Effect of molding conditions on properties of injection-molded polylactic acid parts

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A post-molding stage, in which samples are kept at 105°C, is used to produce semi-crystalline samples in much shorter times than through standard injection into a hot mold.

The physical, thermal, and mechanical properties of thermoplastic polymers are strongly dependent on the crystalline structure and morphology of the materials. An example of a thermoplastic polymer, polylactic acid (PLA), is one of the more versatile bio-based polymers (i.e., synthesized from renewable resources). It has high stiffness and strength, and has thus received a large amount of attention in the search for alternative and biodegradable polymers.[1–5] The remarkably low glass-transition temperature (less than 60°C), however, as well as its consequent low heat-deflection temperature, makes PLA unsuitable for many applications (e.g., for plastic plates and cups for hot food and drinks).[6]

A large crystallinity degree is highly desirable for increasing the heat resistance of PLA, but this can be difficult to achieve during injection molding of PLA because of the material's very slow crystallization kinetics. It is already known, however, that the crystallization kinetics of PLA depend strongly on the thermomechanical evolution of the material. This is because of the degradation experienced by the material in the molten state.[7–10]

In this work,[11] we have therefore investigated the crystallization kinetics of injection-molded PLA. Specifically, the material we used is a commercial-grade PLA from NatureWorks (trade name 2002D).[12–14] Before we conducted any testing or processing of the PLA, we dried the material for 24 hours under vacuum conditions and at a temperature of 60°C. We then formed rectangular bars (with length, width, and thickness of 60, 10, and 1mm, respectively) of the PLA via injection molding with a HAAKE MiniJet system (Thermo Scientific). For this, we set the barrel and mold temperatures at 200 and 25°C, respectively. Due to the high cooling rate during solidification, our resulting samples were completely amorphous.
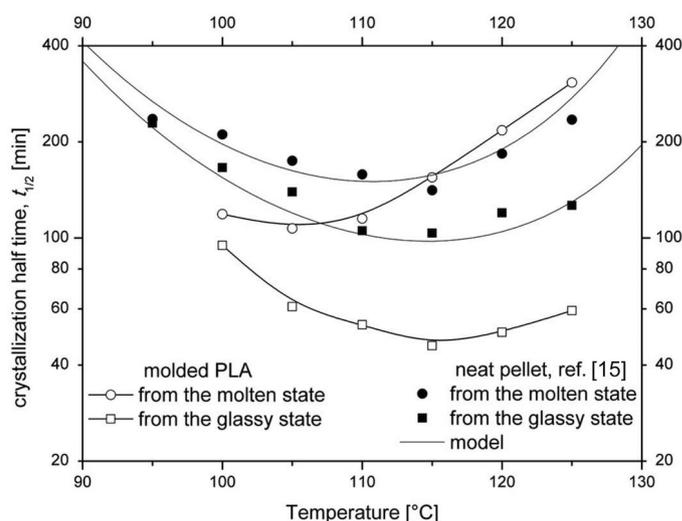
Figure 1. *Experimental crystallization half time for molded polylactic acid (PLA) parts and neat PLA,[15] shown as a function of temperature. Results were obtained following two different differential scanning calorimetry protocols, i.e., where crystallization proceeded from either the molten or the solid state. Model predictions[15] for both the molded PLA and the neat pellet are also shown.*

We conducted differential scanning calorimetry (DSC) to characterize the crystallization of our neat PLA and injection-molded parts. We followed two different protocols so that we considered the crystallization processes starting either from the molten or the solid state (see Figure 1). We found that the crystallization kinetics of the material were much faster when the sample was heated from the amorphous glassy state. On the basis of these results we thus developed a post-molding stage, in which the molded samples are kept at a temperature of 105°C for a specific time (we refer to this stage as the 'molding s' protocol). This stage makes it possible to obtain crystalline samples in

much shorter times (by a factor of about two) than samples that are injection molded in a hot mold (i.e., which is kept at a temperature close to the maximum crystallization rate).

We have also used our DSC crystallization kinetics results to predict (using the Avrami equation[11]) the crystalline content of samples that were molded in both a hot and a cold mold and that were subjected to the post-molding stage. We find that our predictions are accurate for the samples molded without the post-molding step (see Figure 2). For the samples that were subjected to the post-molding step (namely, those that were crystallized from the solid state), however, our predictions underestimated the crystallinity. We ascribe this discrepancy to flow-induced crystallization, which enhances the crystallization kinetics of the material molded in the cold mold.

In another part of our study, we analyzed the dynamic mechanical properties of all our injection-molded samples. For example, our storage modulus results for the samples that crystallized from melt ('molding m') and from solid ('molding s') are shown in Figure 3. These analyses indicate that by increasing the crystallization time (i.e., by increasing the temperature gain), we can achieve better mechanical resistance. We also note that, for the same degree of crystallinity, the heat resistance of samples obtained from the molding m protocol is greater
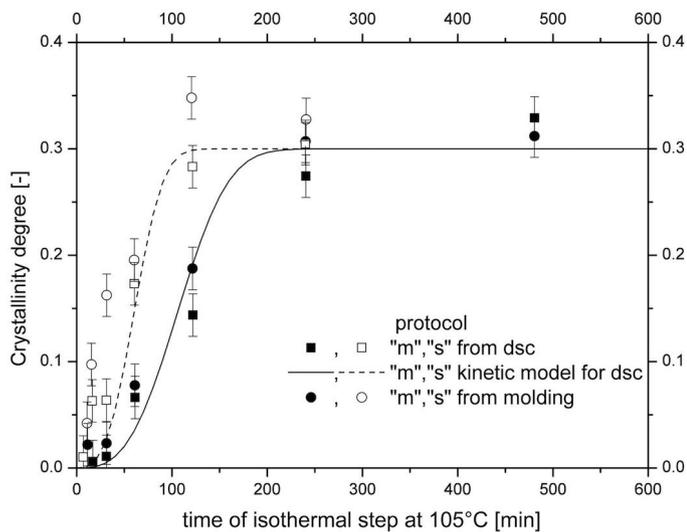
Figure 2. Degree of crystallinity as a function of isothermal crystallization time (at 105°C). The experimental data was obtained from samples that were isothermally crystallized in DSC apparatus (squares) and in the injection-molding machine (circles), and following either the 'm' (crystallization from melt) or 's' (crystallization from solid) protocols (shown by full and open symbols, respectively). Model predictions, according to the Avrami equation,[11] are also shown for the DSC-crystallized samples.
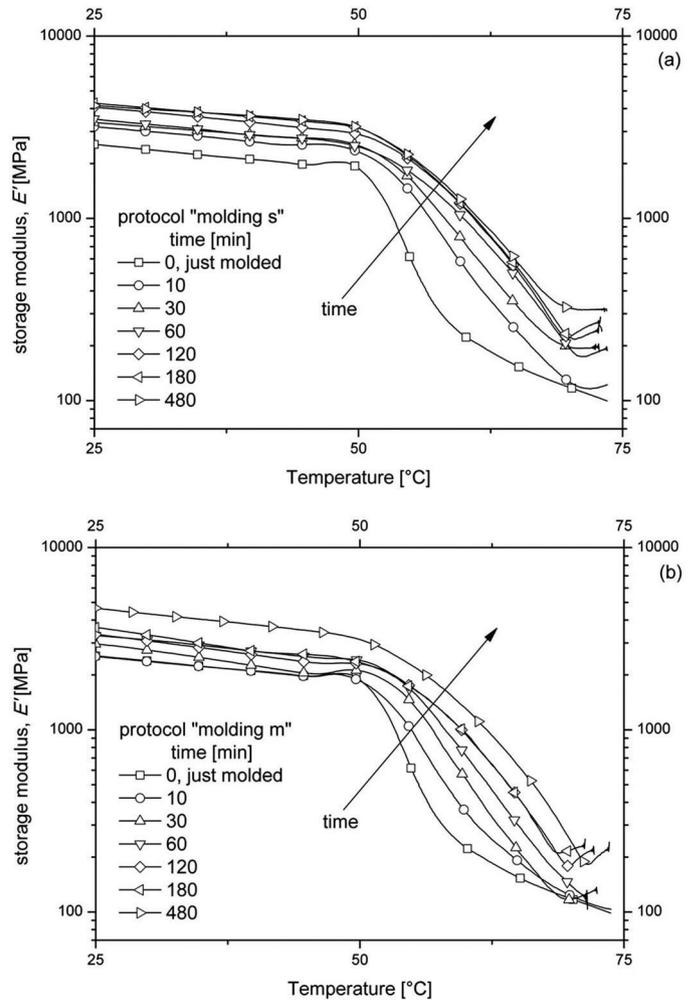
Figure 3. Storage modulus of the PLA samples that were injection molded according to the (a) 'molding s' and (b) 'molding m' protocols, as a function of temperature. Values are given for a range of crystallization times (0–480 minutes).

than that of samples obtained from the molding s protocol. We can explain this result by the fact that larger crystalline structures can impart higher rigidity to the material.

In summary, we have investigated the crystallization kinetics of an injection-molded commercial-grade PLA. For this study we conducted calorimetry according to two different protocols, i.e., where we considered the crystallization process starting from either the molten or solid state. We find that the crystallization kinetics are much faster when the sample is heated from the amorphous glass state. To obtain crystalline samples in much shorter times, we thus adopt a post-molding stage in which the samples are kept at a temperature of 105°C. We have also

used our DSC-obtained crystallization kinetics to satisfactorily predict the crystallinity of PLA (molded in both a hot and a cold mold and subjected to the post-molding stage). Dynamic mechanical testing of all our injection-molded samples showed that better mechanical resistance can be realized by increasing the crystallization time. Furthermore, for the same crystallinity degree, samples that were crystallized from the melt had a higher heat resistance than those that were crystallized from the solid state. Overall, with our post-molding step, it is possible to produce crystalline samples whose mechanical properties are preserved to temperatures that are more than 10°C higher than samples injected into a cold mold. The next stages of our work will be devoted to the addition of new carbon-based nanoparticles in PLA. We plan to investigate these PLA nanocomposites, which are considered the 'holy grail' of materials science, because the addition of the nanoparticles at low concentrations to the polymer matrix causes significant improvements. These include faster melt crystallization kinetics (because of the nucleating effect), enhanced physical performance, thermomechanical reinforcement, higher glass transition temperatures, and preservation of the PLA matrix during melt compounding.

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