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Annealing conditions for injection-molded poly(lactic acid)

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Post-molding annealing increases the degree of crystallinity in injection-molded poly(lactic acid) components and improves their mechanical and heat resistance performance.

Poly(lactic acid) or polylactide (PLA) is a biodegradable thermoplastic polyester obtained from lactic acid (or lactide) that can be produced from renewable resources such as corn or sugarcane. Mass produced and commercially available PLA has been successfully introduced for products where biodegradability or sustainability is required or desired.[1,2] PLA is an enantiomeric polyester including poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA). Fully amorphous materials can be made by the inclusion of a relatively high D content (>20%), whereas highly crystalline materials are obtained when the D content is low (<2%).[3] Obtaining a highly crystalline, injection-molded PLA part remains difficult due to PLA's slow crystallization rate.[4] The polymer's crystallinity plays a significant role in the material's performance. For example, an increase in overall crystallinity leads to improvements in stiffness, strength, heat deflection temperature, and chemical resistance.[5,6] To maximize property enhancements with a high degree of crystallinity in the injection-molded part, the cooling rate has to be slow (leading to a long cycle time), or alternatively, annealing of the post-injection molded part is needed.[4,7] The latter approach can be done offline and in batches, thereby offering a cost-effective way to improve the performance of PLA parts without affecting the cycle time.

We investigated the degree of crystallinity in injection-molded and annealed PLA specimens under different annealing times and temperatures. The relationship between annealing time and temperature was studied by time-temperature superposition following the Arrhenius and Williams-Landel-Ferry (WLF) equations.[8,9] Furthermore, the heat resistance and mechanical performance of as-molded and annealed specimens were assessed.

We laid out injection-molded and annealed parts as shown in Figure 1(a) and placed them in an oven at 65°C to observe the heat resistance and deformation of the specimens. Figure 1(b) shows that the as-molded PLA specimen (the first specimen), which had the lowest degree of crystallinity, exhibited the maximum deformation at 65°C. Annealed specimens showed very little or no deformation at all, suggesting annealing results in better heat resistance.

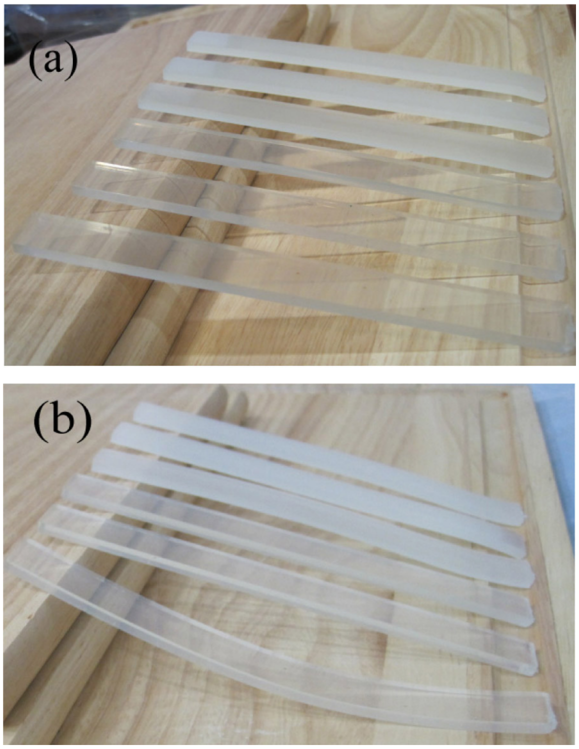

Figure 1. *Heat resistance comparison of as-molded (first specimen) and annealed poly(lactic acid) (PLA). (a) As-molded and annealed PLA of different annealing times at an annealing temperature of 80°C. (b) As-molded and annealed PLA after heating in an oven at 65°C for 3min.*[10]

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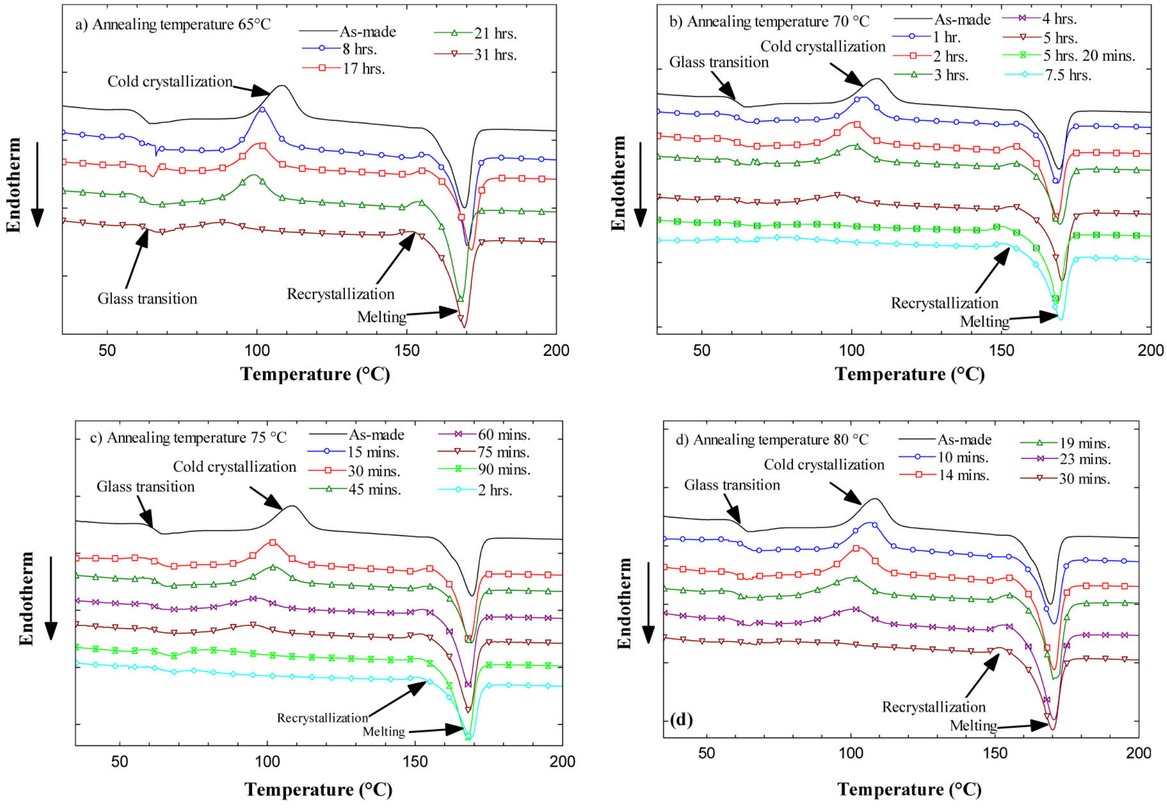

***Figure 2.** Differential scanning calorimetry heating scans showing the effect of annealing time at (a) 65°C, (b) 70°C, (c) 75°C, and (d) 80°C.*[10]

Meanwhile, the differential scanning calorimetry heating scans of the injection-molded PLA specimens heat treated for varying amounts of time at annealing temperatures of 65, 70, 75, and 80°C are presented in Figure 2(a) through (d), respectively. As shown, the enthalpy of the cold crystallization peaks decreased with increasing annealing time, indicating annealing enhanced PLA crystallization. Moreover, longer annealing times shifted the cold crystallization temperatures to a lower value. The recrystallization peak, which was observed just before the melting peak, may be due to the restructuring of certain existing crystalline structures at high temperatures.

Figure 3 shows the evolution of crystallinity as a function of annealing time and temperature. The maximum crystallinity of all PLA samples was around 48–49%. At 65°C, PLA reached 43% crystallinity in 31 hours, whereas at 80°C, PLA reached its maximum crystallinity of around 49% in 30 minutes. The log-log plot of the degree of crystallinity versus the annealing time at various temperatures from Figure 3 is shown in Figure 4. Note that the crystallinity versus time plot shows the same slope at different annealing temperatures.

Given the respective effects of annealing time and temperature on the crystallinity of PLA, and the fact that the curves in Figure 4 resemble each other, we employed the time-temperature superposition technique to construct the master curve in Figure 5. We shifted curves of the degree of crystallinity versus the log of the annealing time at a given temperature horizontally by a shift factor (a_T) to overlap with an adjacent curve at a reference annealing temperature. The empirical

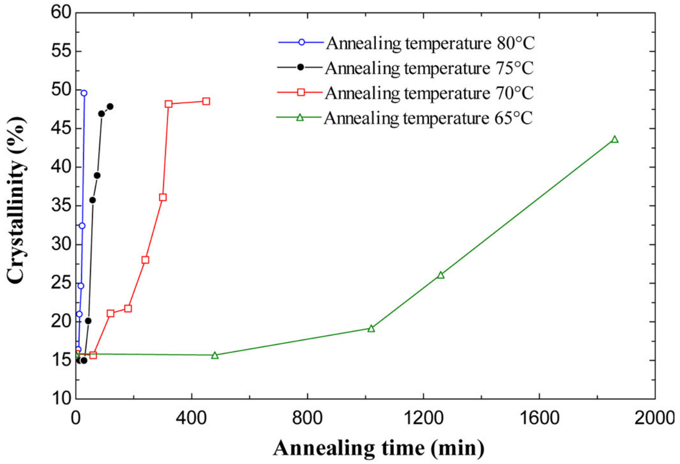

***Figure 3.** Degree of crystallinity versus annealing time at annealing temperatures of 65, 70, 75, and 80°C.*[10]

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relationship between the time and temperature effects can be formulated via a mathematical relationship known as the Arrhenius and WLF equations. This shifting equation is very useful if information is available for only one temperature and information for other temperatures needs to be computed. This technique reflects the fact that the same degree of crystallinity can be achieved by either a higher annealing temperature or a longer annealing time period. The shift factor as a function of temperature provides the mathematical relationship between the annealing temperature and the annealing time.

We also performed tensile tests on our as-molded and annealed PLA tensile bar specimens. The tensile strength of the annealed PLA blends was noticeably higher compared to that of as-molded specimens: see Figure 6.

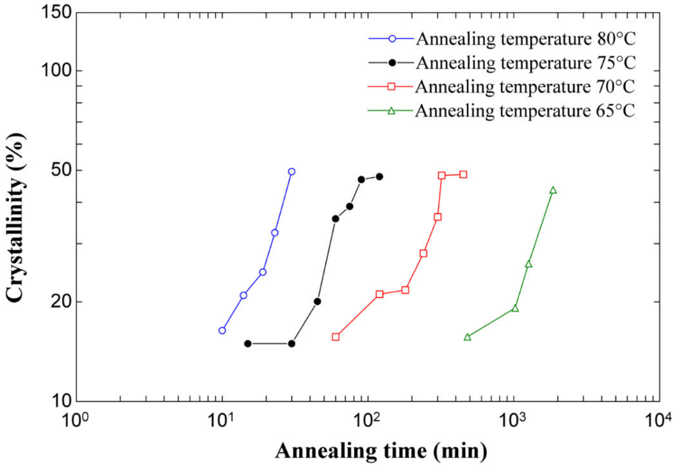

Figure 4. *Log-log plot of the degree of crystallinity versus the annealing time at different annealing temperatures.*[10]

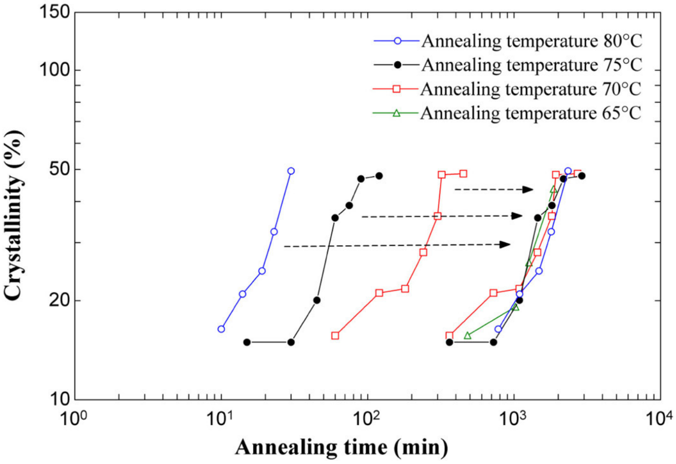

Figure 5. *The master curve with respect to the 65°C curve.*[10]

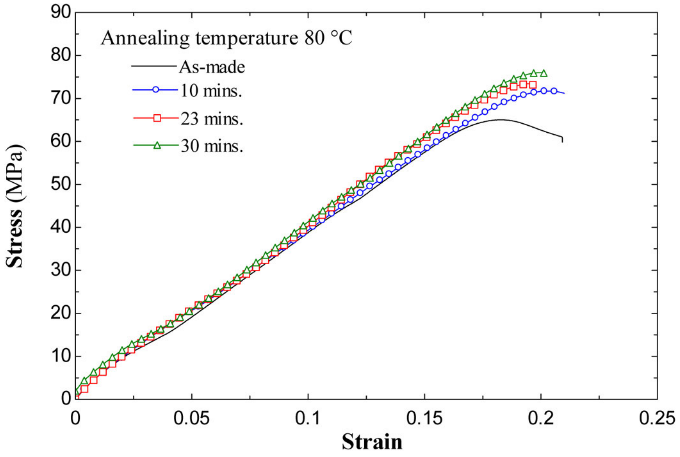

Figure 6. *Tensile stress versus strain curve of the as-molded and annealed PLA at 80°C.*[10]

In summary, we have studied the effect of annealing time and temperature on the crystallinity and mechanical performance of injection-molded PLA parts. The degree of crystallinity depended upon time and temperature, and we confirmed the Arrhenius and WLF relationships between crystallinity, annealing time, and temperature, which provide useful guidelines for heat treating molded PLA parts. Moreover, increasing the overall crystallinity improved the mechanical performance and heat resistance of PLA. In future work, we will develop a viable and scalable process to effectively anneal injection-molded PLA parts to improve their heat resistance properties.

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