

Biodegradable materials from grafting of modified PLA onto starch nanocrystals

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ABSTRACT

PLA was grafted onto starch nanoparticles using a novel synthetic strategy consisting of three reaction steps. The first step was aimed to protect the hydroxyl groups of PLA by benzylation (PLABz), the second one involved the activation of carboxyl groups using thionyl chloride and the last reaction was the grafting of the modified PLA onto the starch nanoparticles (PLASTARCH). The thermal behavior of the composite obtained by this method was very different from that displayed by the physical mixture of PLA and the starch nanoparticles (PLA-NC blend). The benzylation step that leads to PLABz produces an increase of the molecular mobility, resulting in lower glass transition temperature, T_g , than that of the original PLA; a change that was observed in the DSC thermograms of the samples. On the other hand, the T_g of the PLASTARCH was similar to that of the PLA as a consequence of two opposite effects acting simultaneously: a free volume increase due to the presence of benzoyl groups and a confinement of the polymer chain, originating from the grafting onto NC. The material obtained by chemical modification (PLASTARCH) has a degradation temperature slightly lower than that of PLA, which does not affect its potential use in the packaging industry.

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1. Introduction

The diminishing fossil resources and the consequently increasingly higher costs have generated numerous initiatives aimed at replacing these sources by renewable ones. Poly (lactic acid) (PLA) is a biodegradable, thermoplastic polymer, available from annually renewable sources and thus, an ideal candidate to replace some petroleum derivatives [1–3]. In the last years, PLA and their copolymers have become materials of large interest in biomedical and pharmaceutical applications [4]. Additionally, PLA can be used in packaging applications due to its processability by standard melt processes such as injection molding, film blowing or melt spinning [5–7].

On the other hand, starch is a cheap, abundant, renewable and biodegradable biopolymer. In particular, starch nanoparticles or nanocrystals can be obtained that have many potential applications, such as plastic fillers, food additives, drug carriers, implant materials, fillers in biodegradable composites, coating binders, adhesives, etc. [8]. Starch nanoparticles also have a great potential

for use in papermaking wet end, surface sizing, coating and paperboard as part of biodegradable adhesives for substitution of petroleum based ones. In previous works, the production and characterization of starch nanoparticles have been reported in relation to their interesting performance as reinforcing agents [8,9].

Starch-PLA composites seem to be a most promising combination for starch-based packaging, but PLA and starch are thermodynamically immiscible [10,11] and thus, compatibility problems must be solved first in order to obtain competitive materials. Although in the last years, there have been some reports on blends of these polymers [12,13], the chemical grafting is a new and better alternative to overcome the incompatibility problems between starch and PLA.

The aim of this work was the development of new biodegradable materials with high thermal stability to be used in packaging. To accomplish this goal, we used a strategic synthetic pathway not reported before, which consists of three reaction steps to modify PLA, and further allowing an appropriate grafting of PLA onto the surface of starch nanocrystals (NC). PLA was subjected to the following modifications. The first reaction was carried out to protect the PLA hydroxyl groups with benzoyl chloride and a new material was obtained (PLABz). The second one was performed to activate the terminal carboxylic acid by treatment with thionyl

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chloride (PLAM). Then, the PLASTARCH was obtained by grafting PLAM onto (NC). The evolution of the reactions was studied by infrared spectroscopy, which confirmed the success of each step. The grafting was investigated by TGA, FTIR and DSC. Furthermore, large differences were observed between the material consisting of a physical mixture of PLA and NC (PLA-NC blend) and that obtained by chemical modification (PLASTARCH).

2. Experimental

2.1. Materials

Waxy maize starch (N-200) was kindly provided as white powder by Roquette Frères S.A. (Lestrem, France). PLA pellets (90% L-LA, 10% D-LA; $M_n = 49860$ g/mol determined by SEC) were manufactured by Shenzhen Bright China Industrial Co., Ltd (Wuhan, China). All the reagents: benzoyl chloride, pyridine, thionyl chloride and solvents were obtained from commercial suppliers (Aldrich Co). They were used without further purification.

2.2. Procedure

2.2.1. Preparation of starch nanocrystals (NC)

Waxy maize starch nanocrystals were obtained according to a previously described method [8,9]. Briefly, acidic hydrolysis of 36.725 g of waxy maize starch granules was performed in a 250 ml 3.16 M H_2SO_4 solution, at 40 °C and 100 rpm. The mixture was subjected to an orbital shaking action during 5 days. Subsequently, the ensuing insoluble residue was washed with distilled water and separated by successive centrifugations at 10,000 rpm and 5 °C, until neutrality. The aqueous suspensions of starch nanoparticles were stored at 4 °C after adding several drops of chloroform. Finally, the NC were lyophilized and stored so until further use.

2.2.2. PLA modification and grafting onto starch nanocrystals

The synthetic pathway applied involves three reactions. The first reaction consists of the protection of PLA hydroxyl groups by

benzylation to obtain PLABz. The second one is the activation of PLABz carboxyl groups, and in the third one, the resulting product is used immediately in the last reaction, which is the grafting of the modified chains onto the starch nanoparticles. In all the cases, the reaction mixture was sonicated with the washing solvent during 10 min before filtration and centrifugation. At the end of each reaction step, the washing procedure was repeated several times, until no reactive was observed in the discarded liquid. In Fig. 1 the synthetic route applied to obtain PLASTARCH is shown.

2.2.2.1. Synthesis of PLABz by protection of hydroxyl PLA groups (reaction 1). In a first step the hydroxyl groups of PLA were protected by benzylation. For this purpose, PLA (5 g) and chloroform (28 mL) were placed into a three-neck flask; 30 mL of toluene were incorporated and the mixture was heated at 45 °C under constant stirring until complete dissolution. The benzylation was carried out with benzoyl chloride (0.3 mL) and pyridine (0.3 mL) at room temperature during 24 h. Then, distilled water was added to induce the precipitation. The mixture was filtered and removal of unreacted chemicals was performed by repeated washing of the products with hot water under sonication (10 min) followed by filtering, until the residual water was completely clean.

The product, PLABz, was left at room temperature for 24 h and then dried in a vacuum oven until further use.

2.2.2.2. Synthesis of PLAM by activation of carboxyl groups of PLABz (reaction 2). In order to activate carboxyl groups, PLABz (3.824 g) was dissolved in 60 mL of a mixture of CH_2Cl_2 and toluene (50% v/v), at 70 °C, in a three-neck flask and thionyl chloride (0.2 mL) was added. Then, 0.5 mL of triethylamine (TEA) was used to neutralize the reaction mixture under constant stirring during 3 h. The product obtained was named PLAM and it was used without further purification.

2.2.2.3. Synthesis of PLASTARCH by grafting PLAM on NC (reaction 3). A given amount of NC (0.21 g, or 5.2 wt%), previously sonicated in toluene (10 mL, for 10 min), was added to PLAM to

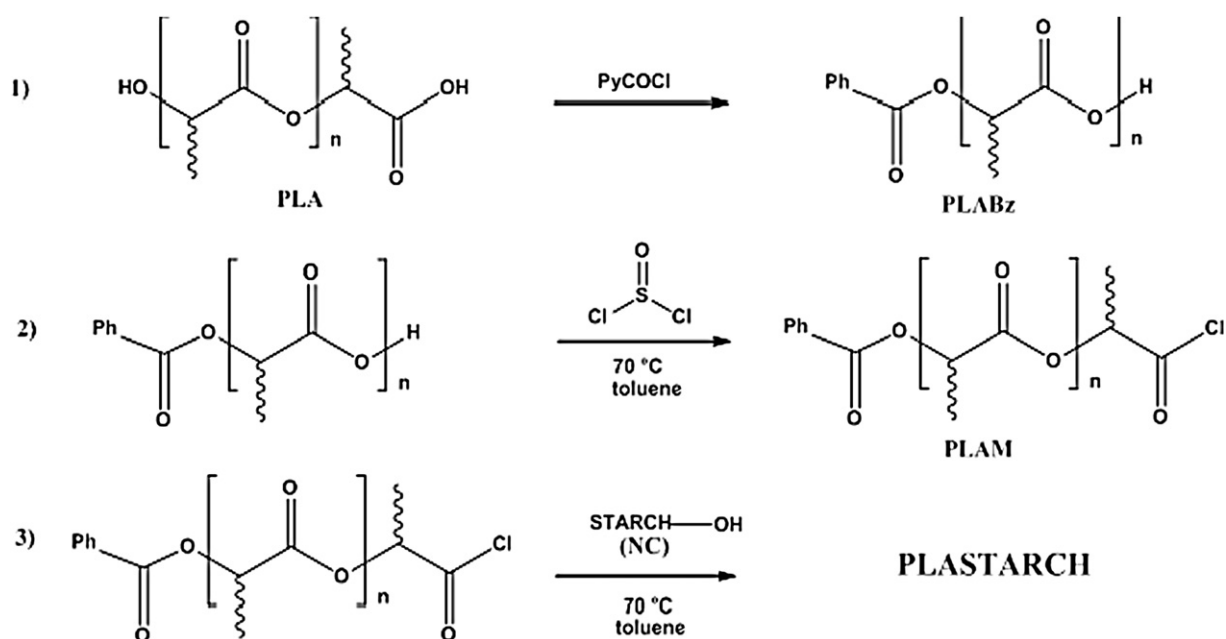


Fig. 1. Synthetic route to obtain PLASTARCH.

perform the esterification reaction. The evolution of the reaction (Fig. 1) was followed by FTIR analysis. After 3 days, distilled water was used to stop the esterification reaction. Then, the precipitate was washed with ethanol several times and finally, this solid was centrifugated with methyl ethyl ketone four times (3000 rpm, 15 min) until NC were not observed in the supernatant. The solid obtained (PLASTARCH) was left at room temperature for 24 h, dried in a vacuum oven and stored under vacuum until further use. To estimate the NC content of PLASTARCH, the successive washing liquids were collected and analyzed, finding 0.08 g of NC. From this data, the content of NC in the PLASTARCH was estimated as 3.2 wt%.

Fig. 2 shows the results of SEC experiments for the different samples, PLA, PLABz, PLAM and PLASTARCH. A slight decrease of the molecular weight can be observed due to the benzoylation step. It is related to the change of the coil size because of the increased free volume produced by the modification of PLA (increased flexibility of the chain).

2.2.3. Preparation of blends

Physical blends were prepared by mixing PLA powder with 3.2 wt% NC to obtain a visually homogeneous material. It was used to evaluate the differences between the physical mixture and PLASTARCH obtained from the chemical modification.

2.3. Characterization and measurements

Infrared spectra were recorded on a Nicolet FTIR Instrument 510P from 400 to 4000 cm^{-1} . For this purpose, the solid polymer was mixed with KBr powder and pressed to prepare thin pellets.

Molecular weight distributions were measured by SEC using a Styragel column (HR-4) from Waters, with THF as solvent at a flow rate of 1.0 mL/min. Number- and weight-average molecular weights were calculated using a universal calibration method using PS standards.

Thermal analyses were performed at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere. DSC measurements were performed on a Q20 TA Instrument calibrated with indium. In all cases, two heating scans were performed, with an intermediated cooling step performed at a rate of 50 $^{\circ}\text{C}/\text{min}$. From the DSC thermograms (second heating scans), the glass transition temperature (T_g) was determined as the inflection point of the transition region. The crystallization temperature (T_c) and melting temperature (T_m) were obtained as the values of the temperature at the maxima of the peaks related to those thermal events.

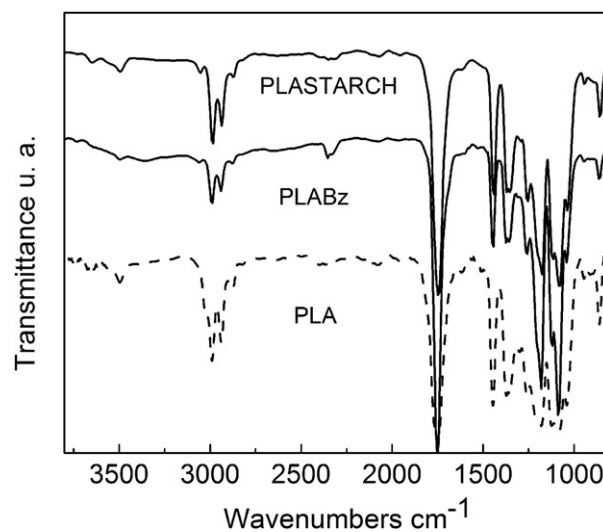


Fig. 3. FTIR spectrum of the PLA, PLABz, and PLASTARCH.

Thermal analyses curves were obtained using a TGA-60 Shimadzu thermogravimetric analyzer under 40 ml/min of nitrogen flux rate.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FTIR)

In Fig. 3 the FTIR spectra of PLA, PLABz and PLASTARCH are shown. All the spectra show a band at 1750 cm^{-1} , which can be attributed to C=O of the ester groups. The FTIR spectrum of PLA has a small and broad signal at 3400 cm^{-1} corresponding to hydroxyl groups of the carboxyl function. In addition, small peaks also appear above 3500 cm^{-1} , which are due to the stretching of hydroxyl groups. These signals (hydroxyl stretching) do not appear in the PLABz spectrum, as a consequence of the benzoylation reaction. However, the broad band corresponding to the hydroxyl stretching in carboxyl groups is similar to that in the spectrum of the original PLA. Meanwhile, the broad signals (around 3500 cm^{-1}) are absent in the FTIR spectrum of the final composite, due to the ester formation between of PLABz and NC.

3.2. Differential scanning calorimetry (DSC)

Fig. 4a shows the DSC thermograms (first heating scan) for the PLA, PLA-NC blend, PLABz and PLASTARCH while Fig. 4b shows the

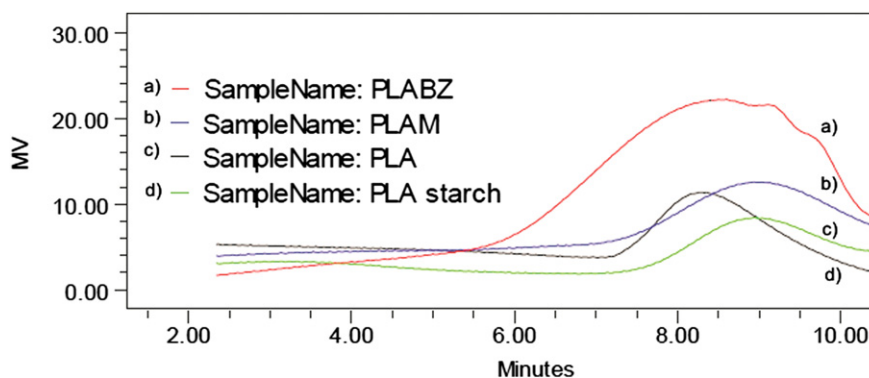


Fig. 2. SEC of PLA, PLABz, PLAM, and PLASTARCH.

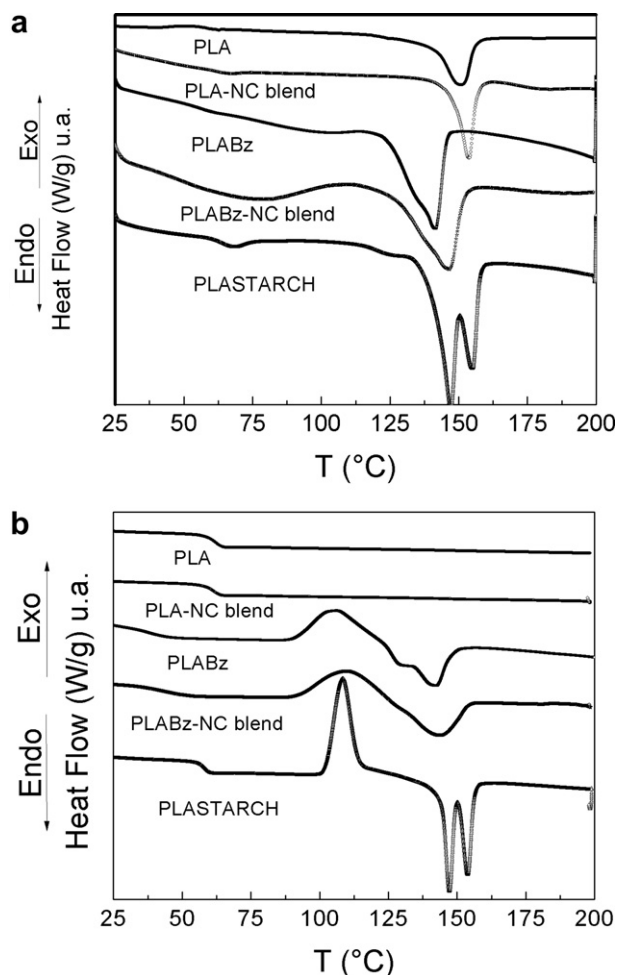


Fig. 4. DSC thermograms: a) first heating scan, b) Second heating scan.

second heating scan. Clear differences can be seen between the first scans of the samples (Fig. 4a). While the thermograms of the PLA and PLA-NC blend samples show only one endothermic peak, associated with the melting transition, PLABz shows a broader melting peak, which appears to be the result of two superimposed endothermic peaks, suggesting that the incorporation of benzoyl groups leads to important changes in the way that PLA chains are arranged.

A very different thermal response to that of the physical mixture (PLA-NC blend) was observed for the sample obtained from the grafted starch (PLASTARCH). Note that, in this case, two endothermic peaks appear which are associated to the melting of two different crystalline arrangements. These results suggest that the NC plays a very different role depending on whether they are chemically attached to PLA or not.

In view of these results we tried to evaluate if the difference between PLA-NC blend and PLASTARCH was only due to the introduction of benzoyl group or was a consequence of both the incorporation of this group as well as the final grafting to NC. In order to evaluate the influence of these effects a new physical mixture between PLABz and 3.2 wt% of NC was prepared. This material was called PLABz-NC blend. The thermogram obtained during the first scan for PLABz-NC blend was added in Fig. 4a, while the one corresponding to the second heating scan is shown in Fig. 4b.

Fig. 4a shows that the only difference between PLABz-NC blend and PLABz is a slight shift toward higher values of the melting peak

temperature. Similar effect can be seen when comparing PLA-NC blend with PLA. This result suggests that there is a physical interaction between both components of the mixture.

Comparing the thermograms obtained during the first and the second heating scan (Fig. 4a and b), it is interesting to notice that while the thermal response of the PLA and PLA-NC blend evidenced extensive structural differences (PLA amorphization due to its slow crystallization kinetics during the fast cooling rate used in this work [7]), the thermograms of the chemically modified materials still show a melting peak during the second heating scan. The chemical modification of PLA with the benzoyl group increases the local free volume, increasing the molecular mobility of the PLA chains allowing the re-crystallization of the material (clearly seen in the second heating scan, Fig. 4b). This assumption is supported by large changes observed in the glass transition zone. From Fig. 4b it can be seen that PLA and PLA-NC blend show well-defined glass–rubber transition zones, with T_g values around 62 °C. On the other hand, the second heating scans for the PLABz and PLABz-NC blend display very wide glass–rubber transitions, with T_g values around 40 °C and 45 °C, respectively. This means that the chemical modification significantly increases the free volume facilitating the movement of the PLA chains and causing a large increase in the number of relaxation mechanisms that are active during the glass transition.

Fig. 4b also shows that in the case of PLASTARCH, the temperature range where the glass transition occurs is much narrower than that of the PLABz, and its T_g increases considerably compared with the corresponding values for PLABz or PLABz-NC blend (PLASTARCH $T_g = 59$ °C). This indicates that the chemical bonding between NC and PLABz induces a confinement of the polymer hindering the molecular mobility of PLABz chains and generating the opposite effect to the one produced by increasing the free volume due to benzylation.

Besides affecting the T_g , the increased molecular mobility favors the re-crystallization of the material. This is observed for the PLABz and the PLABz-NC blend as an exothermic re-crystallization peak and an endothermic one corresponding to the melting (Fig. 4b). The last peak is broad and appears to have an overlapped small second endothermic peak, which is more notorious than in the thermogram of the first heating scan, and especially so in the curve of the blend (Fig. 4a).

Martin and Averous [7] reported the presence of two melting peaks in PLA plasticized with 20% and 10% of oligomeric lactic acid. According to these authors the addition of a plasticizer to the PLA induces crystallization and thus, fusion. Typically, the plasticizers can promote crystallinity due to the enhanced chain mobility. In our case, this increase in the chain mobility is generated by the attached benzoyl group, which induces new conformational arrangements in its surroundings.

The fact that the NC are chemically bound to PLA not only affects the amorphous component, which is reflected by changes in T_g , but also strongly affects re-crystallization. Thermograms in Fig. 4b show that the re-crystallization of PLABz and PLABz-NC blend occurs in a wide temperature range, while PLASTARCH re-crystallization occurs in a narrower temperature range, suggesting that the NC chemically attached to PLABz acts as a nucleating agent for PLABz during the crystallization.

Moreover, while in the second heating scan of PLABz and PLABz-NC blend, the melting appears as a wide event that results from the overlapping of a large peak and a smaller one, two very well-defined endothermic peaks appear for the PLASTARCH, indicating that there are two clearly different crystalline forms. In addition, the widths of these two peaks are much narrower than in the case of PLABz or PLABz-NC blend, which suggests the formation of crystals with more uniform sizes in PLASTARCH as compared to those formed in the other two cases.

Jimenez et al. [14] studied the crystallization of polycaprolactone/clay composites and reported that the crystallization was governed by two processes, diffusion and nucleation. The results of Fig. 4b clearly indicate that the presence of the benzoyl group in the PLA modifies its ability to crystallize and is strongly affected by the addition of NC only when these are chemically bound to PLA.

3.3. Thermogravimetric analysis (TGA)

Fig. 5 shows the thermal analyse (TGA) results for PLA, NC, PLA-NC blend, PLABz and the final product, PLASTARCH. The original PLA degrades in a single stage within a narrow temperature range (307–377 °C) with a maximum degradation rate at 358 °C, in agreement with literature reports. The TGA curve of the NC shows multiple degradation steps, one below 100 °C and two more with maximum loss rates at 233 and 350 °C. The first step corresponds to the loss of water because of the hydrophilic character of starch. The second step is due to the initial decomposition of nanocrystals through its hydroxyl groups, and the third step corresponds to the degradation of the partially decomposed starch [9].

The physical mixture (PLA-NC blend) has its main degradation located at the same temperature as the unmodified PLA. The content of NC corresponds to 3.2 wt%, a very small concentration that would produce a minimum change with respect to the PLA response if no interactions between PLA and NC were present in the blend. However, the TGA curve of the blend differs considerably from that of the PLA. The degradation begins at lower temperature than for PLA, but the residual char is higher. The experimental curve can be very well predicted from the weighed curves of the PLA and the NC, using a mixing rule, but the NC content should be taken equal to 21 wt%, clearly a concentration much higher than the experimental one. This result indicates a strong physical interaction between the NC and PLA. It is well known that in the thermal behavior of a composite, the interface plays an important role. That is, the application of a mixing rule is only a first approximation and is inappropriate in the present case.

The presence of NC reduces the onset of thermal degradation as a consequence of the higher content of hydroxyl groups, which can be hydrogen bonded to PLA. On the other hand, the increase of the char at 500 °C indicates that the fraction of PLA that interacts with NC is also involved in the formation of the residue. Additionally, the

NC may contain some sulfate groups due to the initial acid hydrolysis treatment (small signal at 1080 cm^{-1} in NC FTIR spectrum), which could lead to a higher char.

The analysis of the PLABz degradation curve (Fig. 5) shows a first degradation step in the 100–280 °C range (maximum at 137 °C) that is explained by the scission of free end carboxylic groups that are lost as CO_2 , as it has been described for other polymers with carboxylic groups [15]. There is another degradation step between 280 and 370 °C (maximum at 355 °C), which corresponds to the degradation of PLA, mainly due to ester scission.

The lower thermal stability of this intermediate product is the result of the reduced interactions between carboxylic and hydroxyl groups, since the last ones are blocked, after the reaction.

As the PLABz reacts with the starch NC producing ester groups, the degradation step at 100–280 °C related to the CO_2 formation disappears; the onset of the PLASTARCH degradation is shifted to much higher temperatures, closer to that of unmodified PLA. The results of the degradation study clearly support the success of the last step of PLA-starch reaction. The degradation step for PLASTARCH occurs between 278 and 366 °C with a maximum rate at 353 °C. The DSC results already discussed, showed crystallinity changes between PLASTARCH and PLA. In the first DSC scan, the PLA melting enthalpy is similar to the sum of the two melting enthalpies of PLASTARCH, but in the second DSC scan, PLA suffers an amorphization while the PLASTARCH continues having a crystalline component. The results are in agreement with the observations of other authors [16] on blends of PLA and a polyester amide. They found a strong effect of the crystallinity of the sample on the TGA results, and a reduction of the degradation onset as the concentration of polyester amide increased due to the interactions developed between the polymers, which affected the PLA crystallinity. Because of the good compatibility of the blend, they also found single stage decomposition at low concentrations of the polyester amide. In the present case, starch chemically bound to the PLA, introduced changes in its crystallization, and due to the strong interactions the decomposition still occurs in one stage with a lower onset than for the unmodified PLA.

Additionally, the TGA curve for PLASTARCH shows a char at 500 °C higher than the chars obtained in the degradation of PLA, but also higher than that of the physical mixture (PLA-NC blend), which is another indication of covalent functionalization.

4. Conclusions

A new and reproducible methodology of grafting PLA onto NC was successfully developed. By mean of FTIR analysis, the PLA chemical modification as well as PLABz grafting onto NC were confirmed. The benzoylation in PLABz generates an increase of molecular mobility leading to a T_g value lower than that of the PLA, as it was shown from DSC thermograms. The T_g of PLASTARCH is similar to that of PLA, as a consequence of two opposite effects that act simultaneously: a free volume increment due to the presence of benzoyl groups and a confinement of the polymer chain, induced by the grafting onto NC. Besides, it can be concluded that PLASTARCH has a very different thermal response from that of the physical mixture. In particular, it was demonstrated that the presence of the benzoyl group in the PLA modifies its ability for crystallizing, and this process is strongly affected by the addition of NC only when these are chemically bound to PLA. The material obtained by chemical modification (PLASTARCH) has a degradation temperature slightly lower than that of PLA, although remaining high so that it does not affect its potential use in packaging.

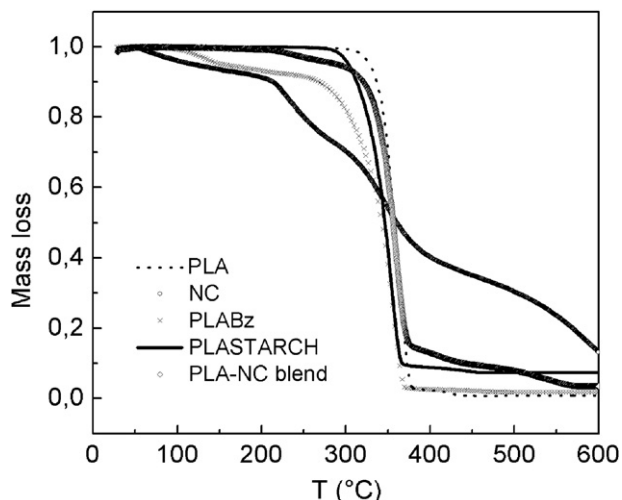


Fig. 5. Thermograms of PLA, NP, PLABz, PLASTARCH and PLA-NC blend.

Acknowledgements

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