**ORIGINAL PAPER** 



# Effect of the Temperature and of the Drawing Conditions on the Fracture Behaviour of Thermoplastic Starch Films for Packaging Applications

Andrea Dorigato<sup>1</sup> · Davide Perin<sup>1</sup> · Alessandro Pegoretti<sup>1</sup>

Published online: 7 August 2020 © Springer Science+Business Media, LLC, part of Springer Nature 2020

#### Abstract

In this work the effects of testing temperature and drawing orientation on the fracture behaviour of biobased and biodegradable thermoplastic starch based films, currently applied in the food packaging field, were investigated. At this aim, the Essential Work of Fracture (EWF) approach was applied on samples tested at 0 °C, 25 °C and 50 °C both in machine (MD) and in cross (CD) directions. The specific essential work of fracture ( $w_e$ ) values strongly decreased with the testing temperature, and  $w_e$  values of CD samples were systematically higher than those of the corresponding MD samples. Considering that photograms of the CD samples taken during the EWF tests highlighted that the yielding zone became progressively opaque as an effect of the strain induced crystallization, it was hypothesized that in CD specimens part of the tensile energy applied during the straining process was utilized for the orientation of the macromolecules along the strain direction, rather than for the propagation of the crack in the ligament zone. Tensile tests under quasi-static conditions on dumbbell specimens highlighted that, regardless to the drawing direction, the stiffness and the resistance at yield and at break decreased with the temperature, while the strain at break was considerably enhanced. Moreover, because of the strong anisotropy induced by the molecular orientation in the drawing direction, MD tested samples had higher elastic modulus, yield resistance, and stress at break compared to CD samples.

 $\overline{\mathbf{S}}$ 

Keywords Starch · Fracture · Mechanical properties · Drawing · Temperature

## **List of Symbols**

List of Syn		5	Standard deviation of W <sub>f</sub> values
DENT	Double edge notched tension	S <sub>11</sub> , S <sub>12</sub> , S <sub>22</sub>	Parameters of the linear regression
E	Tensile modulus	$W_{f}$	Total work of fracture
β	Plastic shape factor	w <sub>f</sub>	Specific total work of fracture
$\sigma_{v}$	Yield stress	$\overline{\mathrm{W}}_{\mathrm{f}}$	Arithmetic mean of W <sub>f</sub> values
Ĺ	Ligament length	W <sub>e</sub>	Essential work of fracture
L	Arithmetic mean of the ligament length	w <sub>e</sub>	Specific essential work of fracture
W	Width of the DENT specimens	W <sub>p</sub>	Non-essential work of fracture
t	Thickness of the DENT specimens	Wp	Specific non-essential work of fracture
n	Number of specimens	W <sub>prop</sub>	Specific essential work for crack
$\mathbb{R}^2$	Coefficient of determination	1 1	propagation
S	Standard error of the linear regression	w <sub>ini</sub>	Specific essential work for crack initiation

Andrea Dorigato andrea.dorigato@unitn.it

Alessandro Pegoretti alessandro.pegoretti@unitn.it

<sup>1</sup> Department of Industrial Engineering and INSTM Research Unit, University of Trento, Via Sommarive 9, 38123 Trento, Italy

## Introduction

Plastic materials are widely employed in everyday life and their use in textiles, electronics, aerospace components, healthcare products, toys, and packaging applications is steadily increasing [1, 2]. The extreme adaptability of polymeric materials is allowed by their fascinating properties

Standard deviation of W values

like good mechanical strength, lightness, flexibility, chemically inertness and durability. These peculiar features, combined with a limited cost and the capability to replace products made from other materials (i.e. paper, glass, and metals), could explain their success in industrial applications [3]. For all these reasons, the worldwide plastic production has steadily increased over the past 50 years, with an average growth rate of about 9% per year [4]. In 2016, global plastic productions reached 335 million tonnes per year, with Europe alone producing 60 million tonnes, and in the next 20 years it is expected to double [5].

Moreover, the packaging field is one of the most important applicative sectors for polymers, as it represents nearly 26% of the total worldwide volume of plastic consumption. Considering that plastic packaging generally has a shorter life in comparison to plastics used in other applications, like building and automotive, it represents the majority of the waste production. Plastic producers and transformers are keen to highlight the benefits deriving from plastic packaging in order to enhance their profits and reduce the plastic and food waste as far as possible [5]. Currently, one of the main problems in the packaging field is the short usage time (i.e. time that the packaging is effectively useful), which is in the range of some days to one month. Even if some of these plastic products are re-used, they inevitably become waste at the end of their life cycle, with a consequently strong environmental impact [6]. A considerable fraction of the plastic waste (up to 43%) ends up in landfills, causing the soil to lose its fertility. This phenomenon is due to the fact that most of the plastic wastes are non-biodegradable and, even if they are chemically inert, they contain small amounts of toxic additives that can be released in the environment [7].

In order to reduce the environmental impact of plastic packaging, many research efforts have been made in the development of novel reusable or recyclable plastics [8]. According to the EU 2015/720 European Commission Directive, by 2030 all plastic packaging in the EU should be reusable or recyclable in a cost-effective manner, and more than one half of all plastic waste generated in Europe must be recycled. Because of these reasons, a great interest has recently emerged towards the use of bioplastics. As a general definition, bioplastics can be made of biodegradable petroleum-based polymers, like  $poly(\varepsilon$ -caprolactone) (PCL), or they can be produced from renewable materials that are non-biodegradable, like polyamide 11 (PA11) [9, 10]. Bioplastics can also derive from renewable resources and could be even biodegradable, like polylactic acid (PLA) [11, 12], starch, cellulose, chitosan, lignin, and proteins [13, 14]. According to the ASTM D6002 standard, a polymer is compostable if at least 90% of it will degrade within 180 days in a controlled humidity environment, at a temperature of 60 °C and in presence of bacteria or algae [15]. The biodegradability of a polymeric material strongly depends

on several factors such as its chemical structure, melting temperature, crystallinity [16] and molecular weight [17]. One of the major advantages of bioplastics is that they can significantly reduce carbon dioxide production and, if they are biodegradable or compostable, they can also reduce the total amount of waste sent to landfilling or incineration [18]. Even if the current bioplastics market represents less than 1% of the entire plastic packaging market, the total bioplastic production will increase from 2.11 million tonnes in 2018 to nearly 2.62 million tonnes in 2023 [19]. One of the leading biopolymers is PLA, a commercially successful biodegradable thermoplastic polyester that could potentially replace low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene (PS), polypropylene (PP) and acrylonitrile butadiene styrene (ABS) [18-22]. Also, polyhydroxyalkanoates (PHAs) have recently attracted the attention of the industries and of the researchers [23]. Production capacities of PHAs and PLA are estimated to quadruple and to double in the next 5 years, respectively [19]. Beside them, one of the most interesting renewable resources for producing bioplastics is starch [24, 25]. Starch is one of the most abundant biomolecules on earth and it is one of the most important energy sources for human beings [26]. From a chemical point of view, it is a carbohydrate composed of a large number of glucose units joined together by glycosidic bonds containing, usually, 20-25% amylose, which is a mostly linear alpha-D-(1-4)-glucan, and 75-80% amylopectin, which is an alpha-D-(1-4)-glucan owning an alpha-D-(1-6) linkages at the branch point. It is abundantly present in plants, like rice, corn, and potatoes, it is relatively cheap and it is totally biodegradable. In all these types of plants, starch is produced in granules, differing in size and in composition, with relatively high hydrophilicity [27]. The structure of starch is strongly dependent on the relative amount of amylopectin and amylose, as the branched amylopectin regions contain crystalline areas while the linear amylose is mostly amorphous. Granules of thermoplastic starch (TPS) can be also incorporated into traditional plastics (like polyethylene [28]) in order to enhance their degradability or to increase their stiffness, thanks to a particular process which involves the gelatinization in water at low temperature in alkaline solution [29]. Nowadays, several bioplastic grades have been produced starting from starch [30, 31], mainly because of its capability to be blended with conventional polymers, and the possibility to process the resulting blends through conventional thermoplastic transformation technologies, like extrusion and injection molding [32]. In order to overcome the problem related to its elevated hydrophilicity, some attempts have been made to modify the starch structure by acetylation, while in other cases TPS was blended with other biopolymers (like PCL or polyhydroxybutyrate-co-valerate (PHBV)), to retain the biodegradability of the blends [27, 33, 34]. Moreover, TPS can be also blended with other

Journal of Polymers and the Environment (2020) 28:3244-3255

polymers (i.e. polyethylene, polypropylene and polystyrene), in order to improve its processability and thermal stability [35]. One of the most important starch-based commercial materials is Mater-Bi<sup>®</sup>, produced by Novamont Spa in Italy starting from 1989. Several classes of biodegradable Mater-Bi<sup>®</sup>, containing different amounts of thermoplastic starch and differing in their constituents, are nowadays produced by this company [36, 37]. These films can be produced by using the traditional film blowing and sealing technologies, resulting in products with mechanical properties comparable to those of petroleum-based polymers.

One of the main problems associated to the use of biodegradable materials in plastic bags is the marked sensitivity of their fracture resistance from the temperature. In order to face this problem, researchers focused their attention on the addition of fillers that could increase the T<sub>g</sub> (glass transition temperature), and thus their service life [38]. Moreover, the mechanical properties of thermoplastic starch are strongly dependent on temperature, as its T<sub>g</sub> is around 55 °C. At room temperature it will therefore show a brittle behaviour (without the addition of plasticizers), while at a temperature close to T<sub>o</sub> it will manifest a marked viscoelastic behaviour [39]. It is also clear that other environmental parameters (like relative humidity) could strongly influence the fracture behaviour of thermoplastics starch. In this sense, the comprehension of the mechanisms that govern the transition from a brittle to a viscoelastic behaviour is a key issue to optimize the mechanical performances of these materials in the packaging applications. Moreover during the production of plastic shoppers through extrusion and film blowing, the material will no longer possess isotropic mechanical properties, as the material will be stretched along the machine direction (MD), resulting in an increase in longitudinal properties with respect to the orthogonal one [named cross direction (CD)] [40]. Therefore, both the temperature and the drawing conditions will strongly affect the fracture resistance of thermoplastic starch based products. Considering that thermoplastic starch manifests a ductile behaviour when it is used for thin products (i.e. films or sheets) [41, 42], an elasto-plastic fracture mechanics approach, based on the essential work of fracture (EWF) concept, could be applied to characterize the material fracture toughness under plane-stress conditions. In fact, the EWF method has gained a wide interest for the evaluation of the fracture toughness of highly ductile polymers, like thermoplastic starch, low density polyethylene (LDPE) and polyamide 66 (PA66) [43–45].

On the basis of these considerations, in the present paper the attention was focused on the effect of the temperature and of the drawing direction on the tensile and fracture properties of thermoplastic starch based materials, produced by film extrusion. This matrix was selected as a model polymer to investigate the fracture behaviour under different environmental and processing conditions of biobased plastic films for food packaging applications. Therefore, tensile tests were carried out at different temperatures on samples cut out both along MD and CD, while their fracture behaviour was investigated applying the EWF approach.

# **Experimental Part**

#### Materials

The material investigated in the present work was a commercial grade of Mater-Bi<sup>®</sup> EF51V (density = 1.22 g/cm<sup>3</sup>, MFI at 190 °C and 2.16 kg = 4 g/10 min, T<sub>g</sub> = 55 °C), kindly supplied by Novamont Spa (Novara, Italy) in form of opaque extruded films with an average thickness of 100 µm. According to the technical datasheet provided by the supplier, this particular type of Mater-Bi<sup>®</sup> is biodegradable, compostable and soluble. Its biodegradability and compostability have been certified by several different accreditation systems following the EN 13430, EN 13431, EN 13432 standards. It had a starch content higher than 85% and, for this reason, it can be defined as thermoplastic plasticized starch.

#### **Preparation of the Samples**

Quasi-static mechanical tests were performed on ISO 527 type 1BA specimens, having a gage length of 30 mm, punchcut from the supplied films both in MD and CD direction.

Double edge notched tension (DENT) specimens for the EWF tests were cut from the supplied films both in MD and CD direction, following the ESIS-TC4 protocol [46]. Even if the EWF approach has not been yet standardized, testing protocols have been developed by ESIS TC4 committee and proposed to ensure the reliability of this approach [43]. DENT specimens had a length of 50 mm, a width of 30 mm and a thickness of about 100  $\mu$ m. Notches were produced on thermoplastic starch strips by using a razor blade (notch radius of 5  $\mu$ m), in order to obtain a very sharp crack tip and to generate DENT specimens with ligament length of 5, 7, 9, 11, 13 and 15 mm. In order to perform a correct statistical evaluation of the obtained data, at least 6 specimens for each ligament length have been tested.

#### **Experimental Techniques**

#### **Quasi-Static Tensile Tests**

Quasi-static uniaxial tensile tests were performed by using an Instron<sup>®</sup> 5969 electromechanical testing machine (Norwood, MA, USA) equipped with a 50 kN load cell and an Instron<sup>®</sup> 3119-409 thermostatic chamber. The tests were performed on ISO 527 type 1BA specimens. According to this standard, the elastic modulus was evaluated as secant modulus between deformation levels of 0.05% and 0.25%, while the tensile properties at break were determined setting a crosshead speed of 10 mm/min. This testing speed was the same utilized for the EWF tests. The tests were performed on samples cut both along MD and CD, at three different temperatures (0 °C, 25 °C, 50 °C). At least five specimens were tested for each sample.

#### **Essential Work of Fracture (EWF) Approach**

Since the matrix selected for this study is a polymer having a relatively high ductility, suitable for the production of thin sheets or films, an elasto-plastic fracture mechanics approach was applied to characterize its fracture resistance under plane-stress conditions. To achieve this aim, the essential work of fracture (EWF) protocol has been adopted [43, 44, 47]. This approach is based on the hypothesis that the total work of fracture  $(W_f)$  of notched specimen results from the summation of two different contributes. The first contribution is given by the work expended in the fracture process zone (We) which is considered to be essential for the generation of new fracture surfaces, while the second contribution is the work associated to the plastic deformation outside the fracture zone  $(W_p)$  [48, 49]. Figure 1 shows the fracture process zone in a DENT specimen, while in Fig. 2a representative load-displacement curve obtained in a tensile test on a DENT specimen is reported. In Fig. 2 it is also indicated uini, which is the displacement corresponding to the initiation of the crack, at which corresponds  $F_{max}$  (i.e. the maximum sustained load) and also umax, which is the maximum displacement measured during the test. As explained in the ESIS-TC4 protocol, under plane-stress conditions, the essential work for creating new fracture surfaces, which is also known as work of fracture (W<sub>f</sub>), is proportional to the ligament cross-section  $(L_t)$ , and the work associated to the



Fig. 1 Representative image of a DENT specimens for EWF tests



Fig. 2 Representative curve of a tensile test performed at 25 °C on a MD DENT thermoplastic starch specimen with L=13 mm

plastic deformation outside the fracture zone is proportional to the outer plastic volume ( $\beta L^2$ ), as reported in Eq. (1):

$$W_f = w_e L t + w_p \beta L^2 t \tag{1}$$

where t is the specimen thickness,  $\beta$  is a shape factor for the outer plastic zone and it changes with the shape of the plastic zone. For circular, elliptical and diamond-type zones  $\beta$  is given by  $\pi/4$ ,  $\pi$  h/4L, and h/2L, respectively [50]. Normalizing Eq. (1) by the cross-section of the samples, the specific total work of fracture (w<sub>f</sub>) can be obtained, as reported in Eq. (2):

$$w_f = w_e + w_p \beta L \tag{2}$$

where  $w_e$  and  $w_p$  are the specific essential and specific nonessential work of fracture terms.

The specimen's dimensions were selected following the indications reported in the paper of Williams and Rink regarding the standardization of the EWF approach [43]. In principle, the specimens should have a thickness lower than 1 mm, the ligament length should range between 5 and 15 mm, while their width and length should be at least 30 mm. With the aim to obtain a standard deviation over the mean value of we lower than 1%, as the ESIS-TC4 protocol states, at least five specimens should be tested for each ligament length. In agreement with these indications, DENT specimens dimensions were selected as follows: W = 30 mm, H = 30 mm, total length = 50 mm, 5 mm < L < 15 mm. In order to correctly apply the EWF approach, a complete yielding of the ligament zone must be obtained before the initiation of the crack propagation. A way to ensure that the fracture process occurred only after a complete yielding of the ligament zone is to compare the maximum stress ( $\sigma_{max}$ ) acting on the ligament, obtained dividing the maximum load  $(F_{max})$  by the ligament cross-section, with the tensile yield stress ( $\sigma_{v}$ ), determined at the same crosshead speed in quasistatic conditions on 1BA specimens. By considering that the ligament is constrained laterally, the value of  $\sigma_{max}$  would be expected to be equal to 1.15  $\sigma_v$ , and it should be independent on the ligament length [45]. Therefore, the results of the EWF tests are assumed to be valid if the value of the maximum stress of each sample is between 0.9-1.1 times the average value of  $\sigma_{max}$ . Subsequently, the total specific work of fracture (w<sub>f</sub>) can be calculated from the load-displacement curves, and the w<sub>f</sub> values can be then plotted against the ligament length, to be then subjected to a linear regression procedure. During this fitting procedure the parameters reported in Eqs. (3)–(7) can be computed:

$$S_{11} = \sum \left( w_{fi} - \overline{w_f} \right)^2 \tag{3}$$

$$S_{22} = \sum \left( L_i - \overline{L} \right)^2 \tag{4}$$

$$S_{12} = \sum \left( w_{fi} - \overline{w_f} \right) \left( L_i - \overline{L} \right)$$
(5)

$$n\overline{L} = \sum L_i \tag{6}$$

$$n\overline{w}_f = \sum w_{fi} \tag{7}$$

where the total summation is taken over i = n - 1, being n the number of specimens. Thereafter, the determination of  $w_e$  and  $\beta w_p$  is possible, as expressed in Eqs. (8) and (9):

$$w_e = \overline{w}_f - \overline{L} \frac{S_{12}}{S_{22}} \tag{8}$$

$$\beta w_p = \left(\frac{S_{12}}{S_{22}}\right) \tag{9}$$

The standard deviation S of  $w_e$  is defined as reported in Eqs. (10) and (11):

$$S^{2} = \left(\frac{1}{n} + \frac{\overline{L}^{2}}{S_{22}}\right) \frac{1}{(n-2)} \left(S_{11} - \frac{S_{12}^{2}}{S_{22}}\right)$$
(10)

$$R^2 = \left(\frac{S_{12}^2}{S_{11}S_{22}}\right) \tag{11}$$

A second verification should be performed to ensure that if a data point is laying outside the interval  $\pm \overline{S}$ , where  $\overline{S}$  is the standard deviation of the w<sub>f</sub> values evaluated from the linear regression procedure, then it will be excluded and the linear regression line will be recalculated. The value of  $\overline{S}$  can be calculated as expressed in Eq. (12):

$$\overline{S} = \frac{1}{(n-2)} \left( S_{11} - \frac{S_{12}^2}{S_{22}} \right)$$
(12)

All the different exclusion criteria were systematically utilized to assess the quality of the data in this analysis, and eventually, a final least squares regression line was performed. Its intercept represents the specific work of fracture ( $w_e$ ), while its slope is the non-specific work of fracture ( $\beta w_p$ ). Furthermore, as reported in several papers on the EWF approach [51, 52], it was also possible to calculate the total work of fracture initiation ( $W_{ini}$ ) by performing integration of load–displacement curves from zero to the maximum load reached. By the fact that  $W_{ini}$  is proportional to the ligament cross-section, the specific essential work of crack initiation ( $w_{ini}$ ) was computed following the same procedure used for determining the specific work of fracture. It is also possible to evaluate the specific essential work of crack propagation ( $w_{prop}$ ) by subtracting the value of  $w_{ini}$  from  $w_f$ .

## **Results and Discussion**

#### **Quasi-Static Tensile Tests**

It is well known in literature that both the mechanical and thermal properties of TPS products are significantly affected by the processing parameters, the plasticizer concentration and the moisture content [53]. Therefore, quasi-static tensile tests have been performed on the investigated material. Representative stress-strain curves from quasi-static tensile tests at break performed at different temperatures on TPS specimens and tested along machine direction and cross direction are reported in Fig. 3a, b, while the most important results are summarized in Tables 1 and 2. Regardless to the temperature and the testing direction, the elastic region at low deformation level is followed by the yielding and by an extended plasticization zone, until the breakage of the samples. This trend is typical of polymeric materials having an elasto-plastic behaviour, and it can be therefore inferred that the EWF could be successfully applied to characterize these materials. It could be interesting to notice that in the samples tested in MD a slight decrease of the stress can be detected immediately after the yield point, and only at deformation levels higher than 25% the stress starts to increase. In the materials tested in CD, a sudden increase of the sustained stress can be noticed immediately after the yield point. This different behaviour can be probably described to the strong orientation of the macromolecules in MD during the production process [54]. Considering the samples tested both



Fig. 3 Representative stress-strain curves from quasi-static tensile tests on thermoplastic starch samples tested along different orientations. **a** Machine direction (MD) and **b** cross direction (CD)

Table 1	Results	s of	quasi-sta	atic	tensile	test	s on	ther	moplastic	starch
samples	tested	at	different	ten	nperatu	res a	along	the	machine	direc-
tion (MI	D)									

T (°C)	E (MPa)	$\sigma_y$ (MPa)	$\sigma_{b}$ (MPa)	$\epsilon_{b}(\%)$
0	$108.3 \pm 2.6$	$27.4 \pm 0.4$	$36.0 \pm 4.0$	213.7±38.8
25	$99.8 \pm 1.5$	$19.5 \pm 0.3$	$26.8 \pm 2.3$	$284.4 \pm 37.5$
50	$71.3 \pm 2.5$	$10.3 \pm 0.2$	$18.7 \pm 0.2$	$410.7 \pm 4.4$

 Table 2 Results of quasi-static tensile tests on thermoplastic starch samples tested at different temperatures along the cross direction (CD)

T (°C)	E (MPa)	$\sigma_y$ (MPa)	$\sigma_{b}\left(MPa\right)$	$\epsilon_{b}(\%)$
0	$45.0 \pm 2.4$	$18.4 \pm 0.6$	$30.4 \pm 3.8$	229.1 ± 27.1
25	$38.0 \pm 1.4$	$12.1 \pm 0.2$	$16.9 \pm 1.4$	$231.7 \pm 18.5$
50	$13.3 \pm 1.3$	$6.5 \pm 0.4$	$6.9 \pm 2.0$	$305.9 \pm 25.7$

in machine and in cross direction, it can be noticed that by increasing the temperature from 0 to 50 °C the elastic modulus (E), the yield stress ( $\sigma_y$ ) and the stress at break ( $\sigma_b$ ) tend to decrease, while the deformation at break ( $\varepsilon_b$ ) increases significantly. It could be important to underline that it was not possible to test the samples at higher temperatures (i.e. above the T<sub>g</sub> of the material) because the tensile properties of the material were too low to be detected. Comparing the elastic and failure properties of these materials in MD and CD (see Tables 1 and 2, respectively), it is immediately evident that samples tested in MD are stiffer and have higher  $\sigma_y$  and  $\sigma_b$  values in comparison to the specimens tested along the CD. By looking at the  $\varepsilon_b$  data of CD specimens tested at 25 °C, a slightly lower value with respect to the corresponding MD samples has been detected, and this difference is even more evident at 50 °C. However, considering the standard deviation values associated to these measurements and that the defomation at break in thin plastic films is strongly affected by the presence of defects within the samples, it can be seen that the observed differences are not so pronounced. These results can be explained considering that the molecular orientation induced by the drawing during the production of the films led to a strong anisotropy of the material and to an increase of the elastic properties and of the yield resistance, regardless to the testing temperature [41].

The dependency of the mechanical propertie on the processing conditions can be ascribed to the fact that they are directly dependent on the combined interaction of polymer crystallized and amorphous phases during the elongational flow [55]. In fact, when the full plasticization of the material occurs (i.e. at high strain level), the original orientation of the macromolecules is completely lost and the MD and CD samples show similar  $\varepsilon_{\rm b}$  values. Therefore, quasi-static tensile tests indicate that both the temperature and the drawing conditions strongly influence the mechanical properties of the material.

#### **Essential Work of Fracture (EWF) Approach**

The evaluation of the fracture behaviour through a specific elasto-plastic fracture mechanics approach is of utmost importance. EWF tests have been performed with the purpose of understanding the elasto-plastic fracture behaviour of thermoplastic starch as a function of the temperature and of the molecular orientation induced by the drawing operations. Therefore, EWF analysis was carried out on DENT specimens conditioned at different temperatures (0 °C, 25 °C and 50 °C) and tested along machine direction and cross direction. DENT geometry was selected in order to correctly fullfill the standardized procedure and also because, thank to this particular geometry, the non-essential work of fracture is lower in comparison to other specimens geometries [56]. Even for EWF tests it was impossible to test the samples at temperatures above the T<sub>o</sub> of the thermoplastic starch, because the mechanical properties were too low to obtain reliable results. Representative load-displacement curves from EWF tests performed at various ligament length on samples tested at different temperatures and both in MD and CD are reported in Fig. 4a-f. In all the curves the load tends to increase reaching a maximum value  $(F_{max})$ . This point is generally associated with the full yielding of the cross-section and to the initiation of the fracture propagation stage. The load then progressively decreases until the breakage of the samples. Therefore, it can be concluded that all the tested specimens display a typical elasto-plastic load-displacement curve, in which a stable crack propagation takes place after the complete yielding of the ligament zone. It is interesting to notice that samples tested in MD (see Fig. 4a, c, e) manifest a sharp decrease of the load after F<sub>max</sub>, while in the CD samples (see Fig. 4b, d, f) the drop of the load after F<sub>max</sub> is less pronounced, especially at elevated temperatures. Once again, this different behaviour can be related to the different molecular orientation induced by the drawing procedure which tends to induce anisotropy in the material [41]. In particular, the behaviour of MD specimens can be explained considering that the structure of the material, during the extrusion process, can be transformed from a semicrystalline structure with some amorphous region into a much more ordered structure, with the majority of the crystalline domains oriented along the strain direction and a lower amorphous phase content [57]. As it could be expected, the sustained load strongly increases with the ligament length for all the samples, increasing thus the total  $(W_f)$  and the specific  $(w_f)$  work of fracture. Regardless to the drawing orientation, rising the testing temperature the material tends to become more and more ductile, increasing thus its tendency to an elasto-plastic fracture behaviour. In fact, as temperature rises from 0 to 50 °C, the maximum displacement (umax) tends to increase and the maximum load  $(F_{max})$  decreases. Once again,  $F_{max}$  values of samples tested in MD are systematically higher than those detected for CD samples, because of the enhancement of the yield resistance due to the molecular orientation induced by the drawing.

It is also interesting to directly compare the obtained load-displacement curves at the same ligament length and at different temperatures, in order to better highlight the role played by the temperature on the fracture behaviour of the tested materials. Figure 5a–f report representative load-displacement curves of DENT specimens with ligament length equal to 5, 9, and 13 mm, tested along machine and cross direction. A direct comparison between MD and CD samples is possible through these plots, and it is even more evident that  $F_{max}$  values of MD samples are superior to those of the corresponding CD specimens. Moreover, these images clearly evidence the decrease of the sustained load with the testing temperature, associated to an increase of the u<sub>max</sub> values.

Figure 6 reports photograms of DENT specimens taken during EWF tests, after the complete yielding of the ligament length. It demonstrates that the full yielding of the ligament zone occurs for all the samples, and an ellipticalshaped zone can be seen, regardless to the testing temperature and/or the drawing conditions. Moreover, by increasing the temperature the volume of the plastic deformation zone tends to increase, independently from the testing direction. It is worhtwhile to observe that MD samples present a transparent yielding zone at 25 °C, and it becomes translucid only at elevated testing temperature (i.e. 50 °C). This is due to the fact that the thickness of the samples is progressively reduced in the ligament area during the tests. Moreover, the macromolecules are already oriented along the straining direction, and further crystallization of the material is not possible. Only at temperatures near the T<sub>o</sub> of TPS (i.e. 50 °C) a further crystallization could be favoured by the higher mobility of the macromolecules, and the ligament zone becomes translucid. Interestingly, in CD specimens the plastic deformation zone does not appear transparent neither at 25 °C. It is probable that in CD samples the orientation of the macromolecules along the strain direction is possible, with a sudden crystallization of the ligament zone. It is generally known that during the stretching of TPS samples, either during processing or testing, some new crystal forms could be generated, the kinetics of crystallization are strongly accelerated, and even crystalline morphology could change from spherulite type to shish-kebab or rownuclei structures [58, 59]. The crystalline morphology of the shish-kebab is composed of a long central fiber core, named shish, surrounded by lamellar crystalline structures, named kebab, periodically attached along the shish. This particular morphology can be generated by nuclei aligned parallel to the flow direction, and then lamellar crystals can be formed and grow in transversal direction [60, 61]. In this particular case study, as stated before, a further orientation of the macromolecule along MD occurs at a temperature close or above 50 °C, leading to higher strength and a lower haze. On the contrary, in CD samples there is not a decrease in haze and also there is an increase in the maximum displacement and a decrease in the maximum load. This last sentence is in agreement with the fact that, during the application of a strain along CD, the macromolecules are able to move with greater mobility, because the whole system is trying to move towards a thermodynamically stable configuration.



Fig. 4 Representative load-displacement curves from EWF tests on DENT specimens tested at various temperatures and along different orientation: **a** MD 0 °C, **b** CD 0 °C, **c** MD 25 °C, **d** CD 25 °C, **e** MD 50 °C, **f** CD 50 °C

This greater mobility leads thus to a further crystallization along CD [62]. However, DSC tests on the material taken from the yielding zone should be performed in the future to have a better explanation of these mechanisms.

Figure 7a, b report the plots of specific work of fracture  $(w_f)$  versus ligament length (L) of thermoplastic starch

specimens tested at different temperature and along different orientation. The most important results of this analysis for MD and CD samples are summarized in Tables 3 and 4, respectively. The reported data have been already selected according to the exclusion criteria reported in the Experimental Techniques section. First of all, it is important to



Fig. 5 Representative load-displacement curves from EWF tests on DENT specimens tested at various temperature and along different orientation: **a** MD L=5 mm, **b** CD L=5 mm, **c** MD L=9 mm, **d** CD L=9 mm, **e** MD L=13 mm, **f** CD L=13 mm

underline that  $w_f$  values follow a linear trend with the ligament length at all the testing conditions, meaning that careful preparation of the samples and a rigid application of the testing procedure suggested by the ESIS-TC4 protocol was carried out. In fact, from Tables 3 and 4 it is evident

that  $R^2$  values associated to the linear regression operations are higher than 0.95 for all the samples. An  $R^2$  value close to 1 is a requisite for the applicability of the methods, as reported by Williams and Rink in their paper concerning the EWF approach standardization [43]. In agreement



Fig.6 Representative images collected during the EWF tests on DENT specimens with ligament length L=13 mm at different temperatures and along different orientation

with quasi-static tensile tests on un-notched specimens, it is proven that both the temperature and the testing orientation significantly influence the essential work of fracture  $(w_e)$  values. The value of  $w_e$  tends to strongly decrease by increasing the temperature, passing from 36.0 down to 16.0 kJ/m<sup>2</sup> for the MD samples, and from 42.5 down to 19.5 kJ/m<sup>2</sup> for the CD samples. This means that at 50 °C the resistance offered by the material against the propagation of the fracture within the ligament zone is about one half than that detected at 0 °C. It is important to underline that the obtained  $w_e$  results are considerably higher than those obtained by Chaleat et al. on a plasticised starch/high molecular weight polyol blend tested at ambient temperature and different moisture contents (i.e. from 3 to 11 kJ/m<sup>2</sup>) [63]. This discrepancy could be explained by the fact that the TPS grade utilized in the present paper has a negliglible water content at ambient temperature, as detected through thermogravimetric tests reported in our previous work on this matrix [25]. However, it has to be considered that a direct comparison between the fracture behaviour of different TPS systems is very difficult, because there are too many factors (like type of plasticizer, molecular weight and crystallinity of TPS, etc.) that could strongly affect the resistance to crack propagation of the material.

A less clear dependency can be detected in  $\beta w_p$  values, even they seem to slightly decrease with the testing temperature. Quite surprisingly, we values of CD samples are systematically higher than those observed in MD samples at all the temperature levels, while comparable results can be seen in  $\beta w_p$  values. The higher  $w_e$  values observed for CD samples could be explained considering that along cross direction no molecular orientation occurred during the production process. During the tests, the macromolecules tend to orient themselves along the strain direction, promoting thus the crystallization of the material. Therefore, part of the tensile energy applied during the tests is utilized to orient the molecules rather than to propagate the crack within the material. This hypothesis is supported by the photograms of the CD samples reported in Fig. 6, in which the yielding zone becomes opaque during the tests.

As reported in Tables 3 and 4, both the essential work of crack initiation  $(w_{ini})$  and the essential work of crack propagation  $(w_{prop})$  are considerably affected by the testing temperature, and they tend to considerably decrease passing from 0 to 50 °C, regardless to the testing orientation. Accordingly to the we results, we prop values of CD samples are systematically higher that those detected for MD samples, probably because during the fracture propagation process part of the energy is utilized to orient the macromolecules along the strain direction. It is therefore demonstrated that in the design of biodegradable plastic packaging products particular attention should be taken to the in-service conditions of the materials, especially at temperatures approaching the T<sub>o</sub>, and that anisotropy of plastic bags deriving from the drawing operation can have an important effect of the elastoplastic fracture mechanisms of the produced materials.

### Conclusions

The aim of this paper is to shed some light over the influence of the temperature and of the drawing conditions on the elasto-plastic fracture behaviour of thermoplastic starch based films for food packaging application. At this aim, quasi-static tensile tests and the essential work of fracture



Fig. 7 Specific total work of fracture as a function of the ligament length from EWF tests on DENT specimens tested at various temperatures and along different orientation. a Machine direction and b cross direction

Table 3 Results of EWF tests on DENT samples tested in machine direction (MD)

T (°C)	w <sub>e</sub> (kJ/m <sup>2</sup> )	$\beta w_p (MJ/m^3)$	$\mathbb{R}^2$	w <sub>ini</sub> (kJ/m <sup>2</sup> )	w <sub>prop</sub> (kJ/m <sup>2</sup> )
0	$36.0 \pm 2.5$	$6.7 \pm 0.3$	0.9566	$7.5 \pm 0.7$	$28.5 \pm 2.3$
25	$26.4\pm0.9$	$6.2 \pm 0.1$	0.9954	$7.1 \pm 0.8$	$19.4 \pm 1.1$
50	$16.0 \pm 2.3$	$7.0 \pm 0.2$	0.9783	$3.5 \pm 0.3$	$12.5 \pm 2.1$

 Table 4
 Results of EWF tests on DENT samples tested in cross direction (CD)

T (°C)	w <sub>e</sub> (kJ/m <sup>2</sup> )	$\beta w_p (MJ/m^3)$	R <sup>2</sup>	w <sub>ini</sub> (kJ/m <sup>2</sup> )	w <sub>prop</sub> (kJ/m <sup>2</sup> )
0	$42.5 \pm 1.5$	$8.4 \pm 0.1$	0.9942	8.8±1.2	$33.7 \pm 1.8$
25	$32.6 \pm 1.2$	$7.9\pm0.1$	0.9953	$4.7 \pm 0.6$	$27.9 \pm 1.4$
50	$19.5 \pm 1.0$	$6.1\pm0.2$	0.9942	$1.2 \pm 0.3$	$18.3 \pm 1.0$

(EWF) approach have been considered, testing samples from 0 up to 50  $^{\circ}$ C and both in machine and in cross direction.

Quasi-static tensile tests highlighted that the elastic modulus (E), the yield stress ( $\sigma_y$ ) and the stress at break ( $\sigma_b$ ) considerably decreased at elevated temperature (i.e. 50 °C), while the deformation at break ( $\varepsilon_b$ ) was noticeably enhanced, regardless to the testing direction. Moreover, samples tested in MD were stiffer and presented higher stress at yield and at break with respect to the CD tested specimens, probably because of the strong anisotropy induced by the molecular orientation along the drawing direction. EWF tests demonstrated that both the temperature and the testing orientation significantly influenced the essential work of fracture (w<sub>e</sub>) values, as  $w_e$  values tended to strongly decrease with the temperature. Moreover,  $w_e$  values of CD samples were systematically higher than those detected in MD samples, probably because part of the tensile energy applied during these tests was utilized to orient the molecules along the strain direction rather than to propagate the crack within the material. This hypothesis was supported by the photograms of the CD samples taken during the tests, in which the yielding zone became progressively opaque due to the strain induced crystallization. Therefore, both the exercise conditions and the structural anisotropy induced by the material processing strongly affect the fracture behaviour of these materials, and EWF could be successfully applied to investigate the elasto-plastic mechanisms that govern the fracture process of these materials.

# References

- 1. Hottle TA, Bilec MM, Landis AE (2013) Polym Degrad Stab 98:1898
- 2. Thakur S, Chaudhary J, Sharma B, Verma A, Tamulevicius S, Thakur VK (2018) Curr Opin Green Sustain Chem 13:68
- Albuquerque PBS, Malafaia CB (2018) Int J Biol Macromol 107:615
- Ryberg M, Laurent A, Hauschild MZ (2018) Mapping of global plastic value chain and plastic losses to the environment: with a particular focus on marine environment. United Nations Environment Programme, Nairobi
- 5. Drzyzga O, Prieto A (2019) Microb Biotechnol 12:66
- Agarski B, Vukelic D, Micunovic MI, Budak I (2019) J Environ Manage 245:55
- Verma R, Vinoda KS, Papireddy M, Gowda ANS (2016) Waste Manag Resour Util 35:701
- 8. Wright SL, Kelly FJ (2017) Environ Sci Technol 51:6634

- Benobeidallah B, Benhamida A, Dorigato A, Sola A, Messori M, Pegoretti A (2019) J Renew Mater 7:89
- Oulmou F, Benhamida A, Dorigato A, Sola A, Messori M, Pegoretti A (2019) J Elastomers Plast 51:175
- Tait M, Pegoretti A, Dorigato A, Kalaitzidou K (2011) Carbon 49:4280
- 12. Dorigato A, Sebastiani M, Pegoretti A, Fambri L (2012) J Polym Environ 20:713
- Goncalves I, Vasconcelos A, Machado ASL, Alves AV (2017) Bioplastics from agro-wastes for food packaging application. In: Grumezescu AM (ed) Food packaging, 1st edn. Academic Press, Cambridge, pp 223-263
- Reddy MM, Misra M, Mohanty AK (2012) Chem Eng Prog 108:37
- Ludevese-Pascual G, Laranja JL, Amar E, Bossier P, De Schryver P (2019) Aquac Res 50:1269
- Xie FW, Zhang TL, Bryant P, Kurusingal V, Colwell JM, Laycock B (2019) Prog Polym Sci 90:211
- 17. Haider TP, Volker C, Kramm J, Landfester K, Wurm FR (2019) Angew Chem Int Ed 58:50
- 18. Dorigato A, Pegoretti A (2012) Colloid Polym Sci 290:359
- Byun Y, Kim YT (2014) Bioplastics for food packaging. In: Han JH (ed) Innovations in food packaging. Academic Press, San Diego, p 353
- Peelman N, Ragaert P, De Meulenaer B, Adons D, Peeters R, Cardon L, Van Impe F, Devlieghere F (2013) Trends Food Sci Technol 32:128
- 21. Drumright RE, Gruber PR, Henton DE (2000) Adv Mater 12:1841
- Massardier-Nageotte V, Pestre C, Cruard-Pradet T, Bayard R (2006) Polym Degrad Stab 91:620
- Valentini F, Dorigato A, Rigotti D, Pegoretti A (2019) J Polym Environ 27:1333
- 24. Dorigato A, Negri M, Pegoretti A (2018) J Renew Mater 6:493
- Dorigato A, Fredi G, Pegoretti A (2019) Thermo-mechanical behavior of novel wood laminae-thermoplastic starch biodegradable composites with thermal energy storage/release capability. Front Mater 6:76
- Halley PJ, Avérous L (2014) Chapter 5—Starch modification to develop novel starch-biopolymer blends: state of art and perspectives. In: Halley PJ, Avérous L (eds) Starch polymers from genetic engineering to green applications. Elsevier, Amsterdam, p 105
- Averous L, Fauconnier N, Moro L, Fringant C (2000) J Appl Polym Sci 76:1117
- 28. Maharana T, Singh BC (2006) J Appl Polym Sci 100:3229
- 29. Nayak PL (1999) J Macromol Sci Rev Macromol Chem Phys C39:481
- Doi Y, Fukuda K (1994) Biodegradable plastics and polymers, vol 12. Elsevier, Amsterdam
- 31. Lawton JW (1996) Carbohyd Polym 29:203
- Yew GH, Chow WS, Ishak ZAM, Yusof AMM (2009) J Elastomers Plast 41:369
- 33. Ayucitra A (2012) Int J Chem Eng Appl 3:156
- Chi H, Xu K, Wu X, Chen Q, Xue D, Song C, Zhang W, Wang P (2008) Food Chem 106:923
- 35. Kaseem M, Hamad K, Deri F (2012) Polym Sci Ser A 54:165

- 36. Bastioli C (1998) Polym Degrad Stab 59:263
- 37. Colonna P, Mercier C (1985) Phytochemistry 24:1667
- Ibrahim MIJ, Sapuan SM, Zainudin ES, Zuhri MYM (2019) Int J Food Prop 22:925
- 39. Ali R, Iannace S, Nicolais L (2003) J Appl Polym Sci 88:1637
- 40. Laftah WA, Rahman WAWA (2019) Polytechnica 2:51
- Thunwall M, Kuthanová V, Boldizar A, Rigdahl M (2008) Carbohyd Polym 71:583
- 42. Zhang Y, Rempel C, Liu Q (2014) Crit Rev Food Sci Nutr 54:1353
- 43. Williams JG, Rink M (2007) Eng Fract Mech 74:1009
- 44. Prashantha SH, Lacrampe MF, Krawczak P (2011) Compos Sci Technol 71:1859
- Bárány T, Czigány T, Karger-Kocsis J (2010) Prog Polym Sci 35:1257
- 46. Clutton EQ (2000) ESIS TC4 experience with the essential work of fracture method. In: Williams JG, Pavan A (eds) Fracture of polymers, composites and adhesives, second ESIS TC4 conference on fracture of polymers, composites and adhesives. Elsevier, New York, p 187
- 47. Dorigato A, Pegoretti A (2012) Eng Fract Mech 79:213
- Musto P, Ragosta G, Scarinzi G, Mascia L (2004) Polymer 45:4265
- 49. Zhang H, Zhang Z, Yang JL, Friedrich K (2006) Polymer 47:679
- 50. Mai YW, Wong SC, Chen X (2000) Polymer blends: formulations and performance. Wiley, New York, p 172
- 51. Rodolfo A (2018) J Vinyl Additive Technol 25:3
- 52. Benavente R, Perez E, Quijada R (2001) J. Polym Sci Pol Phys 39:277
- Zhang Y, Rempel C, McLaren D (2014) Chapter 16—Thermoplastic starch. In: Han JH (ed) Innovations in food packaging, 2nd edn. Academic Press, San Diego, p 391
- 54. Dunn T (2015) Oriented plastic films. In: Dunn T (ed) Flexible packaging. William Andrew Publishing, Oxford, p 177
- 55. Fambri L, Lutterotti L (2019) Effect of Processing and orientation on structural and mechanical properties of polypropylene products. In: Wang W (ed) Polypropylene. IntechOpen, Hamilton
- 56. Hashemi S (2000) Polym Eng Sci 40:798
- 57. Selling GW, Sessa DJ (2007) Ind Crops Prod 25:266
- Kumaraswamy G, Kornfield JA, Yeh FJ, Hsiao BS (2002) Macromolecules 35:1762
- Kimata S, Sakurai T, Nozue Y, Kasahara T, Yamaguchi N, Karino T, Shibayama M, Kornfield JA (2007) Science 316:1014
- Nagasawa T, Shimomura Y (1974) J Polym Sci Polym Phys Edit 12:2291
- 61. Somani RH, Yang L, Zhu L, Hsiao BS (2005) Polymer 46:8587
- Larrañaga A, Lizundia E (2018) Strain-induced crystallization. In: Thomas S et al (eds) Crystallization in multiphase polymer systems. Elsevier, Amsterdam, p 471
- 63. Chaléat CM, Halley PJ, Truss RW (2008) Carbohyd Polym 71:535

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.