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Toughness Enhancement of Commercial Poly (Hydroxybutyrate-co-Valerate) (PHBV) by Blending with a Thermoplastic Polyurethane (TPU)

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Poly(hydroxyl butyrate-co-valerate) (PHBV) is a biopolymer synthesized by microorganisms that is fully biodegradable with improved thermal and tensile properties with respect to some commodity plastics. However, it presents an intrinsic brittleness that limits its potential application in replacing plastics in packaging applications. Films made of blends of PHBV with different contents of thermoplastic polyurethane (TPU) were prepared by single screw extruder and their fracture toughness behavior was assessed by means of the essential work of fracture (EWF) Method. As the crack propagation was not always stable, a partition method has been used to compare all formulations and to relate results with the morphology of the blends. Indeed, fully characterization of the different PHBV/TPU blends showed that PHBV was incompatible with TPU. The blends showed an improvement of the toughness fracture, finding a maximum with intermediate TPU contents.

Keywords: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); polyurethane; biodegradable; blends; essential work of fracture.

1. Introduction

The fracture behavior of materials that present high plastic deformation can be described by post-yielding fracture mechanics (PYFM).[1] The essential work of fracture (EWF) method provides a technique for obtaining toughness parameters for the ductile fracture process in either tensile or tearing configurations. Deeply double edge notched tensile (DDENT) specimens are the most used geometry in EWF determinations in tensile mode.[2,3]

The EWF concept initially states that the energy involved during a ductile fracture (W_f) can be partitioned into two components. One component, the essential work (W_e) is associated with the energy spent at the fractured surface and is therefore proportional to the fracture area ($\ell \cdot t$), where ℓ is the ligament length and t is the specimen thickness. The second component is the non-essential work of fracture or plastic work (W_p), which is related to the energy of the process that takes place out of the fracture surface and involves extensive plastic deformation and other dissipative energy processes. W_p is proportional to the volume of the deformed region surrounding the crack process zone, that is proportional to $\ell^2 \cdot t$. The relation between W_f, W_e, and W_p is described in Eq. (1):

$$W_f = W_e + W_p = w_e \ell \cdot t + \beta \cdot w_p \ell^2 \cdot t, \tag{1}$$

where w_e and w_p are the specific EWF and the specific non-essential work of fracture, respectively, whereas β is a dimensionless shape factor for the plastic zone. Dividing both terms of Eq. (1) by the ligament section, $\ell \cdot t$, we obtain that the specific work of fracture, w_f is then:

$$W_f/(\ell \cdot t) = w_f = w_e + \beta \cdot w_p \ell. \tag{2}$$

According to this equation, w_e and $\beta \cdot w_p$ can be obtained from linear regression of a set of values represented in a diagram of specific total fracture energy versus ligament length. It has been shown that the specific essential work, w_e is in theory of a material constant dependent only on thickness and equivalent to J_{IC},[4] which has also been supported experimentally and compared with the CTOD values.[5] It is assumed that for the correct application of the EWF method, some experimental constraints must be accomplished, including pure plane stress conditions, no border effect, full yielding of the ligament length prior to crack propagation, a geometrical similarity between the fracture load versus. displacement (L–d) curves (Fig. 1(a)) of specimens with different ligament lengths and steady crack propagation during fracture.[6] If these criteria are not accomplished, the results cannot be regarded as true fracture toughness values.

However, there are some works[7–9] in which the energy spent on the fracture process is split into different terms (initiation, necking, plastic work, viscoelastic energy, etc.), so called "partition energy" approaches. The main terms are, generally the initiation process (mainly yielding of ligament section, $w_{f,y}$) and crack propagation process (i.e., ligament necking and tearing, $w_{f,n}$), treated as if they were independent phenomena. According to the approach described in Ref. 7 these terms can be related with the fracture L–d curves, as shown in Fig. 1(b). Hence, Eq. (2) can be rewritten as:

$$w_f = w_y + w_n = (w_{e,y} + \beta \cdot w_{p,y}\ell) + (w_{e,n} + \beta \cdot w_{p,n}\ell) \tag{3}$$

where w_y and w_n can be calculated from L–d curves for each specimen and therefore the specific initiation EWF parameters ($w_{e,y}, \beta \cdot w_{p,y}$) and propagation ones ($w_{e,n}$, $\beta \cdot w_{p,n}$) can be obtained.

From this approach, if the criteria previously exposed for applying the EWF method applies to the initiation part of the fracture of DDENT specimens, the EWF technique can be used to assess toughness and resistance to initiation of

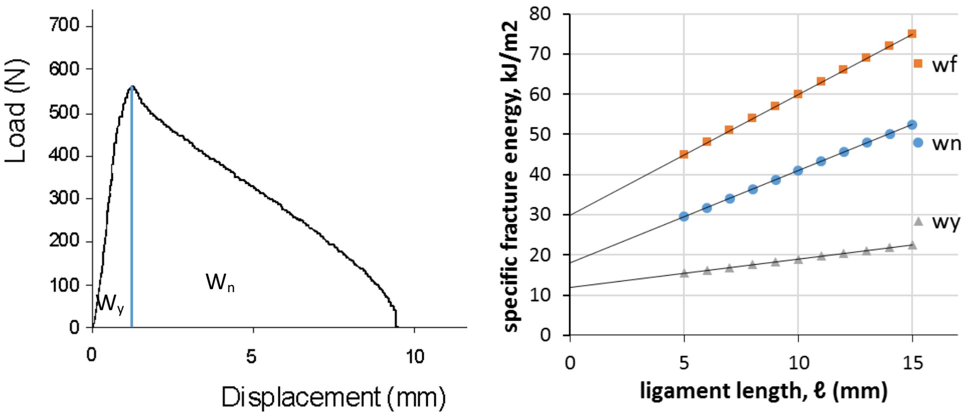

Fig. 1. Schema showing the L–d curves where the work of fracture can be obtained, the partition energy based on yielding criterion and the w_f versus ℓ theoretical plots for assessment of fracture parameters.

crack propagation in materials which show overall ductile fracture behavior, even though the propagation of the crack does not fulfill the self-similarity or steady crack growth conditions.

In this work Polyhydroxybutyrate-co-valerate) (PHBV) films have been prepared, with different percentages of thermoplastic polyurethane (TPU) as an additive in order to improve the fracture toughness and brittleness of virgin PHBV. PHBV is a biopolymer synthesized by microorganisms that is fully biodegradable with improved thermal and tensile properties with respect to some commodity plastics but too brittle to replace commodity plastics in day-to-day packaging applications. As the crack propagation was not always stable in those films, in order to optimize the TPU content in the film formulations, the EWF energy partition approach has been used, in combination with other techniques that provide information about the morphology and tensile behavior.

2. Experimental

PHBV with 3 mol% hydroxyvalerate (HV) content was supplied by Tianan Biologic Material Co. (Ningbo, P. R. China) in pellet form (ENMATTM Y1000P). The TPU Elastollan® 880[a] 13N000 was purchased from BASF. Both materials were used as received. PHBV and the TPU used in this study were dried at 80°C for 2 h before use. The PHBV/TPU blends were obtained by a single screw extruder (Haake Rheomex 252p) with a Maddock screw with an L/D ratio of 25. The temperature profile was set to 120°C/160°C/750°C, a die temperature of 175°C and a typical residence time of 3 min. Films of nominal thickness of 0.2 mm with different TPU contents were obtained: 0% (referred as Neat PHBV), 15wt% TPU (15-TPU), 20wt% TPU (20-TPU) and 25wt% TPU (25-TPU). The morphology

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of the cryofractured surface of the films and post-mortem DDENT specimens was observed by Scanning Electron Microscopy (SEM) using a JEOL 7001F.

DDENT and tensile dumbbell specimens (ASTM D638 Type IV) were cut from the films.[7] For EWF tests, five ligament lengths between 5 mm and 15 mm with a step of 2–3 mm were prepared and for each ligament length, three replicas were tested. All the experiments were conducted in a universal testing machine, Shimazdu AGS-X 500N. The crosshead speed for mechanical and fracture characterization was 5 mm/min and tests were conducted at room temperature ($22 \pm 1°C$).

3. Results and discussion

Blends showed a continuous PHBV matrix with evenly distributed TPU fibers oriented along the melt flow axis during film processing in all case, as shown in Fig. 2. The size of the fibrils did not vary significantly with the TPU content. However, in post-mortem DDENT specimens, the PHBV containing 25% TPU showed some necking with extensive plastic deformation and a close look revealed formation of fibrils along the crack propagation direction.

With respect to tensile performance, all films showed strong anisotropy between the extrusion direction (MD) and the transverse one, as observed in the representative stress versus strain curves in Fig. 3. This behavior is quite typical for extruded films, being especially enhanced in highly crystalline systems, such as PHBV, where crystals grow in a preferred orientation [REF]. Neat PHBV showed brittle behavior without yielding, whereas blends with TPU showed in all cases a yielding point with some plastic deformation. The films blended with TPU showed fast crack propagation after yielding, always at higher deformation values than those obtained by Neat PHBV. Table 1 summarizes the main values obtained from tensile tests; it

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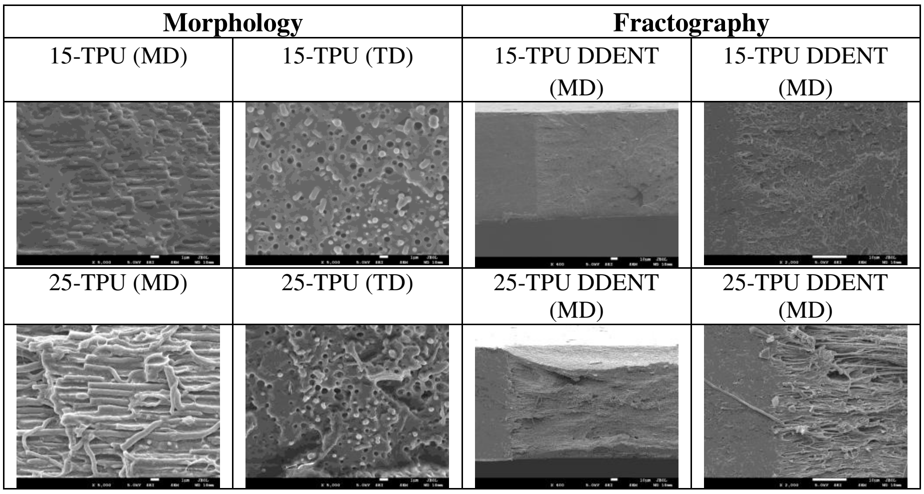

Fig. 2. Morphological and fractographic SEM micrographs.

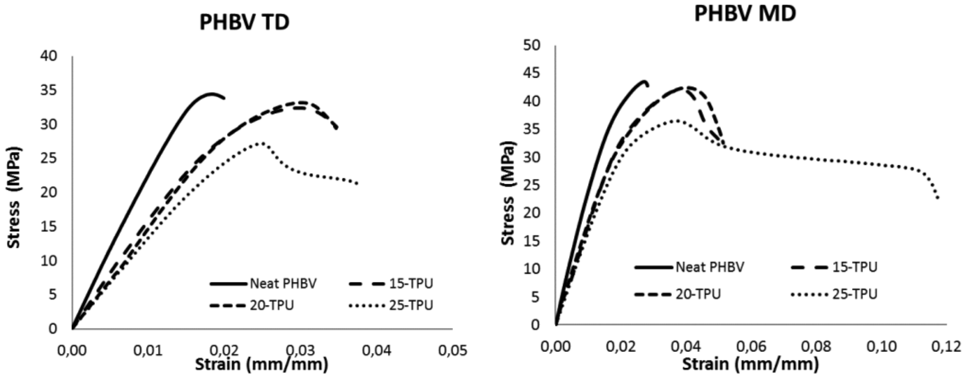

Fig. 3. Representative stress versus strain curves of all compositions studied.

Table 1. Summary of tensile and fracture properties of PHBV and PHBV-TPU films.

	Tensile Properties			Fracture Parameters			
	E (MPa)	σ_y (MPa)	ε_r (mm/mm)	w_e (kJ/m^2)	βw_p (J/m^3)	$w_{e,y}$ (kJ/m^2)	$\beta w_{p,y}$ (J/m^3)
Neat PHBV TD	2200 ± 200	33 ± 1	0.021 ± 0.003				
15-TPU TD	1800 ± 100	31.6 ± 0.5	0.034 ± 0.002	3.4	0.19	2.9	0.16
20-TPU TD	1800 ± 100	32.5 ± 0.7	0.032 ± 0.002	2.0	0.45	0.7	0.45
25-TPU TD	1500 ± 100	27 ± 1	0.034 ± 0.002	5.1	0.75	0.9	0.83
Neat PHBV MD	2500 ± 100	42 ± 1	0.027 ± 0.003				
15-TPU MD	2000 ± 200	41 ± 1	0.047 ± 0.002	8.8	0.23	6.3	0.18
20-TPU MD	2000 ± 100	41 ± 1	0.047 ± 0.004	4.8	1.38	2.4	0.93
25-TPU MD	1700 ± 100	36.0 ± 0.8	0.09 ± 0.02	4.3	0.82	0.8	0.84

can be seen as a trend where there is an increase in deformation at rupture as more TPU is added.

Even though adding TPU reduced the Young Modulus in all cases by at least 20%, the values obtained for tensile strength did not vary that much in formulations with 15% and 20% TPU content. The reason for such small differences is the fact that Neat PHBV films break before reaching plastic yielding by spontaneous crack generation and propagation.

In terms of fracture behavior, Load versus displacement curves, like the ones shown in Fig. 4, were self-similar up to yielding in all PHBV-TPU systems. After maximum load, some sort of disagreement in the tails of the curves was observed. Generally, this type of behavior would prevent from applying the EWF method or, at least, the values obtained should be taken carefully. However, by using the partition approach with the energy values corresponding to the yielding of the DDENT samples, some certitude can be obtained in terms of energy absorbed to crack initiation.

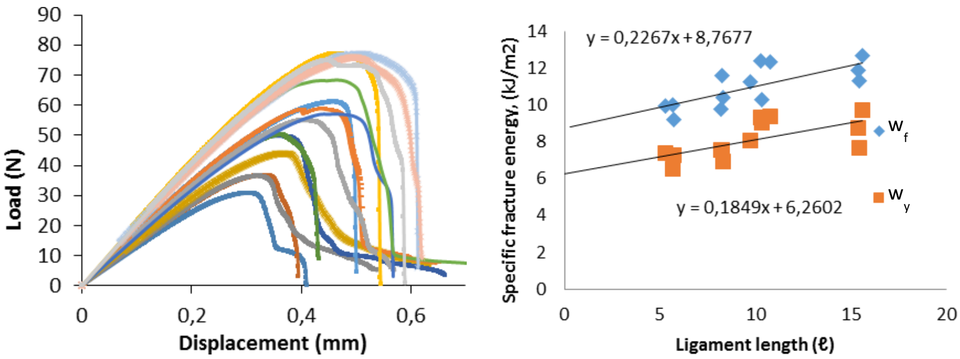

Fig. 4. L–d curves and w versus ℓ plots for determination of EWF parameters for films 15-TPU MD.

Therefore, the specific work of fracture as well as the specific initiation work of fracture were determined and plotted as a function of the ligament length to assess the EWF parameters and the parameters corresponding to the proposed energy partition procedure. The values obtained for all films are summarized in Table 1. As Neat PHBV did not show yielding at all, the EWF method did not provide any valid parameter.

From the EWF values, some general trends can be appreciated, like the anisotropy found in tensile behavior with higher w_e and βw_p values in MD than in TD, or the fact that as TPU content increases, there is higher deviation of w_e values with respect to $w_{e,y}$. A close look to these values show that the $w_{e,y}$ decreases as TPU content increases. This indicates that the contribution of generation of two new surfaces at the initiation of the crack propagation decreases by adding TPU.

However, during this process there is also some plastic deformation with the ligament yielding, which also contributes to energy absorption, represented by the term $\beta \cdot w_{p,y}$. This term, however, is tricky to evaluate, since it represents the plastic work developed by initial volume unit, and this value depends on the stress required to produce plastic work and the extension at which the plastic deformation has been carried out. An increase in TPU makes on one hand to decrease the stress required to produce plastic deformation and on the other hand, to absorb more energy because more plastic deformation is promoted, in agreement with the tensile characterization.

So the global balance in the fracture process initiation is either to ease the plastic deformation at lower energy levels, which decreases w_e but increases the extension of plastic work or difficult the plastic deformation with higher w_e values and a raise in the stress needed to produce plastic deformation. In any case, the EWF method and its partition energy approach allow to determine parameters that can be used to tune the amount of TPU to be used and predict the different fracture behavior of the films.

There is also another observation that is worth to comment with respect to the energy partition analysis. By looking at the differences between w_e and $w_{e,y}$ and $\beta \cdot w_p$ and $\beta \cdot w_{p,y}$, it can be argued that most of the fracture energy spent in 15-TPU films is produced during initiation of the crack (similar values of initiation and overall fracture parameters), whereas the TPU content increases, more energy is dissipated during the crack growth and hence initiation values differ more from the overall fracture ones.

4. Conclusions

As the PHBV-TPU films show ductile behavior, EWF approach is the only one that can be used to assess fracture parameters. It has been shown that increasing TPU content decreases stiffness and yield strength, but allows higher plastic deformation in tensile tests. By using the partition energy approach of the EWF method, it has been shown and quantified the influence of the aforementioned phenomena on the initiation of the crack propagation of the films.

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