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THE FOLLOWING ARTICLE:**

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Polymer Engineering and Science  
Volume 57, Issue 3, 1 March 2017, Pages 306-311  
DOI: 10.1002/pen.24414

**WHICH HAS BEEN PUBLISHED IN FINAL FORM AT**  
<https://onlinelibrary.wiley.com/doi/abs/10.1002/pen.24414>

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**Effect of molding conditions on crystallization kinetics and mechanical properties of Poly(lactic acid)**

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**Abstract**

Although Polylactic acid (PLA) possesses many desirable properties, above all biodegradability, its heat deflection temperature is too low for many desirable applications. Similarly to any other polymers, also for PLA the physical and mechanical properties in the solid state depend on the morphology and crystallinity degree, which in their turn are determined by the thermomechanical history experienced during solidification. A large crystallinity degree is highly desirable to increase the heat resistance of PLA but is rather difficult to reach during injection molding due to the very slow crystallization kinetics of this material. In this work, the crystallization kinetics of an injection molded PLA grade was assessed in function of the thermal history by using calorimetric analysis. The cold crystallization kinetics (starting from the amorphous glassy sample) turned out to be faster than melt crystallization kinetics. Following the indications gained from crystallization kinetics, some samples were injection molded imposing different thermal histories. The effect of molding conditions on crystallinity was determined. This finding was adopted to develop a post-molding stage which allows obtaining crystalline samples in times much shorter (of a factor about two) with respect to samples injection molded in a hot mold kept at temperatures close to the maximum crystallization rate.

The effect of molding conditions on crystallinity was determined to develop a post-molding stage obtaining crystalline samples in times much shorter with respect to samples injection molded in a hot mold.

**Keywords**

polyesters; mechanical properties; injection molding; crystallization; biopolymers.

## INTRODUCTION

Physical, thermal and mechanical properties of thermoplastic polymers are strongly dependent on the crystalline structure and morphology. For this reason, crystallization is a major research interest in the field of polymer physics. The growing environmental awareness in the recent decades has allowed the widening of the researchers interest to the crystallization behavior of biodegradable polymers. Poly(lactic) acid is one of the more versatile bio-based polymers synthesized from renewable resources, with high stiffness and strength, that has received much attention in the research of alternative biodegradable polymers [1-5]. However, its remarkably low glass transition temperature (lower than 60 °C), and the consequent low heat deflection temperature makes it inadequate for many applications [6].

A possibility to improve chemical and thermal resistance of the PLA is to increase the polymer overall crystallinity [7, 8]. Harris and Lee [9] evaluated the effect of crystallinity on the mechanical performance of PLA samples showing that an increase of crystallinity can effectively increase the heat deflection temperature. For this reason, researchers attention was focused on the study of the crystallization kinetics of PLA [10-13]. Pantani et al. in 2010 [14] stressed the significance of the melt processing on the crystallization kinetics: melt processing can induce a reduction in molecular weight due to mechanical and thermal degradation and this can enhance crystallization kinetics. Furthermore, crystallization kinetic of PLA is strongly influenced by the previous thermal history. Sanchez et al. [15] and Pantani et al. [14] demonstrated that there is a significant difference between melt crystallization and cold crystallization of PLA. In a previous work [16] the crystallization kinetics constants of PLA for melt and cold isothermal crystallization at different temperatures was evaluated by means of differential scanning calorimetry. Already some papers in literature discussed the relationship between molding conditions and crystallization of PLA. Tábi et al. [17] focused on the effect of crystalline structure on the processing by injection molding. Harris and Lee also [9] studied how to improve the mechanical performance of injection molded PLA by controlling crystallinity.

In this work, the crystallization kinetics in glassy solid and molten samples were studied using DSC analysis. PLA samples were prepared by injection molding imposing different thermal histories. The effect of molding conditions on crystallinity, mechanical properties and thermal resistance of molded samples were examined.

## EXPERIMENTAL

### *Polylactic acid*

The material adopted in this work is a commercial grade Polylactic acid (PLA) produced by Natureworks with the trade name 2002D [18, 19] comprising D% comonomer of up to  $4.25 \pm 0.55\%$  [20]. The glass transition temperature ( $T_g$ ) and the melting point temperature ( $T_m$ ) of PLA 2002D are 58 °C and 153 °C, respectively [8]. The average molecular weight and polydispersity of the neat resin are  $215 \times 10^3 \text{ g mol}^{-1}$  and 1.9 [21], respectively. Before any test or processing, the material was dried for 24 h under vacuum at the temperature of 60 °C.

As mentioned above, the crystallization kinetics of PLA strongly depends on the thermomechanical history followed by the material, because of the degradation experienced by the material in the molten state [22-25]. The analysis of crystallization kinetics and mechanical properties were consequently conducted on samples taken from injection molded specimens.

### *Differential scanning calorimetry (DSC)*

A differential scanning calorimeter DSC 822e from Mettler Toledo Inc. was used for determination and measurement of the thermal behavior of molded PLA. The calibration of the temperature was done with the extrapolated onset temperature of the phase transition of indium. The samples, obtained from injection molded specimens, with a weight of about 10 mg were put into an aluminum pan and hermetically sealed. All the experiments were conducted in nitrogen, flow rate  $50 \text{ ml min}^{-1}$ , in order to prevent oxidative degradation at high temperature. The protocols adopted to characterize the crystallization kinetics are reported in Fig. 1a and Fig. 1b.

The crystallization kinetics was investigated starting from both the melt and the glassy amorphous material. Both conditions were obtained after holding the sample at 200 °C for 5 min in order to erase the effect of previous thermomechanical history. Preliminary tests were performed and the “couple” 200 °C for 5 min was selected as standard procedure to obtain an amorphous disordered melt, without thermal degradation [16].

The cooling and the heating rate were previously checked to be suitable, i.e. preventing any crystallization phenomena during temperature change before reaching the isothermal test temperature. For example cooling and heating at  $10 \text{ K min}^{-1}$  the initial amorphous sample does not show any peak related to crystallization [16].

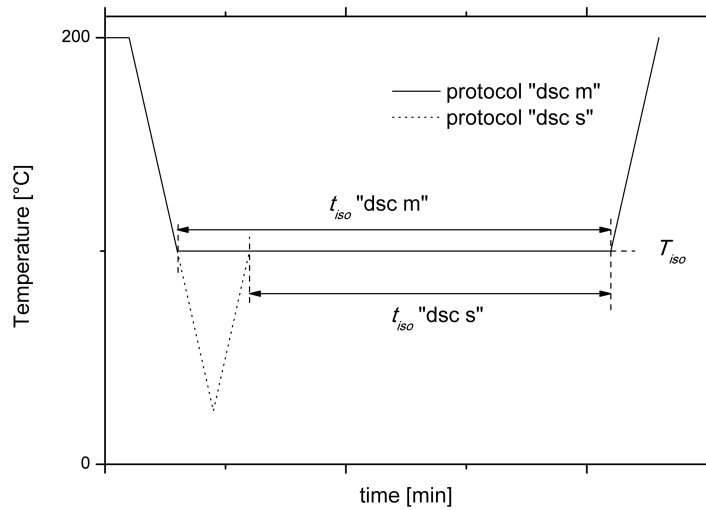
The experimental protocol followed to investigate the isothermal crystallization kinetics for samples cooled from the melt (protocol "dsc m") is showed in the left plot in Fig. 1, and described in the following:

- the sample was kept at 200 °C for 5 min and then cooled at the rate of  $10 \text{ K min}^{-1}$  to the chosen crystallization temperature,  $T_{iso}$

- at  $T_{iso}$  the sample was kept for a given time,  $t_{iso}$
- after this isothermal step, the sample was heated at the rate of  $10 \text{ K min}^{-1}$  to  $200 \text{ °C}$ .

The experimental protocol followed to investigate the isothermal crystallization kinetics for samples heated from the solid [16, 26] (protocol "dsc s") is showed in the right plot in Fig. 1, and described in the following:

- the sample was kept at  $200 \text{ °C}$  for 5 min and then cooled at the rate of  $10 \text{ K min}^{-1}$  to  $25 \text{ °C}$
- then it was immediately heated at the rate of  $10 \text{ K min}^{-1}$  to the chosen crystallization temperature,  $T_{iso}$
- at  $T_{iso}$  the sample was kept for a given time,  $t_{iso}$
- after this isothermal step, the sample was heated at the rate of  $10 \text{ K min}^{-1}$  to  $200 \text{ °C}$ .



**Figure 1.** Experimental protocol followed to investigate the isothermal crystallization kinetics for samples cooled from the melt, with protocol "dsc m", and from the solid, with protocol "dsc s".

The results of the isothermal step at  $T_{iso}$ , from the molten and the glassy state, according to the protocols in Fig. 1, show that crystallization develops, at the maximum of crystallization rate, very slowly, as previously evaluated on the virgin neat material [16] on a time scale of the order of 10000 s.

For this reason, the relative crystallinity degree was calculated by dividing the heat absorbed,  $\Delta H(t_{iso})$ , during subsequent heating ramp at the rate of  $10 \text{ K min}^{-1}$  to  $200 \text{ °C}$ , after a linear baseline subtraction, by the latent heat of a sample that has crystallized at the maximum possible value for that condition,  $\Delta H_{max}$ .

In a similar way, differential scanning calorimetry was also used to determine the relative crystallinity degree of injection molded parts, with different thermal histories, with a simple heating ramp at the rate of 10 K min<sup>-1</sup> to 200 °C and evaluating the related melting enthalpy.

### *Injection molding*

The injection molding machine, Haake MiniJet II by Thermo Scientific, is not a conventional processing device. This equipment has a pneumatic piston that pushes the material from the hot cylinder to the mold for the production of test specimens of few grams. All processing parameters such as temperature (separate for injection cylinder and mold), injection pressure and duration, and post-pressure can be controlled. Management of the post-pressure during sample creation enables optimum compensation for material shrinkage due to the cooling of the sample. In Table 1, the processing conditions adopted to obtain rectangular bars (with length of 60 mm, width of 10 mm, and thickness of 1 mm) for further characterizations are summarized.

The samples adopted for the characterization of the crystallization kinetics were injection molded in a mold at 25 °C. These samples resulted being completely amorphous, due to high cooling rate during solidification.

TABLE 1. Processing conditions for the injection molding of rectangular bars

Injection temperature [°C]	200
Injection pressure [bar]	600
Injection time [s]	10
Mold Temperature [°C]	25 or 105

In order to mimic the experimental protocols used in calorimetric analysis from the glassy and melt amorphous sample, showed in Fig. 1, two protocols were adopted.

According to the first protocol, the samples previously molded with a mold temperature of 25 °C were closed in the same mold but kept at 105 °C and kept in those conditions for a given time. The mold was then cooled so that the sample reached ambient temperature in about 60 s. Since this protocol allows crystallization from the solid glassy state, it will be referred to as "molding s".

According to the other protocol, some samples were injection molded directly in a mold at the temperature of 105 °C and kept inside the mold for a given time. The mold was then cooled so that the sample reached ambient temperature in about 60 s. Since this protocol allows crystallization from the molten state, it will be referred to as "molding m".

In both the protocols "molding m" and "molding s", the temperature of 105 °C was selected since, according to the results of the analysis of crystallization kinetics (reported in the following), it is the temperature at which the material presents the maximum crystallization kinetic rate constant when cooled from the melt.

### 2.4 Dynamic mechanical thermal analysis

The dynamic mechanical thermal analysis was carried out in the tensile mode using a DMTAQ800 (TA Instruments) with a strain of 0.8%, a frequency of 1 Hz and a heating rate of 2 K min<sup>-1</sup> in the range 0-140 °C. Results will be given in terms of storage modulus ( $E'$ ) and loss tangent  $\tan(\delta)=E''/E'$ ,  $E''$  being the loss modulus.

## 3 Results and Discussion

### 3.1 Crystallization kinetics

The isothermal crystallization kinetics for samples cooled from the melt and the solid was investigated by the two different protocols, "dsc m" and "dsc s", described in the previous section. For both protocols, the heat absorbed by the sample during the heating stage following the isothermal step was analyzed. In previous works [14, 16], the crystallization kinetic rate constants for melt and cold isothermal crystallization were evaluated starting from the neat material in the form of a pellet. In this present work, crystallization kinetic was investigated starting from molded samples.

It is worth mentioning that during cooling at 10 K min<sup>-1</sup> the sample remains fully amorphous. Isothermal crystallization kinetics were investigated at different temperatures each 5 K apart within the range 100–125 °C. For each crystallization temperature, different crystallization times were applied. Time integration of the melting peaks, obtained during heating ramps performed at 10 K min<sup>-1</sup> after isothermal crystallization, lets to evaluate indirectly the enthalpy associated with each crystallization time. Assuming the validity of Avrami equation, it was possible to calculate the kinetic rate constants, at the temperature  $T_{iso}$ , of the two processes, namely the crystallization from the glassy state and the molten state. Avrami equation can be expressed as:

$$\chi(t_{iso}) = \Delta H(t_{iso}) / \Delta H_{max} = \left[ 1 - \exp\left(-\ln(2)k^n t_{iso}^n\right) \right] \quad (1)$$



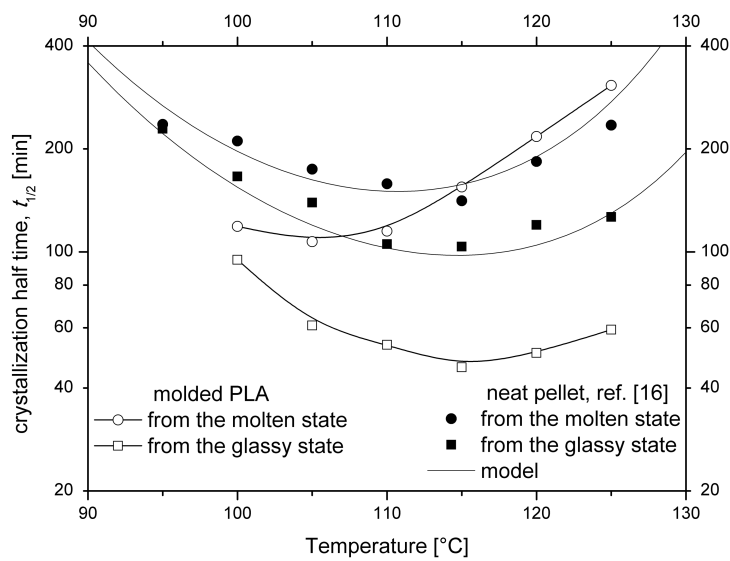
Where  $\chi$ ,  $t_{iso}$ ,  $k$ , and  $n$  are the relative crystallinity, time of isothermal step, the kinetic constant and the Avrami index, respectively.

The Avrami equation describes how solids transform from one phase (state of matter) to another at a constant temperature. At each temperature, the values of  $k(T)$  and  $n$  were identified by the best fitting of the calorimetric data of crystallinity. For each test, it was found that it was possible to obtain a good description of data by adopting a single value of the Avrami index for all tests, which resulted being equal to 3, as for the neat material, and  $\Delta H_{max}$  value of 24.22 J g<sup>-1</sup>.

The value of Avrami index,  $n=3$ , is the same evaluated for the neat resin [16], for a three-dimensional spherulitic growth of heterogeneous random nuclei. The crystallization half time at each temperature, as reported in Fig. 2, were evaluated from Eq. 2, checking, if possible, the coherence with crystallization peak during the isothermal step.

$$t_{1/2}(T_{iso}) = \frac{1}{k(T_{iso})} \quad (2)$$

In agreement with literature indications, at each temperature, the material crystallizes much faster when heated from the solid state. It is worth mentioning that, for the same protocol ("dsc m" or "dsc s" i.e. from the molten or solid glassy state) the crystallization kinetics, namely reciprocal of half crystallization time, of the molded samples, using Haake MiniJet, is similar or faster than that measured on the virgin 2002D [16] and slower than that measured on reciprocating screw injection molded samples [14]. This happens because the samples obtained by HAAKE MiniJet injection molding machine have surely experienced a lower thermomechanical degradation with respect to samples processed by conventional injection molding.



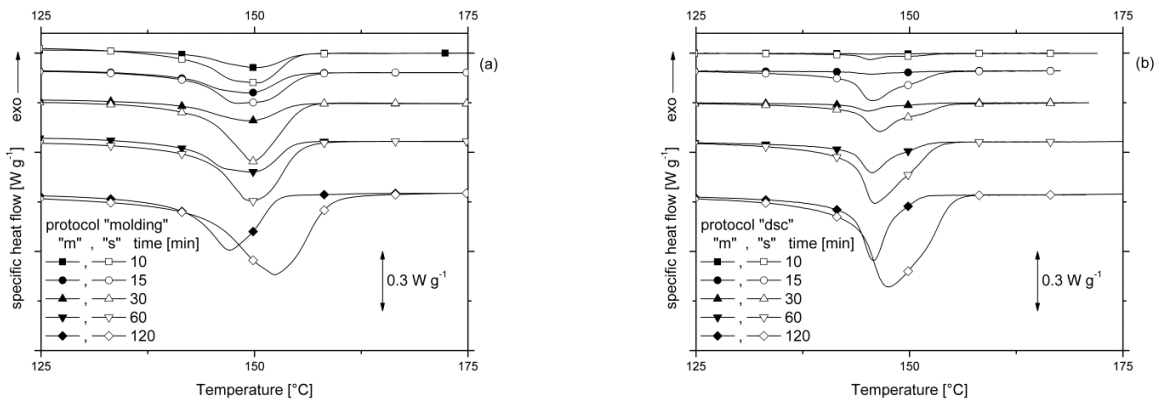
**Figure 2.** Experimental crystallization half time, for the molded PLA and neat pellet [16] vs temperature, from the molten and the glassy state. Lines are eye guides for the molded PLA and model prediction for neat pellet [16].

### 3.2 Characterization of molded samples

Thermal histories, following protocols "molding m" and "molding s", similar to those adopted in the DSC apparatus were imposed also during injection molding by HAAKE MiniJet machine.

The resulting samples were then analyzed by DSC during a heating scan at  $10 \text{ K min}^{-1}$  in order to determine the effect of molding conditions, in particular of mold temperature, on crystallinity. For each molded specimen, the central part, namely at 30 mm from the injection point, was analyzed.

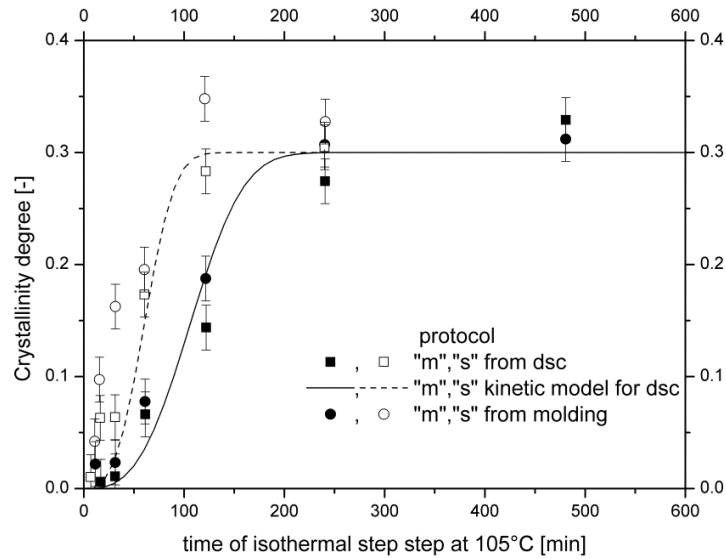
The DSC thermograms, during a heating scan at  $10 \text{ K min}^{-1}$ , of the injection molded samples, solidified in the mold according to the protocols "molding m" and "molding s" are reported in Fig. 3a.



**Figure 3.** Thermograms of the samples analyzed: a) samples solidified in the mold, according to the protocols "molding m" and "molding s"; b) samples solidified in the DSC apparatus, according to the protocols "dsc m" and "dsc s". In all these samples the isothermal temperature is  $105 \text{ }^\circ\text{C}$ .

The DSC thermograms reveal the effect of molding conditions on the crystalline degree of molded samples, obtained according to protocols molding "m" and "s" varying the time at the final temperature of  $105 \text{ }^\circ\text{C}$ . For residence time into the mold of 10 min or longer, the sample presents a quite large melting peak. This peak increases on increasing the residence time. Consistently with the results of crystallization kinetics, for the same residence time, the melting peaks are larger for the samples which underwent protocol "s". This obviously means that the crystalline content is larger for these samples. The crystallinity degrees of the molded samples according to the protocols molding "m" and "s" are reported in Fig. 4. The

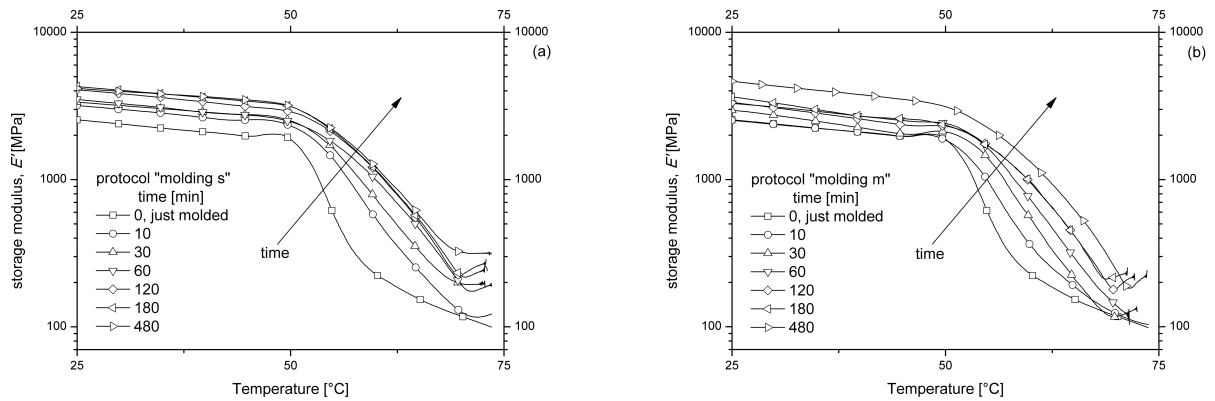
thermograms of the molded resin solidified in the DSC apparatus according to the protocols "dsc m" and "dsc s" are reported in Fig. 3b. The results are qualitatively similar to those reported in Fig. 3a. However, some differences among the protocols "molding" and "dsc" become evident by comparing the crystallinity degrees reported in Fig. 4.



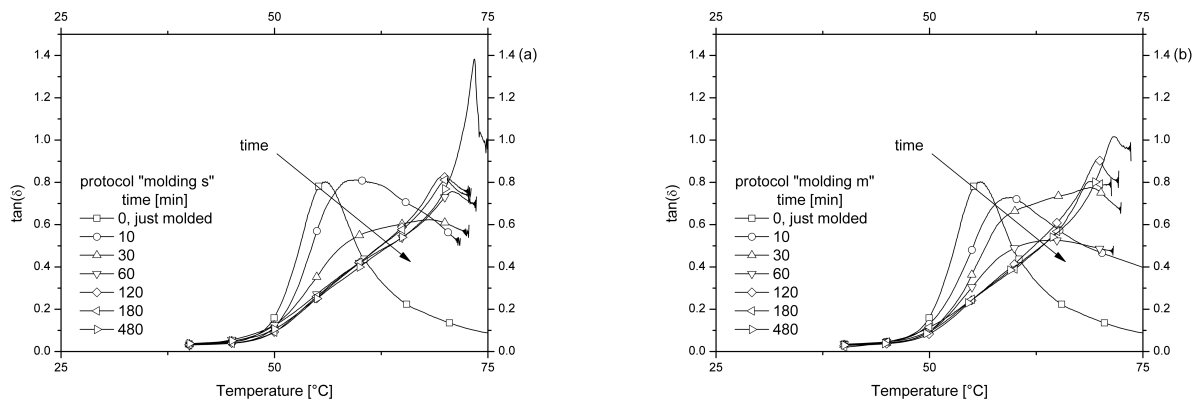
**Figure 4.** Crystallinity degree vs isothermal crystallization time at the temperature of 105 °C. Experimental data obtained from samples isothermally crystallized in DSC apparatus (square symbols) and in injection molding machine (circle symbols) with "m" and "s" protocols (full and open symbols, respectively); model predictions for the samples crystallized in DSC (lines) according to Eq. 1.

The samples crystallized from the melt present about the same crystallinity degree either when crystallized inside the mold or when crystallized inside the DSC apparatus. The samples crystallized from the solid present a larger crystallinity degree when crystallized inside the mold. This can be ascribed to the flow-induced crystallization, which induces an increase of nuclei and thus faster kinetics. This effect is less significant for the protocol "m" because the orientation levels are much lower due to the faster relaxation times. The identification of the values of the kinetic parameters allows to describe, using Eq. 1, the evolution of crystallinity degree, also reported in Fig. 4 for the samples crystallized isothermally in DSC, from the molten and the glassy state, at the temperature of 105 °C. Similar evaluations satisfactory compare with experimental data at each crystallization temperature, in agreement with the fitting procedure.

DMA analysis was conducted on the molded samples obtained at the isothermal temperature is 105 °C. The thermo-mechanical behavior of the samples deeply changes according to the particular protocol (namely the particular thermal history) adopted, as clear from Fig. 5a, Fig. 5b and Fig. 6, representing the storage modulus and  $\tan(\delta)$  respectively.



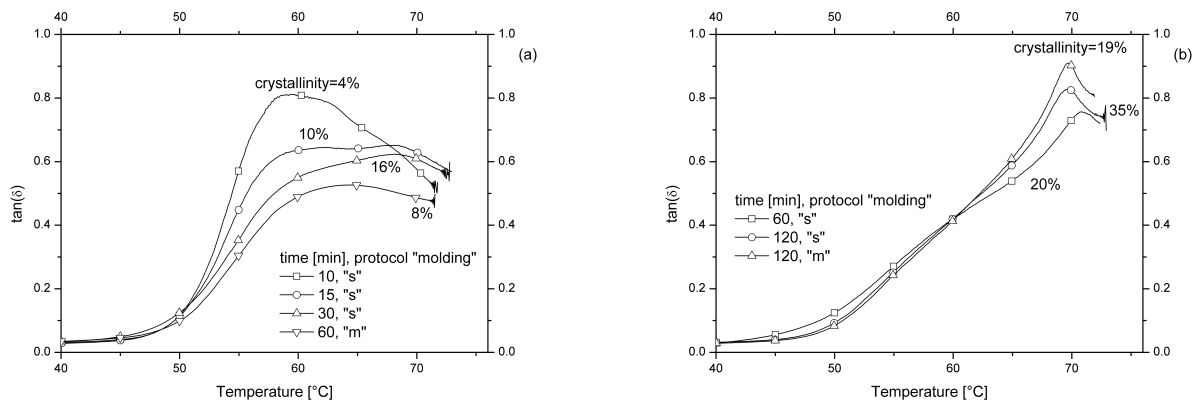
**Figure 5.** Storage modulus  $E'$  of the samples solidified in the mold, according to the protocol: a) "molding s"; b) "molding m".



**Figure 6.**  $\tan(\delta)$  of the samples solidified in the mold, according to the protocol: a) "molding s"; b) "molding m".

From Fig. 5 it is possible to observe that the storage modulus of the samples generally increases on increasing the crystallization time. Furthermore, on increasing the crystallization time a better resistance of mechanical properties with temperature is gained: the same value of the modulus is reached at higher temperatures. Obviously, the same effect is reached at shorter isothermal times if protocol "s" is adopted. In particular, an increase of about 10 °C is reached in the deflection temperature if a treatment time of about 30 min is carried out according to protocol "s" whereas about 1 h is needed for the same result according to protocol "m". On increasing the crystallization time (Fig. 6a, Fig. 6b) the loss

tangent  $\tan(\delta)$  decreases (indicating an increase of the elastic behavior of the material) and the maximum moves toward higher temperatures, indicating an increase of the glass transition temperature on increasing crystallization time. It is interesting to compare the curves of the loss tangent for samples presenting about the same crystallinity degree but obtained according to different protocols (Fig. 7). It can be noticed that the curves obtained for samples solidified according to the protocol "molding m" follow the same trend of curves obtained according to the protocol "molding s" but presenting a much higher crystallinity degree. In Fig. 7a, the  $\tan(\delta)$  of the sample having a crystallinity of 8% solidified according to protocol "molding m" runs close to the curve of the sample having a crystallinity of 16% solidified according to protocol "molding s". Similarly, in Fig. 7b, the  $\tan(\delta)$  of the sample having a crystallinity of 19% solidified according to protocol "molding m" runs close to the curve of the sample having a crystallinity of 35% solidified according to protocol "molding s". The reason of this difference can be ascribed to the different morphology presented by the samples. On the basis of the different protocols adopted, it is in fact expected [21] that larger spherulitic structures are found in the samples solidified according to the protocol "m", with respect to those found in the samples solidified according to the protocol "s" for the same crystallinity degree. These larger structures can infer a higher rigidity to the material. Obviously, a longer time could also influence the rigidity of the amorphous phase. Some studies in the literature [27, 28] also assert that the presence of larger crystalline and rigid amorphous fraction leads to a large improvement in stiffness of PLA. However, this effect should be less significant since the isothermal step is carried out at temperatures significantly higher than the glass transition temperature of the material.



**Figure 7.**  $\tan(\delta)$  of the samples solidified in the mold according to different protocols, having similar crystallinity degree.

#### 4 Conclusions

A characterization of crystallization kinetics of an injection molded commercial grade PLA was carried out by DSC according to two different protocols, considering the crystallization processes starting from the molten or from the solid state. It was found that crystallization kinetics of the material is much faster when the sample is heated from the amorphous glassy state. This finding was adopted to develop a post-molding stage (protocol "molding s") in which the molded samples are kept at the temperature of 105°C for selected times. This stage allows to obtain crystalline samples in times much shorter (of a factor about two) with respect to samples injection molded in a hot mold kept at temperatures close to the maximum crystallization rate (protocol "molding m"). The crystallization kinetics obtained by DSC was adopted to predict the crystalline content of samples molded in a hot mold and in a cold mold and then subjected to the post-molding stage. It was found that the predictions were accurate for samples molded according to protocol "molding m" (namely crystallized from the melt). The predictions underestimated the crystallinity of the samples subjected to the post-molding step (protocol "molding s", namely crystallized from the solid). This was ascribed to the flow-induced crystallization, which enhances the crystallization kinetics of the material molded in the cold mold. All the injection molded samples were analyzed by dynamic mechanical tests. It was found that, on increasing the crystallization time, a better resistance of mechanical properties with temperature is gained. It was also noticed that, for the same crystallinity degree, the heat resistance of samples obtained by the protocol "molding m" is larger than that of samples obtained by the protocol "molding s". This result was ascribed to the fact that larger crystalline structures can infer a higher rigidity to the material.

By adopting the post molding step procedure, it was possible to produce crystalline samples which preserved the mechanical properties at temperatures more than 10 °C higher with respect to samples injected into a cold mold.

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