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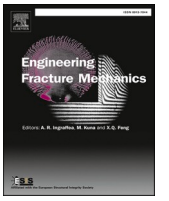

Tearing fracture of poly(lactic acid) (PLA)/ poly(butylene succinate-co-adipate) (PBSA) cast extruded films: Effect of the PBSA content

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ABSTRACT

The development of bio-based film formulations that show mechanical properties comparable to current fossil films is a challenging technological goal. Poly(lactic acid) (PLA) is the most attractive bio-based polymer; however, its poor ductility limits its use for film application. To overcome this issue, in this work PLA was blended with a ductile poly(butylene succinate-co-adipate) (PBSA) bio-based polymer, and cast extruded PLA/PBSA films were produced with differing PBSA amounts (20, 30 and 40 wt%). The mechanical properties of the film were evaluated both in machine and cross direction. The tearing resistance of the produced film was implemented with the essential work of fracture approach to explore the mode III out-of-plane fracture resistance.

1. Introduction

The growing awareness regarding the disposal of conventional plastics has, in recent years, stimulated both academics and industries to dedicate huge efforts to the development and production of a new portfolio of sustainable and eco-efficient bioplastics [1–3]. Particular attention has been dedicated to the production of film and sheets for packaging applications [4]. The replacement of conventional plastics with bioplastics does not necessarily solve the problem of resource exhaustion and plastic waste growth [5]. In fact, as the production of bioplastics increases, these materials will continue to co-exist with conventional plastics for decades to come. For the latter reason it is crucial to find the best solutions to phase out each of the most common plastics [6].

Despite the consistent growth of bioplastics, their waste streams are still small and fragmented, and currently there are not separate recycling streams for bio-based polymers, notwithstanding the fact that there are many patents on biopolymer recycling activities [7]. In this context it is necessary to underline that bio-based, biodegradable or recyclable alternatives, including their environmental sustainability, must guarantee technological performance so that they may represent a viable alternative to conventional plastics [8].

Considering the specific final properties and commercial availability of bioplastics that can be employed in flexible packaging application, poly(lactic acid) (PLA)/poly(butylene succinate-co-adipate) (PBSA) blends are considered very attractive for preparing suitable film with 100 wt% of renewable content [9–11]. PLA is a well-known bio-based polymer, with a mature production (2.23

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Table 1
Blend names and compositions.

Blend name	PLA content wt.%	PBSA content wt.%
PLA80_PBSA20	80	20
PLA70_PBSA30	70	30
PLA60_PBSA40	60	40

million tonnes in 2022 [12]) which has been used in several applications, mainly in packaging [13,14]; it possesses good mechanical properties, especially from the point of view of stiffness but, on the other hand, it is very brittle [15]. For this reason the physical blending with ductile polymers, like PBSA, has been carried out, and this results in improved ductility [16,17]. Compared to other ductile biopolymers on the market, PBSA possesses excellent impact strength and ductility; it has a very good processability and thermal and chemical resistance, as well as better eco-efficiency [18,19]. Consequently, PLA/PBSA films are very attractive as potential substitutes for traditional fossil-based polymers in film applications.

From a purely technical point of view, one of the main characteristics required of a polymeric film, especially in the packaging sector, is tear resistance [20]. In fact, it needs to be considered that in order to be suitable for industry, polymeric film undergoes many mechanical stresses during handling and usage. To this end, the attractiveness of essential work of fracture (EWF) of tear in thin polymer film has increased as it allows the characterization of out-of-plane shear fracture toughness [21].

It is of paramount importance to know the fracture behavior and the critical energy release rate during fracture for an accurate material design. The EWF approach, used also for metallic films [22], was already adopted to characterize the tearing behavior of fossil based thin polymeric films (like low-density polyethylene (LDPE), polyethylene terephthalate (PET), polycarbonate (PC) [23,24]). Recently, EWF methodology has also been adopted on biopolymeric matrices like PLA [25] and its blends (with poly(alkylene furanoate)s (PEFs) [26] or poly(butylene adipate-co-terephthalate) (PBAT) [20]), for sheets based on other co-polyester sheets [27] and fiber-reinforced viscoelastomers [28], but it has not yet been investigated in trouser configuration for PLA/PBSA films.

In this work, cast extruded PLA/PBSA films with increasing PBSA amount (20, 30 and 40 wt% of PBSA) have been mechanically characterized in tensile and tear mode, with particular attention being paid to the critical tearing energy through the essential work of fracture (EWF) approach. Trouser tests at different ligament lengths were carried out, and the contribution of the essential and non-essential work of fracture was separated better to highlight the effect of PBSA in hindering the crack propagation.

2. Materials and methods

2.1. Materials

The materials used in this work are listed below:

- Poly(lactic) acid (PLA), trade name Luminy LX175, provided by Total Corbion PLA (Gorinchem, The Netherlands). This is a bio-based and biodegradable PLA that contains about 4% of D-lactic acid units. Being a general-purpose extrusion grade PLA, it can be used alone or blended with other polymers (density: 1.24 g/cm^3; melt flow index (MFI) (210 °C/2.16 kg): 6 g/10 min).
- Poly(butylene succinate-co-adipate) (PBSA), trade name BioPBS FD92PM, purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). This polymer is a copolymer of succinic acid, adipic acid and 1,4-butandiol. Being a soft and flexible semi-crystalline polyester, it may be used alone in blown or cast film extrusion or blended with other stiffer polymers (density of 1.24 g/cm^3; MFI (190 °C, 2.16 kg): 4 g/10 min).

2.2. Blends preparation

PLA/PBSA blends, having different PBSA amount (from 20 wt% to 40 wt%), were extrusion-compounded according to the compositions listed in Table 1, in a semi-industrial Comac EBC 25HT (L/D = 44) (Comac, Cerro Maggiore, Italy) twin-screw extruder.

Both PLA and PBSA pellets were dried at 60° C for 8 h in a Piovan DP 604 dryer (Piovan S.p.A., Verona, Italy) before their extrusion with an airflow of 50 m^3/h and a sew point of −40 °C. The extruder was equipped with eleven heating zones and the temperature profile adopted was: 150/175/180/180/180/185/185/185/185/185/190 °C, with the die zone at 190 °C for the blends containing up to 30 wt% of PBSA. Increasing the PBSA amount to 40 wt%, the melt viscosity significantly decreased due to the low melting temperature of PBSA. The same viscosity decrement was registered in a previous work [16], and to guarantee optimum extrusion conditions the entire temperature profile was decreased by 5 °C for the PLA60_PBSA40 blend. The extruder mass flow rate was set at 20 kg/h and 300 rpm. The extruded strands were then cooled in a water bath at room temperature and reduced to pellets by an automatic knife cutter. The pellets of the extruded blends were then dried again at 60 °C. The granules were then reprocessed by cast extrusion with a cast extrusion line (eLab cast – EUREXMA – Italy), diameter 35 mm, with a die head width of 400 mm and L/D ratio 33:1. The temperature profile adopted was 170–175-180 °C along the screw in the extruder, while the flat die was set at 170 °C. The films were then collected through a calender apparatus regulated by setting the cooling rollers at 25 °C and the windup roll speed at 28 rpm. The obtained films were 20 mm width and 40 μm thick.

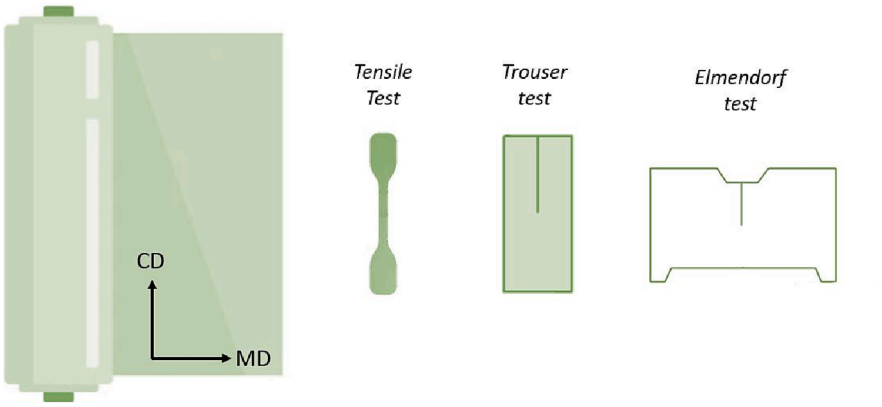

Fig. 1. Cast-extruded film orientation and film specimen geometry adopted for the mechanical characterization.

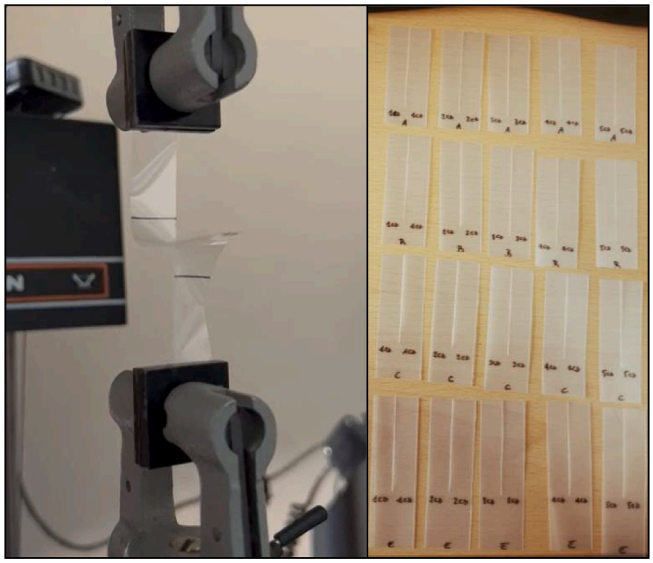

Fig. 2. Film specimens in trouser tear test configuration.

2.3. Mechanical characterization

The mechanical characterization of the cast-extruded films was carried out from a roll of films in machine and cross direction (indicated MD and CD) as shown in Fig. 1.

2.3.1. Tensile tests

Tensile tests were carried out using an Instron universal testing machine model 5500R (Canton, MA, USA) equipped with a 100 N load cell. The machine was interfaced with MERLIN software (INSTRON version 4.42 S/N–014733H) and compressed air grip was used. The initial grip separation was 25 mm, and the deformation rate was set at 50 mm/min. The tensile tests were performed on ISO 527–2/5A dumbbell specimens (gauge length: 25 mm, width: 4 mm; thickness: 40 μm) obtained with a Manual Cutting Press EP 08 (Elastocon, Brahmult, Sweden). At least five specimens both in MD and CD for each blend compositions were tested at room temperature to obtain the main mechanical properties (elongation at break and stress at break) of the cast-extruded films. The elastic tensile modulus was determined by dynamic mechanical analysis (DMA) carried out on a Gabo Eplexor (Gabo, Ahlden, Germany), equipped with a 100 N load cell. At least three specimens were tested cutting the test bars from the dumbbell specimens (gauge length: 20 mm; width: 4 mm; thickness: 40 μm). During the test the temperature and the frequency were kept constant and equal to 25 °C and 1 Hz respectively.

2.3.2. Trouser tests

Trouser tests were carried out to measure the critical fracture energy of the films. The ‘legs’ of the trouser specimen were pulled in

opposite directions to create tearing action. Thanks to this test it is possible to determine the force necessary to propagate a tear in a plastic film and thin sheeting materials [29]. A picture of the film specimens in trouser configuration is given in Fig. 2.

The tearing tests were carried out on the previously mentioned INSTRON universal testing machine model 5500R (Canton, MA, USA) equipped with a 100 N load cell. A quasi-static loading was applied at a crosshead speed of 100 mm/min. The load and extension values were recorded during the specimen loading, tearing and unloading. Five specimens for each type of film in MD and CD were tested. The critical tearing energy (T_c) was calculated according to the following equation [24]:

$$T_c = \frac{2F}{B} \tag{1}$$

where F is the maximum load registered during the test and coincides with the maximum tearing force, and B is the film thickness.

2.3.3. Elmendorf tests

The Elmendorf test is a special case of tear test at high-speed; it is one of the most important tests to be carried out on blown and cast manufactured films [30]. Based on the results obtained with this test it is possible to determine the range of film applications. Elmendorf pendulum (MESDAN, Puegnago del Garda, Italy) according to ISO 6383 with a weight of 1.6 kg. The tests were carried out at room temperature; at least five specimens for each film in MD and CD were tested and **Eq.1** was adopted to calculate the tearing energy at higher speeds (50,000 mm/min).

2.3.4. Essential work of fracture

The essential work of fracture (EWF) approach, developed originally by Cotterell-Mai [31–33] may be successfully applied to ductile polymer thin films or sheets having thickness between 1 and 0.2 mm [34–36]. The main EWF concept is the separation of the total fracture energy of a pre-cracked specimen into two components: one geometry-dependent (the non-essential work, W_p) and the other geometry-independent (the essential work, W_e). The total work of fracture (W_f) may be written as follows:

$$Wf = Wp + We = w_e lt + w_e \beta l^2 t \tag{2}$$

w_e is associated with the energy spent in the inner fracture process and is proportional to the fracture area ($l*t$); where l is the ligament length and t is the film thickness. W_p is correlated to the energy of the process that takes place in the outer plastic deformation zone and is correlated to plastic deformation and other dissipative processes. This term is proportional to the volume fraction of the deformed region (l^2*t) that surrounds the crack process zone; the β parameter is a shape factor for the plastic zone. Simplifying, the **Eq.(2)** can be re-written as follows [25]:

$$w_f = w_e + w_p \beta l \tag{3}$$

Assuming that w_e is a material constant and w_p and β are not dependent on the ligament length [35], it is possible to obtain w_e and w_p from **Eq. (3)** by a linear regression of the values reported in a graph w_f vs l.

Much interest has been shown in recent years to the application of the EWF approach in tearing mode at different ligament length, especially with the advent of new bioplastic film formulations. In fact for biopolymeric film, mode III out-of-plane tearing is the most common failure mode [37]. The tearing resistance of plastic film assumes great importance and can be measured by the single-tear (2-leg trousers-tear) specimen [38]. Wong et al. [39] demonstrated that a distinct initial crack growth region exists where the outer plastic zone was developing prior to the initial crack-tip. In this area, the plastic zone is growing and its size increases with increasing torn ligament length. In the present work the EWF approach was applied for all blend compositions, both in MD and CD, at different ligament lengths (10, 15, 20, 25 and 30 mm). The selected ligament lengths fall within the Wong statement and thus at the maximum ligament length the plastic zone is still in development. The shape factor β can be calculated by applying the **Eq.(4)** in which S_{pa} is the plastic zone area and l the ligament length [24].

$$\beta = \frac{S_{pa}}{l^2} \tag{4}$$

The above mentioned INSTRON universal testing machine model 5500R was equipped with a 100 N load cell and was set at a crosshead speed of 100 mm/min. The tests were performed at room temperature and at least 5 specimens for each ligament length were tested. The total area under the tearing load–displacement curves, which represents the total fracture work, was used to evaluate the total specific fracture work (w_f).

2.4. Morphological characterization

To investigate the final morphology of the developed films, scanning electron microscopy analysis (SEM) was carried out with a FEI Quanta 450 FEG instrument (Thermo Fisher Scientific, Waltham, MA, USA). The micrographs of samples fractured with liquid nitrogen were prior sputtered (with a LEICA EM ACE 600 High Vacuum Sputter Coater, Wetzlar, Germany) with a thin layer of Platinum to avoid charge build up.

Table 2
Tensile tests results.

Blend name	Stress at break (MPa) MD	Stress at break (MPa) CD	Elongation at break (%) MD	Elongation at break (%) CD	Elastic modulus (GPa) MD	Elastic Modulus (GPa) CD
PLA80_PBSA20	21.84 ± 3.41	26.82 ± 1.96	48.77 ± 9.05	35.65 ± 7.12	1.81 ± 0.2	1.72 ± 0.1
PLA70_PBSA30	20.20 ± 4.41	21.84 ± 1.64	107.94 ± 13.06	42.41 ± 13.65	1.31 ± 0.05	1.07 ± 0.07
PLA60_PBSA40	18.07 ± 4.55	15.87 ± 2.01	295.86 ± 31.25	111.30 ± 24.65	0.99 ± 0.06	0.96 ± 0.08

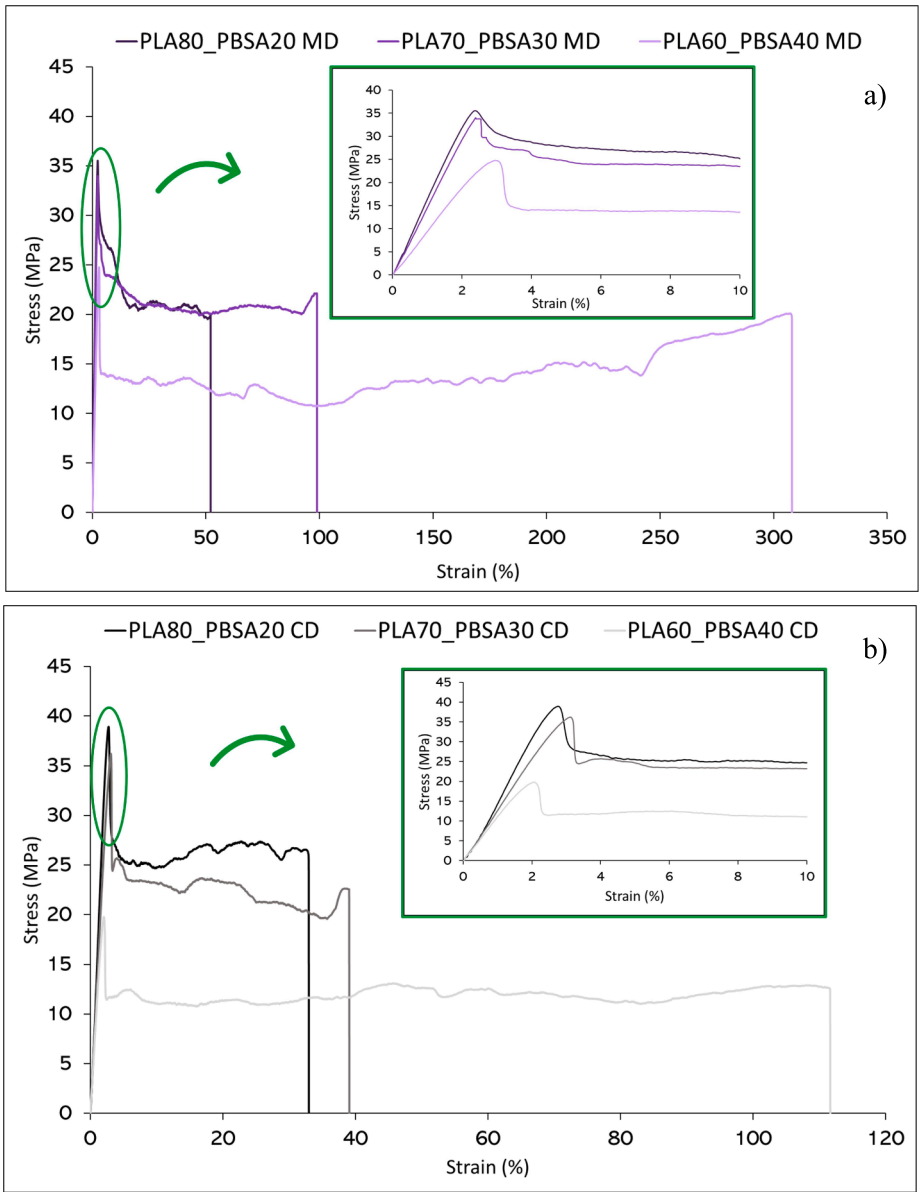

Fig. 3. Stress–strain curves in **a)** MD and **b)** CD.

3. Results and discussions

The results of uniaxial tensile and DMA tests are summarized in Table 2. By increasing the more ductile PBSA phase a decrement of the material stiffness was observed. On the other hand, an increment of films ductility with PBSA content was obtained according with

Table 3
Trouser and Elmendorf results.

Blend name	Trouser tearing energy (N/mm) MD	Trouser tearing energy (N/mm) CD	Elmendorf tearing energy (N/mm) MD	Elmendorf tearing energy (N/mm) CD
PLA80_PBSA20	4.69 ± 0.80	11.01 ± 0.91	3.72 ± 0.01	9.01 ± 0.08
PLA70_PBSA30	14.49 ± 1.11	31.18 ± 1.27	6.88 ± 0.01	13.74 ± 0.06
PLA60_PBSA40	19.37 ± 1.39	41.37 ± 0.93	7.85 ± 0.01	22.77 ± 0.09

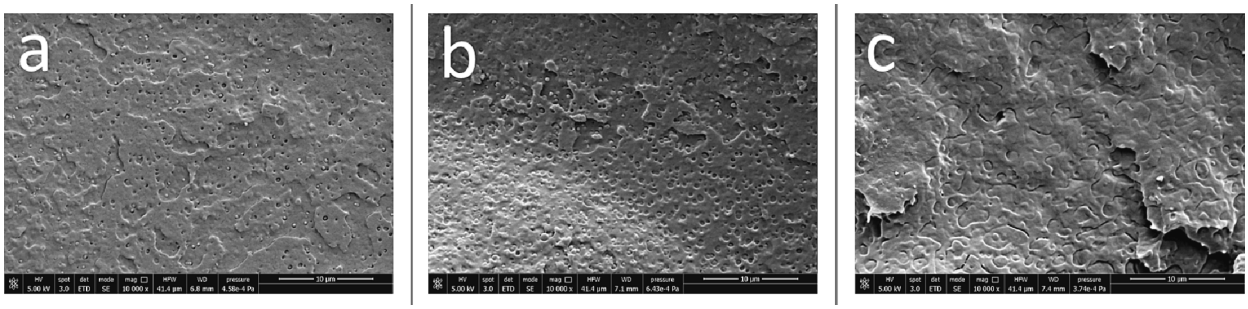

Fig. 4. SEM micrographs at 10000x of a)PLA80_PBSA20, b)PLA70_PBSA30, c)PLA60_PBSA40.

Table 4
Tearing properties of some bio-based and fossil-based polymeric films.

Blend name	Film thickness (μm)	Manufacturing process technique	Elmendorf tearing energy (N/mm)	Trouser tearing energy (N/mm)	Ref.
PLA60PBSA40 MD	40	Cast	7.85	19.37	This article
PLA60PBSA40 CD	40	Cast	22.77	41.37	This article
LLDPE MD	50	Cast	58.8	60	[51]
LLDPE CD	50	Cast	133.2	130	[51]
PP MD	30	Cast	8	8	[51]
PP CD	30	Cast	20.67	20	[51]

literature data [16,40]. Furthermore, the stress–strain curves, reported in Fig. 3, better highlight how increasing the PBSA content the stress at yielding (corresponding to the maximum stress of the stress–strain curve) decreases, but in combination with a marked increment of the elongation at break.

The films obtained by cast-extrusion exhibit anisotropy for all compositions. The elongation at break in MD is higher with respect to CD, and the elastic modulus is also slightly higher in MD with respect to CD. This behavior is coherent with other literature studies carried out on cast-extruded films and may be ascribed to the partial alignment of the polymeric chains in machine direction induced by the elongational flow [41–43].

Interesting results of trouser and Elmendorf tests are carried in Table 3. In contrast to the tensile tests, the tearing resistance of the films is better in CD. In CD the films are more prone to reduce the crack propagation. In fact, while the partial chain alignment improves elongation at break in the MD, it also facilitates crack propagation, which is more hindered in the CD [20,44]. The energy absorbed during the film tearing is therefore greater in CD than in MD. This inversion of the trend with respect to tensile tests depends precisely on the type of test. While in the uniaxial tensile tests the machine stretching direction corresponds to the direction of tension; in trouser tear test the crack propagates in a transverse direction with respect to the direction of tension (mode III fracture out-of-plane). Thus, fracture propagation is hindered when it encounters transversely oriented macromolecules.

An effect due to the test speed may also be observed. Increasing the speed rate, passing from tear to Elmendorf test, the materials are more fragile with lower tearing energy.

The toughening effect of PBSA is noteworthy; already observed in tensile mode, this is more marked in tearing mode (the critical tearing energy increases significantly with the PBSA content). Nevertheless, this result is due to the inclusion of a more ductile polymer (PBSA) in a brittle matrix (PLA) However, quantifying this improvement (without losing properties such as mechanical strength) and evaluating as this improvement is correlated with the test speed and fracture mode is, at the best of our knowledge, innovative for biodegradable blends. The introduction of a ductile dispersed phase is a not a sufficient condition also to guarantee improved toughness, especially when the loading conditions and the speed tests vary. Krishnan et al. [45] published a very exhaustive review about the PLA toughening and the necessity to increase the ductility without losing too much the pristine PLA characteristics (i.e. high elastic modulus, good processability, impressive tensile strength). In this work they underlined that the toughness is a complicated property; although it may be relatively easy to improve the elongation at break, it is much more challenging to increase the impact

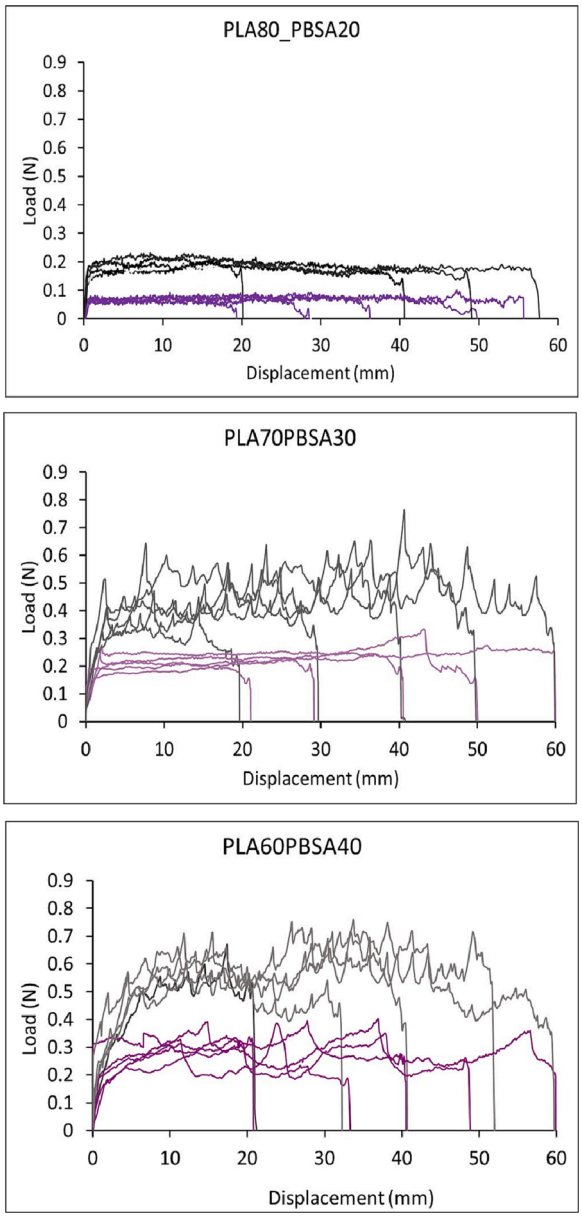

Fig. 5. Tearing load–displacement curves at various ligament lengths MD and CD for **a)** PLA80_PBSA20 **b)** PLA70_PBSA30 and **c)** PLA60_PBSA40.

toughness of PLA. Indeed, high speed toughness depends on many extrinsic and intrinsic variables. Several published works [46–49] demonstrate how the enhancement of ductility is not accompanied by toughness increment in terms of absorbed energy, especially at high test speeds; the hypothesis is that dilatational yielding, that is the key to a successful toughening under the more severe testing conditions, does not start, i.e. a high level of energy absorption must be reached. Furthermore, the test speed is a determining factor that modifies the brittle-to-ductile transition of the polymeric blends [50].

In any case the SEM micrographs (Fig. 4) demonstrate that passing from a structure in which PBSA is dispersed in a PLA matrix (PLA80PBSA20, Fig. 4**a**) to a co-continuous morphology (Fig. 4**c**), the improvement in ductility becomes associated to an improvement in toughness (as proved by Elmendorf tests).

The tearing properties are remarkable, especially for the PLA60_PBSA40 formulation. The results obtained for PLA60_PBSA40 were compared with other bio-based and fossil-based data reported in relevant publications (Table 4).

Nevertheless, it must be pointed out that, to the best of our knowledge, no quantity of published data exists regarding the Trouser/Elmendorf comparison for cast-extruded film formulations. Research becomes more complicated when it refers to bio-based or biodegradable film formulations like those developed in this paper. Moreover, it is challenging to make an equal comparison between bio-based and petro-based films given that the production processes (cast-extrusion, strongly directional with respect to blown

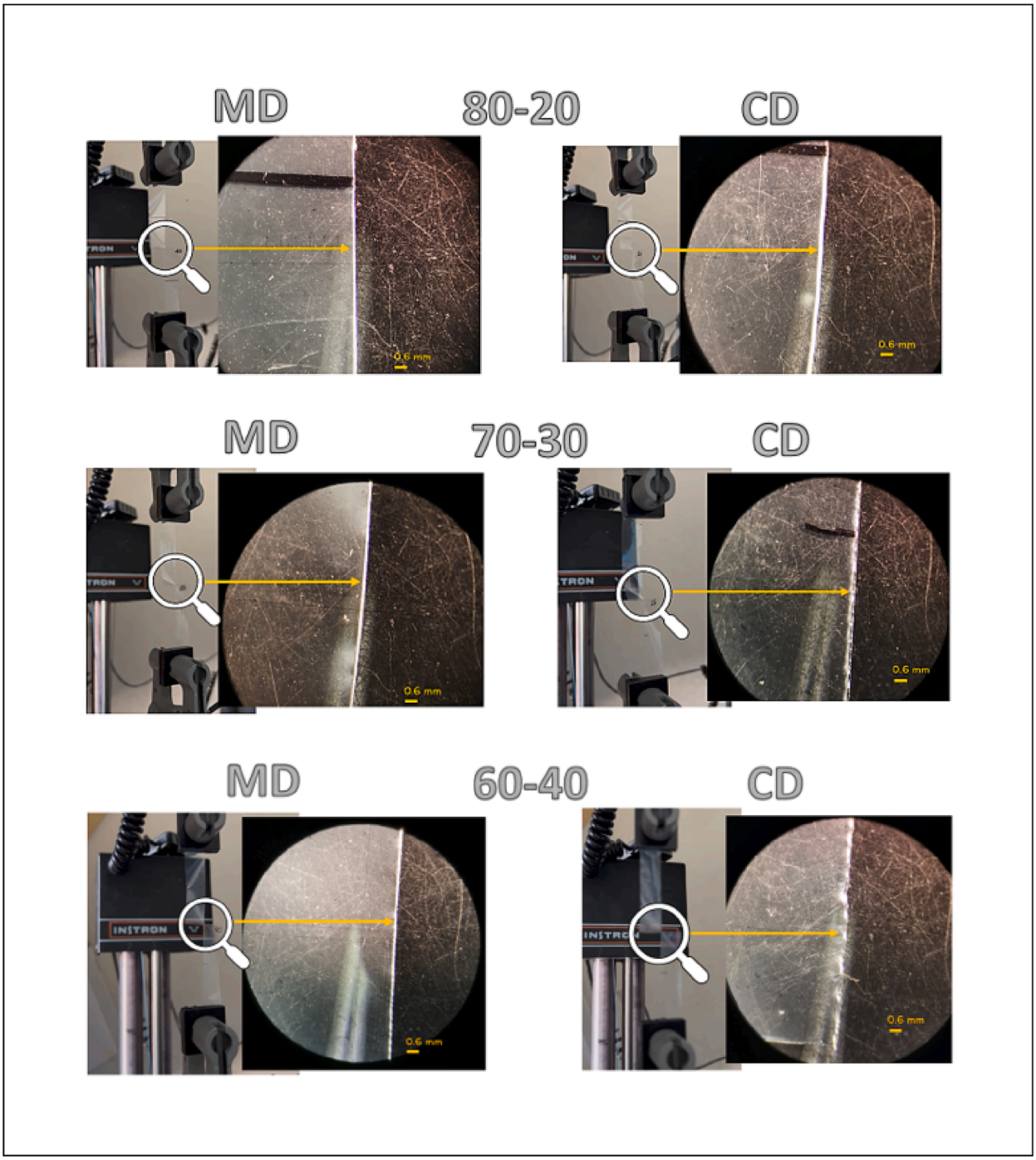

Fig. 6. Optical micrographs at 16X of trouser specimens at ligament = 25 mm.

extrusion), draw ratio speed and thickness are parameters that strongly influence tearing resistance, in addition to the nature of the polymer itself.

In all cases, PLA60_PBSA40 tearing resistance is encouraging both in trouser and Elmendorf test, the values achieved being higher than cast-extruded PP films. However, more effort needs to be dedicated so as further to improve the tearing properties that are far from LLDPE, with respect to current commercial available bio-based film formulations achieved by blown extrusion, PLA60_PBSA40 results are significantly higher than Ecovio P50 (MD: 10 N/mm; CD: 30 N/mm) and Materbi P25 ((MD: 4 N/mm; CD: 18 N/mm) [52].

Fig. 5 shows the load vs. displacements curves at various ligament length in MD and CD for all the blends composition.

The fluctuations in the force values registered during tearing are not instrument noise, but may be ascribed to the stick–slip

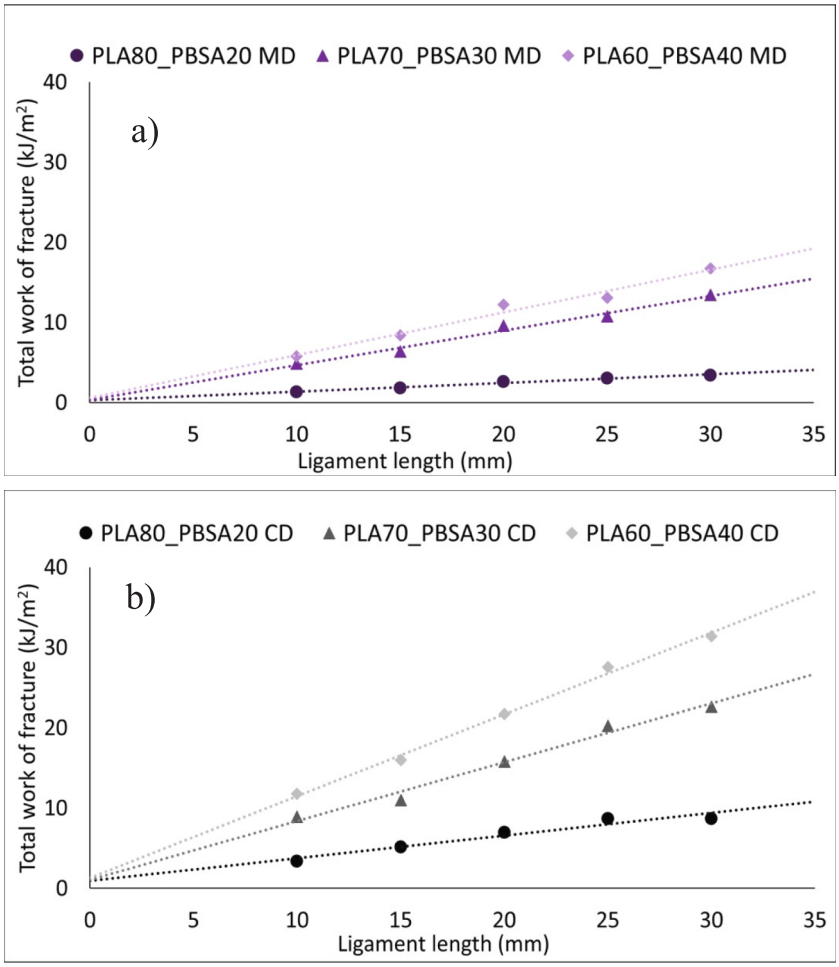

Fig. 7. Specific total work of fracture versus ligament length for PLA/PBSA cast-extruded films in **a)** MD and **b)** CD.

Table 5
EWF fracture parameters.

Blend name	w_e (kJ/m^2)	βw_p	w_p (MJ/m^3)	β	R^2
PLA80_PBSA20 MD	0.26	0.11	11.00	0.010	0.98
PLA70_PBSA30 MD	0.39	0.43	36.32	0.012	0.98
PLA60_PBSA40 MD	0.58	0.53	37.86	0.014	0.97
PLA80_PBSA20 CD	0.91	0.28	18.62	0.015	0.94
PLA70_PBSA30 CD	1.05	0.73	39.00	0.020	0.98
PLA60_PBSA40 CD	1.33	1.02	40.73	0.025	0.99

behavior observed during fracture that occurs in the polymeric systems. The tearing curves better highlight the critical tearing energy results, showing how at different ligament lengths the energy absorbed during the tearing process is always higher in CD than in MD for all formulations. Analyzing in greater detail the tearing curves reported in Fig. 5, it may be noticed that for PLA80_PBSA20, the shape of the curves as a function of the ligament, both in MD and CD, are quite flat, with low peak fluctuations. This behavior is ascribed to the higher PLA content in the blend, which does not guarantee an evident resistance to tearing.

Contrary to this, by increasing the amount of PBSA, as in the PLA70_PBSA30 formulation, the shape of the curves in MD remains rather flat, while in CD there is an evident alternation of maxima and minima peaks; this latter aspect is a symptom of a laceration that occurs in successive steps due to the opposition to crack propagation.

Finally, for the PLA60_PBSA40, in both MD and CD the fracture is characterized by stick–slip behavior, but still with improved tear resistance in CD. These observations are confirmed by the optical micrographs, at 16X, of the broken trouser specimens shown in Fig. 6.

The PLA80_PBSA20 confirms a more fragile fracture propagation profile, with no ridges developing in either MD or CD. Conversely, for PLA70_PBSA30 and PLA60_PBSA40, in CD ridges caused by the transversal polymeric chain orientation, due to the cast-extrusion,

are clearly visible, guaranteeing a better obstacle to the crack propagation.

The total area under the tearing load–displacement curves is the total work of fracture (w_f). In Fig. 7, the specific total work of fracture versus ligament length for the different blend compositions and ligament lengths is plotted. A good linear fitting between w_f and l was found both in MD and CD, with the regression coefficients reported in Table 5 that lie in a range between 0.94 and 0.99.

From an analysis of the obtained fracture parameters (Table 5), it emerges that both the essential work of fracture and non-essential work of fracture increase with the PBSA content in the film. The anisotropic film behavior was also evident as the fracture parameters are higher in CD than in MD, confirming the results observed in the trouser and Elmendorf tests. βw_p increases with the material ductility similarly to the findings of Arkhireyaya et al. [53] and in accordance to tensile test results.

Optical microscopy analysis, illustrated in Fig. 6, also revealed useful information for separating the geometric contribution (β factor) from the w_p. In this regard, it was observed that the plastic zone development occurs with a shape similar to a rectangle rather than the classic semi-elliptical shape found in other published works [39,54]; these values are shown in Table 4.

From the separation of the geometric factor, the EWF parameters are well distinguished and highlight the PBSA toughening effect. In particular PBSA hinders the crack propagation once it has been initiated, as may be seen from the higher w_p values compared to w_e, the latter representing the energy needed to start the crack advancement. Moreover, the plastic zone increases with PBSA content; it is clearly visible from β values for all formulations in CD and in MD.

4. Conclusions

The improvement of bio-based film properties, specifically from a technological perspective, is of paramount importance to allow their widespread use and to meet market requirements. PLA/PBSA blends containing different PBSA amounts (20, 30 and 40 wt%) were cast-extruded to obtain films 40 μm thick. The film anisotropy induced by the cast-extrusion process was evaluated by tensile and tearing tests. Particular attention was dedicated to the tearing properties of the films as these are fundamental from a practical point of view. The essential work of fracture approach was indeed investigated in tearing mode. Interesting results were obtained: increasing the PBSA amount an increment of ductility, and trouser resistance was observed. The PBSA content additionally improves the film anisotropy. In conclusion, the films containing 40 wt% of PBSA possess very good elongation at break value, but they also possess tearing properties better than some commercial bio-based polymeric films. Definitely, in the present work the influence of the test speed on PLA-PBSA films with different PBSA contents was tested, showing how achieving morphological co-continuity guarantees a higher barrier to crack propagation even under the most severe conditions (proved by Elmendorf tests), thus achieving a clear toughening of the PLA matrix.

CRediT authorship contribution statement

Laura Aliotta: Writing – original draft, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Vito Gigante:** Writing – original draft, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Bianca Dal Pont:** Writing – review & editing, Visualization, Investigation, Data curation. **Filip Miketa:** Writing – review & editing, Visualization, Resources. **Maria-Beatrice Coltelli:** Writing – review & editing, Visualization, Validation, Resources. **Andrea Lazzeri:** Writing – review & editing, Visualization, Validation, Supervision.

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

Data will be made available on request.

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