB mixtures through a melting-method followed by incorporation of α-tocopherol [37]. The Authors of this study highlighted the possibility of having chemical reactions with α-tocopherol since the polyester matrix of PLA-PHB contains carboxylic chemical groups that can interact with the hydroxide groups of α-tocopherol. Additionally, TOC is an effective biobased compound adequate for melt-processing, which can replace phenolic stabilizers in many fossil-based polymers [38,39]. To the best of our knowledge, only Sin et al. have previously investigated the possibility of using TOC as an additive in PVOH/starch biocomposites for the preparation of films by casting technology [40]. The results show an increase in tensile strength of different wt/wt% PVOH/starch mixtures containing between 1 wt% and 3 wt% which was ascribed to the compatibilizing effect of TOC, reducing surface energy of the PVOH/starch matrix due to the presence of a long apolar alkyl "tail" together with a polar "head" which can improve interfacial adhesion between the apolar PVOH and polar starch. In conclusion, Sin and coworkers highlighted that TOC acts simultaneously as a plasticizer, a compatibilizer, and a thermal stabilizer for PVOH/starch blends.

Within this context, the present work is the first of its kind validation of the use of TOC to increase the physical and mechanical properties of PBS/BSG biocomposites. PBS/BSG blends (75/25 wt/wt%) were prepared with the addition of 2 wt%, 4 wt%, 8 wt%, and 10 wt% of TOC. The chemical, physical, mechanical, rheological, and morphological characteristics of the PBS/BSG/TOC mixtures were compared with those of the PBS/BSG (75/25 wt/wt%), chosen as the reference formulation based on our previous studies [16].

According to current knowledge, this is the first study addressing PBS/BSG blends that include α-tocopherol as a natural plasticizer/compatibilizer to have a fully green bio-composite. This study provides additional scientific insight on the enhancement of the performance of PBS/BSG mixtures (without an additive) previously studied in two of our previous works, through an integrated approach combining mathematical modelling and rheological, physical, mechanical, and morphological characterization [16,41].

2. Materials and methods

2.1. Filler, matrix, and additive

Filler: Brewer's grains (code: "BSG") are derived from the production of lager beer from malted barley and were pre-dried by the brewing company (Birrificio Messina Società Cooperativa - Larderia Inferiore, Messina, Italy).

Matrix: Polybutylene succinate (code: "PBS") was produced by Mitsubishi Chemical Performance (Japan), grade FZ71PM. According to the product data sheet, the density value is 1.260 g/cm^3, and the melt flow rate (MFR) is 22 g/10 min (190°C/2.16 kg).

Additive: α-Tocopherol (purity ≥95.5%, purchased from Sigma-Aldrich and used as is, code: "TOC") was used as a natural antioxidant molecule in the PBS/BSG blend to prevent thermos-oxidative degradation that occurs during technological processes for transforming thermoplastic materials (such as melt blending and thermoforming, discussed here). As mentioned before, since both PBS and BSG are bio-derived materials, the antioxidant molecules were also chosen from among the bio-derived ones to obtain a fully bio-derived composite material.

Generally, the numbers after the filler or additive codes specify the percentage by weight.

2.2. Bio-composites

Bio-composites preparation started from the filler treatment. Thus, as received beer spent grain was ground with a ball milling machine (model: RETSCH-MM301) for 1.5 h, frequency = 20 Hz. The fraction smaller than 100 micrometres was collected through a sieving process in stainless steel filters (by Endecotts, 200 mm diameter, supplied by ENCO Scientific Equipment – Venezia, Italy) with the help of an automatic sieving machine (by Filtra Vibration, mod. Filtra IRIS FTL-0200). Finally, the fraction < 100 μm was placed in a convection oven at 80 °C for 4h to evernight (depends on the quantity of BSG and pre-moisture level) to lower the moisture level below 2 wt% [16,41].

Before mixing, PBS has been pre-dried at 60°C for 4 h to reach a moisture content lower than 0.06 wt%.

Dried PBS and BSGF have been mixed inside a Brabender Plasticorder-PL2100 chamber (by Belotti Instruments, Milan, Italy) by measuring the torque at 140°C, 40 rpm (rotational speed), and mixing time of 10 min. The "WINMIX" software was used to monitor the torque during the melt mixing process. Then, all the blends were thermoformed in a uniaxial press at 140°C, by applying pressure in a stepwise manner: 0 MPa for 7 min, 5 MPa for 5 min, and 10 MPa for 3 min. The final cooling was achieved by utilizing recirculating cold water to obtain square sheets measuring 6 × 6 cm with a thickness of 1 mm. Different sheets of Bio-Composite (BC), in which the BSGF content has been fixed at 25 wt%, the PBS content at 75 wt% (codified as "BC25") without and with TOC additive (at 2–4–8–10 wt%) have been obtained. A simple BC25 blend was used as a control sample. Table 1 lists all the bio-composite blends studied in this work, along with their identification codes and composition details.

The value of the BSG content was set at 25% by weight from previous studies performed on PBS/BSG [16], where the best overall performances were obtained for PBS/BSG 75/25 wt/wt. Therefore, the BC25 blend (*i.e.,* PBS 75 wt% and BSG 25 wt%) is considered as a starting point for further investigations aimed at improving its properties using

Table 1
Additive content, maximum torque, and viscosity of Bio composites with 75 wt% of PBS and 25 wt% of BSGF.

Code	Additive (wt%)	Torque (Nm)	η* x 10^8 [mPa x sec]	η* x 10^6 [mPa x sec]
	TOC	*Max peak*	*0.1 rad/sec*	*10 rad/sec*
PBS	0	19,193	0.92 ± 0.04	1.52 ± 0.00
BC25	0	39,118	1.30 ± 0.09	1.60 ± 0.09
BC25-TOC2	2	17,890	0.89 ± 0.08	1.10 ± 0.02
BC25-TOC4	4	17,325	0.016 ± 0.01	0.85 ± 0.04
BC25-TOC8	8	8498	0.029 ± 0.01	0.67 ± 0.04
BC25-TOC10	10	7616	0.018 ± 0.02	0.59 ± 0.09

the antioxidant additives mentioned above.

Subsequently, from all sheets, several dog-bone shape samples were cut by means of a Ray-Run cutting instrument (ASTM D638 standard), specifically for tensile test [42]. Fig. 1 shows the photographs of dog-bone-shaped specimens of BC25, BC25-TOC2, BC25-TOC4, BC25-TOC8, and BC25-TOC10.

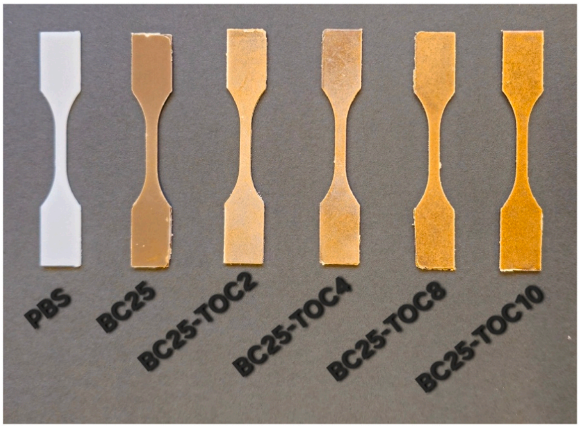

Fig. 1. Photos of PBS, BC25, BC25-TOC2/BC25-TOC10 dog-bones.

2.3. *Chemical, physical, and mechanical characterization tests*

The ATR spectra of BSG and PBS–BSG samples were obtained using a spectrometer mod. PerkinElmer Spectrum Two FT-IR. The instrument is equipped with a $LiTaO_3$ detector (Waltham, Massachusetts, USA). Spectral investigated range was within 600 cm^{-1} and 4000 cm^{-1} . The resolution was of 2 cm^{-1} and 100 accumulated scans.

An ATS120 Moisture Analyzer (AXIS Sp. z o.o., 80–125 Gdańsk, ul. Kartuska, n. 375B, state of Poland) evaluated the moisture content of BSG. The chemical constitution of BSG was analysed according to the standard methods AOAC (2000) applied by Sobukola et al. and by Hejna et al. [43,44].

The torque generated during the melt-mixing (described in the following Section 2.1) was monitored throughout the experiment. A representative torque–time curve was obtained by averaging three independent measurements.

The complex viscosity (η*), storage modulus (G') and loss modulus (G'') were evaluated using a rheometer, rotational type, (model: MC-502, of Anton Paar; in Graz, state of Austria). The instrument has been equipped with a cone–plate geometry (diameter of 25 mm, and gap was of 1 mm), where the rotating rod was submerged in the molten polymer."Amplitude-sweep-test" measurements have been conducted at 140 °C. The frequency has been fixed at the constant value of 1 Hz to establish the Linear Viscoelastic Region (LVR), applying a shear strain ranging from 0.01% to 1000%. Subsequently, "frequency-sweep-tests" were done within the range of 0.01–100 rad/s at a strain fixed at the value of 0.1%, chosen within the LVR. All rheological experiments were performed in triplicate.

Mechanical tensile properties were determined using a universal testing machine (Lloyd LR10K, supplied by Elis–Electronic Instruments & Systems S.r.l., site in Rome, state of Italy). Mechanical tensile tests have been conducted according to the ASTM D638 standard [42], at 25 °C and 21% relative humidity (RH), by using a 0.5 kN load cell. The applied preload was of 1.0 N. The crosshead speed was of 2 mm/min. We considered the following mechanical parameters: Young's modulus (E, MPa); tensile strength at break (σb, MPa); elongation at break (εb, %); work at break (Wb, J). Wb is the area under the stress-strain curve. Values shown are derived from eight measurements for each sample.

Thermal analysis was investigated by a Differential Scanning Calorimetry (DSC). Tests were performed using a Mettler Toledo DSC 3 Thermal Analysis System (Mettler Toledo, Milan, Italy). The analyses were conducted in a nitrogen environment with a flow rate of 20 mL/min, over a temperature interval of 25–160 °C, and a heating rate of 10 °C/min. Samples of PBS and BC25 (~10 mg) were first heated from 25 °C to 160 °C to erase any prior thermal history, then cooled back to 25 °C and reheated to 160 °C in order to determine the crystallization temperature (Tc) and melting temperature (Tm). Each measurement was repeated three times to ensure reproducibility. The degree of crystalline order for PBS and BC25 composites was calculated according to the following Eq. (1) [45]:

$$\chi_c(\%) = \left(\frac{\Delta H_c}{\Delta H_0 * (1 - w)}\right) * 100 \tag{1}$$

In Eq. (1), χc represents the crystallinity degree (%), ΔHc is the crystallization enthalpy of the sample (J/g), and ΔH° corresponds to the melting enthalpy of fully crystalline PBS, reported as 110.3 J/g [45]. The parameter w denotes the weight fraction of BSG in the composite materials.

The fracture surfaces of the dog-bone specimens obtained after the tensile tests were examined by *Scanning Electron Microscopy (SEM)* using a ZEISS Crossbeam 540 manufactured by Carl Zeiss Microscopy GmbH (Jena, Germany). Observations were performed at a voltage of 5 kV, and magnifications of 300 × and 2000 × . Prior to SEM imaging, the samples were sputter-coated with a thin layer of chromium using a Quorum Q150T-ES (Quorum Technologies, West Sussex, UK) to provide sufficient electrical conductivity.

Torque, viscosity, and tensile mechanical data were statistically analyzed using GraphPad Prism 8, developed by GraphPad Inc. (address: La Jolla, CA, state of USA). Data are expressed in terms of mean ± standard deviation (SD), with a significance level of $p < 0.05$.

Data normality and lognormality were assessed using the D'Agostino–Pearson test, while the Brown–Forsythe test was applied to verify the homogeneity of variances. Since the assumptions were met, a two-way ANOVA followed by Tukey's post hoc test was performed to determine significant differences between groups at a significance level of 0.05.

3. Results and discussion

3.1. *Effect of α Tocopherol on the processability and tensile properties*

To evaluate the effect of TOC on the stability of PBS/BSG blend during melt processing, the components were first processed separately (Fig. 2a) and then simultaneously (Fig. 2b).

In Fig. 2a, the torque vs time curves of PBS, PBS+BSG25, and PBS+TOC4 +BSG25 are plotted. For clarity, PBS+BSG25 is a blend of PBS with the addition of 25 wt% BSG after 4 min of mixing, whereas PBS+TOC4 +BSG25 is a blend of PBS with 4 wt% TOC added after 3 min of mixing, followed by the addition of 25 wt% BSG after 4 min.

As expected, at the beginning of the PBS melt mixing process, the torque increases from zero (empty chamber) up to the maximum peak value, which is about 20,000 Nm (Table 1). This effect arises from the semi-solid PBS pellets, which start melting during the process. As the pellets melt, the torque decreases to a minimum value of about 4800 Nm after 2 min of mixing. The addition of BSG25 after 4 min raises the torque to about 10.000 Nm.

Instead, as TOC4 is added to the chamber, the torque of PBS immediately decreases from about 4800 to zero, eliminating any shear stress on the bioplastic. The subsequent addition of BSG25 causes the torque to rise again, but to a lower value (about 7000 Nm) because it is partially compensated by the TOC4 presence. After 10 min of mixing, the torque value of the PBS+TOC+BSG mixture is always higher than that of PBS+TOC and of PBS.

These results clearly show that the BSG improves the melt viscosity and the mechanical stress in the bioplastic. Thus, the presence of a

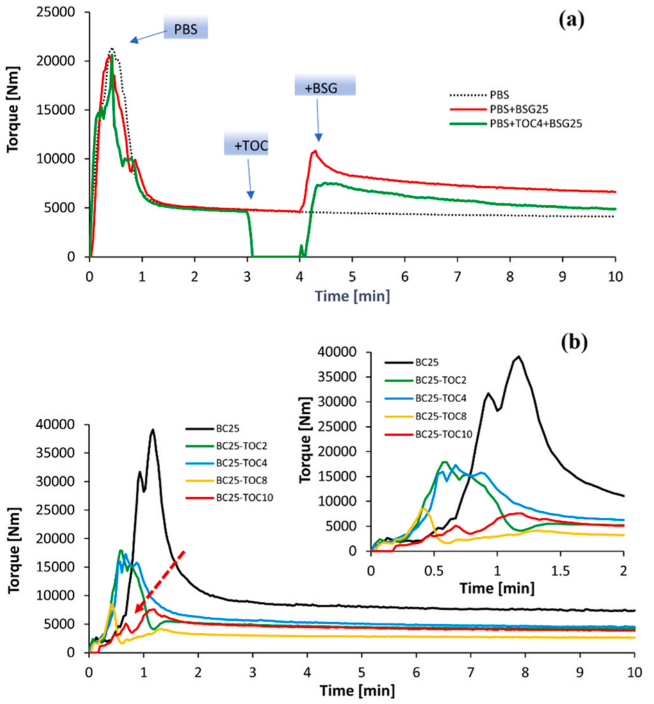

Fig. 2. Torque vs time of mixtures of PBS, PBS+BSG25, PBS+TOC4 +BSG25, whose components are added separately and at different times into the mixing chamber (a), and of all the mixtures studied in this paper, whose components are all inserted simultaneously into the mixing chamber (b).

plasticizing additive such as TOC is necessary to decrease the melt viscosity and to limit the thermo-mechanical stress during the melt mixing of the polymer blend.

Fig. 2b shows the torque evolution during 10 min of all the mixtures in which all components were inserted simultaneously into the mixing chamber at the beginning of the process. The curves reveal the variations resulting from the mixing of PBS with BSG (25 wt%) to create BC25, without and with TOC (from 0 wt% to 10 wt%). The torque analysis showed an increase in the material fluidity with increasing TOC in the following order:

BC25 > PBS>BC25-TOC2 > BC25-TOC4 > BC25-TOC8>BC25-TOC10

(see the detailed torque values in Table 1).

Confirming the data of (Fig. 2a), TOC lowers the viscosity of the molten BC25 mixture by acting as a plasticizing additive. Being an oil, TOC significantly lowers the viscosity of the melt (from 39,118 Nm to 17,325 Nm when added at 4% by weight, corresponding to a decrease of −56%, and from 39,118 Nm to 7616 Nm when added at 10% by weight, corresponding to a decrease of −80.53%).

It is known that thermo-mechanical stress during processing induces the breaking of chemical bonds in the macromolecular chain of the polymer, resulting in the formation of free radicals. The latter, being highly unstable by their nature, easily react with oxygen, forming new functional groups (e.g., hydroxyl, carboxylic, carbonyl), thereby varying the molecular weight, the molecular weight distribution, forming new chain rearrangements, double bonds, etc [46]. The macroscopic variation that indicates degradation is a general worsening of the physical-mechanical properties of the polymer that generally changes its mechanical performance from ductile to brittle [47]. Studies on the thermomechanical degradation and recyclability of PBS have shown that PBS undergoes degradation reactions when reprocessed at temperatures above 190°C [48], above the temperature used in our experimentation (140°C). However, since the torque curves of the BC25-based blends in (Fig. 2b) show a nearly constant torque value after about 4 min of mixing, the residence time in the thermal chamber could be reduced from the 10 min used. This would reduce the thermo-mechanical stress acting on the polymer melt.

The mixtures were then used to prepare sheets, which were cut into dog-bone-shaped specimens for physical- mechanical tests. Tensile tests were performed to evaluate the degree of homogeneity of the samples containing different amounts of TOC. For this purpose, stress-strain curves of BC25, BC25-TOC2, BC25-TOC4, BC25-TOC8, BC25-TOC10 were obtained from six tensile tests for each mixture. When the tensile curves overlap (BC25-TOC4, Fig. 3c), this behaviour can be attributed to good homogeneity of the mixture and strong filler-matrix interaction that minimizes voids at the fiber-matrix interface [49]. On the contrary, when the curves do not overlap, the mixture shows lower reproducibility. The higher the distance between the curves indicates the non-homogeneous dispersion of the filler within the polymer and consequently low compatibility between the filler and the polymer matrix [16,41].

The tensile behaviour of the BC25 blend is shown in (Fig. 3a), the six stress-strain curves obtained do not perfectly overlap, suggesting a poor distribution of the BSGF within the PBS polymer matrix. The six mechanical curves of BC25-TOC2 are closer than those of BC25 (Fig. 3b), and even closer for BC25-TOC4, indicating an improvement in homogeneity. In particular, the BC25-TOC4 sample exhibits the best overlap of the curves among all the investigated blends, with the curves begin very close to one another (Fig. 3c). This result suggests that the ratio PBS/BSG/TOC of 75 wt%/25 wt%/4 wt% (in BC25-TOC4) is the most suitable among the investigated mixtures to achieve a good filler-matrix interaction, thus improving the dispersion of the BSG filler within the PBS matrix. Consequently, the tensile behaviour of BC25-TOC4 provides evidence of a possible interaction between the BSG filler and the PBS macromolecular chains, favoured by the presence of the optimal TOC content (4 wt%).

The average values of mechanical parameters are listed in Table 2. Mechanical tensile data for pure PBS have been added for comparison and deeply already discussed in our previous papers [16,41]. As already known, pure PBS is a ductile bioplastic with young modulus of ∼328 MPa, stress at break of ∼37 MPa, elongation at break of ∼354%, and work at break of ∼ 4 J. As already discussed in our previous paper, the addition of BSG filler, changes the mechanical performance of the PBS [16]. In fact, the BC25 blend exhibited a Young's modulus, tensile strength, elongation at break, and work at break of about 440 MPa, 19 MPa, 30%, and 0.16 J, respectively.

The addition of 2 wt% of TOC decreases all the mechanical parameter values in BC25-TOC2 compared with BC25 (approximately 398 MPa ($p < 0.001$), 14 MPa ($p < 0.001$), 25% ($p < 0.001$), and 0.11 J ($p < 0.001$), respectively).

Instead, the blend BC25-TOC4 shows a slightly lower modulus (376 MPa, $p < 0.001$), while the tensile strength remains practically unchanged (around 19 MPa, $p < 0.9994$). However, the elongation at break and work at break increase (from 30.74% to 41% ($p < 0.001$), and from 0.16 J to 0.23 J ($p < 0.001$), respectively) compared to BC25. These latter values indicate an increase in deformability of approximately 36%, and an increase in toughness of approximately 43%, suggesting again that in the BC25-TOC4 mixture a filler-matrix interaction is established compared to the reference mixture (BC25), favoured by the presence of TOC4 in the blend.

It should be noted that, although the improvements in deformability and toughness are significant with respect to the PBS/BSG reference system, a comparison with more flexible biodegradable polymers such as Poly (butylene succinate- co -butylene adipate) (PBSA) would further clarify the practical relevance of these results. This aspect was not addressed in the present study and will be the subject of future investigations.

Further additions of TOC (8 wt% and 10 wt%) significantly decrease the mechanical stiffness, strength, and deformability of the material, resulting in values of approximately 145 MPa, 5.86 MPa, 7.8%, and 0.07 J in BC25-TOC10 for modulus, strength, elongation at break, and

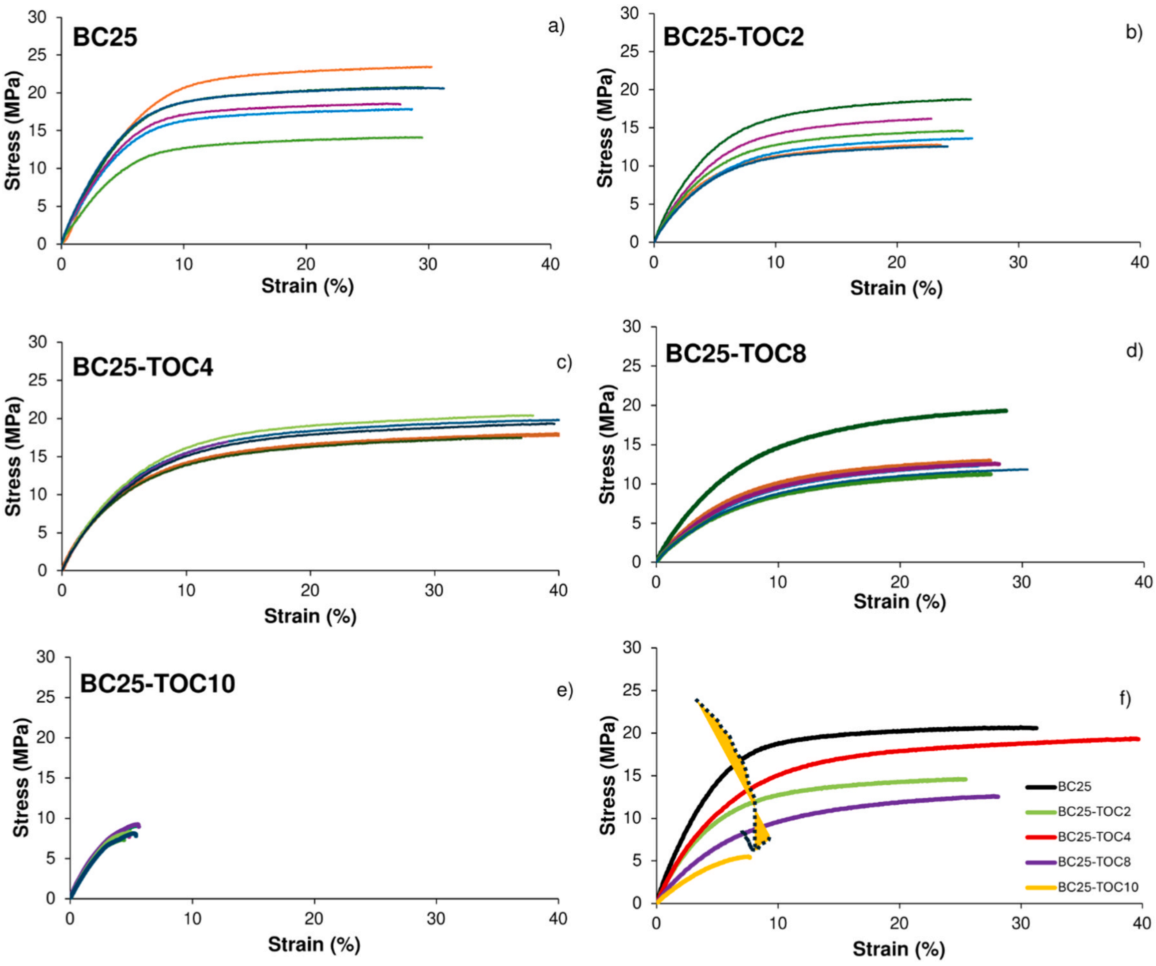

Fig. 3. Tensile test behaviour of BC25 (a), BC25-TOC2 (b), BC25-TOC4 (c), BC25-TOC8 (d), BC25-TOC10 (e), and comparison of the representative curves of all the blends (f). Statistical differences between the groups were evaluated using Tukey's post hoc test. (significance level: 0.05).

Table 2
Average mechanical tensile parameters.

Sample	Young's Modulus, E (MPa)	Tensile Strength at Break, σ_b (MPa)	Elongation at Break, ε_b (%)	Work at Break, W_b (J)
PBS	328.25 ± 18.82	37.15 ± 0.9	353.57 ± 1.30	4.45 ± 1.93
BC25	440.37 ± 8.88	19.18 ± 1.99	30.74 ± 0.35	0.16 ± 0.002
BC25-TOC2	398.15 ± 15.14	14.42 ± 1.84	25.14 ± 0.59	0.11 ± 0.006
BC25-TOC4	376.00 ± 9.11	19.00 ± 2.71	41.00 ± 0.40	0.23 ± 0.002
BC25-TOC8	225.59 ± 22.56	13.04 ± 2.86	28.56 ± 0.37	0.11 ± 0.005
BC25-TOC10	145.95 ± 18.41	5.86 ± 1.45	7.80 ± 0.29	0.07 ± 0.004

work at break, respectively (Fig. 3d and e). Although the curves can be considered relatively superimposable, the excess amount of tocopherol negatively affects the blend, compromising the macromolecular structure of the PBS.

In Fig. 3f, the representative curves for each type of mixture are compared. It can be observed that the slope of the BC25 blend curve progressively decreases (as indicated by the arrow inside the graph), confirming the hypothesized plasticizing effect of TOC discussed above. Only by adding 4 wt% of α-tocopherol led to the maximum values of ultimate tensile strength (19 MPa, $p = 0.9994$), deformability (41%, $p < 0.0001$), and work at break (0.23 J, $p < 0.0001$) among all the blends analysed be achieved. Young's modulus progressively decreased with increasing TOC content, from 440 MPa (0 wt% TOC in BC25) to 146 MPa (10 wt% TOC in BC25-TOC10, $p < 0.0001$).

TOC amounts exceeding 4% (i.e., 8 wt% and 10 wt%) caused a deterioration in the mechanical performance of the blends due to excessive additive load in the blend. An excessive amount of plasticizer in a filled polymer matrix can alter its structure/microstructure and adversely affect the material performance, shifting the behaviour from tough to soft and mechanically unstable. Furthermore, an excess of TOC compromises the long-term durability of the material, accelerates the aging and degradation processes, and favors the migration of additives from the polymer matrix, raising critical issues for applications such as packaging and medical [50].

The rheological tests are shown in Fig. 4, while the complex viscosity values (at two different angular frequencies) are listed in Table 1. The complex viscosity at 0.1 rad/sec of the BC25 blend is higher compared that of pure PBS as expected, due to the presence of brewer spent grain filler inside the polymeric matrix, according to previous paper [16]. Then, the complex viscosity of the blend progressively decreases with increasing TOC content in this order:

BC25 > PBS>BC25-TOC2 > BC25-TOC4 > BC25-TOC8>BC25-TOC10

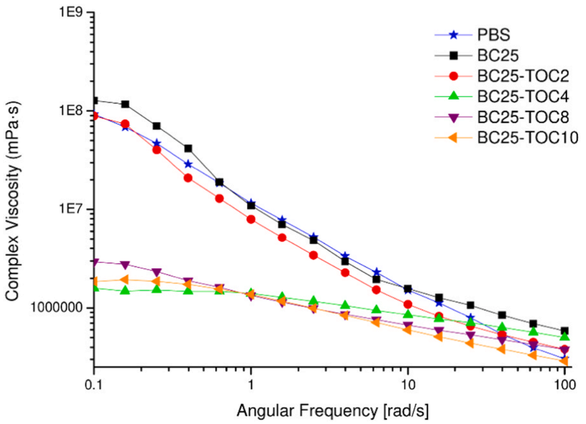

Fig. 4. Rheological analysis of BC25 with different TOC amounts, from 2 to 10 wt%.

In particular, it decreases by approximately 2 orders of magnitude in the BC25-TOC10 blend (from 1.3×10^8 mPa x sec to 0.018×10^8 mPa x sec). The same trend is observed at higher angular frequencies (10 rad/sec), where the viscosity decreases from 1.6×10^8 mPa x sec to 0.59×10^8 mPa x sec. However, the values show that the addition of 4 wt% TOC already significantly reduces the viscosity (i.e.: from 1.3×10^8 mPa x sec to 0.016×10^8 mPa x sec at 0.1 rad/sec, reducing by about 99%, and from 1.6×10^8 mPa x sec to 0.85×10^8 mPa x sec at 10 rad/sec, reducing by about 50%). Therefore, a further increase to 8–10 wt% TOC in the mixture appears necessary, since the viscosity remains within the same range (i.e., between 0.016 and 0.029×10^8 mPa x sec at 0.1 rad/sec, and between 0.6 and 0.8×10^8 mPa x sec at 10 rad/sec). The results of these rheological tests suggest that 4 wt% TOC is sufficient to have a plasticizing effect in the mixture, in agreement with the mechanical tensile results and with the torque results.

3.2. Effect of α-tocopherol on the structure of the blends

To understand the effect of α-Tocopherol on the structure of the blends, DSC, ATR, and SEM were performed. The Cole-cole plots have been also considered in the discussion to evaluate the effect of BSG and of TOC in the blends.

DSC analysis of all samples was carried out to achieve further information on the effect of TOC on the macromolecular structure of PBS by evaluating crystallization temperature (Tc), melting temperature (Tm), and crystallinity degree (χ_C).

By comparing the T_c of BC25 with those of specimens containing increasing quantities of TOC, it can be noticed that, although values do not follow a regular trend, the T_c of BC25-TOC4 (84.47 °C) is significantly higher than that of all other specimens containing TOC and of BC25 (see data listed in Table 3). This result suggests that the addition of 4 wt% of TOC improves the dispersion of the BSG particles. Additionally, the sample BC25-TOC4 has the highest crystallinity degree (χ_c = 62.54%) among all the blends, exceeding by approximately 15% that of BC25 (χ_c = 54.42%)

This evidence indicates that TOC presence helps the macromolecular chains' mobility in PBS by acting as a lubricant (since it is an oil), allowing them to organize more easily into a more ordered structure with a higher crystalline degree, in agreement with the findings of Visco et al. [34]. Furthermore, these results highlight that the amount of 4 wt % of TOC is confirmed again to be suitable to reach the highest structural order inside the polymeric matrix, suggesting that an optimal compatibility effect of TOC is achieved [40,51].

Table 3
Melting and crystallization temperature (T_m and T_c), and crystallinity degree of BC25 blends.

Sample	T_m (°C)	T_c (°C)	χ_c (%)
BC25	113.76 ± 0.06	82.72 ± 0.11	54.42 ± 0.60
BC25-TOC2	113.73 ± 0.04	76.17 ± 0.10	58.97 ± 0.25
BC25-TOC4	113,64 ± 0.03	84.47 ± 0.10	62.54 ± 0.60
BC25-TOC8	113.02 ± 0.09	72.82 ± 0.23	59.64 ± 0.65
BC25-TOC10	112.63 ± 0.09	76.03 ± 0.19	58.36 ± 0.72

Higher concentrations of TOC (8 wt% and 10 wt%) instead show a significant decrease in T_c and χ_c, possibly due to an overload of additive, which reduces the mobility of the polymer chains, further confirming that quantities of TOC above 4 wt% are detrimental, in agreement with tensile and rheological test results. Conversely, T_m remained relatively constant across all samples (around 114 °C) and comparable to that of PBS [16].

The reason for the positive effect of TOC in the sample BC25-TOC4 is probably due to the chemical nature of α-tocopherol which possesses an amphiphilic polar head and an apolar tail (Fig. 5). Its nature could interact both with the crystalline region (with the apolar tail) and the amorphous region (with the polar head), increasing the interactions among these two components (compatibilization effect).

As reported in the literature [52], adding amphiphilic compounds into bio-composites is an example of non-reactive compatibilization, which exerts its activity at the blend interface to facilitate interfacial adhesion. The non-reactive compatibilization may improve plasticization and processability, enhance elasticity, increase crystallinity, decrease stiffness, and strength at break [53].

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To investigate possible interactions among the components, Attenuated Total Reflectance (ATR) spectroscopy was performed on the bio-composites with and without TOC (Fig. 6) [40,54]. The most diagnostic signals are located in the 1700–1800 cm^{-1} region, corresponding to the C=O stretching band. As reported in the literature [55], the formation of intermolecular interactions such as hydrogen bonding may

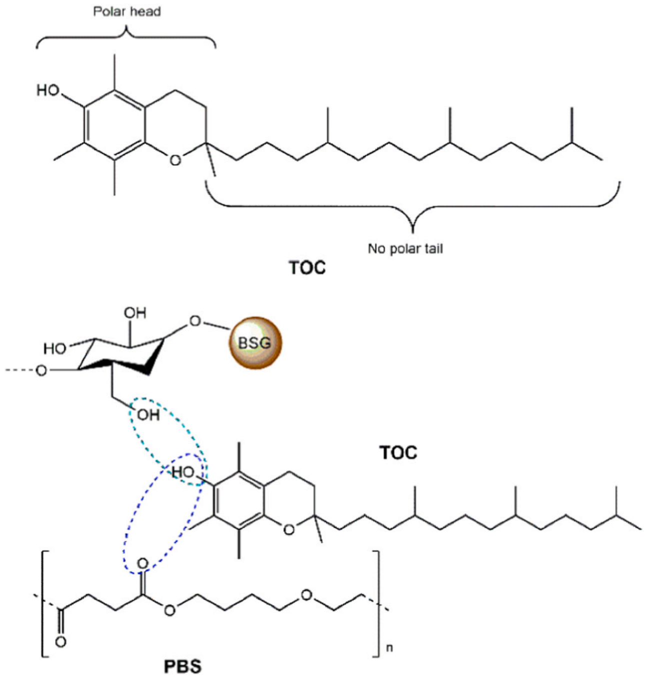

Fig. 5. Chemical structure of α-tocopherol (TOC)and schematic H-bond formation between PBS, BSG, and TOC.

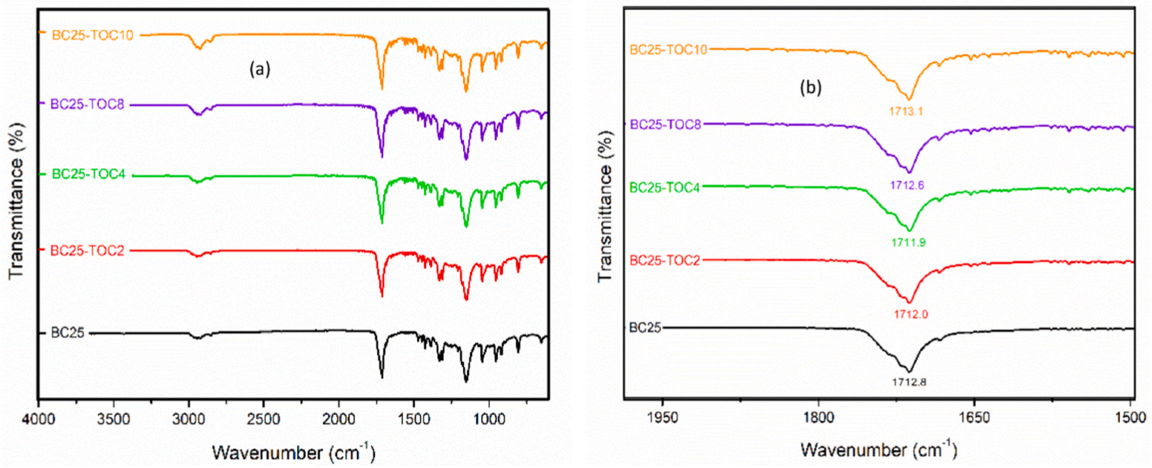

Fig. 6. ATR spectra of BC25, BC25-TOC4, BC25-TOC10 (a) and magnification between 2000 cm^{-1} and 1500 cm^{-1} (b).

lead to a shift of this band toward lower wavenumbers. In the present case, a slight shift of the C=O stretching band from 1712.8 cm^{-1} (BC25) to 1711.9 cm^{-1} (BC25-TOC4) is observed. This minor variation may indicate the presence of weak intermolecular interactions, such as hydrogen bonding, between PBS, BSG, and TOC. However, considering the limited magnitude of the shift close to the instrumental resolution, this observation alone cannot be regarded as conclusive evidence and should be interpreted with caution. Nevertheless, this spectroscopic indication is consistent with the overall behavior of the system. In particular, the BC25-TOC4 formulation exhibits improved mechanical performance, enhanced filler–matrix interaction (as suggested by tensile behavior and SEM observations), and increased crystallinity degree from DSC analysis, all pointing toward improved interfacial compatibility. Therefore, while ATR alone does not provide definitive proof, the combined results support the presence of enhanced intermolecular interactions in the system, likely associated with the amphiphilic nature of α-tocopherol.

Conversely, at higher TOC content (BC25-TOC10), the C=O stretching band shifts toward higher wavenumbers (1713.1 cm^{-1}), approaching the value of pure PBS, suggesting a reduction in such interactions due to excess additive loading. This further supports the existence of an optimal TOC concentration (4 wt%) for achieving effective compatibilization within the composite.

The filler-matrix interaction in the BC25-TOC4 blend can also be observed through morphological analysis using a scanning electron microscope (SEM). SEM micrographs at low magnifications (300x) show the fracture surfaces of the blends. The morphologies of these surfaces are irregular; elongated BSG particles can be seen, often protruding from the surface (Fig. 8a and d). The presence of voids on the fracture surface is due to the extraction of the filler (BSG) following sample fracture.

However, the general irregularity of the surface does not allow the identification of a significant morphological change that could indicate variations in the homogeneity of the BSG dispersion within the polymer matrix as the TOC content varies. SEM analysis can nevertheless provide evidence of the filler-matrix interaction induced by TOC when higher magnifications are considered (2000x).

SEM micrographs at 2000x magnification (Fig. 7f and i) focus on the filler particles protruding from the matrix, highlighted by red arrows. In the BC25 (Fig. 7f), BC15-TO2 (Fig. 7g), and BC25-TOC8 (Fig. 7i) blends, the BSG particles appear detached from the matrix and are surrounded by voids (indicated by the arrows). The fibrous BSG particles appear smooth and elongated, due to their lignocellulosic composition [16].

In contrast, the BSG particle in the BC25-TC4 sample shows good anchoring to the polymer matrix thanks to a continuous phase that forms at the filler/matrix interface and envelops the polymer particle (Fig. 7h). This result is consistent with that of Sin et al., who verified that α-tocopherol can act as an "interacting agent" between polyvinyl alcohol and starch [40].

Regarding the BC25-TOC10 blend, the situation differs from that observed in the other blends, as it is not easy to distinguish the BSG particles from the matrix at low magnifications (Fig. 7e). At high magnifications, a possible filler particle has the usual elongated shape, suggesting it is a BSG fiber; however, the latter does not have the typical smooth morphology due to its lignin-cellulosic composition, but rather appears to be covered by a phase of different origin, likely due to the excess TOC present (10 wt%).

Therefore, the results of the SEM morphological observation confirm that a proper balance between the amount of TOC in the mixture is necessary and agree with the results of the previously performed characterizations (tensile strength, ATR, DSC) which highlight how the presence of TOC at 4% by weight is the optimal one, ensuring good ductility of the matrix and good physical filler-matrix interaction, avoiding the use of chemically reactive and harmful compatibilizers. This result is in a good agreement with the article by Jiang et al. [37] and Sin et al. [40].

In polymer composites, the filler dispersion and interfacial interactions between filler and matrix are a critical issue. Effective filler dispersion in the matrix promotes a homogeneous structure, while poor compatibility induces filler aggregation and marked heterogeneity [56].

These structural features are directly reflected in the rheological response. The Cole–Cole plot (G″ vs G′) represents a sensitive indicator of system homogeneity: a quasi-semicircular arc is associated with a simple viscoelastic behaviour characterized by a single dominant relaxation time [57]. Deviations from this behaviour, including distorted arcs or quasi-linear trends, indicate a broader distribution of relaxation times and increased microstructural complexity [58]. Hence, the Cole-Cole plots from our rheological analysis have been considered to evaluate the compatibility effect of TOC in the blend compared to pure PBS, considered as reference. Fig. 8 shows the Cole-Cole plots of all the blends (BC25, BC25-TO2/TOC4/TOC8/TOC10). In the same graph, neat PBS has been added as reference. Neat PBS exhibits a quasi-semicircular Cole–Cole profile, consistent with a relatively simple viscoelastic response and a narrow relaxation time distribution. This behaviour is typical of homogeneous polymer melts and has been widely reported in the literature [59].

Sample BC25 shows a marked change compared to pure PBS, tending towards linearity. The Cole–Cole plot deviates significantly from the semicircular shape, displaying a non-closed, monotonically increasing trend. Such a response is typically associated with the absence of a dominant relaxation time and the presence of a broad and continuous relaxation spectrum. This behaviour suggests the formation of a highly heterogeneous structure, likely related to the development of a partially

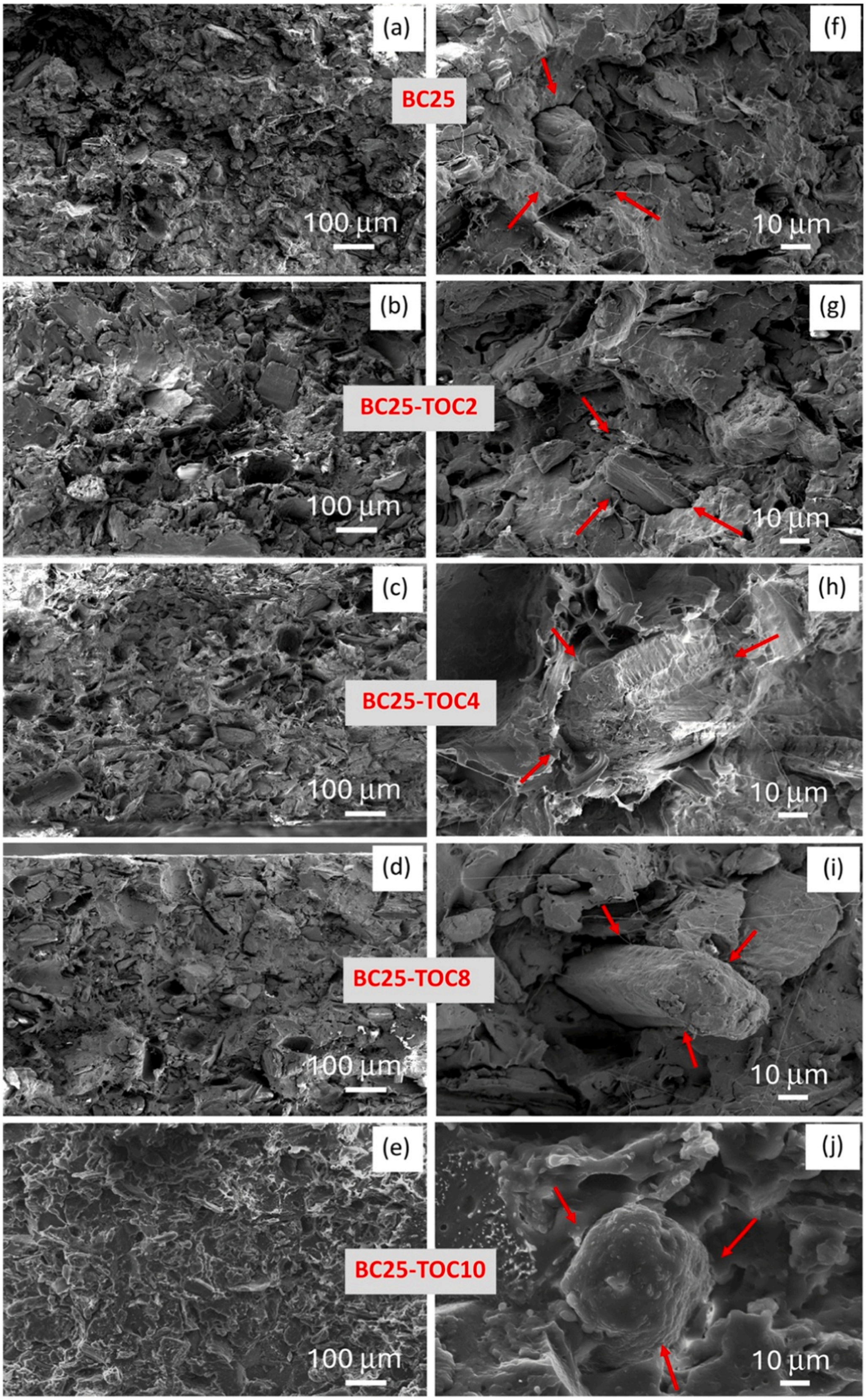

Fig. 7. SEM images of BC25 (a, f), BC25-TOC2 (b, g), BC25-TOC4 (c, h), BC25-TOC8 (d, i), BC25-TOC10 (e, j), at low (left 300x) and high (right, 2000 x) magnifications.

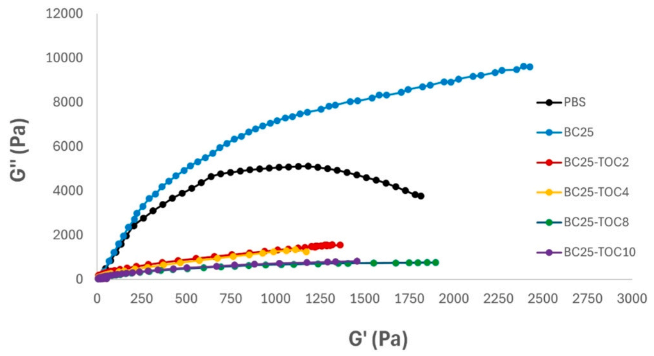

Fig. 8. Cole-Cole plot of PBS, BC25, BC25-TOC2, BC25-TOC4, BC25-TOC8, BC25-TOC10.

percolated network of BSG fibres within the PBS matrix [60]. The strong filler-filler interactions and the resulting structural connectivity could be due to the high BSG content in the blend (25%) and their high aspect ratio [24]. This indicates a significant increase in structural heterogeneity, consistent with literature data [61].

The presence of TOC in BC25-TOC2, BC25-TOC4, BC25-TOC8, and BC25-TOC10 does not restore a homogeneous filler distribution within the matrix, as clearly evidenced by the persistent deviation from the ideal semicircular Cole–Cole profile. Nevertheless, TOC induces a marked restructuring of the viscoelastic response, indicating a significant reduction in filler–filler interactions and a progressive disruption of the percolated network formed by the high aspect ratio BSG fibers. Compared to the highly distorted response of BC25, TOC-containing systems exhibit a substantially simplified quasi-linear behaviour, reflecting a shift in the governing relaxation mechanisms. These findings strongly suggest that TOC drives a transition from a BSG network-dominated regime to a matrix-controlled viscoelastic response, although full microstructural homogenization is not achieved [62].

Finally, one of the key limitations of PBS is its relatively poor resistance to UV radiation, which remains a critical drawback for its broader application. [63].

To improve its stability to UV light, stabilizers are often added to PBS. Among these, carbon black is one of the most effective due to its ability to absorb UV rays and reduce polymer degradation processes [64]. Appropriately modified lamellar double hydroxides (LDH) also help protect the material by limiting the breakage of polymer chains during exposure to light. [65,66]. Additional strategies include the use of lignin or specific UV absorbers, which improve the material's shielding properties [67]. α-Tocopherol can contribute to photo-protection by absorbing part of the UVB radiation and acting as an antioxidant. For this reason, further future studies could continue our previous research [64] by verifying the effect of TOC as a UV filter both alone and in combination with other specific additives such as carbon black and even the spent grains themselves which, given their ligno-cellulosic nature, could help preserve the material.

4. Conclusions

Since fossil-based plastics have caused significant environmental pollution, scientific interest has shifted towards renewable, biodegradable, and compostable plastics. Considering their high cost and the high cost of disposal of large amounts of industrial agro-food waste (such as spent beer grain, BSG), the solution proposed in this work is to combine PBS (a bioderived and biodegradable bioplastic) with 25 wt% of BSG (BC25 blend), thus reducing bioplastic use by 25 wt% and favouring the consumption, by same amounts, of agro-food waste. An additive (α-tocopherol at 2–4–8–10% by weight) is added to the BC25 mixture to enhance the mobility of the macromolecular chains, facilitate processability, and to improve the compatibilization between the filler and the matrix. Several tests (chemical-physical, rheological, mechanical, and morphological) were performed on all the blends to check the effect of the addition of α-tocopherol in different amounts.

The analysis of the torque and the rheological test during mixing indicates that TOC acts as a plasticizing agent, reducing the torque stress generated on the PBS melts, whereas BSG increases it. Therefore, the presence of an additive such as TOC is beneficial for minimizing the thermomechanical stress during the melt processing of PBS. In particular, the addition of 4 wt% of TOC reduces the viscosity of the mixture by two orders of magnitude compared with that of neat BC25.

The plasticizing effect increases macromolecular mobility, affecting the crystallization kinetics of PBS. To verify this at the structural level, it would be useful to analyse these kinetics, for example using polarized optical microscopy (POM), which was not explored in this work.

In addition, TOC improves the dispersion of the filler (BSG) inside the polymeric PBS matrix when it is added in 4% by weight. In fact, BC25-TOC4 rises of ~36% in deformability and of ~43% in toughness with respect to BC25. The crystalline order rises from 54.42% (in BC25) to 62.54% (in BC25-TOC4), suggesting that TOC acts as a lubricant and helps the macromolecular chains' mobility, which can better organize themselves in a more ordered structure.

Lower amounts of TOC (2 wt%) are not enough to have a positive effect, while higher amounts (8–10 wt%) are excesses that destabilize the macromolecular structure of PBS.

The positive effect of TOC (at the threshold value of 4 wt%) is due to its dual nature, which has a polar amphiphilic head and an apolar tail and can bring filler and matrix closer because the head interacts with the amorphous parts, therefore facing the BSG, while the apolar tail interacts with the crystalline parts, facing the semi-crystalline PBS. The possible interactions are of a physical nature, such as hydrogen bonds among the PBS and BSG.

Further specific studies on PBS-BSG-TOC blends will be dedicated to exploring other aspects not yet analyzed, such as recyclability/re-workability, and mathematical modeling studies to create a predictive model of mechanical behavior at any chemical composition. All this will help define the shelf life of these biomaterials over time and their recyclability before final biodegradation.

Additionally, the stability and possible migration of α-tocopherol within the PBS/BSG matrix were not investigated in the present study. Although this aspect is less critical for the currently targeted applications, such as flowerpots, it remains important for assessing long-term performance and reliability and will be addressed in future work through dedicated retention/migration studies.

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CRediT authorship contribution statement

Salim Brahimi: Visualization, Investigation, Formal analysis, Data curation. **Silvia Conca:** Visualization, Investigation, Formal analysis, Data curation. **Valentina Beghetto:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Funding acquisition, Data curation, Conceptualization. **Annamaria Visco:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Funding acquisition, Data curation, Conceptualization. **Cristina Scolaro:** Visualization, Methodology, Investigation, Formal analysis, Data curation.

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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Data availability

Data will be made available on request.

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