IMPACT BEHAVIOR OF PLA/PCL BIOBLENDS

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RESUMEN

Se ha evaluado el efecto de la adición de policaprolactona (PCL) sobre el comportamiento a impacto del ácido poliláctico (PLA). Las bio-mezclas (con y sin compatibilizante) fueron preparadas en una planta piloto (extrusión doble-husillo, 5 kg/h) en diferentes proporciones. Los ensayos fueron realizados mediante impacto por caída de dardo instrumentado a temperatura ambiente sobre placas obtenidas por moldeo por compresión (100x100x1 mm^3). Este método ha servido como técnica de control de calidad y ha permitido optimizar las condiciones de proceso a escala pre-industrial así como la proporción de los diferentes componentes de la mezcla. Los resultados ponen de manifiesto que la eficiencia del compatibilizante no solo viene dictada por su proporción en la mezcla sino también por la homogeneidad y uniformidad de la morfología de mezcla obtenida.

PALABRAS CLAVE: Bio-mezclas, PLA, PCL, Impacto instrumentado, Morfología

ABSTRACT

The effect of adding polycaprolactone (PCL) on the impact behavior of poly(lactic acid) (PLA) has been evaluated. Bioblends (with and without compatibilizer) were prepared in a pilot plant (twin screw extrusion, 5kg/h) in different compositions. Impact testing was carried out using instrumented falling weight impacts at room temperature on plates obtained by compression moulding (100x100x1 mm^3). This method has served as a quality control technique and has allowed optimizing the processing conditions at a pre-industrial scale, as well as the composition of the different blends. The results revealed that the compatibilizer efficiency is not only governed by its weight fraction in the blend but also by the homogeneity and uniformity of the obtained blend morphology.

KEYWORDS: Bioblends, PLA, PCL, Instrumented impact, Morphology

1. INTRODUCTION

Regarding bio-based polymeric materials, poly(lactic acid) (PLA) has been viewed as a promising material to replace conventional polymers. Nevertheless, the use of PLA in some specific applications is still complicated, mainly due to its brittleness due to its high physical aging rate at room temperature [1]. Consequently, in the last decade a particular interest has been observed in many laboratories around the world both in academia and industry in order to solve these limitations. Among the ways used to solve those limitations is of particular interest the blending with other thermoplastics for developing bio-based formulations with tailored performances. This is a relatively quick and inexpensive way to adapt the properties which could play a crucial role in increasing the competitiveness of PLA [2].

Blends based on PLA using poly(ε-caprolactone) (PCL) as minority phase are of great interest because of their wide variety of physical properties and bio-based nature. In these blends, at room temperature the glassy PLA shows excellent tensile strength, while the rubbery PCL would bring toughness to the blend [3]. However, due to the lack of miscibility between PLA and PCL, a phase separated morphology is generated with low interfacial adhesion which tends to degrade their mechanical properties [4].

Therefore, the addition of a compatibilizer is required to ensure the transmission of tensions between the phases when the system is subjected to a mechanical loading. For these blends, different strategies of compatibilization can be identified: reactive and non-reactive. In the case of non-reactive methods copolymers such as block copolymers are added to the blend. In contrast, in the reactive compatibilization the block copolymers form in situ during blending thanks to the addition of a polymer with reactive groups or an additional reagent. In both cases, one type of constitutive blocks of the copolymer is miscible with one blend component while the other block of the copolymer is miscible with the second component [5].

This work summarizes the results within a collaboration between the company Ercros S.A. and the technological center Centre Català del Plàstic (CCP). Ercros, producer of PLA compounds, set as the main objective to develop a bioblend (i.e. biodegradable) based on PLA with impact behavior similar to the one of polypropylene (PP). This communication presents the stages of the work from blend conception until formulation optimization.

With that aim in mind, bioblends with different compositions of PLA, PCL and a compatibilizer C were prepared. To find an optimal composition, instrumented falling weight impact tests were performed using the flexed plate test configuration. This configuration allows a multi-axial loading at high rate which is more representative of the real end-use conditions [6].

2. EXPERIMENTAL PROCEDURE AND MATERIALS

2.1. Materials

The base materials used in this study were PLA (PLA ErcrosBio® LL712, Ercros S.A., Barcelona, Spain) as matrix of the blend and PCL (PCL CAPA® 6500, Ingevity, North Charleston, SC, USA) as a second phase. In addition, a suitable compatibilizer of both phases was used. Due to a confidentiality agreement between Ercros S.A. and the Centre Català del Plàstic no more details about materials can be provided.

2.2. Processing

Prior to processing, all materials were dried at 80 °C for 4h using a dehumidifier hopper (DSN506HE, Piovan S.p.A., Santa Maria di Sala, Italy) with a dew point of -40 °C. Processing was performed in three consecutive steps: (1) compatibilizer masterbatch preparation, (2) bioblend production, and (3) sample manufacturing (square plates).

The masterbatch was produced by compounding PLA and the compatibilizer at 20% w/w in a single-screw extruder with a screw diameter of 30 mm and L/D ratio of 25 (IQAP-LAP E30-25D, IQAP Masterbatch Group S. L., Les Masies de Roda, Spain). The screw speed and the barrel temperature profile were 60 rpm and 140-145-150-150 °C, respectively. Once the masterbatch was obtained, it was recrystallized for 1.5h at 90 ºC.

Bioblend pellets of PLA/PCL with and without compatibilizer (i.e. masterbatch) were prepared by melt mixing in a co-rotating twin-screw extruder with a screw diameter of 25 mm and L/D ratio of 36 (Collin Kneter 25x24D, Collin Lab & Pilot Solutions GmbH, Maitenbeth, Germany). The screw speed and the barrel temperature profile were 40 rpm and 50-160-165-170-175-180-180 °C, respectively. The composition and codification of the prepared bioblends are indicated in Table 1, respecting the confidentiality agreement between Ercros and CCP.

From the bioblend pellets previously obtained, square plates of 100 x 100 x 1 mm^3 were manufactured by compression moulding in a hot plate press (IQAP LAP PL-15, IQAP Masterbatch Group S. L., Les Masies de Roda, Spain) using a moulding pressure and temperature of 4 MPa and 180 °C, respectively. The processing time was 3 minutes. After moulding the plates were cooled to room temperature at a cooling rate of around -50 ºC in the cold stage of the press.

Table 1. Prepared materials and codification

Reference material	Composition	Thickness (mm)
PLA	100% PLA	1.08 ± 0.14
PP	100% PP	1.23 ± 0.04
3PCL-0C	PLA + 3x% PCL	1.04 ± 0.01
3PCL-3C	PLA + 3x% PCL + 3y% C	0.96 ± 0.02
2PCL-2C	PLA + 2x% PCL + 2y% C	0.93 ± 0.02
1PCL-1C	PLA + 1x% PCL + 1y% C	0.96 ± 0.02
3PCL-1C	PLA + 3x% PCL + 1y% C	0.98 ± 0.01
2PCL-1C	PLA + 2x% PCL + 1y% C	0.95 ± 0.04

2.3. Instrumented falling weight impact tests

Impact tests were carried out on fully clamped square plates employing an instrumented vertical drop weight testing machine (CEAST Dartvis, Instron, Norwood, MA, USA) at room temperature (23°C). A hemispherical striker of 3.243 kg with 12.7 mm in diameter was dropped from a fixed height (500 mm), preserving the quasistatic conditions required for the validity of parameter estimations, i. e. the impactor velocity at the end of the event (v_f) is not less than 90% of the initial one (v_0). Under these conditions, the curves of reaction force (F) vs. striker-test specimen contact time (t) were recorded [7].

The characteristic parameters of maximum registered force, or peak force, (F_p), energy consumed until this point (E_p), and total energy at the end of the impact event, (E_t), were determined. The energetic parameters were calculated applying the quasistatic model for this kind of loading. According to this model, as the striker mass (m), the striker velocity at the initiation of contact (v_o) and the registered $F(t)$ in every instant "i" of the contact striker-test sample are known, the displacement (x) of the striker (which is assumed is the same as the sample), can be determined according the following expressions [8]:

$$F = ma = m\frac{dv}{dt} \quad (1)$$

$$Fdt = mdv \quad (2)$$

then,

$$v = v_o - \frac{1}{m}\int Fdt \quad (3)$$

$$v = \frac{dx}{dt} \quad (4)$$

$$x = \int vdt = v_o t - \frac{1}{m}\iint Fdt^2 \quad (5)$$

The energy consumed as a function of time (*E(t)*) can be calculated if the kinetic energy of the striker is known at the contact initiation (E_0) and the kinetic energy at every instant "i":

$$E = \frac{1}{2}m{v_0}^2 - \frac{1}{2}mv^2 = v_0\int Fdt - \frac{1}{2m}\left[\int Fdt\right]^2 \quad (6)$$

Prior to testing, plates were stored during a week at room temperature in order to reach the thermodynamic equilibrium state of end use (physical aging). For each material studied, a total number of 5 samples were tested.

3. RESULTS AND DISCUSSION

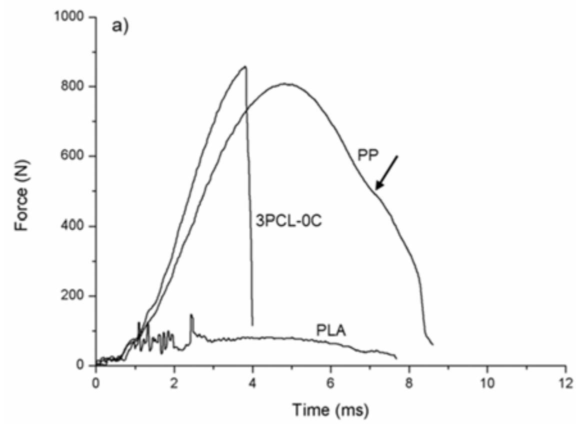
3.1. Effect of PCL addition on PLA

Figure 1a shows 3 typical *F(t) vs. t* traces obtained during the impact tests for PLA, PP, and 3PCL-0C respectively, while in Table 2 the characteristic numerical parameters obtained are shown.

For PP a characteristic ductile behavior is observed. First, the force increased until a unique maximum where it began to decrease in a continuous way until a clear change in the decrease is observed. Inspection of the broken sample (Figure 1b) let infer the deformation events: At the maximum force registered (F_P) the striker began to plastically deform the surrounding ductile material, forming a cup into the square plate. As the striker advanced, this region began to neck until the tear and rupture of the sample occurred. This point was reached at about 7 ms (arrow in Figure 1a).

In the case of PLA, the *F(t) vs. t* trace highlights a brittle behavior with multiple peaks related to unstable crack propagation. Here, the initial crack could be generated at the region where unstability of the *F(t) vs. t* traces was observed and showed an unstable propagation at about 1 ms. The photograph in Figure 1b shows four cracks at about 90° departing from the center of the specimen where it was struck by the hemispherical tip. As can be seen in Table 2, the mean value of F_P for the PLA was approximately 85 N, much lower than that for PP. Mean E_p and E_t values are not reported because they could not be determined with sufficient precision due to the high instability and variability in the trace.

The addition of PCL to PLA caused an almost ten-fold increase of the maximum registered force. However, after the maximum force was reached an abrupt fall in load-carrying capacity was observed, indicating that an uncontrolled crack was propagating. As observed in Figure 1b, the bioblend accomplished a certain degree of plastic deformation but still retained its inherently brittle nature that led to breakage without significant tearing. The energy at the peak force values were close to those of PP, considering the dispersion of the mean.



b)

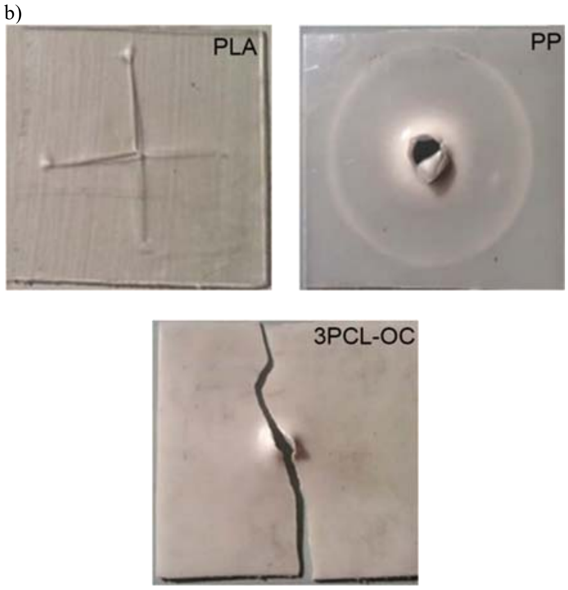


Figure 1. a) Representative force versus time curves recorded by instrumented falling weight impact tests for PLA, PP, and 3PCL-0C; b) Representative photographs of specimens after impact tests: PLA, PP, 3PCL-0C.

Table 2. Characteristic mechanical parameters obtained

from the instrumented falling weight impact tests performed on the selected material shown in Figure 1.

Material	Peak Force (N)	Peak Energy (J)	Total Energy (J)
PLA	85.2 ± 14.0	–	–
PP	788.1 ± 27.1	5.5 ± 0.5	10.3 ± 0.9
3PCL-0C	838.1 ± 28.6	3.9 ± 0.4	3.9 ± 0.4

3.2. Effect of the compatibilizer

To improve the behavior of the 3PCL-0C bioblend, in a way that the occurrence of brittle fracture was diminished or even avoided, both PLA and PCL were compatibilized with different weight percentages of a product C whose details cannot be given.

Figure 2a shows a representative *F(t) vs. t* curve of 3PCL-3C bioblend and the mean characteristic parameter values obtained as well as a picture of the broken specimen (Figure 2b).

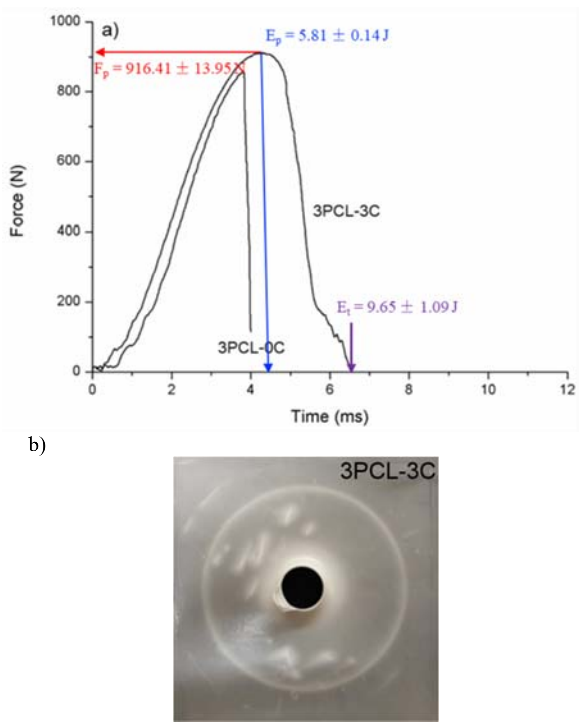


Figure 2. a) Representative force versus time curve recorded by instrumented falling weight impact tests for 3PCL-3C; b) Representative photograph of specimen after impact test.

For comparison purposes, the representative trace obtained for 3PCL-0C was also included in Figure 2a. It is apparent that the addition of the compatibilizer, in the relative proportion used, eliminated the brittle behavior as observed for 3PCL-0C. In this case, the broken surface showed the necked cup similar to what was observed for PP (see Figures 1b and 2b). When 3PCL-3C characteristic parameter values are compared to those obtained for PP (Table 2), it can be observed that both were quite similar.

3.3. Combined effect of PCL and compatibilizer content: Formulation optimization

It is of interest to optimize the cost of the blend. Increasing the PLA content in the bioblend would reduce the cost (since PLA is currently cheaper than PCL) and increase the bio-based content of the formulation, maintaining the biodegradability properties. For this reason, 2 additional bioblend compositions were prepared, changing the relative proportion between PLA and PCL and preserving the relative amount of compatibilizer with respect to PCL, the blends analyzed were those identified as: 1PCL-1C, 2PCL-2C and 3PCL-3C.

Figure 3a shows the representative impact *F(t) vs. t* traces obtained. In addition, representative photographs of broken test specimens for each material are included (Figure 3b). In Table 3 the mean values of the characteristic parameters obtained are shown. In the case of bioblend 1PCL-1C, some specimens failed in a brittle manner (Figure 3b), but others failed in a ductile way. This caused a wide dispersion of impact test results, as can be seen in Table 3. This fact would indicate that the relative amount of PCL added to PLA is not enough to stabilize the crack propagation at high loading rates. Perhaps the size of the PCL phase and its distribution act as a stress concentrator, preventing local triaxiality relief. Therefore, the formulation was discarded because it could not guarantee a regular and repetitive behavior.

Both 2PCL-2C and 3PCL-3C bioblends showed a quite similar fracture behavior, namely a necked cup formation without crack outside the cup zone (see Figure 3b).

In the case of 2PCL-2C, the *F(t) vs. t* traces revealed a greater extent of cup elongation until the crack initiated and propagated. This situation could indicate that with this proportion of PCL the minimum required condition about size and distribution of PCL phase was reached to act as an effective local triaxiality reliever. Yet, from an industrial point of view the 2PCL-2C formulation is more attractive.

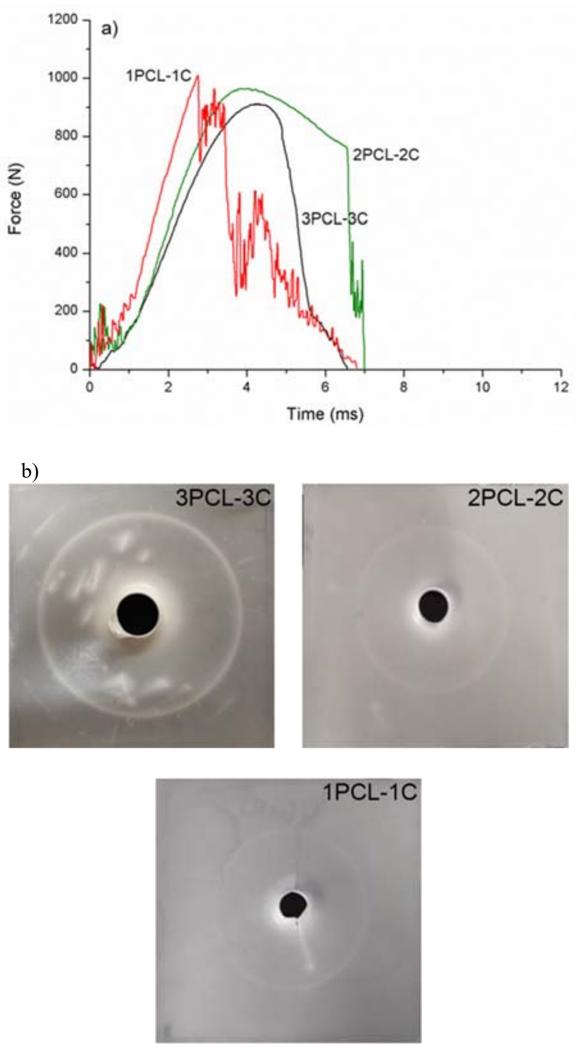


Figure 3. a) Representative force versus time curves recorded by instrumented falling weight impact tests for 3PCL-3C, 2PCL-2C, and 1PCL-1C; b) Representative photographs of specimens after impact tests: 3PCL-3C, 2PCL-2C, and 1PCL-1C.

Table 3. Characteristic mechanical parameters obtained from the instrumented falling weight impact tests performed on the selected material shown in Figure3.

Bioblend	Peak force (N)	Peak energy (J)	Total energy (J)
3PCL-3C	916.4 ± 14.0	5.8 ± 0.1	9.7 ± 1.1
2PCL-2C	1025.0 ± 63.3	6.0 ± 0.5	11.2 ± 0.7
1PCL-1C	1096.9 ± 86.3	5.9 ± 2.0	11.0 ± 3.1

In an attempt to optimize the content of compatibilizer, its relative amount with respect to the PCL phase was reduced. For this purpose, the 3PCL-1C and 2PCL-1C bioblends were prepared and compared to bioblends 3PCL-3C and 2PCL-2C. Figure 4a shows a representative *F(t) vs. t* trace for each new blend composition. In the same figure photographs of tested specimens are included (Figure 4b). Also, Table 4 shows the mean values of the characteristic parameters for each blend extracted from the *F(t) vs. t* traces.

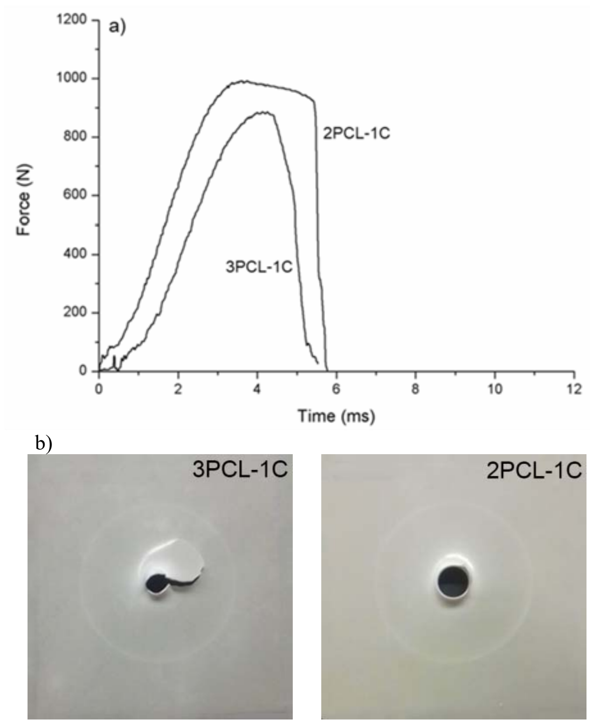


Figure 4. a) Representative force versus time curves recorded by instrumented falling weight impact tests for 3PCL-1C and 2PCL-1C; b) Representative photographs of specimens after impact tests: 3PCL-1C and 2PCL-1C.

Table 4. Characteristic mechanical parameters obtained from the instrumented falling weight impact tests performed on the selected material shown in Figure4.

Bioblend	Peak force (N)	Peak energy (J)	Total energy (J)
3PCL-1C	790.2 ± 100.0	3.6 ± 1.2	5.0 ± 1.7
2PCL-1C	965.4 ± 29.1	5.6 ± 0.3	10.9 ± 1.1

Both blends showed the typical ductile *F(t) vs t* trace with cup formation. However, 2PCL-1C presented a higher extension of cup deformation before rupture. Observing the broken region of the tested sample, it is clear that in the case of 3PCL-1C developed cracks that spread out of the cup region in all the square plates, while for 2PCL-1C the crack was located at the region of the hemispherical striker base (Figure 4b). The situation presented in 3PCL-1C indicates that the amount of compatibilizer added was not sufficient to homogenize the obtained phase morphology and/or to generate an effective anchor for the stress transfer between phases during mechanical loading at high rate. So, the bioblend with relative proportion of parent polymer identified with

3PCL was discarded.

Comparing the mean values of total energy absorbed (E_t) for 2PCL-2C (Table 3) and 2PCL-1C (Table 4) bioblends, it can be observed that for bioblend 2PCL-1C this value was close to the one obtained by 2PCL-2C, but with greater relative error (10% vs. 6%). The higher dispersion in the impact test results for 2PCL-1C could be attributed to the fact that this relative proportion of compatibilizer was not sufficient to ensure a good homogenization and/or local stress transfer between phases.

4. CONCLUSIONS

A PLA-based bioblend with impact behavior similar to the one of PP was obtained. The composition of this bioblend was optimized by instrumented falling weight impact tests, analyzing the impact behavior of different compositions of PLA, PCL and a compatibilizer C. Instrumented falling weight impact tests can be considered valid tests for applying quality control and a relatively quick assessment of the behavior of these materials. Flexible materials of series ErcrosBio® LM82000 and LM50005 commercialized by Ercros are based on the PLA-based bioblends with similar impact to PP developed in this work.

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REFERENCES

[1] J. Cailloux, O.O. Santana, E. Franco-Urquiza, J.J. Bou, F. Carrasco, M.Ll. Maspoch. Sheets of branched poly(lactic acid) obtained bu one-step reactive extrusion-calendering process: physical aging and fracture behavior. J Mater Sci (2014) 49: 4093-4107. https://doi.org/10.1007/s10853-014-8101-y.

[2] J. Cailloux, T. Abt, V. García-Masabet, O.O. Santana, M. Sánchez-Soto, F. Carrasco, M. Ll. Maspoch. Effect of the viscosity ratio on the PLA/PLA10.10 bioblends morphology and mechanical properties. Express Polym Lett (2018) 6: 569-582. https://doi.org/10.3144/expresspolymlett.2018.47.

[3] D. Wu, Y. Zhang, M. Zhang, W. Zhou. Phase behavior and its viscoelastic response of polylactide/poly(ε-caprolactone) blend. Eur Polym J (2018) 44: 2171-2183. https://doi.org/10.1016/j.eurpolymj.2008.04.023.

[4] M. Todo, T. Takayama. Fracture Mechanisms of Biodegradable PLA and PLA/PCL Blends. Biomaterials - Physics and Chemistry, R. Pignatello (Ed.), InTechOpen 2011, pp. 490. https://doi.org/10.5772/24199.

[5] B. Imre, B. Pukánsky. Compatibilization in bio-based and biodegradable polymer blends. Eur Polym J (2013) 49: 1215-1233. https://doi.org/10.1016/j.eurpolymj2013.01.019.

[6] M.M. Gauthier (Ed.). Engineered Materials Handbook Desk Edition. ASM International Handbook Committee, United States of America 1995, pp. 1317.

[7] A.B. Martínez, D. Arencón, J. Navas, J.L. Velasco. Low Energy Impact Indentation of a Modified Polyethylene Terephthalate by Instrumented Falling Weight. J Appl Polym Sci (2012) 127: 2983-2989. https://doi.org/10.1002/app.37969.

[8] A.B. Martínez (Ed.). Técnicas de impacto de materiales plásticos y compuestos. Universitat Politècnica de Catalunya (UPC), Barcelona 1988, pp. 111.