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Epoxidized linseed oil as a plasticizer for All-Cellulose Composites based on cellulose acetate butyrate and micronized pulp fibers

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ABSTRACT

All-Cellulose Composites (ACCs) with cellulose derivatives have been neglected in the composite industry due to their high brittleness, low impact strength, and flowability. Epoxidized vegetable oils are well-known plasticizers for several polymers and composites but have never been exploited on the production of ACCs. The present work investigates the potential of an epoxidized linseed oil (ELO) as a cost-effective additive to enhance the properties and processability of ACCs made with cellulose acetate butyrate (CAB) and micronized *Eucalyptus* pulp fibers. The thermo-mechanical characterization of the composites, obtained by melt-mixing, revealed that ELO significantly decreases the glass transition temperature (Tg) of the obtained composites without compromising their thermal stability. Moreover, an 84-fold improvement was achieved on the melt flow rate (MFR) with 30 wt% ELO, and growing amounts of this additive caused an augment on the elongation and flexural strains at break. High loads of ELO resulted also on a substantial improvement of the impact strength, with values raising from 5.3 ± 0.9 $kJ·m^{-2}$ up to 29.5 ± 1.7 $kJ·m^{-2}$. Furthermore, this eco-friendly plasticizer also led to higher water uptake values, as well as higher biodegradation rates than the non-plasticized ACCs. Therefore, these results evince a remarkable improvement on the ACCs processability, performance, and biodegradation upon addition of a bio-based and cost-effective plasticizer.

1. Introduction

Biocomposites have been a subject of great interest for over a decade. In particular, natural fiber-reinforced composites have gained momentum as replacements for the widely used and more traditional glass fiber-reinforced composites (Arif et al., 2022; Jariwala and Jain, 2019). However, some limitations, such as the non-renewability and non-biodegradability of the commonly used thermoplastic matrices, which are typically petrochemical-based polyolefins, and the unfeasibility to recycle the composites, still raises questions about their environmental impact (Arif et al., 2022; La Mantia and Morreale, 2011). Also, since incineration is not an ecological viable option, and with shortage of landfill availability, it becomes imperative to shift the paradigm towards the design of biocomposites made entirely from renewable resources and with sustainable end-of-life alternatives (Mohanty et al., 2000; Morici et al., 2022). The social and political environmental consciousness over the overexploitation and accumulation of petroleum-based thermoplastics on the environment is on an all-time high, with international entities, such as the European Union, defining carbon neutrality goals for the next decades ("European comission, climate action-, 2050 long-term strategy"). Therefore, it is of the overall best interest to turn the attention to bio-based and biodegradable thermoplastic polymers that could gradually replace the petroleum-based counterparts.

On that perspective, cellulose derivatives, such as cellulose acetate (CA), cellulose acetate butyrate (CAB) or cellulose acetate propionate (CAP), are potential candidates given their thermoplasticity and relatively good properties (Zepnik et al., 2013). These cellulose derivatives were very popular in the industry by the middle of last century. However, in recent times, research activities on their application as matrices for composite materials have been limited due to the focus on petroleum-based polymers, given their lower cost and better processability (Gilbert, 2017; Teramoto, 2015; Toriz et al., 2005) and, more recently, on the bio-based polymers such as poly(lactic acid) (PLA)

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(Ranakoti et al., 2022), poly(hydroxybutyrate) (PHB) (Ranakoti et al., 2022), and thermoplastic starch (TPS) (Ruhul Amin et al., 2019). For those reasons, the potential of cellulose derivatives as sustainable matrices for the development of natural fiber-reinforced composites has been clearly overlooked (Gilbert, 2017; Teramoto, 2015; Toriz et al., 2005).

Cellulose acetate butyrate, introduced in the 1940s as a tougher version of CA, is one of the most relevant cellulose esters produced at a commercial scale (Edgar et al., 2001; Gilbert, 2017). The properties of CAB, that is obtained through the esterification of cellulose with butyric and acetic anhydrides, can be tuned by varying the degree of substitution and the acetate/butyrate ratios (Edgar et al., 2001; Gilbert, 2017). Due to the longer chain length butyrate substituent groups, CAB has naturally lower water absorption, higher flexibility, and better flowability than the more popular and widely used CA (Edgar et al., 2001; Gilbert, 2017). Additionally, its good appearance, high gloss, and clarity, as well as good stability to ultraviolet light, are also attractive characteristics for various applications, including the production of filtration membranes, packaging materials, biomedical products, polymeric composites, and particularly coatings ("Eastman Chemical Company", 2022; Edgar et al., 2001; Petersson et al., 2009; Sudhakar, 2022; Toriz et al., 2005). In the composites field, CAB has been used as the polymeric matrix reinforced with diverse natural fibers, including flax (Carrillo et al., 2011; Toriz et al., 2003), hemp (Ouajai and Shanks, 2009; Wibowo et al., 2006), wood fibers (Glasser et al., 1999), cellulose nanowhiskers (Ayuk et al., 2009; Bondeson et al., 2008), and regenerated fibers (Carrillo et al., 2011), giving rise to a variety of composite materials commonly denominated as All-Cellulose Composites (ACCs), viz. composites composed mostly of cellulose.

Besides the appealing properties of CAB, its narrow processing window, high brittleness, relatively low impact strength, and short elongation at break are still disadvantages in regard to its petroleum-based counterparts. Even though CAB can be processed at lower temperatures and require lower amounts of plasticizers than CA, due to its longer substituent groups, the use of plasticizers on CAB-based composites is still highly desirable to overcome the aforementioned issues (Edgar et al., 2001; Podshivalov et al., 2018). Plasticizers are conveyed to reduce intermolecular interactions between the polymeric chains and to improve the processability by lowering the melting and softening points, as well as the viscosity of the polymer (Gilbert, 2017; Phuong and Lazzeri, 2012; Wypych, 2017). To that purpose, and given their high availability and low cost, phthalates and citrate esters are two of the most extensively studied families of compounds used as plasticizers on thermoplastic cellulose derivatives-based materials (Gilbert, 2017; Toth et al., 2022; Wojciechowska and Foltynowicz, 2009). However, phthalates have been under strong scrutiny over the undesired health side-effects and due to the increasing directives and regulations prohibiting them, implemented by several countries ("Plasticizers market by type (low plasticizers market by type (phthalates, non-phthalates), application (flooring & wall covering, wire & cable, coated fabric, consumer goods, film & sheet), and region (asia pacific, europe, north america) - global forecas"; Wojciechowska, 2012). Besides, more sustainable and non-toxic alternatives, namely the citrate esters, such as triethyl citrate (TEC) and tributyl citrate (TBC), have shown some volatilization at processing temperatures and imparted a decrease on the thermal stability of the composites (Ayuk et al., 2009; Ouajai and Shanks, 2009; Quintero et al., 2013).

Taking everything into consideration, an appropriate plasticizer should be selected, not only by considering its renewability and lack of toxicity , but also on desired characteristics, such as high resistance to migration, high boiling point, low volatility and high thermal stability, meant to prevent, or at least reduce, the plasticizer loss during processing and usage (Wojciechowska, 2012). Herein, epoxidized vegetable oils, such as epoxidized linseed oil (ELO), fulfil such requirements and have been, in fact, successfully used in green composites of PLA and PHB (Immonen et al., 2019; Peltola et al., 2019; Valente et al., 2022). However, the potential of these vegetable oil derivatives on All-Cellulose Composites has not been tested yet. Following that line of thought, in this work, ELO was proposed as a green plasticizer to enhance the processability and overall performance of ACCs based on cellulose acetate butyrate as the matrix and micronized pulp fibers as reinforcements.

2. Materials and methods

2.1. Materials

Two different grades of cellulose acetate butyrate: CAB 381–0.1, with average butyryl, acetyl, and hydroxyl contents of 38.0%, 13.5% and 1.2%, respectively, and CAB 553–0.4 with 47.0% butyryl, 2.0% acetyl, and 4.8% hydroxyl were acquired from Eastman Chemical Company (Kingsport, Tennessee, USA). Both CAB grades have the same density (1.2 $g·cm^{-3}$) and number-average molecular weight (M_n) (20,000). The viscosities of CAB 381–0.1 and CAB 553–0.4 are 38 cP and 114 cP, respectively. The micronized bleached *Eucalyptus* kraft pulp fibers, with average length and width of 332 ± 211 μm and 12.5 ± 5.4 μm, respectively, were kindly provided by The Navigator Company (Aveiro, Portugal). The epoxidized linseed oil, with viscosity values between 0.08 and 0.12 cP, density of 1.1 $g·cm^{-3}$ and minimum oxirane oxygen of 8%, was provided by Traquisa (Barcelona, Spain). The composition of the ELO is as follows: stearic (3–5%), palmitic (5–7%), oleic (18–26%), linoleic (14–20%), and linolenic (51–56%) acids. Nutrimais Pulverulento compost medium, acquired from Nutrimais (Gondomar, Portugal), was obtained by selective compositing of food wastes and lignocellulosic leftovers from forest exploration. The compost medium has 57.66 ± 11.5% of organic matter, pH of 8.9 ± 0.6, moisture content of 29.23 ± 1.41%, water-holding capacity of 170.33 ± 12.34%, and an elemental composition of 32.03 ± 2.66% (total carbon (C)), 2.41 ± 0.48% (total nitrogen (N)), 1.96 ± 0.39% (total potassium (K)), 0.71 ± 0.14% (total magnesium (Mg)), 14.50 ± 2.90% (total calcium (Ca)), and 1.33 ± 0.27% (total phosphorous (P)).

2.2. Composites production and processing

The non-plasticized ACCs were obtained by melt-mixing the CAB samples with a 40 wt% reinforcement of micronized fibers. For the plasticized ACCs, ELO was pre-blended with the CAB prior to the melt-mixing stage. Then, the pre-blend was melt-mixed with the micronized fibers at 50 rpm, during 10 min, at 170 °C, in a Brabender W 30 EHT Plastograph EC mixer (Brabender GmbH&Co. KG, Duisburg, Germany). The ratio of CAB to reinforcing fibers was maintained at 60:40 for all formulations and the content of ELO varied between 7.5 and 30.0 wt%, relative to the total weight of the composite (Table 1).

Dog-bone shaped and rectangular specimens were obtained through injection moulding in a Thermo Scientific Haake Minijet II (Waltham, Massachusetts, USA). The cylinder temperature was set at temperatures between 180 °C and 195 °C and the mould temperature varied between 70 °C, for ACCs with higher loads of ELO, and 160 °C to the non-plasticized ACCs. The injection pressure was maintained at 800 bar for all samples and the post-injection set at 200 bar.

2.3. Composites characterization

2.3.1. Colour coordinates

CIELab parameters of lightness, L* (black (0) to white (100)), and colour coordinates, a* (green = –a* to red = +a*) and b* (blue = - b* to yellow = +b*) were acquired on a Konica Minolta CM-2300d portable sphere type spectrophotometer (Konica Minolta Sensing Europe BV, UK). All measurements were performed on injection moulded test specimens.

2.3.2. Torque measurements

The torque measurements of all composite mixtures, as function of

Table 1
Composition of the non-plasticized and plasticized ACCs, and respective density values.

Sample	CAB (wt %)[a]	Micronized fibers (wt%)[a]	ELO (wt %)[a]	Density (g·dm^{-3})[b]
ACC 381[c]	60.0	40.0	0.0	1.30 ± 0.03
ACC 381_7.5ELO[c]	55.5	37.0	7.5	1.30 ± 0.01
ACC 381_15ELO[c]	51.0	34.0	15.0	1.28 ± 0.00
ACC 381_22.5ELO[c]	46.5	31.0	22.5	1.26 ± 0.00
ACC 381_30ELO[c]	42.0	28.0	30.0	1.24 ± 0.00
ACC 553[d]	60.0	40.0	0.0	1.30 ± 0.01
ACC 553_7.5ELO[d]	55.5	37.0	7.5	1.28 ± 0.00
ACC 553_15ELO[d]	51.0	34.0	15.0	1.28 ± 0.00
ACC 553_22.5ELO[d]	46.5	31.0	22.5	1.25 ± 0.00
ACC 553_30ELO[d]	42.0	28.0	30.0	1.23 ± 0.00

ACC – All-Cellulose composite, CAB – Cellulose acetate butyrate, ELO – Epoxidized linseed oil

[a] Relative to the total weight of the composite.

[b] The density was determined by dividing the specimen's weight by their volume (3.2 cm^3).

CAB grade: [c] CAB 381–0.1; [d] CAB 553–0.4

the ELO load, were obtained at the end of 10 min on a Brabender W 30 EHT Plastograph EC mixer (Brabender GmbH&Co. KG, Duisburg, Germany).

2.3.3. *Scanning electron microscopy (SEM)*

The micrographs of the fracture zones of the composites, after tensile testing, were acquired on a FE-SEM Hitachi SU70 microscope (Hitachi High-Technologies Corporation, Tokyo, Japan), operated at 15 kV. The samples were coated with a carbon film prior to the analysis.

2.3.4. *Thermogravimetric analysis (TGA)*

The thermal stability and degradation profiles of the composites were assessed by TGA. Approximately 10 mg of each sample were heated from room temperature to 800 °C, under inert atmosphere (N_2), using a gradient of 10 °C·min^{-1}. The tests were carried out on a SETSYS Setaram TGA analyser (SETARAM Instrumentation, Lyon, France) equipped with a platinum cell.

2.3.5. *Dynamic mechanical analysis (DMA)*

DMA curves of rectangular specimens (30 × 5 × 1 mm^3) of the composites were obtained on a Tritec 2000 DMA (Triton Technologies, London, UK) apparatus operating on tensile mode at 1 Hz with 0.01 displacement. The temperature was sweep from 25° to 170°C with a heating rate of 2 °C·min^{-1}.

2.3.6. *Mechanical testing*

The tensile mechanical properties, namely the Young's modulus, tensile strength, and elongation at break, were determined according to the ISO-527–2 (bar type 5 A). For that purpose, at least six dog-bone specimens were tested at a velocity of 5 mm·min^{-1} using a 10 kN static load cell. For the flexural properties, the tree-point loading model was chosen. The assays were conducted according to ISO 178, where five standard rectangular specimens (80 × 10 × 4 mm^3) were tested with a 500 N load cell at a velocity of 5 mm·min^{-1}. The tensile and flexural assays were both conducted on a universal testing machine Instron 5966 (Instron Corporation, Norwood, MA, USA). The impact strength of at least ten specimens was measured following the international standard ISO 179/1eU. Accordingly, the unnotched charpy (edgewise) tests were conducted on a Ray Ran Universal Pendulum impact system (Ray-Ran Test Equipment Ltd., Nuneaton, UK) operating a 4 J pendulum with the support span set at 62 mm. The statistical analysis of the mechanical properties was done using the analysis of variance (ANOVA) and Tukey's mean comparison test (OriginPro 9.6.5, OriginLab Corporation, MA, USA) with the statistical significance set at $p < 0.05$.

2.3.7. *Melt flow rate (MFR)*

The MFR of the composites was measured according to the standard ASTM D1238. For that purpose, a Melt Flow Indexer Davenport (MFR-9) (Ametek, Denmark) was operated at 190 °C with a 5 kg weight. Five cut-offs for each sample were weighted and the melt flow rate was calculated following Eq. 1:

$$MFR \quad (g.10\text{min}^{-1}) = \frac{600 \times m}{t} \tag{1}$$

where m represents the average mass of the cut-offs, in grams, and t is the cut-off time interval, in seconds.

2.3.8. *Water uptake capacity*

Three rectangular (60 × 10 × 1 mm^3) test specimens of each sample were immersed in distilled water at room temperature. During the course of 31 days, the specimens were removed from the water and wiped with tissue paper in order to remove the excess of water and weighted. The water uptake capacity (%) by immersion was calculated according to the following Eq. 2:

$$Water \quad uptake \quad (\%) = \frac{(W_t - W_0)}{W_0} \times 100 \tag{2}$$

where W_0 is the initial weight of the specimen and Wt is the specimen's weight after immersion for a t time period.

2.3.9. *Degradation in compost medium*

The degradation of the composites was determined by measuring the weight loss of the test specimens as function of the burial time in compost medium. First, the rectangular test specimens (60 × 10 × 1 mm^3) were conditioned by drying them in an oven during 48 h at 40 °C, and the initial weight was registered (W_0). The specimens were then buried in compost medium in a 1 L container, placed at 1 cm from the bottom. The assays were conducted at room temperature and the humidity of the compost medium was maintained at 60 wt% of the water-holding capacity by adding tap water regularly. At time t, tree specimens of each sample were retrieved from the container, washed with distilled water to remove compost residues and then dried at 40 °C until a stable mass was achieved. Lastly, the specimen's weight (W_t) was measured and the weight loss was calculated according to Eq. 3:

$$Weight \quad loss \quad (\%) = \frac{W_0 - W_t}{W_0} \times 100 \tag{3}$$

3. Results and discussion

The current study investigates how effectively an epoxidized linseed oil can function as a low-cost plasticizer to enhance the processability and performance of All-Cellulose Composites made with cellulose acetate butyrate as the matrix and micronized fibers as reinforcements. The composites were prepared with two distinct CAB grades (CAB 381–0.1 and CAB 553–0.4) having different viscosities and percentages of acetyl, butyryl, and hydroxyl groups. The influence of ELO was studied by changing its load from 7.5 wt% to 30.0 wt%, in relation to the total weight of the composite (Fig. 1). To efficiently study the influence of ELO on the ACCs, the ratio between the matrix and reinforcement was maintained at 60:40.

Fig. 1 portrays the digital photographs of the injection moulded ACCs without and with different contents of ELO and their respective colour

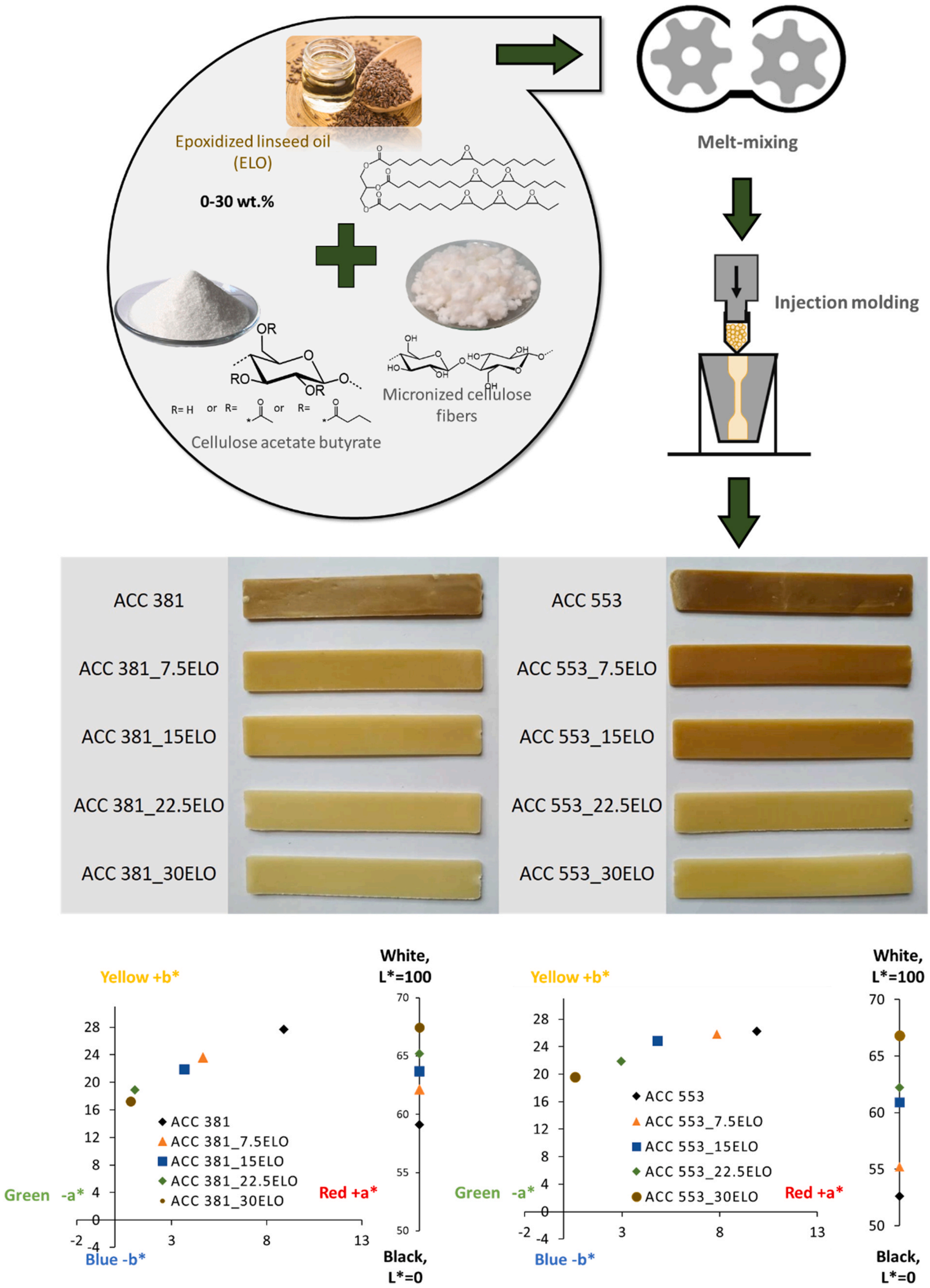

Fig. 1. Scheme showing the production and processing of the ACCs, the digital photographs of the injection moulded test specimens and their colour parameters (CIELab scale: L*, a*, b*).

coordinates. It is clearly visible that the non-plasticized ACCs have a much darker colour in comparison with the respective plasticized composites. The dark colour of cellulose fiber-reinforced composites has been attributed to some degree of thermal degradation of the cellulose fibers during the fabrication and processing of the composites at high temperatures (Ozyhar et al., 2020; Valente et al., 2021). On the contrary, plasticized ACCs gradually become less darker with the increase of the ELO content. In addition to the visual observation of the test specimens, the variation of the CIELab colour coordinates further supported that hypothesis. As verified in Fig. 1, the incorporation of ELO led to a decrease in the yellowness (b* values) and redness (a*values) of the composites, together with an increase in the whiteness (L* values). On a previous work (Valente et al., 2022), ELO was effectively used as plasticizer on formulations of PHB and PLA reinforced with micronized fibers. Similar to the results reported here, the incorporation of ELO also contributed to the whitening of the test specimens, although in a smaller extent given the lower amount of ELO used on that study. The whitening effect was attributed to the plasticizing action of the additive, which lowers the melt viscosity and friction during processing, as evidenced by the decrease on the torque measured during the melt mixing stage (Fig. 2), thus lessening the thermal degradation (Immonen et al., 2019; Valente et al., 2022). Furthermore, it is believed that two other factors might also play a crucial role on the colour of the composites: (i) the mildest injection conditions of the plasticized ACCs (up to 15 °C and 90 °C difference on the cylinder and mould temperature, respectively) and (ii) the gradual decrease on the reinforcing fiber load (Table 1), that further contributes to reduce the fiber/fiber friction.

In the next sections, the influence of different contents of ELO will be discussed regarding its effect on the interfacial morphology, thermal, and mechanical performance, melt flowability and biodegradation behaviour of the composites.

3.1. *Morphology*

The SEM micrographs of the fracture surfaces of the non-plasticized and plasticized ACCs are displayed in Fig. 3. To evaluate the influence of ELO on the interfacial morphology, the intermediate (15 wt%) and maximum (30.0 wt%) ELO loads were selected, alongside with the non-plasticized ACCS. The micrographs reveal that the micronized fibers are well dispersed and present a uniform distribution, without any visible agglomerates at sight, which agrees with the visual observation of the test specimens (Fig. 1). However, fiber pullouts and voids are also visible in the micrographs, especially for the non-plasticized ACCs, which was anticipated given the different phobic natures of the constituents. The same observation has been reported in the past for other CAB-based composites reinforced with different lignocellulosic fibers (Glasser et al., 1999). Despite the pullouts and voids, the interfacial adhesion seems relatively good for all non-plasticized and plasticized ACCs, as demonstrated by the absence of any gaps between the fibers and the matrix. Nevertheless, the compatibility between the thermoplastic CAB and the lignocellulosic fibers is not a consensual issue. In fact, some authors, such as Bondeson (Bondeson et al., 2008) and Seavey (Seavey et al., 2001), also described the good interaction between the CAB matrix and the reinforcing cellulose substrates, namely nanowhiskers or lyocell, respectively, but other authors claimed a weak interfacial adhesion and compatibility between the CAB and lyocell (Carrillo et al., 2011) or hemp (Ouajai and Shanks, 2009) fibers.

To be best of our knowledge, none of the works on plasticized CABs-based ACCs previously reported in the literature investigated how the plasticizer affects the morphology of the composites. In the present work, as the plasticizer content goes up, the fibers are better embedded into the composite matrix. That can be, in part, associated with the large amounts of ELO and consequent reduction of the total percentage of the micronized fibers in the overall mixture (Table 1) and to the plasticizing action of ELO, which increases the molecular mobility (Wojciechowska, 2012) and renders the ACCs with increased ductility, ultimately facilitating the embedment of the fibers. Furthermore, the fatty acids long chains and epoxide groups of ELO may interact with the hydrophobic CAB and hydrophilic micronized cellulose fibers, respectively, thus improving the interfacial adhesion.

3.2. *Thermogravimetric analysis*

The thermal stability of the ACCs was assessed by TGA and the corresponding curves and its derivatives (dTGA) are presented in Fig. 4. All thermograms of plasticized and non-plasticized ACCs display a very similar profile with one minor weight loss at temperatures near 100 °C, related to the evaporation of residual water, and a major weight loss stage associated with the degradation of the three constituents of the composites, namely the CAB matrix, the micronized fibers, and the ELO. Moreover, the maximum degradation temperatures (T_{max}) of the non-plasticized ACCs were very similar to those of the plasticized counterparts. The non-plasticized ACC 381 and ACC 553 had a T_{max} of 354 °C and 351 °C, respectively, while the corresponding plasticized ACCs had T_{max} between 352 °C and 353 °C for the ACCs 381 and between 349 °C and 353 °C for ACCs 553. The observation of only one main weight loss can be correlated with to the good miscibility of three components in the mixture and to the proximity of their degradation temperatures. Cellulose fibers have been reported to have a maximum degradation temperature of near 350 °C (Neto et al., 2021; Valente et al., 2021), while cellulose acetate butyrate has degradation temperatures in the range between 350 °C and 370 °C (Furtado et al., 2020; Zaini et al., 2014) and ELO decomposes at around 380 °C (Supanchaiyamat et al., 2014). Finally, at temperatures above 400 °C, a residue content between 11% and 15% can be noted, which corresponds to the formation of ashes (Quintero et al., 2013).

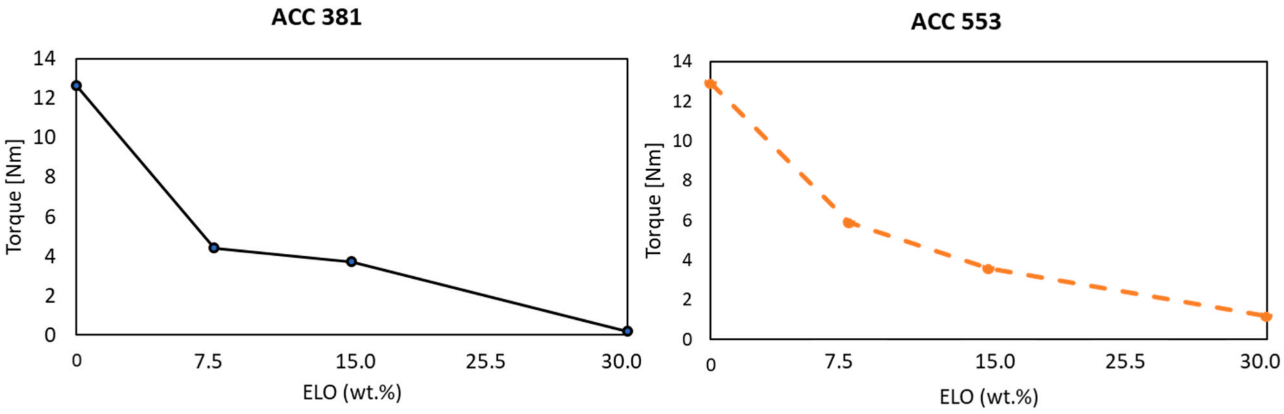

Fig. 2. Torque measurements of the non-plasticized (0 wt% ELO) and plasticized (7.5, 15 and 30 wt% ELO) ACCs.

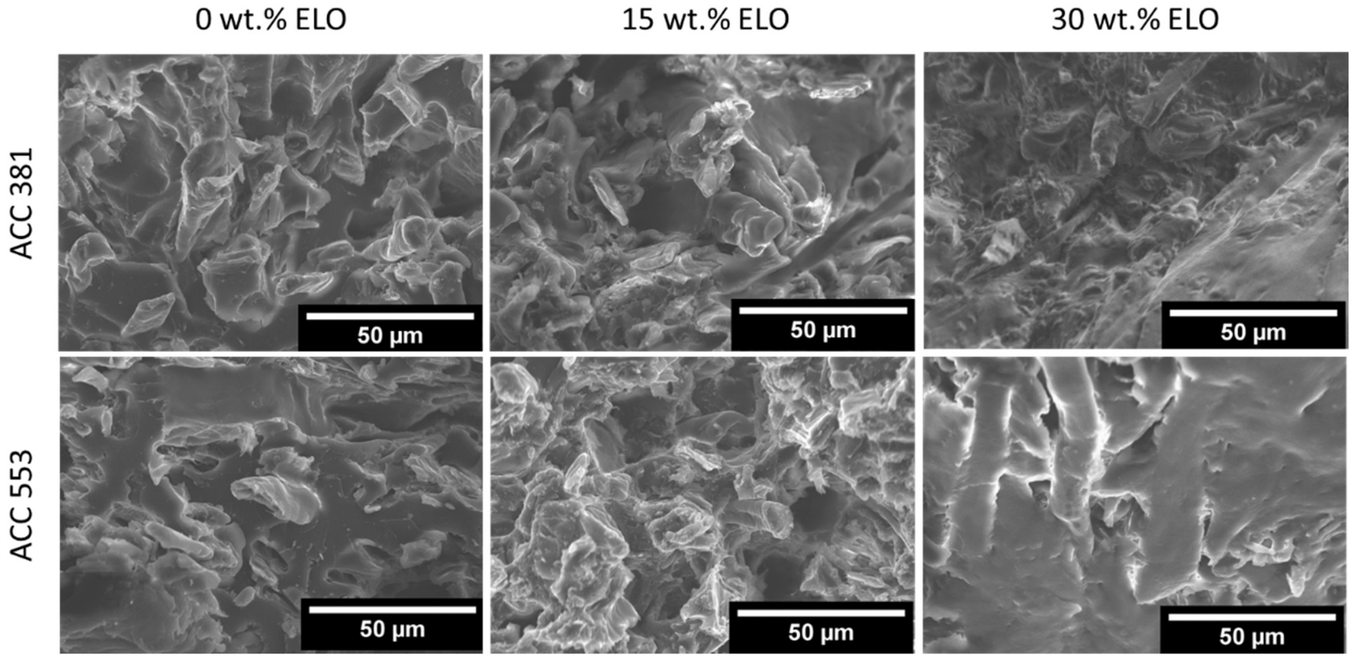

Fig. 3. SEM micrographs of fracture surfaces of non-plasticized (0 wt% ELO) and plasticized (15 and 30 wt% ELO) ACCs.

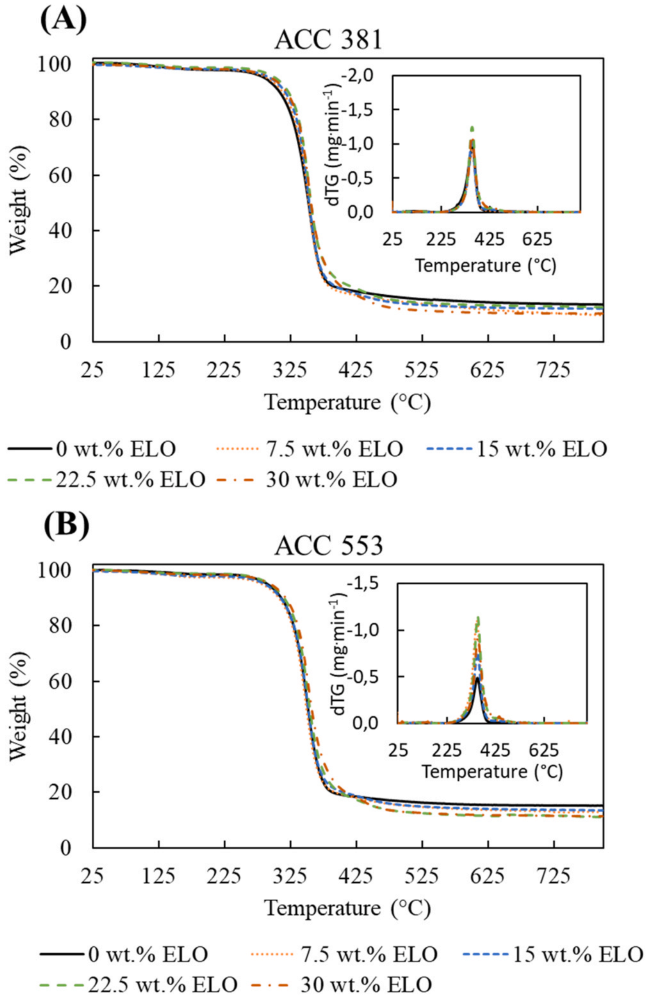

Fig. 4. Thermogravimetric and derivative curves of the non-plasticized and plasticized ACCs 381 (A) and ACCs 553 (B).

It is worth noting that the addition of ELO and its increasing content does not hinder the thermal stability of the ACCs. That achievement presents a remarkable advantage of ELO over other plasticizers, such as TBC or TEC, which are some of the most extensively used bio-based plasticizers on thermoplastic cellulose derivatives and its composites (Ayuk et al., 2009; Bondeson et al., 2008; Ouajai and Shanks, 2009; Tech et al., 2014). For instance, it was found that CAB films plasticized with 20 wt% of TEC had two main weight losses, of which, the first was associated to the loss of the plasticizer, at temperatures below 214 °C (Quintero et al., 2014). On another example, a 5 wt% content of TEC was enough to lower the degradation temperature of CAB-based nanocomposite films with organoclay and antimicrobial agents (Quintero et al., 2013). In plasticized ACCs of CAB with modified hemp cellulose fibers, TBC also caused a decrease on the thermal stability of the composites. Specifically, if from one side, the main degradation temperature of CAB was recorded at approximately 350 °C, on the other side, plasticized CAB composites showed weight losses proportional to the content of TBC, at temperatures between 175 °C and 180 °C, which was credited to the volatilization of the plasticizer (Ouajai and Shanks, 2009). It is worth to emphasize that these lower volatilization temperatures of the aforementioned plasticizers are well in the range of the processing window of biocomposites with natural fibers (up to 200 °C) (Gholampour and Ozbakkaloglu, 2020; Jaafar et al., 2019) and, therefore, the loss of the plasticizer during processing can seriously jeopardize the plasticizing efficiency.

3.3. Dynamic mechanical analysis

Dynamic mechanical analysis is a method for the investigation of the temperature-dependent stiffness behaviour of a sample (Frink et al., 2019) and, as such, it is a helpful tool to assess how the inclusion of a plasticizer affects the properties of the composites. The curves of the storage modulus *E*', i.e., the ability of the material to store energy, and the loss factor (tan δ), i.e., the ratio between the loss modulus and storage modulus, of the ACCs without and with different amounts of ELO are represented in Fig. 5.

As observed in Fig. 5A and B, composites with either CAB 381–0.1 or CAB 553–0.4 have a similar storage modulus profile, with a glassy state at lower temperatures followed by a softening phase. More importantly,

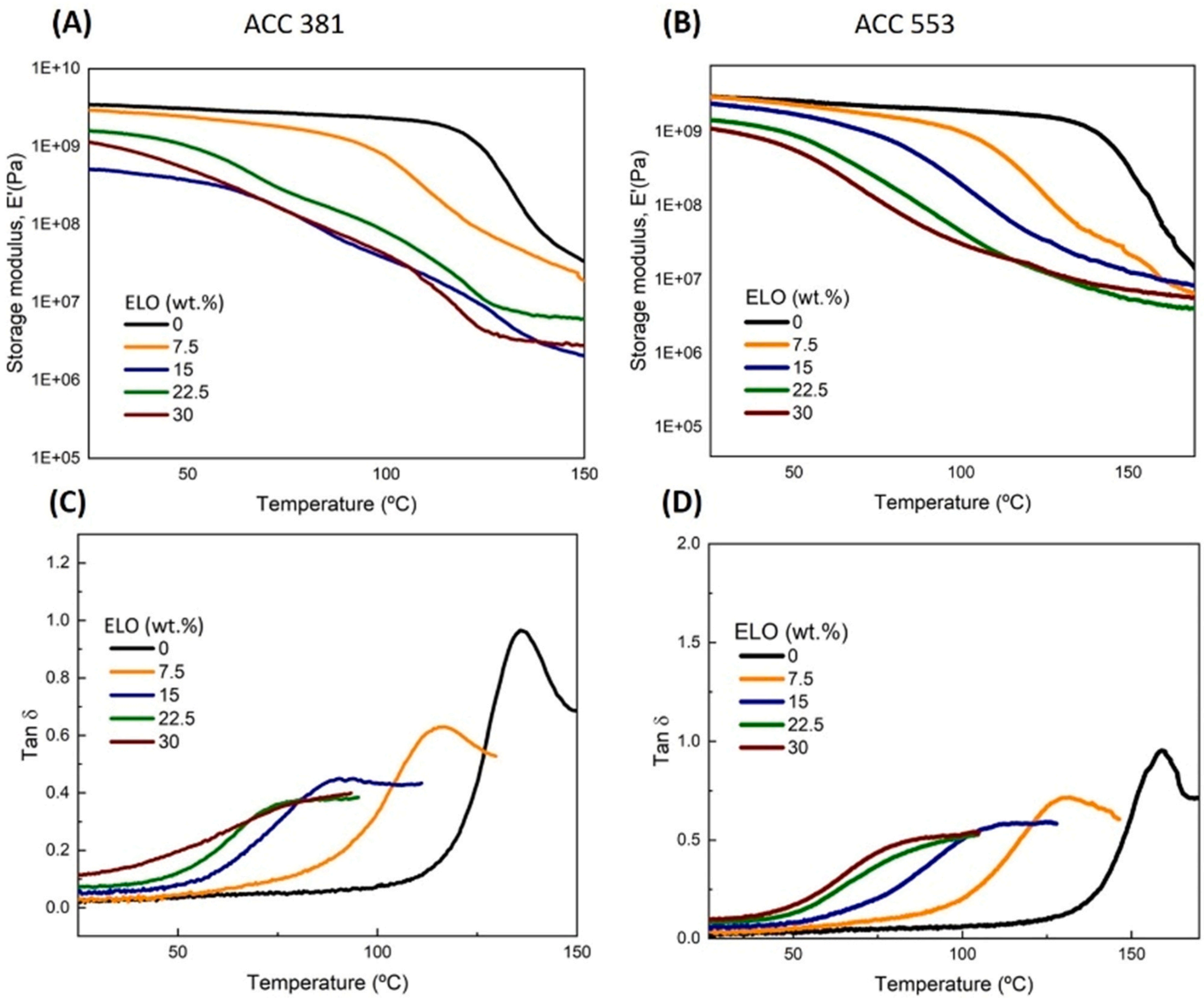

Fig. 5. Storage modulus (A,B) and loss factor (tan δ) (C,D) of the non-plasticized and plasticized ACCs: ACC 381 (A,C) and ACC 553 (B,D).

a considerable downward trend can be noted for the storage modulus as the content of ELO increases. That can be explained, not only with the plasticizing action of ELO, but also with the decrease on the percentage of reinforcing fibers in respect to the total amount of the composite (from 40 wt% for ACC without ELO to 28 wt% for ACCs with 30 wt% ELO). The glass transition temperature (T_g), determined as the temperature at which the peak of the loss factor occurs, also decreases progressively with the increase in the ELO content. While non-plasticized ACCs 381 and ACCs 553 have T_g values of 135.9 °C and 158.8 °C, respectively, the corresponding composites plasticized with 30 wt% presented T_g values under 80 °C. That can be explained by the free volume theory plasticization mechanism, which states that the molecules of a plasticizer increase the free volume (internal space within the polymeric matrix), allowing higher chain rotation and segment mobility, thus reducing the storage modulus and glass transition temperature (Wojciechowska, 2012).

The effect of plasticizers on the viscoelastic behaviour of thermoplastic matrices and composites has been documented on the literature, with studies showing the same trend as the ones observed in the present work. For instance, when tributyl citrate was employed as plasticizer in CAB films, in volume fractions between 10 and 30 vol%, both the storage modulus and glass transition temperature shifted to lower temperatures with the increasing amount of TBC (Ouajai and Shanks, 2009). For example, just 10 vol% of TBC was enough to lower the T_g from around 130 °C to near 90 °C. In a similar fashion, Ayuk and co-authors (Ayuk et al., 2009) manufactured ACCs based on CAB reinforced with cellulose nanowiskers, plasticized with triethyl citrate. Although in a much lower extent, given the significantly lower amount of plasticizer (5 wt%), TEC was responsible for the drop of the T_g from 157 °C to 142 °C. Therefore, the combined results on the storage modulus and glass transition temperature presented in this work are consistent with to the expected behaviour of a plasticizer and with the results shown in literature.

3.4. Tensile, flexural and impact properties

The impact of the ELO content on the tensile, flexural, and impact performance is depicted in Figs. 6 and 7. In a similar manner to what was found for the storage modulus, the plasticization of the ACCs with increasing ELO contents led, for the most part, to a progressive reduction on the Young's and flexural moduli. The Young's modulus for both the ACCs 381 and ACCs 553 decreased from 3.6 ± 0.1 GPa and 3.8 ± 0.1 GPa, for the respective non-plasticized composites, to only 0.7 ± 0.1 GPa after the incorporation of 30.0 wt% of ELO. Similarly, the flexural modulus falls from 4.4 ± 0.1 GPa (ACC 381) and 4.8 ± 0.3 GPa (ACC 553) to only 0.6 ± 0.1 GPa for both plasticized ACCs with 30.0 wt % of ELO. It is worth mentioning however, that in the case of ACC 381, the flexural modulus of ACC 381_7.5ELO is superior to the non-

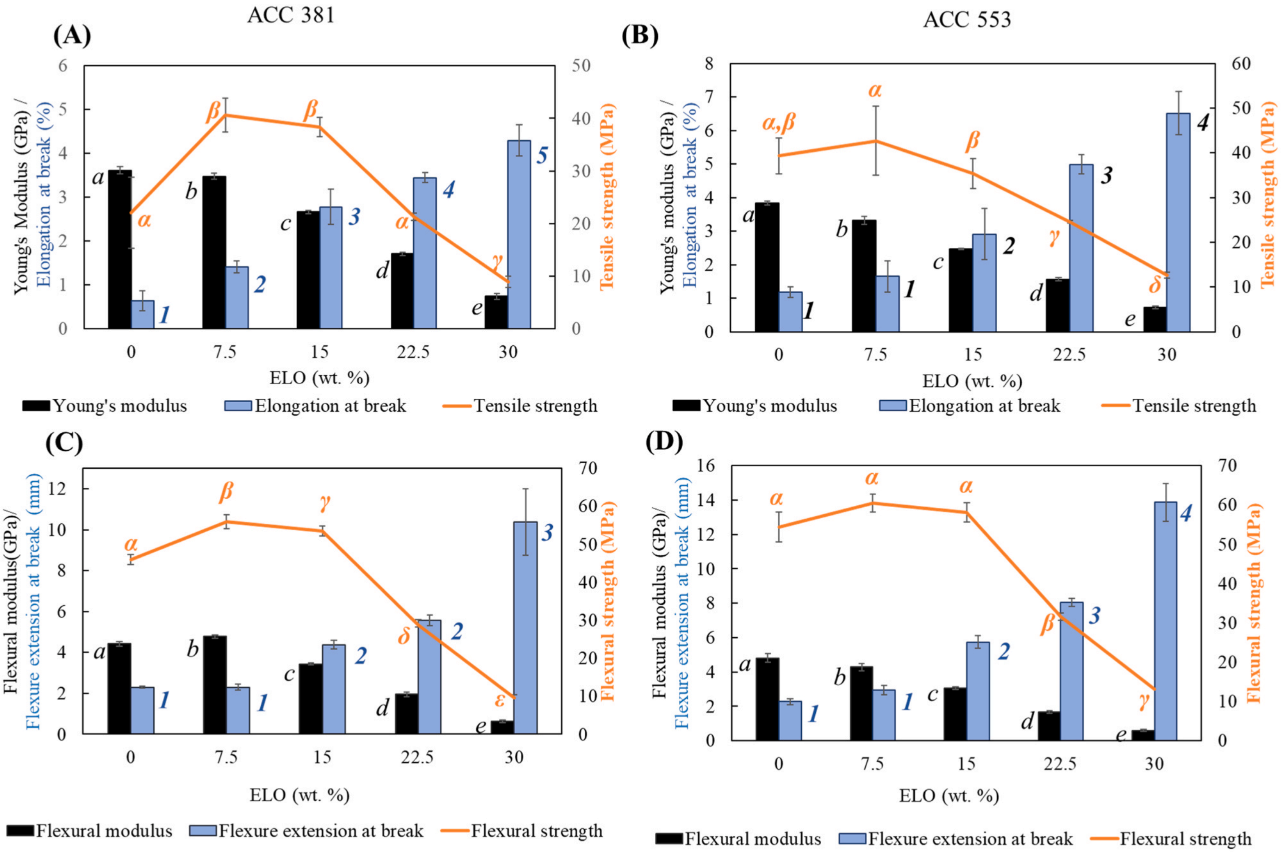

Fig. 6. Tensile (A,B) and flexural (C,D) properties of ACCs as function of the ELO content (the lines are for visual guidance only). Different letters (a,b,c,d,e), (α,β,γ,δ,ε) or numbers (1,2,3,4,5) indicate statistically significant differences ($p < 0.05$).

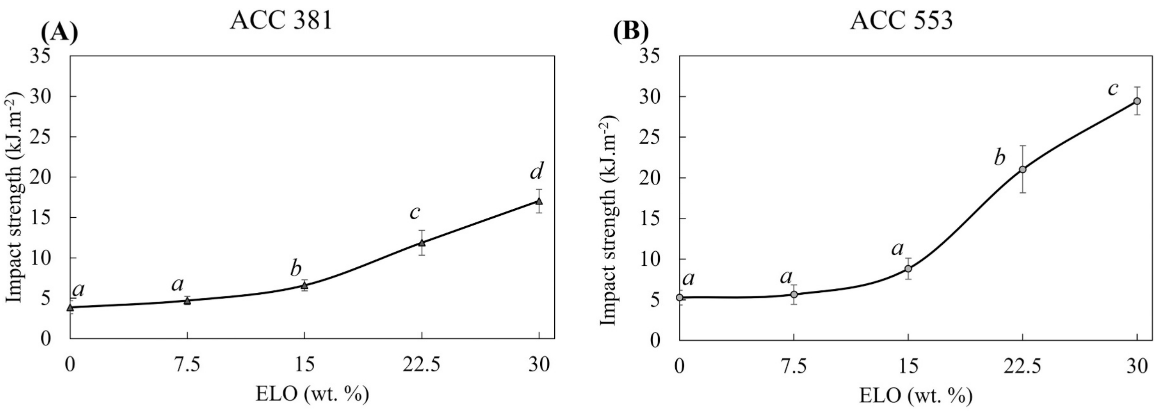

Fig. 7. Impact strength of ACCs 381 (A) and ACCs 553 (B) as function of the ELO content (the lines are for visual guidance only). Different letters (a,b,c,d) indicate statistically significant differences ($p < 0.05$).

plasticized counterpart.

Concerning the tensile and flexural strengths, the addition of 7.5 wt% and 15.0 wt% ELO on ACC 381 yields higher values when compared with the non-plasticized composites. The superior tensile and flexural strengths and, even the higher flexural modulus for ACC 381_7.5ELO over its non-plasticized counterpart are, in fact, opposite to the expected behavior of a plasticized composite. This phenomenon, which may happen when low amounts of plasticizers are added to thermoplastic materials, is called antiplasticization (Wypych, 2017). Although the mechanisms involved are not clear, it has been previously reported for plasticized poly(methyl methacrylate) (PMMA) with 13 wt% TEC or triacetin (Gutierrez-Villarreal and Rodríguez-Velazquez, 2007) and even for CAB/tetraethoxysilane hybrids (Wojciechowska, 2012). On the contrary to the ACCs 381, the tensile and flexural strengths of plasticized ACCs 553 with 7.5 wt% and 15.0 wt% ELO, are not statistically different from the non-plasticized ones. Nevertheless, for higher contents of ELO, more specifically 22.5 wt% and 30.0 wt%, a sharp decline can be noted for both ACC 381 and ACC 553 based materials.

As expected, the reduction on the tensile and flexural moduli and strengths, upon incorporation of plasticizer, is accompanied by a remarkable improvement on the elongation and flexural extensions at break. The elongation at break rises from 0.6 ± 0.2% (ACC 381) and 1.2 ± 0.2% (ACC 553) to a maximum of 4.3 ± 0.4% and 6.5 ± 0.6%, respectively. The flexural extension at break follows the same trend with values jumping from 2.3 ± 0.1 mm (ACC 381) and 2.3 ± 0.2 mm (ACC 553) to a maximum of 10.4 ± 1.6 mm and 13.9 ± 1.1 mm, respectively.

The decrease on the tensile and flexural moduli and strengths, and the increase on the elongation and flexion strain at break are deeply related with two distinct factors, namely the overall content of reinforcing fibers and the plasticization action of ELO. As can be inferred by the information provided in Table 1, although the ratio of matrix to fibers is maintained constant, as the content of incorporated ELO increases, both the amount of matrix and reinforcing fibers falls down. Since it is well known that the content of reinforcing fibers has a major influence on the mechanical properties (Khan et al., 2018; Pickering et al., 2016), the reduction of the reinforcing fiber content certainly contributes to the lower moduli and strengths. Furthermore, and as expected, the increased polymer chain mobility and the decrease of the glass transition temperature originated by the addition of a plasticizer, leads to an improvement on the elongation and flexure strain at break, while compromising the tensile and flexural moduli and strengths (Wypych, 2017). Numerous studies have shown the influence of plasticizers on the tensile and flexural properties of thermoplastic materials. For instance, three citrate esters (TEC, TBC, and acetyl triethyl citrate (ATC)) and three phthalates (diethyl phthalate (DEP), dibutyl phthalate (DBP) and dioctyl phthalate (DOP)) were tested in a CAB/tetraethoxysilane hybrid composite. The results showed that after the anti-plasticization threshold, the majority of the tested plasticizers led to a decrease on the tensile strength and an augment of the elongation at break when the plasticizer content was at 35 wt% (Wojciechowska, 2012). Other studies have demonstrated the same profile either for CAB matrices (Ouajai and Shanks, 2009) or for ACC of CAB reinforced with flax fabric (Tech et al., 2014), both plasticized with TBC.

Cellulose acetate butyrate has a relatively low resistance to impact, which results from its high brittleness (Podshivalov et al., 2018). Consequently, CAB-reinforced composites, as the ones produced on the present work, also have low impact resistance (Fig. 7). For instance, non-plasticized ACC 381 and ACC 553 have impact strengths of 3.9 ± 0.8 kJ·m^{-2} and 5.3 ± 0.9 kJ·m^{-2}, respectively. Nonetheless, higher contents of ELO (22.5 wt% and 30.0 wt%) caused significant improvements on the impact resistance, which can result on values as high as 17.0 ± 1.5 kJ·m^{-2} (ACC 381_30ELO) and 29.5 ± 1.7 kJ·m^{-2} (ACC 553_30ELO). That represents an improvement of ca. 335% and 457% in regard to the non-plasticized composites and brings the impact resistance to the range of commercial products of the biocomposites of polyolefins reinforced with natural fibers (15–45 kJ·m^{-2}) ("beologic,", "SAPPI Symbio", "UPM Formi"). Moreover, the results are in agreement with the previous mechanical properties in the sense that the addition of ELO makes the ACCs considerably more ductile. It is worth mentioning that, for the lower contents of ELO, more specifically 7.5 wt% and even 15.0 wt% in the case of ACC 553, the changes in the impact strength are not statistically different when compared to the non-plasticized composites. A possible explanation might be related with the anti-plasticization phenomenon observed on the tensile and flexural properties, as previously discussed.

Literature on the impact strength properties of CAB or CAB-based composites is very scarce. For instance, Toriz and co-authors (Toriz et al., 2003) reported that CAB composites reinforced with 50 wt% of a flax mat displayed a Charpy (notched) impact strength of approximately 16.5 kJ·m^{-2}. Nonetheless, to the best of our knowledge, the influence of plasticizers on the impact strength of CAB matrices or composites has not been assessed yet. However, previous studies with other thermoplastic cellulose derivatives and respective composites are in line with the results obtained in the present work. As example, different amounts of two plasticizers, namely DEP and triacetin, were tested on cellulose acetate (Charvet et al., 2019). The incorporation of a plasticizer content of 30 wt% lead to a 4-fold increase in the impact strength from around 5 kJ·m^{-2} to approximately 20 kJ·m^{-2} (Charvet et al., 2019). In another study, composites of CA reinforced with Curauá fibers and plasticized with DOP more than doubled their Izod impact strength by increasing the plasticizer content from 20 wt% to 30 wt% (Gutiérrez et al., 2014).

3.5. Melt flow rate

The MFR relates to the amount of material extruded through a nozzle at a predetermined temperature when a standard weight is applied and, as such, is a good indicator of the processability of thermoplastic composites (Singh et al., 2017). As demonstrated in Fig. 8, that illustrates the MFR of the ACCs as function of the ELO content, the non-plasticized ACCs have relatively low MFR values. This is not surprising considering that CAB has been previously reported as a polymer with low melt flowability (Wang et al., 2018, 2017) and that the addition of reinforcing fibers usually reduces even further the MFR (Valente et al., 2021). A difference between the MFR of the ACCs with the two different CAB grades (1.1 ± 0.1 g·10 min^{-1} for ACC 381 and 0.6 ± 0.1 g·10 min^{-1} for ACC 553) can also be noted, which is easily explained by the different properties of these cellulose derivatives. Although both grades have the same molecular number-average molecular weight (20,000 g.mol^{-1}), CAB 553–0.4 has a higher butyryl content and a higher viscosity. Since the viscosity is inversely proportional to the melt flow rate, the higher viscosity of CAB 553–0.4 in comparison with CAB 381–0.1, justifies the lower MFR of the composites with CAB 553–0.4.

The results in Fig. 8 also show that ELO improved the melt flowability of these materials. For example, an intermediate percentage of 15.0 wt% of ELO gave rise to an increase of about 5 times for the ACCs 381 and near 5.5 times for the ACCs 553. Yet, the most significant results were obtained for the higher contents. At 30.0 wt% ELO, the MFR increased to 92.5 ± 7.7 g·10 min^{-1} for ACCs 381 and to 50.9 ± 2.7 g·10 min^{-1} for ACCs 553, which corresponds to an impressive 84-fold increase for both plasticized AACs in comparison with the non-plasticized ones. The strong increase on the chain mobility and the reduced fiber/fiber and fiber/matrix friction are certainly related to the increased flowability of the composites (Valente et al., 2022; Zepnik et al., 2013). In fact, previous studies revealed that the use of a plasticizer and its increasing content reduces the melt viscosity of the thermoplastic polymers/composite and increases the MFR. Zepnik and co-authors (Zepnik et al., 2013) studied the relationship between the MFR of a cellulose derivative (cellulose acetate) and plasticizer amount and type. All three plasticizers, namely allyl alcohol ethoxylate, glycerol triacetate, and TEC, led to an increase on the MFR. In another study, CA was plasticized with poly(ethylene glycol) (PEG) and TEC in amounts ranging from 15 to 25 wt%. Although both plasticizers caused an increase on the MFR, the higher MFR was obtained for 25 wt% of PEG (Wang et al., 2016). In another study, Tech et al. (2014) explored the use of TBC as a bio-based plasticizer for natural fiber-reinforced CAB

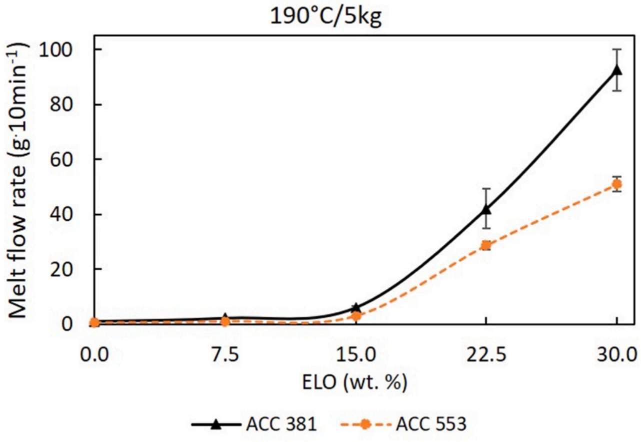

Fig. 8. Melt flow rate of the ACCs as function of the ELO content (the lines are for visual guidance only).

composites. The authors claimed that only 10 wt% of TBC was enough to nearly double the melt volume rate (MVR) of the composites.

Overall, the present work provides enough evidence that the ELO additive, in addition to lowering the processing temperature, also significantly improved the melt flowability of the material and simplified its processing. Moreover, the 84-fold increase on the MFR obtained herein emphasises that ELO is a better plasticizer than the aforementioned examples, particularly if MFR is concerned.

3.6. Water uptake capacity

The water uptake profiles of the ACCs immersed in water, as function of the ELO content, are plotted in Fig. 9. As a rule of thumb, the composites experienced a fast absorption during the first few days of immersion, followed by a stabilization stage. This water uptake profile, previously documented on other works (Valente et al., 2021; Vilela et al., 2019), is predominantly due to the water absorption of the hydrophilic cellulose fibers, who account for the majority of the absorbed water. On its turn, CABs and ELO are hydrophobic, which means that their contribution to the water uptake is almost negligible. This statement is supported by the low water uptake of the CAB matrices used in this study (2.6 ± 0.0% for CAB 381–0.1 and 3.9 ± 0.1% for CAB 5531–0.) and the plasticized CABs (1.5 ± 0.0% and 2.8 ± 0.0% for CAB 381–0.1 and CAB 553–0.4 plasticized with 30.0 wt% ELO, respectively). Carrillo and co-workers also showed that CABs have low water absorption and that the higher water absorptions of CAB-based composites with flax or lyocell were due to cellulosic fibers (Carrillo et al., 2011).

Concerning the plasticized ACCs, after 31 days of immersion, the percentage of water absorbed varies between 9.5 ± 0.1% and 10.3 ± 0.2% for ACCs 381 and between 10.8 ± 0.1% and 12.2 ± 3.8% for ACCs 553. This difference between the water uptake of ACCs with different CAB grades is easily justified but their different characteristics, more specifically related with the nature and content of the substituent groups. The higher hydroxyl content of CAB 553–0.4 (4.8 wt%) make it more prone to absorb water than its CAB 381–0.1 counterpart, which only has 1.8 wt% of hydroxyl groups. This small, yet significant difference, brings some clearance why ACCs 553 have higher water uptakes than ACCs 381 (Edgar et al., 2001). To better elucidate the water uptake results, the percentage of reinforcing fibers also has to be taken into consideration. As previously discussed, as the content of ELO goes up, the percentage of the reinforcing fibers, relative to the weight of the composite, decreases. For instance, while non-plasticized ACCs have 40 wt% reinforcing fibers, the ones plasticized with 30.0 wt% ELO only have 28 wt% of cellulose fibers (Table 1). Therefore, by increasing the amount of hydrophobic ELO and decreasing the load of hydrophilic fibers, ACCs with higher contents of plasticizer would be expected to have lower water uptakes than the non-plasticized ones. However, as can be observed from the results in Fig. 9, the plasticized ACCs tend to have slightly higher values, mainly for the higher ELO contents. Thus, it has to be assumed that the influence of the decreasing percentage of reinforcing fibers is being counterbalanced by the plasticizer action of ELO. In fact, the incorporation of plasticizers in composites is known to increase the water uptake. More specifically, ELO led to a raise of the water uptake of composites based on PLA and PHB (Balart et al., 2018; Valente et al., 2022). It has been proposed that the plasticization increases the free volume allowing water to diffuse more easily into the composite (Burgada et al., 2021; Dominguez-Candela et al., 2022). Moreover, the water absorption of the fibers leads to its sweeling, which subsequently causes internal stresses that finally end up on the formation of cracks, which obviously favour the water absorption of these materials (Balart et al., 2018).

3.7. Degradation in compost medium

The weight loss of the non-plasticized and plasticized ACCs, buried in compost medium, was evaluated in intervals of 30 days, up to 6 months (Fig. 10). Upon observation of the weight loss profiles, it is clear that the ACCs without ELO or with low contents of the plasticizer have low weight losses (1.5 ± 0.3% for ACC 381 and 2.1 ± 0.2% for ACC 553) for the tested conditions. Although CAB is often referred as a biodegradable polymer (Klemm et al., 2005; Sudhakar, 2022), both grades used in the present work showed almost no degradation for the tested conditions (data not shown). The biodegradability of CAB, similar to any other polymer, is dependent on a vast number of variables. For instance, it is known that many intrinsic factors, such as the polymer crystallinity, chemical structure, molecular weight, or external factors, such as the microbial composition, temperature, moisture, and pH of the soil/compost, have a strong impact on its biodegradability (Pires et al., 2022; Yadav and Hakkarainen, 2021). For the case of cellulose esters, it is thought that the biodegradation mechanism first requires the action of an esterase to break the ester bonds, subsequently allowing cellulase enzymes to take action on the cellulose backbone (Edgar et al., 2001; Puls et al., 2011). It is also known that the biodegradation rate is inversely related with the degree of substitution and length of the side chains, which is closely related with their hydrophobicity (Toriz et al., 2005). Since CAB 381–0.1 and CAB 553–0.4 are both hydrophobic, as

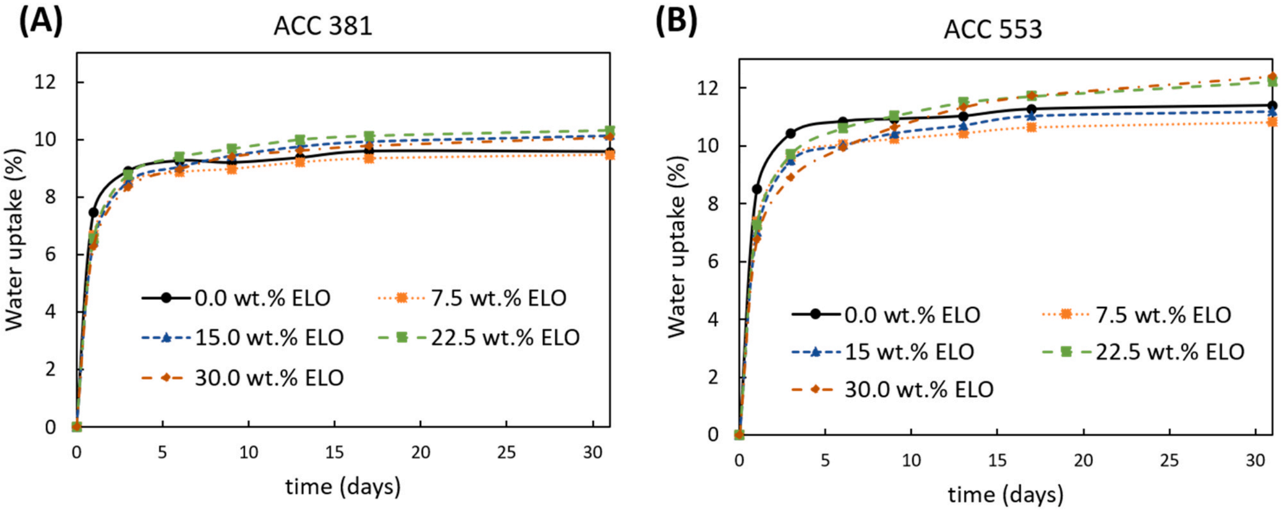

Fig. 9. Water uptake of the non-plasticized and plasticized ACCs 381 (A) and ACCs 553 (B) as a function of time (the lines are for visual guidance only). The standard deviations (not shown) are under 0.3% for all samples except for ACC 553_30 ELO (3.8%).

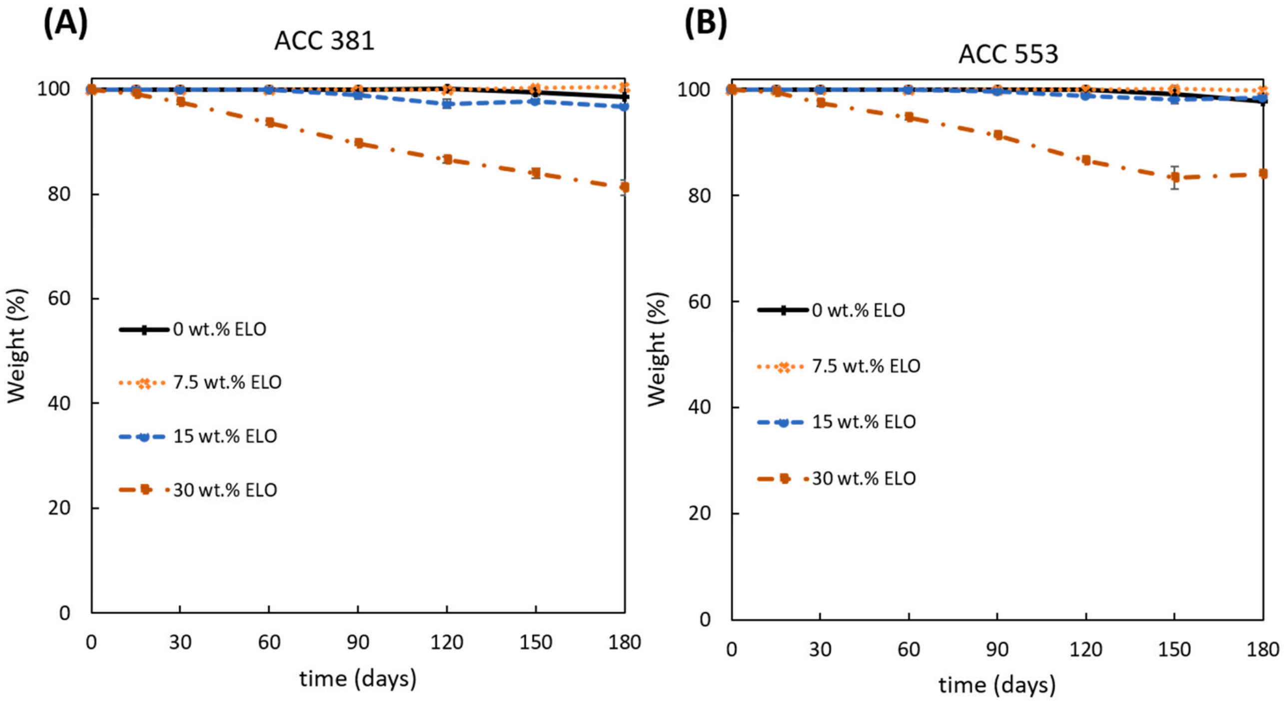

Fig. 10. Weight loss of the non-plasticized and plasticized ACCs 381 (A) and ACCs 553 (B) as a function of time (the lines are for visual guidance only).

proved previously by the water uptake measurements, and have large percentages of the considerable long butyryl side group, the biodegradation can be slowed down. Kunthadong et al. (2015) also reported that CAB did not degrade on the tested experimental composting conditions (temperature: 45–70 °C; moisture content: 40–55% and pH: 4–8), pointing its hydrophobicity, high T_g, and rigidity as the main reasons (Kunthadong et al., 2015).

Nevertheless, the low degradation rates of the CABs alone do not fully justify the low weight loss of the non-plasticized ACCs, as they are also comprised of 40 wt% of micronized cellulose fibers. Since it is well accepted that cellulose fibers are readily biodegradable (Klemm et al., 2005; Pérez et al., 2002), it would be expected that non-plasticized composites showed higher levels of weight losses due to the biodegradation of the reinforcing fibers. As an example, Carrillo and co-authors (Carrillo et al., 2011) demonstrated that, while the CAB matrix only lost 1.3% of its mass over a period of 60 days, the CAB reinforced with a flax content of 34.8 vol% lost up to 25% of its initial weight (Carrillo et al., 2011). However, it is proposed here that the high embedment of the fibers in the matrix of CAB, as observed on the SEM micrographs in Fig. 3, inhibited the access of the compost enzymes and microorganisms to the cellulosic fibers.

The addition of ELO on the ACCs induced considerable changes on its weight loss. As can be clearly concluded from the results in Fig. 10, the degradation of the test specimens is accelerated by the incorporation of high contents of ELO, with prominence for a plasticizer content of 30.0 wt%, where the weight loss reaches values of 18.8 ± 1.5% for ACC 381_30ELO and 15.9 ± 0.4% for ACC 553_30ELO, after 6 months. The influence of plasticizers on the biodegradation of CAB-based materials has been reported before. For instance, the degradation of CAB and CAB/silica hybrids, in sea water, increased from 1.9%, for pure CAB, to values in the range between 7.2% and 17.9%, when 25 wt% of DEP or TBC were incorporated (Wojciechowska et al., 2011). The increase on the free volume through the action of ELO can, in part, be held responsible for the higher weight losses of the plasticized composites as it facilitates the access of microorganisms and enzymes. Moreover, and given that the non-plasticized ACCs did not show any major degradation, as discussed before, it can be hypothesised that, on the initial stage, the majority of the weight loss of plasticized composites is due to the biodegradation and/or leaching of ELO. It is known that epoxidized vegetable oils, such as ELO, are easily degraded in soil/compost medium given that lipases secreted by bacteria can break the ester linkages, and the resulted products are converted into water and carbon dioxide by the action of several microorganisms (Chow et al., 2014; Riaz et al., 2010). Therefore, the biodegradation of ELO would create additional space and increase the susceptibility of the bulk material to enzymes and microorganisms accelerating even further the degradation rate (Iglesias-Montes et al., 2021).

It should be emphasized that the results here presented may differ from those that could have been obtained in a commercial composting facility, since the composting conditions are fundamentally different from those of a laboratorial scale. For instance, the mechanical pretreatment, higher temperatures during the thermophilic phase (up to 75 °C), higher amount of organic matter and larger diversity of microorganisms presented in a commercial composting facility are most likely to accelerate the biodegradation rate of this class of composites (Pires et al., 2022; Puls et al., 2011).

4. Conclusions

An epoxidized linseed oil was proposed as an alternative plasticizer for all-cellulose composites made of cellulose acetate butyrate reinforced with micronized e*Eucalyptus* pulp fibers. The increasing content of ELO, together with the consequent decrease on the fiber load, caused a substantial decrease on the glass transition temperature and on the storage modulus, without compromising the thermal stability of the composite. Alongside with the increase on the melt flow rate, the results clearly evidence a substantial improvement on the processability of ACCs upon the incorporation of ELO.

The raise on the elongation and flexure strains at break with the addition of ELO was accompanied by a decrease on the Young's and flexural moduli, and strengths, which agrees with the expected behaviour of a plasticizer. The impact strength was also remarkably improved to values near the ones of the commercial products available on the market. Alongside with the plasticizing effect of ELO, the decrease on the fiber load with the augment of the percentage of the additive also contributes to the variation of the mechanical and thermo-mechanical properties. Moreover, ELO also led to an increase in the water uptake capacity and accelerated the biodegradation of the ACCs in compost medium.

Due to the different characteristics of the CAB grades tested, some properties of the ACCs changed accordingly. For instance, for the high viscosity grade CAB (CAB 553–0.4), the corresponding composites had better impact strength than for those with the low viscosity CAB 381–0.1. On the other hand, composites with CAB 381–0.1 had higher MFR than the ones based on the more viscous counterpart. Given the similarity on molecular weight of these polymers, these differences on the viscosity can be correlated with variation of the percentages of hydroxyl, acetyl and butyryl substituting groups on the CABs structures.

In sum, the results provideevidence that ELO, a sustainable, non-toxic, and relatively cheap molecule, is an effective plasticizer to drastically improve the processability, elongation and flexibility at break, impact strength, and flowability of all-cellulose composites, without compromising its thermal stability.

CRediT authorship contribution statement

Bruno F.A. Valente: Investigation, Methodology, Writing – original draft, Writing – review & editing, Data curation; **Anna Karamysheva**: Investigation, Writing – review & editing; **Carlos Pascoal Neto**: Resources, Supervision, Project administration, Writing – review & editing; **Armando J.D. Silvestre:** Resources, Project administration, Writing – review & editing.; **Carla Vilela**: Conceptualization, Supervision, Writing – review & editing; **Carmen S.R. Freire:** Conceptualization, Resources, Supervision, Project administration, Writing – review & editing.

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.

Data Availability

All data is included in the manuscript in the form of figures, graphics and tables.

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