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"Processing and characterization of binary polyhydroxybutyrate (PHB) and polycaprolactone (PCL) blends with improved impact properties"

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Abstract

The present work is focused on the development of binary blends from poly(hydroxybutyrate) (PHB) and poly(caprolactone) (PCL). Miscibility, mechanical and thermal properties as well as blends morphology are evaluated in terms of the blend composition. Binary PHB-PCL blends were manufactured by melt compounding in a twin screw co-rotating extruder and injection molded. Composition of PHB-PCL covered the full range between individual polymers at 25 wt% increments. The obtained results show that PCL acts as an impact modifier thus leading to an increase in flexibility and ductility as the PCL content on PHB-PCL blends increases with a noticeable increase in elongation at break and on the energy absorption in impact conditions. The tensile strength and the elastic modulus decrease with increasing PCL content on PHB-PCL blends; nevertheless, the flexural strength and the flexural modulus reach highest values for PHB-PCL blends containing 25 wt% PCL, with a remarkable decrease over this composition. Analysis of fractured surfaces by FESEM and thermal properties obtained by DSC and TGA give clear evidences of the immiscibility of these two biodegradable polymers. Additionally, DSC results showed an increase in crystallinity of both PHB and PCL with regard to individual polymers for PHB-PCL blends containing 25 wt% PCL. Furthermore, an increase in the degradation onset (T_0) of about 30 ºC higher was detected for same blends. DMTA showed slightly shifted glass transition temperatures of each individual polymer thus indicating that although both PHB and PCL are not fully miscible, some interactions between them occur.

Introduction

In the last decades, a remarkable increase in the use and consumption of polymeric materials has been detected; this increase has been particularly noticeable in the packaging industry. This fact has led to large waste generation around the world. An important fraction of these wastes are incinerated or poured into controlled landfills because of technical or economical reasons thus leading to important environmental problems such as waste removal

from environment, soil contamination or toxic gas emissions coming from incineration processes. This acts as leading force to the study, development and use of biobased and/or biodegradable polymers characterized by low environmental impact [1-3].

Poly(hydroxybutyrate)-PHB is one of the most studied biopolymer from the family of poly(hydroxyalkanoates)-PHAs due to its biodegradability and biocompatibility [4]. It is an aliphatic polyester synthesized by controlled bacterial fermentation [5, 6]. It is characterized by a high crystallinity degree and a relatively high melt temperature, near 170 ºC [2, 6]. Despite this, its high production cost in comparison to commercial plastics, its high fragility due to high crystallinity, its relatively low melt viscosity as well as its thermal instability at moderate temperatures restrict its use [2, 7]. With the aim of improving some of its properties PHB has been blended with several biodegradable polymers such as poly(lactic acid)-PLA [2, 8], poly(p-dioxanone)-PPD [5], poly(butylene succinate) (PBS) [9, 10], poly(ethylene succinate) (PES) [11] or poly(caprolactone)-PCL [12-14].

The present work is focused on the use of poly(caprolactone)-PCL as co-component in binary PHB-PCL blends. Poly(caprolactone)-PCL is a readily biodegradable, semicrystalline thermoplastic polyester which is produced by the ring opening polymerization of caprolactone monomer by using a catalyst [15]. PCL is characterized by a low melting point around 60 ºC, a very low glass transition temperature, T_g at about -60 ºC; nevertheless, the thermal decomposition temperature is relatively high, with values around 350 ºC [16, 17]. With regard to its mechanical properties, PCL is extremely ductile with a high elongation at break value and low modulus [18, 19].

Physical blends of polymers by melt compounding is a good and cost effective method to obtain materials with tailored properties [20]. Due to its high ductility, PCL offers attracting properties to PHB as it can reduce its low intrinsic fragility. PCL shows good miscibility behavior with a wide variety of polymers [21]; nevertheless, immiscibility with PHB has been reported in the literature together with different studies to increase compatibility between them [12, 13, 22, 23].

The main aim of this work is to study the PHB-PCL system in terms of miscibility as well as mechanical, thermal and morphological properties of PHB-PCL blends obtained by melt compounding in a twin screw co-rotating extruder. Mechanical properties of PHB-PCL blends are evaluated by tensile, flexural, impact and hardness tests as well as by dynamic mechanical thermal analysis (DMTA) using oscillatory rheometer with accessory for solid samples in torsion-shear mode. The effect of the blend composition on thermal properties has been evaluated by differential scanning calorimetry (DSC) and thermogravymetric analysis (TGA). Miscibility has been assessed by thermal analysis together with morphological characterization by field emission scanning electron microscopy (FESEM).

Experimental

Materials

Poly(hydroxybutyrate)-PHB under the trade name P226E (Mw=426,000 Da) was supplied by Biomer (Krailling, Germany). Poly(caprolactone)-PCL commercial grade CAPA 6500 (Mw=50,000 Da) was supplied by Perstorp Holdings AB (Malmö, Sweden).

PHB-PCL blend preparation

PHB and PCL pellets were dried in an air circulating oven for 24 h at 70 ºC and 40 ºC respectively before further processing in order to remove moisture. The appropriate amounts of each polymer in the blends was weighed and mechanically mixed in a zip bag. After this, the pellet mixtures were compounded in a twin screw co-rotating extruder with a temperature profile ranging from 160 ºC (hopper) to 175 ºC (die) and a screw speed of 40 rpm. The extruded material was cooled in air and subsequently was pelletized in a plastic mill. The compounding was further processed by injection molding in a Mateu & Solé mod. Meteor 270/75 (Barcelona, Spain) at 175 ºC to obtain standard samples for testing. The blend composition ranges from individual PHB and PCL polymers to different compositions with 25 wt% increment. Table 1 summarizes the compositions for all the PHB-PCL blends manufactured.

Table 1

Mechanical properties of PHB-PCL blends

The tensile and flexural properties of PHB-PCL biodegradable blends were obtained using an electromechanical universal test machine Ibertest ELIB 30 from S.A.E. Ibertest (Madrid, Spain) with a 5 kN load cell at room temperature, following the guidelines of ISO 527 and ISO 178 standards respectively. The crosshead speed was set to 5 mm min^{-1}.

The impact absorbed energy was measured in accordance with ISO 179 standard; impact tests were carried out on "V" notched samples ("V" at 45 º and a notch radius of 0.25 mm) in a 1 J Charpy impact pendulum by Metrotec S.A. (San Sebastian, Spain).

Hardness of PHB-PCL blends was determined in a Shore D hardness durometer mod. 676-D from J. Bot Instruments (Barcelona, Spain) according to ISO 868.
The values reported for all mechanical parameters were obtained for, at least, five different samples and averaged.

Thermal properties of PHB-PCL blends

Thermal characterization of PHB-PCL blends was carried out by differential scanning calorimetry (DSC) and thermogravymetric analysis (TGA). Thermal transitions were obtained by DSC in a Mettler Toledo 821 from Mettler-Toledo Inc. (Schwerzenbach, Switzerland). Samples sizing 7-9 mg were placed in standard 40 μL Al crucibles and subjected to an initial temperature program from -50 ℃ up to 180 ℃ at a constant heating rate of 10 ℃ min^{-1} and after this, temperature was maintained at 180 ℃ for 2 min and subsequently cooled to -50 ℃ at a cooling rate of -10 ℃ min^{-1} to remove previous thermal history. Then, samples were subjected to a second thermal program from -50 to 300 ℃ at 10 ℃ min^{-1}. DSC tests were carried out in nitrogen atmosphere (66 mL min^{-1}). The melt temperature of PHB and PCL was determined by considering the information provided by the second heating ramp. The crystallinity degree of both PHB ($X_{c, PHB}$) and PCL ($X_{c, PCL}$) in the blends was calculated by following Eq. (1) where

ΔH_m is the fusion enthalpy and ΔH_0 is the enthalpy related to the corresponding 100 % crystallinity (theoretical value) polymer; these values were assumed as 146 J g^{-1} [1] for PHB and 156.8 J g^{-1} [3] for PCL. Finally, "*w*" represents the weight fraction of PHB and PCL in each PHB-PCL blend.

$$X_c \ (\%) = 100 \ \times \left[\frac{\Delta H_m}{\Delta H_0 \cdot w}\right] \qquad \text{Eq.1}$$

Thermogravymetric analysis was carried in a TGA/SDTA 851 horizontal thermobalance from Mettler-Toledo (Schwerzenbach, Switzerland). Samples sizing 7-9 mg were placed in standard alumina crucibles and subjected to a heating program from 30 ºC to 600 ºC at a heating rate of 10 ºC min^{-1} in nitrogen atmosphere (constant flow rate of 66 mL min^{-1}). The onset degradation temperature (T_0) was determined at 2 wt% mass loss and the maximum rate degradation temperature (T_{max}) was obtained by analyzing the DTG curves (first derivative of TGA curve).

Field Emission Scanning Electron Microscopy (FESEM)

A field emission scanning electron microscope (FESEM) ZEISS ULTRA55 (Oxford instruments) at an acceleration voltage of 2 kV was used to observe fractured surfaces of samples subjected to a cryofracture process. Cryofractured samples of each blend were subjected to a selective extraction of PCL with acetone. Firstly, all samples were dried in an air circulation air oven at 40 ºC for 24 h and subsequently immersed in acetone for additional 24 h at room temperature to selectively remove the PCL portion which allows a better distinguish of the phase distribution in the blend [24]. Prior to sample observation of the samples before and after selective extraction, surfaces were covered with a thin layer of platinum in vacuum conditions with a sputter coater.

Dynamic mechanical thermal analysis (DMTA) of PHB-PCL blends

Dynamic mechanical thermal analysis (DMTA) in torsion mode was carried out in an oscillatory rheometer AR G2 from TA Instruments (New Castle, USA). Rectangular samples sizing 40x10x4 mm^3 were subjected to a dynamic temperature program from -100 to 150 ºC at a constant heating rate of 2 ºC min^{-1} at a frequency of 1 Hz and constant deformation (γ) of 0.1%. The evolution of the storage modulus (G'), loss modulus (G") and damping factor (tan δ) were followed in terms of increasing temperature.

Results and discussion

Mechanical properties

Mechanical properties (tensile and flexural) of PHB-PCL blends system are summarized in Table 2.

Table 2

With regard to tensile properties, we can see that individual PHB is characterized by a remarkable higher tensile strength and elastic modulus if compared to raw PCL, but, obviously, lower deformation ability as it can be derived by the relatively low elongation at break value of 8.1%. PHB is a rigid polymer. As we have indicated, the soft and flexible nature of PCL allows its use as impact modifier for rigid polymers such as PHB. As the PCL content on PHB-PCL blends increases, we observe a decrease in both tensile strength and elastic modulus values but, in contrasts, the elongation at break (ductile properties) is remarkably improved. In fact, raw PCL and high PHB-PCL blends with high PCL content (PHB25/PCL75) didn't break; samples covered the maximum displacement of the machine with elongation values over 1000% [25]. As it can be observed, for PHB-PCL composites with less than 50 wt% PCL, the elongation at break is relatively low and presence of PCL leads to a slight increase in elongation at break from values of 8.1% (raw PHB) up to 17.6% for PHB-PCL blends with 50 wt% PCL. It is expectable that PHB is the matrix in these blends composition as the blend properties are mainly

defined by PHB. Nevertheless, for compositions with high PCL content the elongation at break increases up to values over 1000% and it is expectable that PCL acts as matrix. So that matrix inversion occurs for PCL contents higher than 50 wt% as the properties of the blend are clearly defined by PCL for these composition ranges. PCL acts as an impact modifier with a remarkable increase in flexibility and ductility as PCL content increases and, specifically for composition with more than 50 wt% PCL.

The evolution of flexural properties is similar to those observed in tensile mode. Individual PHB offers higher flexural strength and modulus values than individual PCL; nevertheless, we can see slight differences as the only addition of 25 wt% PCL leads to a slight increase in both flexural strength (from 36.7 MPa to 38.5 MPa) and modulus (from 1515 MPa to 1605 MPa) which represents a percentage increase of almost 5% and 6% respectively. Higher PCL content on blends than 25 wt% lead to the expected behavior with decreasing mechanical resistant properties such as flexural strength and modulus and an improvement on deformation properties.

Fig. 1 shows the evolution of the impact absorbed energy (Charpy pendulum) and Shore D hardness for the PHB-PCL blends system. The absorbed energy is directly related to the ability of the material to absorb energy during the fracture in impact conditions, mainly due to deformation before fracture, so that, this property is representative for ductility while Shore D hardness is representative for resistance. The evolution of the absorbed energy follows similar tendency as that observed for elongation at break. We detect a slight increase from 2 J m^{-2} (individual PHB) up to values around 3.5 J m^{-2} for PHB-PCL blends with 50 wt% PCL and a remarkable increase for higher PCL content (values around 10.6 J m^{-2} for PHB-PCL blends with 75 wt% PCL) up to the maximum value achieved by individual PCL (15.1 J m^{-2}). In general terms we can conclude that addition of PCL leads to an improvement on ductile behavior of PHB-PCL blends which is more evident for compositions with more than 50 wt% PCL. As expected, Shore D hardness offers opposite behavior as it is a mechanical resistant property. PHB is characterized by a Shore D of 57.3 whilst PCL is much softer with a Shore D value of

46.5. As the PCL content on PHB-PCL blends increases we observe a decrease in Shore D values and this decrease is more evident for composition with more than 25-50 wt%

Fig. 1

Thermal properties of the PHB-PCL blends system

Fig. 2 shows a comparative plot of the DSC curves of the PHB-PCL blends system with varying composition. Fig. 2(a) shows the cooling curves after removal of thermal history and Fig. 2(b) shows the DSC curves corresponding to the second heating cycle and the base curve for determining the values of ΔH_m for PHB, PCL and their blends (unnormalized values and normalized values with respect to the sample weight), the melt temperatures (T_m) as well as the crystallinity degree (X_c); all these values are shown in Table 3. As it can be seen in Fig. 2(b), individual PHB shows two melt peaks: one located at 168.3 ºC which is related to the melting of PHB and a small one peak at 52.3 ºC which can be attributable to some low molecular weight additive in the formulation [26, 27]. With regard to the glass transition temperature, typical values of T_g for PHB are located between the 2-7 ºC range. We can see a slight change in the base line in a wide temperature range covering -10 ºC to 10 ºC but no clear evidence of the T_g is detected. With regard to individual PCL we observe a unique peak located at 59.3 ºC and the T_g can't be detected as it is below -50 ºC [16]; for this reason, T_g study was conducted by using DMTA. DSC of the PHB-PCL blends system show a clear evidence of the immiscibility of these two biodegradable polymers as two individual peaks located at the typical temperature values of each melting point can be detected: one at about 170 ºC attributable to PHB and other melt peak located at about 60 ºC which is related to the melting of PCL. Table 3 shows that as the PCL content on PHB-PCL blends increases, a slight increase in both melt peak temperatures of PHB ($T_{m\,PHB}$) and PCL can be detected ($T_{m\,PCL}$).

The normalized melt enthalpy (ΔH_m) for both polymers, obtained in the second heating cycle, was used to calculate the crystallinity degree of each material in the blends. Crystallinity plays an important role in mechanical performance of PHB, PCL and their blends. The

percentage crystallinity of individual PHB ($X_{c\ PHB}$) is higher than 55% while the percentage crystallinity of raw PCL ($X_{c\ PCL}$) is about 46%. The percentage crystallinity of each polymer in the blends is slightly higher for PHB-PCL blends with 25 wt% PCL the percentage crystallinity of PHB ($X_{c\ PHB}$) changes from 55.1% up to 58.2% and the value of ($X_{c\ PCL}$) changes from 46.4% to 51.3%. The percentage crystallinity of each polymer for all the rest blend compositions is slower as observed in Table 3. That's why we have previously observed a slight increase in flexural strength and modulus in PHB-PCL blends with 25 wt% PCL.

Fig. 2

Table 3

Thermogravymetric curves (TGA) of both individual PHB and PCL as well as the PHB-PCL blends are shown in Fig. 3(a) and the main thermal parameters regarding degradation are summarized in Table 4. As it can be observed, PCL degrades in a single step process with an onset degradation temperature ($T_{0\ PCL}$) of 359.5 ℃ and a maximum degradation rate temperature ($T_{max\ PCL}$) of 415.5 ℃ [28]. On the other hand, PHB degradation proceeds in several stages due to the formulation of the commercial polymer which contains plasticizers, nucleating agents and stabilizers [26]. The onset degradation temperature ($T_{0\ PHB}$) for PHB is 231.3 ℃ and the maximum rate ($T_{max\ PHB}$) is achieved at 290 ℃. These values are remarkably lower than those obtained for individual PCL thus giving clear evidence of the lower thermal stability of PHB if compared to PCL. The TGA curves for PHB-PCL blends occurs in two different stages attributable to PHB and PCL. The first degradation stage is related to PHB degradation and the second stage, located at higher temperatures is related to PCL degradation with slight changes in the characteristic degradation temperatures corresponding to each polymer. This is also a clear evidence of the lack of strong interactions between the two biodegradable polymers thus giving evidence of immiscibility (or very low miscibility). In general terms we can see that presence of PCL leads to a slight increase in the thermal stability of PHB. Although PHB and PCL show very restricted miscibility as revealed by the DSC analysis, PCL is characterized by a

10

remarkable high thermal stability compared to PHB and all blends with PCL show a slight increase in the thermal onset degradation temperature which could be related to somewhat interactions between the two components thus it is possible to expect phase separation with a PCL rich phase with very low content on PHB chains and in the same way, a PHB rich phase with very low amounts of dissolved PCL chains. This fact could be responsible for the slight increase in the thermal stability of PHB rich phase and conversely, a slight decrease in the onset degradation temperature of the PCL rich phase. We can see in Table 4, how the onset degradation temperature (T_0) is increased from 231.3 ºC (individual PHB) up to values in the 260-270 ºC for PHB-PCL blends with PCL content in the 25 – 75 wt% range. Similar tendency (but less intense) can be observed for the maximum thermal degradation rate (T_{max}) for both PHB and PCL. With regard to the maximum degradation rate temperature of PHB, $T_{max\ PHB}$ changes from 290.0 ºC (individual PHB) up to values of 296.8 ºC for PHB-PCL blends with 75 wt% PCL. The maximum degradation rate temperature for PCL ($T_{max\ PCL}$) changes in a very narrow range from 413.8 ºC to 415.5 ºC for blend composition containing 75 wt% PCL.

Derivative thermogravymetric curves (DTG) are shown in Fig. 3(b) and we can observe the peak temperatures corresponding to the maximum weight loss rate. DTG curves of PHB-PCL blends are characterized by two main peaks attributable to PHB degradation (low temperature) and PCL degradation (high temperature). As it has been previously discussed, the maximum degradation rate temperature for PHB ($T_{max\ PHB}$) slightly increases while the maximum degradation rate temperature for PCL remains in a very narrow temperature range (413-415 ºC).

Fig. 3

Table 4

Morphological characterization of PHB-PCL blends system

Fig. 4 shows FESEM images of cryo-fractured surfaces of PHB, PCL and their blends in terms of the PCL content. We can observe a clear fragile fracture surface due to cry-fracture

conditions. Fracture surface of individual PHB can be seen in Fig. 4(a) and it is characterized by different immiscible components in the commercial formulation. As we have indicated, this commercial PHB grade is composed of plasticizers and other components which are not fully miscible in PHB [26] thus resulting in very small spherical formations (lower than 500 nm). With regard to PHB-PCL blends morphology, we can clearly see phase separation between PHB and PCL thus giving clear evidence of the immiscibility (or very low miscibility) of these two biodegradable polymers. For all intermediate compositions we observe a matrix phase and dispersed circular shapes sizing between 2 and 10 μm (we don't observe the typical spherical droplets and holes of immiscible polymers, due to the cryofracture process which also breaks dispersed spherical droplets) corresponding to the dispersed phase. In PHB-PCL blend with 25 wt% PCL, Fig. 4(b), the spherical droplets are higher than those observed in PHB-PCL blends in which PCL is the main component and acts as matrix. In addition, for the PHB-PCL blend with 25 wt% PCL we can see the lack of interaction between PCL droplets and the surrounding PHB matrix, Fig. 4(b). The largest droplets can be observed in Fig. 4(c) which corresponds to PHB-PCL blend with 50 wt% PCL. As it can be seen in Fig. 5, we observe a small ring around the dispersed phase which can be representative for some miscibility between the two polymers. In such Fig. 5 it is clearly detectable the generalized lack of interactions between the two polymers.

Fig. 4

Fig. 5

With the aim of analyzing the surface morphology, a selective extraction process was done with acetone for a period of 24 h to selectively dissolve PCL [24]. In Fig. 6(a) and 6(b) we can see how the small PCL droplets have been fully dissolved leading to formation of small voids on the fractured surface while larger PCL droplets have not been fully attacked leading to a flake-like structure. The blend composition with 25 wt% PCL (PHB75/PCL25) shows that PCL is highly dispersed in the PHB matrix that was not clearly detectable by conventional

FESEM without previous selective attack of the PCL rich phase. With regard to the blend compositions with 50 wt% PCL (PHB50/PCL50) we see that PCL acts as the matrix in the blend with the typical flake morphology described before. Such morphology is also observed for PCL rich blend with 75 wt% PCL. In both cases, the selective extraction with acetone leads to appearance of small PHB spherical droplets immersed in the PCL matrix.

Fig. 6

Dynamic mechanical thermal analysis (DMTA)

Fig. 7 shows the evolution of the storage modulus (G'), the loss modulus (G'') and the damping factor (tan δ) for individual PHB and PCL as well as their blends in terms of increasing temperature. As one can see in Fig. 7(a), the storage modulus decreases with temperature. PHB is stiffer than PCL and that's why the G' curve corresponding to PHB is shifted to high values. The storage modulus for PHB shows two main steps: one located at around -7 ºC which is related to its glass transition temperature ($T_{g\,PHB}$) and another one in the temperature range comprised between 55 ºC and 60 ºC which can be attributable to some commercial additive in PHB [26]. With regard to the storage modulus evolution for PCL, a remarkable decrease can be detected once its glass transition temperature ($T_{g\,PCL}$) is surpassed at around -53 ºC. This dramatic drop in G' values for PCL can also be observed in PHB/PCL blends high PCL content (50 wt% and 75 wt%) while not so remarkable peak is observable for blends with 25 wt% PCL. The storage modulus for blends with high PCL contents reaches values nearby 0 MPa once the melt temperature of PCL ($T_{m\,PCL}$) has been surpassed (around 60 ºC) which also gives evidences that PCL acts as the matrix for a polymer blend composition of 50 wt% PCL. The blend composition with 25 wt% PCL (PHB75/PCL25) shows at room temperature, similar storage modulus to that obtained for individual PHB but a remarkable decrease is detected at temperatures higher than 60 ºC in which, PCL melt occurs. As we can see, as the PCL content increases, G' curves are moved to lower values thus indicating that PCL provides an impact modifier effect on PHB.

With regard to the loss modulus (G") and damping factor (tan δ), Fig. 7(b) and 7(c) show their corresponding evolutions with temperature. PHB-PCL blends show two peaks that are attributable to PHB and PCL which in turn, gives evidences of immiscibility or poor miscibility of both polymers in the amorphous regions. The first peak, located at -53 ℃ is representative for the glass transition temperature of PCL ($T_{g\ PCL}$) and the other main peak is located at around -7 ℃ and corresponds to the glass transition temperature of PHB ($T_{g\ PHB}$). Nevertheless, it can be observed that the glass transition temperature of each polymer in the blend is slightly different if compared to the individual material which could be attributable to some interactions between both polymers.

Fig. 7

Conclusions

The main aim of this research work was the development of PHB blends with PCL to improve the high intrinsic fragility of PHB. The obtained results show that PCL acts as an impact modifier thus providing higher flexibility and ductility and, obviously, a decrease in mechanical resistant properties such as strength and modulus. As the PCL content in PHB-PCL blends increases, we observe an increase in the impact absorbed energy as well as the elongation at break in tensile tests. This increase is particularly remarkable for PHB-PCL blends with more than 50 wt% PCL. The elongation at break changes from 11.2% up to values over 1000% for a blend composition of 75 wt% PCL. With regard to flexural strength and modulus, we observe a slight increase for the blend containing 25 wt% PCL. This is related to crystallization phenomena and the DSC study revealed a noticeable increase in the crystallinity degree (X_c) of both PHB and PCL for this particular blend composition. PHB and PCL have been proved to be immiscible as FESEM of cryo-fractured samples revealed. Such immiscibility is also evident by DSC and TGA analysis. DSC study does not show significant changes in the melt peak temperature for PHB and PCL and TGA analysis of PHB-PCL blends shows a slight

improvement on the typical degradation temperatures but it is not significant. The TGA study also reveals the relatively low thermal stability of individual compared to PCL but the addition of PCL to PHB promotes slight improvement on the typical degradation temperatures of PHB. Dynamic mechanical thermal analysis (DMTA) confirmed the very low miscibility between these polymers with two glass transition temperatures located at around -53 ºC and -7 ºC for the PCL-rich phase and PHB-rich phase respectively. Nevertheless, some slight changes in the T_g values are observed which could be representative for some PHB-PCL interactions.

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Figure legends

Fig. 1 Impact energy and Shore D hardness values for the PHB-PCL blends system in terms of the PCL content

Fig. 2 DSC thermograms during the (a) cooling scan and (b) second heating scan of PHB-PCL blends system

Fig. 3 (a) TGA and (b) DTG curves of PHB-PCL blends system

Fig. 4 FESEM images at 5000x of cryo-fractured surfaces of PHB-PCL blends: (a) PHB100/PCL0; (b) PHB75/PCL25; (c) PHB50/PCL50; (d) PHB25/PCL75; (e) PHB0/PCL100.

Fig. 5 FESEM images of cryo-fractured surface of PHB50/PCL50 at 25000X

Fig. 6 FESEM images of cryo-fractured surfaces of PHB-PCL blends subjected to a selective extraction with acetone: (a) PHB75/PCL25 (5000x); (b) PHB75/PCL25 (25000x); (c) PHB50//PCL50 (5000x); (d) PHB50//PCL50 (25000x); (e) PHB25//PCL75 (5000x); (f) PHB25//PCL75 (25000x)

Fig. 7 DMTA (torsion mode) curves of PHB-PCL blends system: a) storage modulus (G'); b) loss modulus (G") and c) damping factor, (tan δ)

Table captions

Table 1 Composition of PHB-PCL blends and labelling of each composition

Table 2 Tensile and flexural properties of the PHB-PCL blends system

Table 3 Thermal parameters of PHB-PCL blends system obtained by differential scanning calorimetry (DSC)

Table 4 Thermal degradation parameters of PHB-PCL blends system obtained by thermogravymetric analysis (TGA)