

Thermal, rheological and microstructural characterisation of commercial biodegradable polyesters

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ABSTRACT

Growing environmental concerns along with new regulations are forcing the industries to seek renewable raw materials for their products. In this sense, this work studies the thermo-rheological properties of commercial biodegradable polyesters: two polylactic acids (PLAs), a polycaprolactone (PCL) and a PLA/PCL blend. A comprehensive material characterization by means of thermogravimetry/differential thermal analysis (TG/DTA), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), frequency sweep tests and polarized light microscopy was carried out. The results have shown that the material thermal/thermo-rheological properties and, therefore, its microstructure, are strongly dependent on its thermal history. This fact arises from the slow recrystallization kinetics shown by PLA. Interestingly, PCL may play the role of nucleating agent for the PLA crystallization, making it faster. This issue must be carefully considered so that a reliable material characterization is achieved.

Keywords: polylactic acid, polycaprolactone, polymer blend, DMTA, nucleating agent, product design.

1. INTRODUCTION

The classic way to manufacture polymers is based on the polymerization of the lightest fractions of crude oil. However, a growing environmental awareness and the rising crude oil prices have motivated researchers from industry and academia to develop biodegradable products from renewable resources [1]. Among bio-based polymers, polylactic acid (PLA) is a promising candidate to replace petroleum-based plastics due to its high stiffness and strength, which are comparable to polystyrene, at least at room temperature. PLA is a versatile polymer synthesized by the biological fermentation of renewable resources, such as corn starch and sugar beet, and thus environmentally and ecologically safe [2]. Initially, PLA development focused on the production of body implants which would degrade within the human body over time [3]. Over the past decades, PLA has been used in a variety of consumer goods, such as single use cutlery or food packaging [4]. This approach involves heating the polymer above its melting point, shaping it to the desired forms, and cooling to freeze form and dimensions.

In this work, two commercial polylactic acids (PLAs) produced by NatureWorks LLC (United States), with the trade names Ingeo 2002D and Ingeo 4032D, have been studied. On account of their applications, Ingeo 2002D is a clear extrusion sheet grade and is easily processed on conventional extrusion and thermoforming equipment. On the other hand, Ingeo 4032D can be converted into a biaxial oriented film with the use of temperatures up to 150 °C. This film has excellent optics, good machinability and excellent twist and deadfold. These properties make it suitable for laminations and other packaging applications.

On the other hand, it is well known that PLA crystallinity can induce significant improvements in stiffness, strength, heat deflection temperature and chemical resistance

[5]. In this sense, different researchers have studied the complex PLA crystallization process and the selection of suitable nucleating agents to improve the crystallization rates [6]. Related to this, the nucleating ability of a commercial polycaprolactone (PCL) (Capa™ FB100 from Perstorp, Sweden), a crystalline and biodegradable petroleum-based polyester, is also evaluated in this work.

PLA, PCL and their blends have been widely investigated elsewhere because of their compelling commercial applications [7-10]. Further to these studies, this paper intends to gain a deeper knowledge on the effect that previous thermal history may exert on the polymer microstructure and, therefore, on its thermo-rheological response at temperatures below its melting point. To accomplish this goal, a comprehensive material characterization has been carried out by means of simultaneous thermogravimetry/differential thermal analysis (TG/DTA), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), frequency sweep tests and polarized light microscopy.

2. EXPERIMENTAL

Two commercial polylactic acids (PLAs), with the trade names Ingeo 2002D and Ingeo 4032D (produced by NatureWorks LLC, United States), and a commercial polycaprolactone, Capa™ FB100 (manufactured by Perstorp, Sweden), were used. These polymers will be referred to as “fresh” PLA 2002, PLA 4032 and PCL samples, hereinafter. Prior to its use, the polymers were dried overnight at 90 and 50 °C for PLAs and PCL samples, respectively.

In addition, a blend 70/30 (wt.%) of PLA 4032/PCL (abbreviated PLA/PCL) was also studied. This blend was prepared with the mixing chamber Rheomix 3000p from Thermo Haake (Germany), equipped with two counter-rotating rollers. PLA 4032 and

PCL were mixed for 20 min at 180 °C, and a rotation speed of 50 rpm. This sample will be referred to as “fresh” PLA/PCL blend.

Simultaneous TG/DTA measurements were conducted using a Seiko TG/DTA 6200 (Japan). Temperature ramps at 10 °C/min, from 40 to 600°C, under N₂ atmosphere, were carried out on 5-10 mg of “fresh” samples.

In order to conduct DMTA/frequency sweep tests, different specimens were prepared by compression-moulding in a hot-plate press. Firstly, the samples were subjected to 50 bar of pressure for 20 min, at 180 °C for the PLA 4032 and PLA/PCL samples, and 80 °C for the PCL sample. Subsequently, the specimens were allowed to cool down to room temperature over a time interval of 5 hours inside the press. This represents a cooling rate of 0.5 °C/min in the PLA 4032 and PLA/PCL blend samples and of 0.17 °C/min in the PCL sample. The resulting material will be referred to as “moulded”, in contrast to the as-received material (referred to as “fresh”). “Moulded” samples were also characterized by DSC and Polarized Light Microscopy.

Differential scanning calorimetry (DSC) tests were performed with a TA Q-100 (TA Instruments, USA). Samples of 5-10 mg were subjected to three different testing protocols, composed of two heating steps (20-200 °C) at a rate of 10°C/min, with an intermediate cooling step conducted at the rates of -70, -10 and -3 °C/min, for protocols I, II and III, respectively. All the tests were performed with a N₂ gas flow rate of 50 mL/min. From these different protocols, the polymers crystalline fractions were determined.

Dynamic Mechanical Thermal Analysis (DMTA) and frequency sweep tests were performed on rectangular samples of 50 mm length, 10 mm width and 3 mm thickness, with a Seiko DMS 6100 (Seiko Instruments Inc., Japan) in double cantilever (bending)

mode. With respect to the DMTA measurements, these were conducted on PLAs and PLA/PCL samples at a constant frequency of 1 Hz and strain within the LVE interval, with the application of a heating rate of 1 °C/min, from 40 °C up to the material cold crystallization temperature. On the other hand, isothermal frequency sweep tests from 0.02 to 100 Hz were carried out on PLA 4032 samples, also within the linear viscoelasticity (LVE) region, at 30, 60 and 80 °C.

The microstructure of the materials was examined with an optical microscope, Olympus (Japan) BX51, equipped with a pair of crossed polarisers. For this analyses, 0.1 mm-thick films (prepared in hot-plate press) were placed on a LTS 350 hot stage (Linkam Scientific Instruments Ltd., UK), and subjected to different temperature programmes controlled by a Linkam TP 94.

3. RESULTS AND DISCUSSION

3.1. Thermal characterization

The thermal characterization of “fresh” neat polymers and the PLA/PCL blend was carried out by simultaneous thermogravimetric/differential thermal analysis (TG/DTA) and by calorimetric (DSC) tests. First of all, the thermal degradation temperatures (T_d), shown by the peak maximum in the DTG curves, were evaluated by TG/DTA tests. This technique allows sample mass loss and phase transitions to be determined simultaneously in an open system (Figures 1A and 1B). However, glass transition temperatures (T_g) and melting points (T_m) can be better visualised by the DSC results shown in Figure 2.

Figure 1A shows the DTG curves for the “fresh” neat polymers and the PLA/PCL blend. It can be observed very similar values of the thermal degradation temperatures

for both PLAs, which are much lower than that showed by PCL (see values in Table 1). As expected, the thermal degradation of the PLA/PCL blend occurs in two overlapped steps, with peaks located at the values for its single components.

Instead, the thermal events observed in these materials before decomposition seem to be more complex, as revealed by DSC results. Figure 2 shows the heat flow thermograms for the first and second heating ramps for “fresh” PLAs and PCL samples. A cooling rate of 10 °C/min, corresponding to protocol II, was applied between them. It can be observed that, for PLAs samples, both first and second heating ramps present a thermal event at around 60 °C, which corresponds to the glass transition of their amorphous fraction. In contrast, only the first ramp shows, at about 150 °C, the melting peak of the PLA crystalline fraction. The absence of the melting peak for the second ramp indicates that recrystallization upon cooling from the melt does not occur at the cooling rate applied (too fast for the polymer chains to reorganise into crystalline regions). Instead, a more pronounced glass transition is observed, as chain mobility is not constrained by PLA crystals. On the contrary, both first and second ramps for the PCL display a melting peak around 60 °C, which indicates that PCL recrystallizes faster than PLA. The glass transition temperature for the PCL, located at much lower temperatures than the interval tested, is not provided. In order to erase the thermal history, the values of T_g and T_m (included in Table 1) were determined from the second heating ramps. However, T_m of PLAs samples were taken from the first scans, as their molecules did not recrystallize at the cooling rate of 10 °C/min.

In order to study the crystallinity of these materials, three DSC protocols with different intermediate cooling rates of 70, 10 and 3 °C/min (protocols I, II and III, respectively) were carried out. In this sense, the following equation was used to calculate the degree

of crystallinity (χ):

$$\chi = \frac{\Delta H}{\Delta H_m^0 \cdot \text{wt.}\%} \cdot 100 \quad (1)$$

where χ may be: a) $\chi_m - \chi_{cc}$, percentage of crystallinity formed during cooling (post-melt crystallization), if $\Delta H = \Delta H_m - \Delta H_{cc}$; b) χ_{cc} , percentage of crystallinity formed during heating (cold crystallization), if $\Delta H = \Delta H_{cc}$; or c) χ_m , total crystallinity, if $\Delta H = \Delta H_m$. ΔH_m^0 is the theoretical heat of fusion for a fully crystalline material. From literature, enthalpies of fusion of 93.1 and 135.3 J/g, for PLA and PCL respectively, have been assigned to 100% crystalline materials [12,13]. Finally, “wt.%” represents the PLA weight fraction, in case of PLA/PCL blend.

The melting enthalpies and percentage of crystallinity for the “fresh” polymers are presented in Table 2. On the one hand, the first heating ramps for both pure PLAs samples show similar crystalline fractions of 31.5 and 30.8, for PLA 2002 and PLA 4032, respectively. These values, which represent the thermal response of the bio-polymer pellets as delivered by the manufacturer, are in accordance with the values found in literature [14]. However, the PLAs melting peaks disappear during a second heating ramp conducted after cooling the material down to room temperature at 10 °C/min (protocol II). Hence, this cooling rate (and those corresponding to protocols I and III, not shown in Table 2) prevented PLA chains from recrystallizing. On the other hand, the heats of fusion measured over the first heating ramps (not affected by type of protocol conducted) for the PCL sample indicates that this material presents an average value of its crystalline fraction of about 44.5 %. No significant differences were either found among the three values obtained for the second heating ramps (average of about 37.5), even though they were subjected to three different intermediate cooling ramps.

However, the percentage of crystallinity decreased 7 % when the samples were subjected to fast/very fast cooling, or even quenching (protocols III, II and I, respectively) from the melt, suggesting that, same as PLAs samples, a different thermal treatment was applied during the manufacture of the “as-received” polymers. This result reveals the PLA, mainly, as well as PCL crystallinity to be hardly affected by the thermal history of the material, and demonstrates the importance of the processing parameters in endowing the polymer the desired properties.

Furthermore, Figure 3 presents the heat flow thermograms, corresponding to the first and second heating ramps, for three selected “moulded” samples: PLA 4032, PCL and PLA/PCL blend. “Moulded” samples were subjected to compression-moulding and subsequently cooled down to room temperature (very slowly, over a 5 h-interval), before testing. In every sample, the same cooling rate of 10 °C/min (protocol II) was applied between the two DSC heating scans and the results are shown in Figure 3. As can be observed, if compared to Figure 2, the new treatment significantly changed the thermal response of PLA 4032. In addition to the glass transition and melting peak above, the first heating ramp for this material presents a new event, more precisely, a cold crystallization, which extends from 105 up to 135 °C. The values of enthalpy associated to these events and the percentage of crystallinity are displayed in Table 3, which shows that only 8.1 % of crystals (if compared to 30.8 % in the “as-received” material) were present in the material before heating. The remaining 15.9% appeared from cold crystallization upon heating. Thus, the total crystallinity was of 24.0 %. However, the second ramp only shows the glass transition. Therefore, the fast cooling rate applied (10 °C/min) again seems to prevent polymer chains recrystallization. With regard to the PCL, no remarkable differences were observed between “fresh” and “moulded” samples. In both cases, this polymer only presented, in the temperature

interval tested, a melting peak. However, the degree of crystallinity achieved was seen to decrease from 42.9 down to 37.5 % from the first to the second ramp. A reduction of 1.5 % in the “moulded” material crystallinity is also noticed when compared to the “fresh” PCL (first heating ramp values).

Concerning the “moulded” PLA/PCL blend, the thermograms in Figure 3 reveal the existence of three thermal events in both heating ramps. The first event corresponds to the overlapping of melting and the glass transition of the PLA and PCL fractions, respectively. The second one relates to the cold crystallization due to the PLA fraction of the blend. Finally, the third event is the melting of the PLA crystals. Interestingly, and in contrast to the “moulded” PLA 4032 sample, the second and third events again arise in the second heating ramp, leading to the formation of 4.2 and 0.8 % of crystals during post-melt crystallization and cold crystallization (both at 10 °C/min), respectively. Hence, this result suggests that PCL may induce a faster formation of PLA crystals upon cooling [15]. Yet, the crystals content is far from that corresponding to the first heating ramp. Moreover, first heating scans of “moulded” PLA 4032 and PLA/PCL blends reveal χ_m - χ_{cc} values of 8.1 and 9.8 %, whilst they present χ_{cc} values of 15.9 and 6.3 %. In consequence, the presence of a higher percentage of crystals formed during cooling in the PLA/PCL blend seems to negatively affect the cold crystallization process, as it may reduce the chains mobility.

3.2. Microstructure and thermal history

Polarized light microscopy images in Figure 4 further confirm the results derived from DSC measurements. Thus, different levels of crystallinity were observed by subjecting the samples to different thermal treatments. As can be observed, the “moulded” PLA 4032 sample presents, at 25 °C, the classic “malt cross” pattern associated to its

crystalline fraction (see Figure 4A). This sample was compression-moulded, at 180 °C for 20 min, and then cooled down (at 0.5 °C/min), to room temperature. As previously mentioned, this thermal treatment allowed for the eventual formation of 8.1% crystals.

Investigations on the crystallization kinetics of PLA and other polymers point out the effect on the polymer crystallinity of both time and temperature during an isothermal crystallization [11,16]. In general, the crystal growth rate for a semi-crystalline polymer becomes faster if the sample is maintained at temperatures close to their crystallization temperature over a certain “annealing” time [12].

Even though the isothermal crystallization conditions need to be optimised in order to achieve the maximum crystals content, the PLA 4032 film was annealed at 120°C (cold crystallization peak, in Figure 3A) for 30 min, with the aim to establish a qualitative comparison. As a result, Figure 4B demonstrates the formation of new crystals upon annealing, if compared to the film which was measured at 25°C. Moreover, as demonstrated by Pluta and Galeski, the new crystals originated via heating from the glassy amorphous state were smaller than those originally obtained via cooling from the melt. Similar results for PLA are reported elsewhere [11, 17].

On the other hand, Figure 4C shows the presence of white spherulites, associated to PLA crystals, when the “moulded” PLA/PCL film was observed at 25 °C. In fact, DSC measurements revealed a content of 9.8 % of crystals in the PLA matrix. In addition, the Figure 4D indicates a much higher crystals density when the sample was annealed at the selected conditions of 120 °C for 30 min. Again, the crystals formed through this treatment are clearly smaller than the original crystals derived from the post-melting crystallization.

3.3. Viscoelastic behaviour in solid state.

In order to study the thermo-rheological behaviour of these polymers in solid state, Dynamic Mechanical Thermal Analysis (DMTA) and isothermal frequency sweep tests (bending mode) were conducted, on “moulded” PLAs and PLA/PCL samples, between 40 °C and the materials cold crystallization temperatures. Again, the samples studied were previously subjected to compression-moulding in a hot-plate press and further cooled down to room temperature over a period of 5 hours (“moulded” samples).

Figure 5 illustrates the temperature dependence of the elastic modulus (E') and loss tangent ($\tan \delta$), obtained through dynamic bending tests carried out at 1 Hz and a heating rate of 1 °C/min. As can be observed in Figure 5A, both “moulded” PLA 4032 and PLA 2002 show very similar viscoelastic response. Between 40 and 50 °C, they present nearly constant values of E' ($>2 \cdot 10^9$ Pa) which slightly decrease with temperature, as expected from the glassy region. Moreover, their elastic modulus experiences a marked decay between 50 and 65 °C, which relates to the transition from the glassy to the rubbery region. Further, a plateau in E' ($\sim 10^7$ Pa) is observed between 65 and 80 °C, temperature at which E' is seen to increase up to about 110 °C, as a consequence of the cold crystallization. Thus, the results of viscoelasticity tests demonstrate the reinforcing effect of the crystals formation. At this point, PLA 4032 sample seems to level off, whilst PLA 2002 sample starts to decrease.

As a result, Figure 5B presents, for PLA 4032 and PLA 2002 samples, well-defined peaks in $\tan \delta$, at about 60 °C, which correspond to the mechanical glass transition temperature determined by DMTA measurements. Similar results have been previously reported for other bioplastics and composites containing PLA in their formulations [20-23]. On the other hand, it can be observed a small peak at about 90 °C, before the steep increase in E' occurs. This event may be possibly related to the density modulation

preceding the formation of a crystalline phase (pre-crystallization), which was already observed by different authors in the crystallization of poly(ethylene terephthalate). Differences with values measured by DSC derive from different heating rates used.

With regard to the “moulded” PLA/PCL sample, the viscoelastic response is very similar to the neat PLA samples. However, $\tan \delta$ peaks are seen to move to lower temperatures. Thus, the peak associated to the material glass transition shifts from 60 °C down to 55 °C, which may be attributed to the PCL content (PCL is nearly molten at that temperature). On the other hand, the small $\tan \delta$ peak at 90 °C for “moulded” PLAs samples transform into a “shoulder” located at about 85 °C for the “moulded” PLA/PCL sample. This corroborates a decrease in the crystallization upon heating and supports the nucleating effect of PCL during post-melt crystallization of the PLA matrix (see results in Table 3). In fact, the rubbery modulus for the “moulded” PLA/PCL sample is about $4 \cdot 10^7$ Pa, higher than the samples which do not contain PCL.

Moreover, in order to gain a deeper knowledge on the rheology of these material in solid state, a new specimen of the “moulded” PLA/PCL sample was placed into the rheometer, heated up to 110 °C, and maintained for 30 min. Then, the specimen was cooled down to 40 °C, and the same DMTA test was conducted. This sample is referred to as “annealed” PLA/PCL sample. Interestingly, this sample does not present any cold crystallization process, and transition from glassy to rubbery region is less pronounced (rubbery modulus of about $1.5\text{-}2.0 \cdot 10^8$ Pa). This result again demonstrates the reinforcing effect of the crystalline domains formed during the isothermal crystallization at 110 °C, which leads to a value of the rubbery modulus much higher than the corresponding to the “non-annealed” samples. Also, the glass transition temperature is shifted about 5 °C to higher temperatures than its parent “moulded” PCL/PLA sample, and the size of the $\tan \delta$ peak is smaller. These two observations usually indicate

restricted movement of amorphous chains because of the presence of reinforcements like fillers and/or crystalline regions. Furthermore, the PLA molecules with the lower molecular weight (higher mobility) are probably those included in the growing crystals during annealing. These molecules are the same that act as plasticizing agents for PLA amorphous part. Thus, it results in an increase of the glass transition temperature.

Finally, Figure 6 compares the frequency dependence of E' and E'' , at three selected temperatures, for “moulded” and “annealed” PLA 4032 samples. The “annealed” specimen was placed into the DMTA rheometer, heated up to 110 °C, and maintained for 30 min. Then, the sample was cooled down to 80 °C, and the first frequency sweep test conducted. Two more tests were later carried out by decreasing temperature down to 60 and 30 °C, respectively.

At 30 °C, both PLAs samples exhibited similar rheological responses, with a well-developed plateau in E' ($\sim 2\text{-}3 \cdot 10^9$ Pa), and E'' decreasing with increasing frequency (typical from the glassy region). At this temperature, the samples show a prevailing elastic response, with much higher values of E' than E'' in the entire frequency interval studied. An increase in the testing temperature leads to a reduction in E' and E'' values and changes significantly the mechanical spectra obtained. At 80 °C, the “moulded” sample shows a weak gel-like behaviour, with E' slightly higher than E'' . Instead, the “annealed” sample exhibits a well-developed rubbery (or “plateau”) region. This region is characterised by nearly constant values of E' , much higher than E'' , which presents an apparent minimum. It has been extensively described in polymer rheology in terms of an entanglement network formed by the simple topological interaction of polymer chains, resulting from polymeric systems behaving like pseudo-gels at frequencies higher (shorter timescale) than the lifetime of the topological entanglements [26]. This

response, which involves a large amount of interactions among chain segments, suggests a material with a higher density of crystalline regions which act as physical crosslinks. However, the most noticeable differences in the viscoelastic response occur at 60 °C, at the polymer glass transition temperature. At this temperature, the “moulded” sample presents a prevailing viscous response, as E' undergoes a remarkable decay with decreasing frequency (Figure 6A). On the contrary, the “annealed” sample shows a much less pronounced decrease in E' , due to the constrained mobility of the polymer chains as a consequence of a higher crystalline fraction (Figure 6B).

4. CONCLUSIONS

Complex thermal and thermo-rheological behaviours, which strongly depend on their thermal history, were exhibited by PLA and its blend with PCL.

On the one hand, cooling scans at different temperatures demonstrated very slow crystallization kinetics of PLA upon cooling from the melt. Interestingly, DSC measurements also revealed that its blend with PCL may induce a faster formation of crystals. On the other hand, polarized light microscopy indicated that PLA spherulites formed by isothermal crystallization (annealing) were significantly smaller than those obtained by post-melting crystallization. Finally, PLA viscoelastic properties were greatly influenced by the higher crystallinity percentage after being annealed for 30 min in the proximity of its cold crystallization temperature. Particularly, $\tan\delta$ peak corresponding to its glass transition decreased as a consequence of the constrained chain mobility, whilst its rubbery modulus presented a very high value, if compared to the “non-annealed” sample. Moreover, the higher crystalline fraction after annealing led to a well-defined “plateau” region at 80 °C, as crystals seem to act like physical crosslinks which favour the existence of interactions among chains.

In consequence, thermal history must be carefully considered in order to conduct a reliable material characterization of PLA.

5. ACKNOWLEDGEMENTS

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Table 1. Glass transition, melting and degradation temperatures for “fresh” neat polymers.

	PLA 2002 “fresh”	PLA 4032 “fresh”	PCL “fresh”
T_g (°C)	58	59	Not determined (*)
T_m (°C)	153	152	56
T_d (°C)	362	354	410

(*) Below the temperature interval tested

Table 2. Melting enthalpies and percentage of crystallinity for “fresh” neat polymers.

	1 st heating ramp		2 nd heating ramp	
	ΔH_m (J/g)	χ_m (%)	ΔH_m (J/g)	χ_m (%)
PLA 2002 “fresh” <i>Protocol II</i>	29.4	31.5	0	0
PLA 4032 “fresh” <i>Protocol II</i>	28.7	30.8	0	0
PCL “fresh” <i>Protocol I</i>	61.0	45.1	50.5	37.3
PCL “fresh” <i>Protocol II</i>	59.7	44.1	50.1	37.0
PCL “fresh” <i>Protocol III</i>	60.8	44.9	51.2	37.8

Table 3. Cold crystallization and melting enthalpies and percentage of crystallinity for “moulded” neat polymers and PLA/PCL blend.

	1 st heating ramp					2 nd heating ramp				
	ΔH_{cc} (J/g)	ΔH_m (J/g)	χ_{cc} (%)	$\chi_m - \chi_{cc}$ (%)	χ_m (%)	ΔH_{cc} (J/g)	ΔH_m (J/g)	χ_{cc} (%)	$\chi_m - \chi_{cc}$ (%)	χ_m (%)
PLA 4032 “moulded” <i>Protocol II</i>	14.83	22.35	15.9	8.1	24.0	0	0	0	0	0
PCL “moulded” <i>Protocol II</i>	-	58.0	-	-	42.9	-	50.8	-	-	37.5
PLA/PCL “moulded” <i>Protocol II</i>	4.12	PLA/PCL 10.5/11.3	6.3(*)	9.8(*)	16.1(*)	2.7	PLA/PCL 3.25/7.7	0.8(*)	4.2(*)	5.0(*)

(*) Percentages of crystallinity corresponding to the PLA matrix.

Figure captions

Figure 1. (A) DTG and (B) DTA curves for “fresh” neat polymers and PLA/PCL blend.

Figure 2. (A) First and (B) second heating scans, at 10 °C/min, for “fresh” pure.

Figure 3. (A) First and (B) second heating scans, at 10 °C/min, for “moulded” PLA 4032 and PCL samples, and “moulded” PLA/PCL blend.

Figure 4. Polarized light micrographs of: A) “moulded” PLA 4032; B) PLA 4032 annealed at 120 °C for 30 min. C) “moulded” PLA/PCL blend; and D) PLA/PCL annealed at 120 °C for 30 min.

Figure 5. DMTA curves, in bending mode at 1 °C/min, for four selected samples: “moulded” PLA 2002, PLA 4032 and PLA/PCL blend, and “annealed” PLA/PCL blend.

Figure 6. Frequency sweep tests, in bending mode, at 30-60-80 °C, for “moulded” and “annealed” PLA 4032 samples.

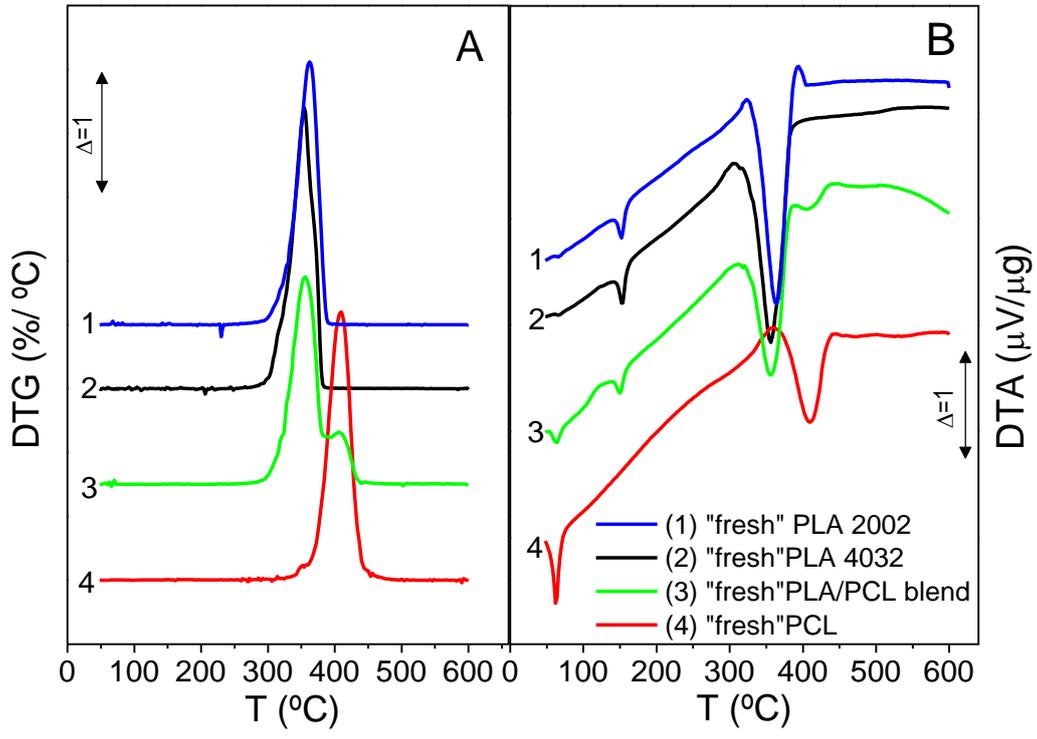


Figure 1.

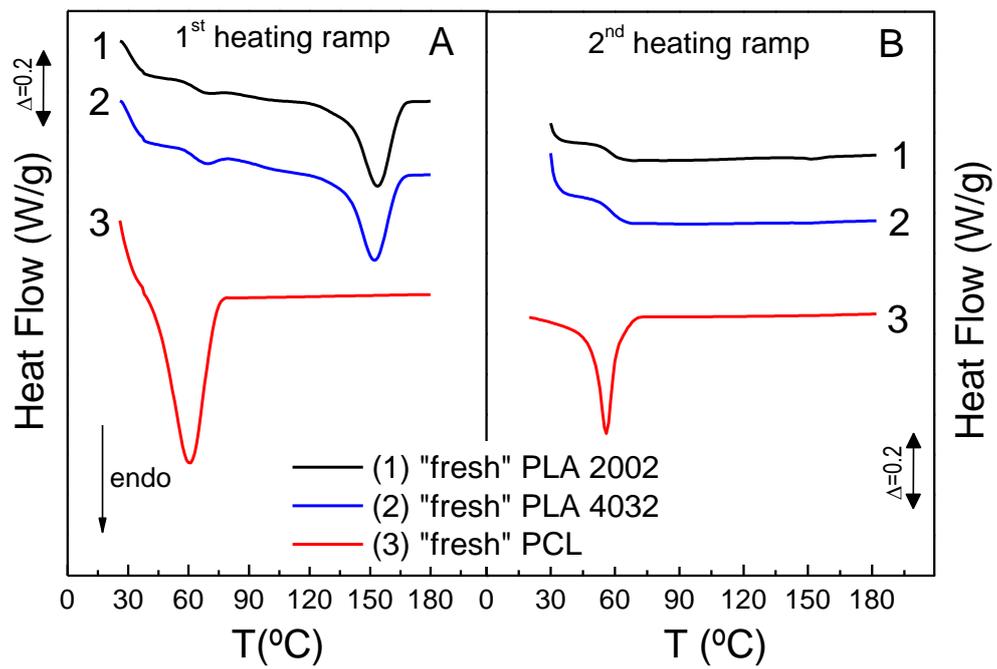


Figure 2.

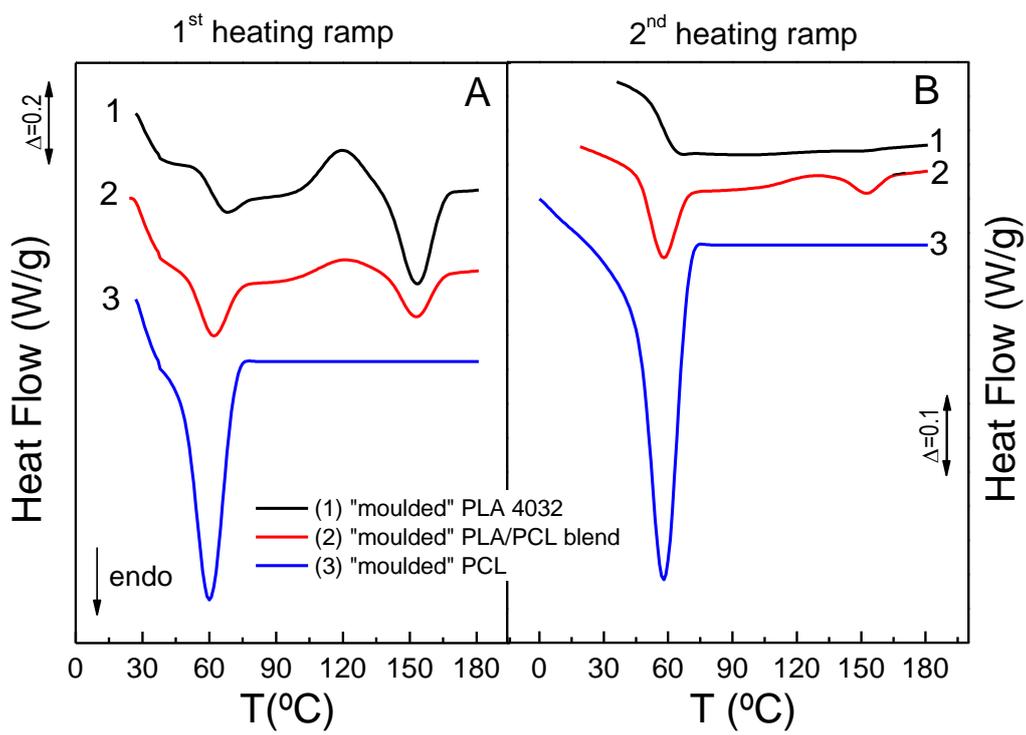


Figure 3.

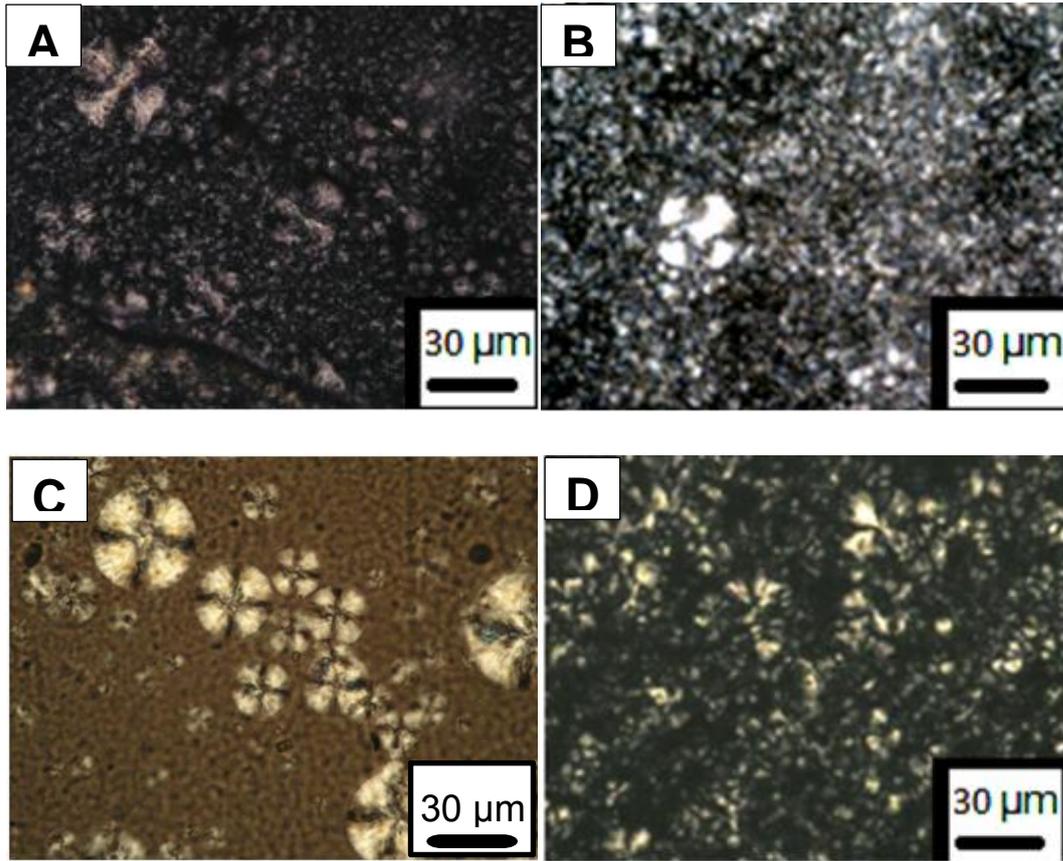


Figure 4.

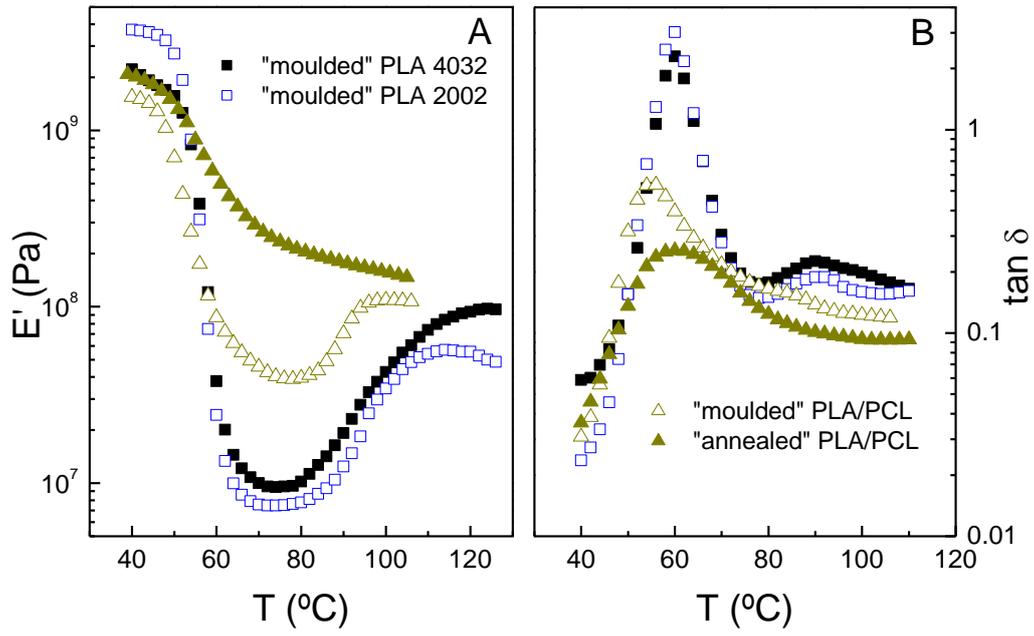


Figure 5.

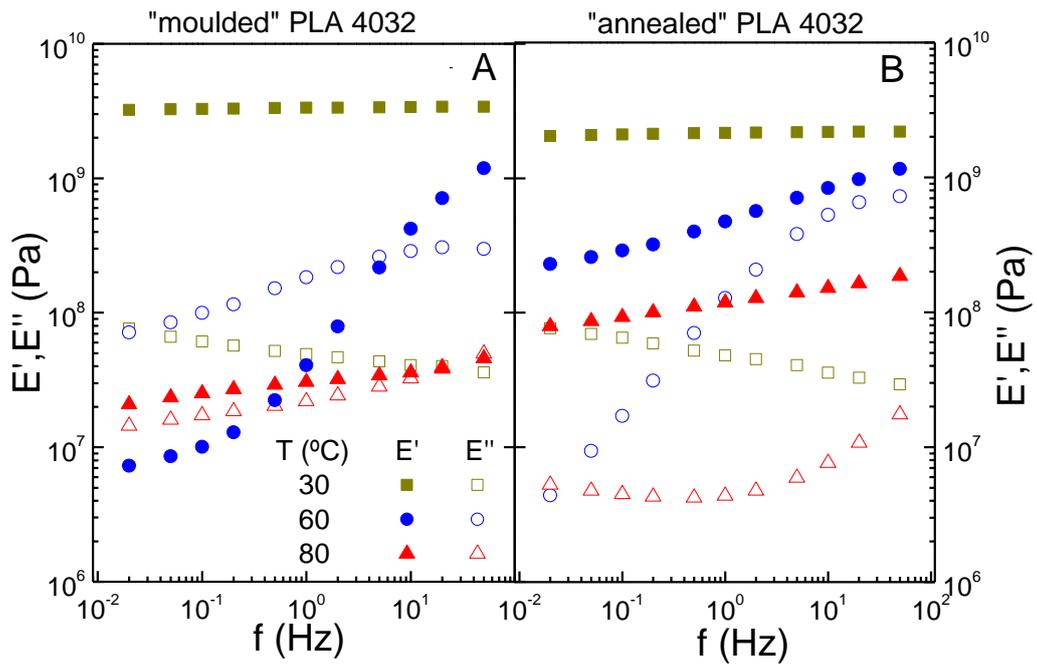


Figure 6.