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Ferri Azor, JM.; Fenollar Gimeno, OÁ.; Jorda-Vilaplana, A.; García Sanoguera, D.; Balart Gimeno, RA. (2016). Effect of miscibility on mechanical and thermal properties of poly(lactic acid)/polycaprolactone blends. *Polymer International*. 65(4):453-463. doi:10.1002/pi.5079.



The final publication is available at

<http://dx.doi.org/10.1002/pi.5079>

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Additional Information

This is the accepted version of the following article: Ferri, J. M.; Fenollar, O.; Jorda-Vilaplana, A.; Garcia-Sanoguera, D.; Balart, R. (2016). "Effect of miscibility on mechanical and thermal properties of poly(lactic acid)/polycaprolactone blends". *Polymer International*. 65(4):453-463. doi:10.1002/pi.5079., which has been published in final form at <http://dx.doi.org/10.1002/pi.5079> .

**“Effect of miscibility on mechanical and thermal properties of poly(lactic acid)-
poly(caprolactone) blends”**

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Abstract

In this work, binary blends based on poly(lactic acid)-PLA and poly(caprolactone)-PCL were prepared by melt mixing in a twin screw co-rotating extruder in order to increase the low intrinsic elongation at break of PLA for packaging applications. Although PLA and PCL show low miscibility, presence of PCL leads to a remarkable increase in ductile properties of PLA. Different mechanical properties were evaluated in terms of PCL content up to 30 weight % PCL. Additionally to tensile and flexural properties, the Poisson's ratio was obtained by using bi-axial extensometry to evaluate transversal deformations when axial loads are applied. Very slight changes in the melt temperature (T_m) and glass transition temperature (T_g) of PLA were observed thus indicating low miscibility of the PLA-PCL system. Field emission scanning electron microscopy (FESEM) revealed some interactions between the two components of the blend since the morphology is characterized by non-spherical poly(caprolactone) drops dispersed into the PLA matrix. In addition to the improvement of mechanical ductile properties, PCL provides higher degradation rates of blends under conditions of composting for contents below 22.5% PCL.

Keywords: Poly(lactic acid)-PLA; poly(caprolactone)-PCL; binary blends; FESEM; mechanical properties; disintegrability.

1.- Introduction.

Nowadays, polymers find a broad number of applications in the fields of packaging, medical and automotive industries due to an excellent balance between processing and overall properties [1]. Among all these polymers, aliphatic polyesters from both renewable and/or fossil fuel resources [2] such as poly(lactic acid)-PLA, poly(caprolactone)-PCL, polyesteramide-PEA, poly(hydroxybutyrate)-PHB, thermoplastic starch-TPS, etc. and their copolymers such as poly(lactic acid)-*co*-poly(ϵ -caprolactone)-PLACL, poly(hydroxybutyrate-*co*-hydroxyvalerate)-PHBV, etc. are increasingly used in the medical[3] and packaging field due to their easy processing[1] and quick degradability in the different environments [4-6]. Some of their uses include films, bottles, homewares, packages, etc. Most of these polymers offer attracting degradation rates in controlled environments, thus avoiding permanent environmental impact. On the other hand, their thermoplastic nature enables easy processing by conventional processes such as melt spinning [7, 8], injection moulding [9], extrusion [1], etc. or other advanced manufacturing processes such as electrospinning [10-12], 3D printing [13-15], etc.

Poly(lactic acid) is one of the most used biocompostable polymers in packaging applications due to its high mechanical performance and balanced barrier properties[16, 17]. PLA is widely used in the manufacturing of biodegradable/biocompostable films for food applications. The main drawback related to PLA is its high intrinsic fragility that is still accentuated as degradation occurs. PLA has low ductility at room temperature because its glass transition temperature (T_g) is located at around 60 °C; so that, below its T_g , it behaves as a glass characterized by high mechanical resistance and modulus and high fragility together with low elongation at break (due to restricted polymer chain mobility below T_g). Conventional plasticizers could potentially be used to allow some elongation at break but typical plasticizers can migrate and this could be responsible for a toxicity as well as a decrease in mechanical properties [18-20]. Another alternative is copolymerization. By using copolymerization processes with appropriately selected monomers it is possible to tailor PLA properties to desired performance. Some examples of PLA-based copolymers are poly(lactic acid-*co*- ϵ -caprolactone)-PLACL, poly(lactic acid-*co*-ethylene glycol)-PLAEG, poly(hydroxibutirate-*co*-

hydroxivalerate)-PHBV, etc [21, 22]. Nevertheless these copolymers are expensive. One attracting solution is manufacturing of binary or ternary PLA-based blends. The use of a flexible polymer can lead to improved ductile properties with similar effects to a plasticizer.

Polymeric plasticizers thus providing improved elongation on PLA. Additionally, by controlling the blend composition it is possible to tailor the desired properties such as toughness, ductility, elongation at break, mechanical strength, etc.

Poly(ϵ -caprolactone)-PCL is partially compatible with PLA as they are aliphatic polyesters. PCL is characterized by a very low glass transition temperature, T_g of about $-60\text{ }^\circ\text{C}$ [23] and this makes it very flexible at room temperature. On the other hand, it melts at relatively low temperatures close to $60\text{ }^\circ\text{C}$, remarkably lower than the melt temperature of PLA located at about $170\text{ }^\circ\text{C}$, so that it can provide similar features than polymeric plasticizers when processed in conjunction with PLA. PCL can provide flexibility and elongation ability depending on the total PCL content. Although PLA and PCL are compatible, some research studies have demonstrated that there is very low interactions between them when melt blended [23, 24]. Broz *et al.* observed that the higher interactions are detected for percentages higher than 50% PCL. Also they do comparative studies with the mathematical model Kerner-Uemura-Takayangi to compare their results [25]. Jen-Taut Yeh *et al.* demonstrated by dynamic mechanical thermal analysis (DMTA) studies that increased interactions or miscibility occur for a mixing ratio of PLA70-PCL30 [23]. Lopez-Rodriguez *et al.* also observed by DMTA studies that there is a weak interaction between these two polymers [26]. The poor interactions are demonstrated because DSC and DMTA studies of PLA/PCL blends showed two T_g at positions close to the raw components revealing a clear phase separation.

The aim of this study is to evaluate the influence of poly(caprolactone)-PCL as minor component in poly(lactic acid)-PLA/poly(caprolactone)-PCL blends. The effect of PCL content in the 0 – 30 wt.% ratio is evaluated in terms of mechanical (tensile, flexural, impact, hardness tests) and thermal properties by differential scanning calorimetry (DSC), thermogravymetric analysis (TGA) and dynamical mechanical thermal analysis (DMTA) in torsion mode.

Qualitative assessment of miscibility/interactions is carried out by characterizing surface morphology of PLA/PCL blends with field emission scanning electron microscopy (FESEM).

2.- Experimental.

2.1.- Materials.

Poly(lactic acid)-PLA from renewable resources Ingeo™ Biopolymer 6201D supplied by NatureWorks LLC (Minnetonka, USA) was used as base polymer. This polymer is characterized by a 2 % D-lactic acid with overall density of 1.24 g cm^{-3} and a melt flow index of 15-30 g/10 min at a temperature of 210 °C. A commercial grade of poly(caprolactone)-PCL, Capa™ 6500 supplied by Perstorp (Warrington, UK) was used to provide ductile properties to PLA. This PCL grade is characterized by a melt flow index of 7.90-5.60 g/10 min at 160 °C, a density of 1.1 g cm^{-3} and a molecular weight of $50,000 \text{ g mol}^{-1}$. Its melt point is located in the 58-60 °C range and it offers a high elongation at break of more than 800%.

2.2.- PLA/PCL blend manufacturing.

Four different PLA/PCL blend compositions were defined, being PLA the major component. Table 1 shows a summary of the compositions and labelling of each PLA/PCL blend. PLA and PCL pellets were previously dried in an oven at 60 °C and 40 °C respectively, for 24 h before melt blending. Appropriate amounts of PLA and PCL were manually mixed in pellet form in a zip bag and after this, mixtures were melt compounded in a twin screw co-rotating extruder at a rotating speed of 60 rpm. The temperature profile was 25°C, 175 °C, 177.5 °C and 180 °C from the hopper to the die. After cooling, the material was pelletized and subsequently injection moulded in a Mateu & Solé mod. Meteor 270/75 (Barcelona, Spain) at a temperature of 180 °C.

Table 1.- Summary of the compositions of PLA/PCL blends and labelling.

Reference	PLA wt. %	PCL wt. %
PLA	100	-
PLA /7.5PCL	92.5	7.5
PLA /15PCL	85	15
PLA /22.5PCL	77.5	22.5
PLA /30PCL	70	30

2.3.- Mechanical characterization of PLA/PCL blends.

Mechanical properties of PLA/PCL blends were measured with tensile, flexural, impact and hardness tests **at time zero and after 8 months. Samples are not stored under special conditions.** Tensile and flexural properties were obtained using a universal test machine from S.A.E. Ibertest mod. ELIB 30 (Madrid, Spain) at room temperature by following the guidelines of the ISO 527-5 and ISO 178 respectively with a load cell of 5 kN and a crosshead speed of 10 mm min⁻¹. At least five different samples were tested in tensile and flexural tests and average values of the relevant parameters were calculated. In addition, elastic modulus and Poisson's ratio were accurately determined by using bi-axial (longitudinal and transversal) extensometers from S.A.E. Ibertest mod. IB/MFQ-R2 (Madrid, Spain) coupled to the universal test machine.

Hardness of PLA/PCL blends were obtained in a Shore D durometer from Instrumentos J. Bot S.A., mod. 673-D (Barcelona, Spain) as recommended in UNE-EN-ISO 868.

Impact absorbed energy values were measured on unnotched samples in a Charpy pendulum (5 J) from Metrotec S.A. (San Sebastián, Spain) as indicated in the ISO 179:1993 standard. The impact test was carried out on five different samples and average values of the impact-absorbed energy were calculated.

2.4.- Characterization of surface morphology of PLA/PCL blends.

All PLA/PCL composites were subjected to a cryofracture process with liquid N₂ and samples were observed in a field emission scanning electron microscope (FESEM) ZEISS

ULTRA55 from Oxford Instruments (Oxford, UK) at an acceleration voltage of 2 kV. Samples for FESEM observation were subjected to a sputtering process with platinum to obtain detailed information of the blend morphology. Cryofractured PLA/PCL samples were also subjected to selective extraction with acetone to selectively remove PCL from surface thus leading to detailed observation of the blends morphology. The samples were immersed in acetone for 12 hours. Then placed in an oven at 40 °C for 1 hour to evaporate the solvent.

2.5.- Dynamic mechanical thermal analysis of PLA/PCL blends.

Dynamic mechanical thermal analysis (DMTA) was carried out in torsion-shear mode in an oscillatory rheometer (OR) from TA Instruments, mod. AR G2 (New Castle, USA) equipped with a torsion clamp accessory for solid samples. Rectangular samples sizing 40x10x4 mm³ were subjected to a temperature ramp from -80 °C up to 130 °C at a constant heating rate of 2 °C min⁻¹. A frequency of 1 Hz was used for all tests and the maximum deformation (γ) was set at 0.1%.

2.6.- Thermal characterization of PLA/PCL blends.

Thermal properties of PLA/PCL blends were studied by differential scanning calorimetry (DSC) and thermogravymetric analysis (TGA). Thermogravymetric analysis was conducted on a TGA/SDTA 851 thermobalance from Mettler-Toledo Inc. (Schwerzenbach, Switzerland) with a temperature program from 30 °C to 700 °C at a heating rate of 20 °C min⁻¹ and nitrogen gas atmosphere (66 mL min⁻¹). The main thermal transitions were obtained with a differential scanning calorimeter (DSC) 821 from Mettler-Toledo Inc. (Schwerzenbach, Switzerland) in air atmosphere. The heating program for DSC runs was from 30 °C to 350 °C at a heating rate of 10 °C min⁻¹. The percentage crystallinity of PLA was calculated by means of the following equation:

$$X_c (\%) = \frac{\Delta H_m - \Delta H_c}{w \Delta H_m^0} 100 \quad (1)$$

where ΔH_m and ΔH_c are the experimental melting enthalpy and cold crystallization enthalpy of PLA, respectively, and w is the weight fraction of PLA. A value of $\Delta H_m^0 = 93 \text{ J g}^{-1}$ was used according to a reported enthalpy of melting of 100% crystalline PLA [23]. The percentage crystallinity value of PCL was 46.4%. Neat PCL had no cold crystallization peak and a value of $\Delta H_m^0 = 139 \text{ J g}^{-1}$ was used according to a reported melt enthalpy of 100% crystalline PCL [26].

2.7.- Disintegrability under composting conditions.

The disintegration of PLA and PLA-PCL blends under composting conditions was investigated attending to the ISO 20200 standard. The composition of the solid synthetic waste was prepared by mixing 40% sawdust, 30% rabbit food, 10% of mature compost supplied by BCM-BRICOLAGE, S.A., 10% starch, 5% sugar, 4% corn oil and 1% urea. The water content was set to 55 wt.% and the aerobic conditions were guaranteed by appropriate and vigorous mixing. Sheets sizing $25 \times 25 \text{ mm}^2$ were initially weighed and buried at 4 - 6 cm depth inside perforated PS boxes containing the prepared mix. The incubation temperature was maintained constant at 58 °C. Each sample was extracted from the boxes at regular periods of 3, 7, 14, 21, 28, 35 and 42 days of disintegration; extracted samples were cleaned softly with distilled water, dried in an oven at 37 °C during 24h and finally, reweighed. The disintegration degree was calculated by referring the sample weight at different days of incubation to the initial weight. The equation to calculate the disintegration in percentage is shown below:

$$D (\%) = \frac{m_i - m_f}{m_i} 100 \quad (2)$$

where m_i is the initial weight of the sample and m_f is the weight of the same sample after the corresponding incubation period.

3.- Results and discussion.

3.1.- Effect of PCL on mechanical properties of PLA/PCL binary blends.

One of the main drawbacks related to PLA is its low intrinsic ductility with low elongation at break values; this is an important issue to be taken into account for uses in packaging applications. Fig. 1 shows the evolution of the tensile properties of PLA/PCL blends in terms of the PCL content. As expected, PCL provides improved ductile properties (with similar effect to plasticizers) that leads to lower tensile strength. The tensile strength of unblended PLA is close to 64 MPa and the only addition of 7.5 wt.% PCL leads to values of 56.8 MPa (a percentage decrease of 12.7%). As the PCL content increases, tensile strength values decrease up to values of 45.8 MPa for a PLA/PCL blend with 30 wt.% PCL, that represents a percentage decrease of about 28.4%. It is evident the plasticization effect that PCL provides to PLA. Similar tendency is observed with regard to the tensile modulus. With regard to elongation at break, it is clearly detectable an improvement. PLA is a quite brittle polymer with a low elongation at break of 8.6%. Addition of 7.5 wt.% of PCL leads to elongation at break values of 19.1% which represents a percentage increase of 122%. Higher PCL contents lead to elongation at break values higher than 70% for compositions containing 22.5 wt.% PCL which represents a percentage increase of more than 715% with regard to individual PLA. For higher percentages over 22.5 wt.% PCL, elongation decreases. When polymers are immiscible, the growth of the minority polymer domains increases (in this case the PCL rich phase), the continuous phase (in this case the PLA rich matrix) shows a clear phase separation. This phase separation is responsible for the interrupt of the blend elongation as observed by other authors [27]. As we have previously described, PLA is a stiff polymer with a tensile modulus of about 3594 MPa. Tensile modulus is defined as the ratio between the strength and the strain values in the linear region. As we have seen, tensile strength decreases with the PCL content but the decrease in elongation at break is remarkably higher and this leads to lower stress/strain ratios, which leads to lower tensile modulus as observed in Fig. 1. The tensile modulus of individual PLA is reduced up to values lower than 3000 MPa for PLA/PCL blends with a PCL content of 22.5 wt.% and higher.

Figure 1

The evolution of the flexural properties is similar to tensile properties (Fig. 2). As the PCL content increases both the flexural modulus and flexural strength decreases due to the plasticization effect provided by PCL. The flexural strength of unblended PLA is 116.3 MPa and we observe a decreasing tendency with values of 91.3 MPa and 86.7 MPa for PLA/PCL blends with 22.5 wt.% and 30 wt.% respectively (21.5% and 25.45% lower values respectively). With regard to the flexural modulus, it represents the ratio between the flexural stress and flexural deformation. In a similar way to tensile modulus, the decrease in flexural stress is lower than the deflection due to increased deformation provided by PCL and this leads to lower flexural modulus. So that, the PLA flexural modulus of 3273 MPa is reduced up to 2701 MPa for PLA/PCL blends with 30 wt.% PCL.

Figure 2

The ability for energy absorption is also reduced with the PCL content (see Table 2). The absorbed energy is directly related to deformation and mechanical resistance. As we have described previously, both the tensile and flexural strength are reduced (mechanical resistant properties) while the elongation at break (deformation property) increases in a great extent. This changes lead to lower impact absorbed energy values as observed in Table 2. Unblended PLA offers an absorbed energy value of 30.9 J m^{-2} due to the combination of high mechanical resistance and very low deformation; as the PCL content in PLA/PCL blends increases, we observe a decrease in the absorbed energy values due to the plasticization effect of PCL which contributes to higher deformation but lower mechanical resistance properties. The maximum decrease in the absorbed energy value is detected for PLA/PCL blends containing 30 wt.% PCL with a value of 23.1 J m^{-2} which represents a percentage decrease of almost 25%. With regard to the hardness (Shore D), the evolution is identical to that observed for other mechanical resistant properties such as strength and modulus. We observe a decreasing tendency in Shore D

hardness values as the PCL content increases. As we have described previously the Poisson's ratio is an important parameter from a design point of view and it is a key parameter for dimensioning plastic parts with potential application in the packaging industry. For this reason, the influence of PCL content on the Poisson's ratio, ν has been evaluated. Table 2 shows Poisson's ratios with varying PCL content in PLA/PCL blends. Individual PLA shows a Poisson ratio of 0.43 [28] [29] and this value does not change in a remarkable way with varying PCL content. This could be related to the high PLA content on PLA/PCL blends which maintains transversal deformations in the same range as for unblended PLA.

Table 2.- Summary of some mechanical properties: impact absorbed energy, hardness and Poisson ratios of PLA/PCL blends in terms of the PCL weight %.

Property	PCL content (wt.%)				
	0	7.5	15	22.5	30
Charpy impact energy (J m ⁻²)	30.9 ± 0.8	28.3 ± 1.8	26.6 ± 0.6	24.9 ± 0.4	23.1 ± 0.4
Hardness (Shore D)	73.9 ± 0.8	71.1 ± 1.0	69.1 ± 0.6	68.2 ± 1.1	66.3 ± 1.2
Poisson ratio, ν	0.43	0.42	0.43	0.42	0.43

Fig. 3 shows FESEM images of fractured surfaces from impact tests corresponding to PLA/PCL blends with different PCL content. Fracture surface of unblended PLA (Fig. 3a) is smooth as typical fragile polymers due to very low deformation as indicated by the very low elongation at break values. As the PCL content increases, we observe rougher surfaces with some voids, flakes structure and some filaments giving some evidences of plastic deformation provided by PCL. These filament structures are related to the plastic deformation of PCL immersed in the PLA matrix. The morphological structure can be identified and phase separation due to immiscibility between PLA and PCL is clearly detectable.

Figure 3

On the other hand, Table 3 shows the potential change in mechanical properties after 8 months from the injection moulding to see how they have changed over time. The obtained results show that the tensile and flexural tests, impact absorbed energy and hardness of virgin PLA and PLA/PCL formulations only varies less than $\pm 5\%$. It means that values are into typical error and do not show an important variation. Only the elongation at break shows an important reduction being up to 25% lower for PLA/PCL blends with 22.5 wt.% PCL.

Table 3. Summary of tensile and flexural tests, impact absorbed energy and hardness of PLA/PCL blends in terms of the PCL weight %, aged at room temperature for 8 months.

Property	Samples (8 months)				
	PLA	PLA/7.5PCL	PLA/15PCL	PLA/22.5PCL	PLA/30PCL
Tensile strength (MPa)	61.4 \pm 1.4	55.4 \pm 0.4	51.8 \pm 0.9	48.5 \pm 1.5	46.8 \pm 0.8
Tensile modulus (MPa)	3453 \pm 128	3555 \pm 21	3131 \pm 110	3113 \pm 34	2687 \pm 62
Flexural strength (MPa)	105.9 \pm 0.7	101.2 \pm 0.8	95.2 \pm 0.6	87.3 \pm 0.9	82.2 \pm 0.2
Flexural modulus (MPa)	3374 \pm 65	3185 \pm 68	2758 \pm 49	2798 \pm 67	2691 \pm 80
Elongation at break (%)	7.8 \pm 0.7	18.2 \pm 2.6	18.0 \pm 1.0	64.5 \pm 7.8	54.6 \pm 8.0
Charpy impact energy (J/m ²)	29.3 \pm 0.7	27.2 \pm 1.1	25.0 \pm 0.9	22.7 \pm 0.6	21.1 \pm 0.5
Hardness (Shore D)	74.7 \pm 0.7	72.1 \pm 1.1	70.5 \pm 0.8	68.9 \pm 0.9	67.3 \pm 1.0

3.2.- Effect of PCL content on thermal and thermomechanical properties of PLA/PCL blends.

Fig. 4 shows a comparative plot of the typical DSC curves of PLA/PCL blends with varying PCL content. Three different thermal transitions can be identified for individual PLA. The glass transition temperature, $T_{g\text{ PLA}}$ is located in the 55 – 65 °C range. The typical cold crystallization process of PLA is located in the 85 – 115 °C range with a peak ($T_{c\text{ PLA}}$) at about 100 °C. Finally, the melt process comprises a temperature range from 155 to 175 °C with a peak ($T_{m\text{ PLA}}$) at 168 °C. With regard to PCL the melt process is located between 45 – 65 °C with a

peak at 59 °C; the glass transition temperature for PCL ($T_{g\text{ PCL}}$) cannot be seen in these DSC runs because the temperature program starts from room temperature and the typical $T_{g\text{ PCL}}$ values are close to -60 °C. DSC curves of PLA/PCL blends are very interesting to assess the miscibility between these two components. As we can see, the DSC curves of PLA/PCL blends in the temperature range between 30 °C and 210 °C, show the same thermal transitions than individual polymers. Table 4 shows a summary of the main thermal parameters obtained from DSC curves. The melt temperature of PLA ($T_{m\text{ PLA}}$) does not change with the PCL addition with values around 168 °C. With regard to the melt peak of PCL ($T_{m\text{ PCL}}$), it is located at about 59 °C and it is overlapped with the glass transition temperature of PLA ($T_{g\text{ PLA}}$), that is located in the same temperature range. Nevertheless, the melt peak of PCL does not change with varying PCL and it remains at values of 59 °C as individual PCL. With regard to the crystallization peak of PLA ($T_{c\text{ PLA}}$), it does not change with the PCL content and remains at constant values at about 101 °C. The fact that all the thermal transitions of PLA and PCL in PLA/PCL blends appear at the same typical temperatures of the corresponding individual polymers is representative for lack (or very low) interactions between these two polymers which indicates no (or poor) miscibility [23-26]. Furthermore, the crystallization enthalpy of PLA decreases with increasing PCL content. Nevertheless, the degree of crystallinity (X_c) of PLA increases with a PCL content of 22.5%. Higher PCL content does not allow PLA spherulites growing. The excessive content of PCL can block or restrict molecular motions of PLA chains and interrupt the growth of PLA spherulites [23].

Figure 4

Table 4.- Summary of the thermal parameters of PLA/PCL blends with different PCL content obtained by differential scanning calorimetry (DSC).

PCL wt. %	PLA thermal properties					PCL thermal properties		
	Melt Temperature $T_{m\text{PLA}}$ (°C)	Crystallization Peak $T_{c\text{PLA}}$ (°C)	Crystallization enthalpy $\Delta H_{c\text{PLA}}$ (J g ⁻¹)	Melt enthalpy $\Delta H_{m\text{PLA}}$ (J g ⁻¹)	Degree crystallinity $X_{c\text{PLA}}$ (%)	Melt temperature $T_{m\text{PCL}}$ (°C)	Melt enthalpy $\Delta H_{m\text{PCL}}$ (J g ⁻¹)	Degree crystallinity $X_{c\text{PCL}}$ (%)
0	168.3	102.1	24.3	39.7	16.5	-	-	-
7.5	168.2	101.5	25.3	38.6	15.5	59.2	0.9	8.6
15.0	168.6	100.6	22.7	36.8	17.8	58.8	4.8	23.0
22.5	168.3	100.5	20.9	33.3	17.2	58.9	8.3	26.5
30.0	168.5	102.2	20.2	29.4	14.1	59.0	11.1	26.6

Fig. 5 shows a comparative plot of the thermogravymetric (TGA) degradation curves of individual PCL and PLA together with the TGA curves of PLA/PCL blends with different PCL content. Although the thermal performance of poly(caprolactone) is not high due to low melt and glass transition temperatures, PCL is characterized by extraordinary thermal stability at high temperatures[30], even more than other biodegradable polymers. In fact, PCL degrades at higher temperatures than those observed for PLA (Fig. 5). PCL addition to PLA blends give more stable materials. We can see that thermal degradation of PLA/PCL blends occur in two different stages: one is located in the temperature range comprised between 300 °C and 370 °C that is attributable to PLA degradation and a second degradation step with typical weight loss in the 370 °C – 440 °C temperature range which is attributable to the PCL degradation. This situation is also representative for poor or lack of polymer interactions thus leading to a blend of immiscible polymers as validated by differential scanning calorimetry.

Figure 5

DSC and TGA studies have revealed poor interactions between the two polymers as both components in PLA/PCL blends maintain their typical thermal transitions. With regard to the combined effect of mechanical loads and temperature, Table 5 shows the evolution of the Vicat softening temperature (VST) and heat deflection temperature (HDT) of PLA/PCL with varying PCL content. As PCL is remarkably more flexible than PLA, addition of PCL leads to a decrease in VST and HDT values due to the plasticization effect provided by PCL but in general terms, the variation in VST and HDT is not high.

Table 5.- Thermomechanical properties (Vicat softening temperature-VST and heat deflection temperature-HDT) of PLA/PCL blends in terms of the PCL weight %.

Property	PCL content (wt.%)				
	0	7.5	15	22.5	30

Vicat softening temperature, VST (°C)	52.8	52.4	51.4	51.2	51.0
Heat deflection temperature, HDT (°C)	47.6	46.4	45.4	44.4	44.2

Fig. 6 shows the plot evolution of the storage modulus (G') of PLA and PLA/PCL blends with varying PCL content. The plasticizing effect provided by PCL is proportional to the total PCL content and this can be observed in Fig. 6 by a displacement of the G' curve to lower temperatures. At a temperature of 37 °C, unblended PLA has a storage modulus G' of 1035 MPa. The only addition of 7.5 wt.% PCL gives a reduction in storage modulus up to values of 1010 MPa which represents a percentage decrease of about 2.4%. As the PCL content increases, we observe a decreasing tendency in the storage modulus values up to 835 MPa for PLA/PCL blends containing 30 wt.% PCL with a reduction of about 19.3%. A remarkable decrease in the storage modulus (three fold) occurs in the temperature range comprised between 60 °C and 75 °C that is attributable to the glass transition temperature of PLA ($T_{g \text{ PLA}}$). Finally, at a temperature range of 80 °C – 100 °C, the storage modulus increases again due to the cold crystallization process of PLA; the crystallization process leads to a more packed structure that improve mechanical elastic behavior. As we can see, PCL addition leads to lower crystallization temperatures[23].

Figure 6

3.3.- Morphology of PLA/PCL blends.

Fracture analysis by FESEM gives some evidences of the fracture type as described before but it does not give evidences of polymer phase separation due to immiscibility. For this reason, PLA/PCL blends were subjected to a cryofracture process and subsequent observation by field emission scanning electron microscopy (FESEM). As described previously, PLA and PCL are not miscible polymers; thermal analysis has given some evidences of this lack of miscibility. By observing FESEM images of cryofractured surfaces of PLA/PCL blends (Fig. 7). PCL appears in the form of circular shapes dispersed in a predominant PLA matrix. The

geometry of dispersed PCL is in the form of regular or irregular spheres but the cryofracture process gives circular cross section from these spheres so that, FESEM observation offers these circular shapes. We can also observe how the sphere size increases with increasing PCL content. For a 7.5 wt.% content on PLA/PCL blends, the particle size is lower than 0.5 μm (Fig. 7a & 7b). In addition we observe some evidences of the plasticization effect through some filament structures representative for plastic deformation. PLA/PCL blends with 15 wt.% PCL show similar structure with a predominant PLA matrix in which, PCL spherical shapes are immersed. For this composition, PCL spheres are characterized by a sphere size comprised in the 0.5 – 1.0 μm (Fig. 7c & 7d). This size is even larger for PLA/PCL blends containing 30 wt.% PCL with an average size of 1.5 – 2.0 μm (Fig. 7g & 7h). The phase separation between these two biodegradable polymers is evident for all the composition range in this study thus giving clear evidences of immiscibility (or very low miscibility). The plasticization effect can be observed in PLA/PCL blends with 22.5 wt.% PCL at 10000x (Fig. 7f) with a PCL sphere linked to the surrounding PLA matrix through different filament formations thus giving evidence of some low interactions between the two polymers. Cryofractured samples from PLA/PCL blends were also subjected to selective extraction with acetone. This solvent causes PCL extraction but also some swelling on PLA occurs (probably due to some PCL domains dissolved in the PLA matrix). This situation can be observed in Fig. 8. The selective extraction of PCL leads to a porous structure of PLA because the spherical PCL domains have been removed by the action of acetone. We also observe the same for cryofractured images in Fig. 7: the sphere diameter increases with increasing PCL content in PLA/PCL blends. FESEM gives a clear evidence of phase separation so that PCL and PLA are immiscible in a great extent but the plasticizing effect of PCL leads to attracting elongation at break values as described previously with regard to tensile properties.

Figure 7

Figure 8

3.4.- Disintegration under composting.

Fig. 9 shows the visual appearance of PLA, PLA/PCL blends before and after different times of disintegration in composting conditions; it is clearly evident the biodegradable character of all the formulations studied.

Figure 9

Before placing the samples in composting conditions, we observed that neat PLA is transparent and PLA/PCL blends have a whitish color. After 3 days of incubation PLA sample became opaque thus giving evidence of the hydrolysis process [6, 31, 32]. For an incubation period of 14 days, samples became brittle and acquired a light yellow hue. After this day, the degradation process was accelerated in a remarkable way. At an incubation period of 21 days, the neat PLA shows lower degradation than all PLA/PCL blends. It is clear that the higher PCL content percentage of PCL blend contains, the degradation is lower. This is due because the PCL degrades less than PLA[33]. The PCL acts as a nucleant agent for degradation process. In fact, the samples with minor percentage of PCL are more suitable to degradation than the higher percentage of PCL. For further degradation time, samples acquired a light brown hue and the pieces were increasingly smaller. For an incubation period of 42 days, PLA and PLA-PCL blends were totally disintegrated. PLA with 7.5 wt.% PCL is the blend composition with higher disintegration rate as detected by visual appearance.

Figure 10

Furthermore, the mass loss as a function of incubation time of neat PLA and PLA/PCL blends was evaluated (Fig. 10). It can be seen that from day 14 the mass loss increases significantly. At about an incubation period of 35 days almost a 50% of the initial mass is lost. After an

incubation period of 42 days, all samples are completely disintegrated. In Fig. 10 one can see that degradation is lower at higher PCL percentages. In fact, from 0 to 28 days mass loss is lower than neat PLA. The nucleating effect of the PCL in the PLA crystallization decreases the disintegrability rate of PLA-PCL samples due to an increase in the degree of crystallinity.

4.- Conclusions.

The results show that PCL provides attracting ductile properties to PLA with a remarkable increase in elongation at break values from 8% for unblended PLA up to values higher than 70% for PLA/PCL blends with 20-30 wt.% PCL. Although these two polymers seem to be highly immiscible, the increase in ductile properties is quite good without compromising mechanical resistant properties. Thermal analysis by differential scanning calorimetry (DSC) revealed high immiscibility of both polymers since the main thermal transitions for PLA and PCL in PLA/PCL blends are independent of the blend composition. FESEM analysis of cryofractured samples from PLA/PCL blends revealed a morphology with a clear phase separation; PCL appears in the form of variable size spheres dispersed in the predominant PLA matrix. The size of PCL phase domains changes from 0.5 μm for PLA/PCL blends with 7.5 wt.% PCL up to values of 1.5-2 μm for blends containing 30 wt.% PCL. With regard to mechanical properties, the plasticizing effect of PCL leads to lower tensile and flexural strength and modulus values. Overall, addition of PCL to PLA provides PLA with enough flexibility to be used in packaging uses such as those that require flexible materials to be adapted to different geometries (homewares) or to extrude films to conserve food products. Furthermore PLA-PCL blends under composting conditions have a mass loss higher than neat PLA. This is due to PCL as it acts as a nucleant agent to accelerate the disintegrability process for lower PCL content. Nevertheless, for contents over 22.5 wt.% PCL the mass loss is less than neat PLA.

Acknowledgements

This research was supported by the Ministry of Economy and Competitiveness - MINECO, Ref: MAT2014-59242-C2-1-R. Authors also thank to the "Conselleria d'Educació, Cultura i Esport" - Generalitat Valenciana, Ref: GV/2014/008 for financial support.

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Table captions

Table 1.- Summary of the compositions of PLA/PCL blends and labelling.

Table 2.- Summary of some mechanical properties: impact absorbed energy, hardness and Poisson ratios of PLA/PCL blends in terms of the PCL weight %.

Table 3. Summary of tensile and flexural tests, impact absorbed energy and hardness of PLA/PCL blends in terms of the PCL weight %, aged at room temperature for 8 months.

Table 4.- Summary of the thermal parameters of PLA/PCL blends with different PCL content obtained by differential scanning calorimetry (DSC).

Table 5.- Thermomechanical properties (Vicat softening temperature-VST and heat deflection temperature-HDT) of PLA/PCL blends in terms of the PCL weight %.

Figure legends

Figure 1.- Plot of the evolution of mechanical properties from tensile tests (tensile strength, elongation at break and tensile modulus) in terms of the PCL wt.%.

Figure 2.- Plot of the evolution of mechanical properties from flexural tests (flexural strength and flexural modulus) in terms of the PCL wt.%.

Figure 3.- FESEM images of fractured surfaces from impact tests of PLA/PCL blends with different weight % PCL at 5000x , a) 0 wt.%, b) 7.5 wt.%, c) 15.0 wt.%, d) 22.5 wt.% and e) 30.0 wt.%.

Figure 4.- Comparative plot of DSC curves of individual PLA and PCL and PLA/PCL blends with different weight % PCL showing the main thermal transitions.

Figure 5.- Comparative plot of thermogravymetric TGA curves of individual PLA and PCL and PLA/PCL blends with different PCL content.

Figure 6.- Plot comparison of the evolution of storage modulus, G' with temperature for PLA/PCL blends with different weight % PCL.

Figure 7.- FESEM images of cryofractured surfaces of PLA/PCL blends with different wt.% PCL and different magnifications, a) 7.5 wt.% PCL; 5000x, b) 7.5 wt.% PCL; 10000x, c) 15 wt.% PCL; 5000x, d) 15 wt.% PCL; 10000x, e) 22.5 wt.% PCL; 5000x, f) 22.5 wt.% PCL; 10000x, g) 30 wt.% PCL; 5000x and h) 30 wt.% PCL; 10000x.

Figure 8.- FESEM images of cryofractured surfaces of PLA/PCL blends with different wt.% PCL and different magnifications after selective extraction with acetone, a) 7.5 wt.% PCL; 5000x, b) 7.5 wt.% PCL; 10000x, c) 15 wt.% PCL; 5000x, d) 15 wt.% PCL; 10000x, e) 22.5 wt.% PCL; 5000x, f) 22.5 wt.% PCL; 10000x, g) 30 wt.% PCL; 5000x and h) 30 wt.% PCL; 10000x.

Figure 9.- Visual appearance of PLA and PLA/PCL samples before and after different incubation days under composting conditions.

Figure 10.- Disintegrability in percentage of neat PLA and PLA-PCL blends under composting conditions as a function of time.