

Acceleration of the Molding Cycle of Semi-crystalline Polylactic Acid by Cellulose Nanofibers Reinforcement

(Graduate School of Agriculture,
Laboratory of Active Bio-based Materials, RISH, Kyoto University)

Lisman Suryanegara

The main drawback of semi-crystalline type of polylactic acid (PLA) for industrial application is the longer injection molding cycles compared with conventional polymers such as polypropylene (PP). We found that the combination of nucleant addition and cellulose nanofiber reinforcement had a synergetic effect to accelerate the injection molding cycle of PLA.

Introduction

PLA has a great potential to replace petroleum-based plastics because of its high stiffness and strength. However, semi-crystalline PLA designed for semi-structural purpose has slower crystallization speed. Hence, when semi-crystalline PLA molding product at amorphous condition is subjected to above T_g , the product gives poor mechanical properties causing creep deformation as well as shrinkage due to crystallization.

Considering industrial applications, the slower crystallization speed of PLA resulting in longer molding cycle, is a significant drawback. The prolonged molding cycle in order to obtain fully crystallized PLA decreases productivity and increases the cost. Thus, the main objective of this study is to assess the possibility to accelerate the injection molding cycle of PLA by cellulose nanofibers reinforcement and nucleant addition. Our goal is to process PLA as productively as PP while keeping the advantage of mechanical reinforcement of cellulose nanofibers, which are the high thermo-mechanical properties.

Materials and Methods

To evaluate the effect of reinforcement, PLA and microfibrillated cellulose (MFC) at fiber content of 0, 3, 5, 10, and 20 wt% were mixed in an organic solvent. After the solution was dried at room temperature followed by vacuum-drying, a kneader was used to obtain a homogenous compound which was hot pressed. The melted samples were immediately quenched in liquid N₂ to bring them to a fully amorphous state. To obtain fully crystallized state, the amorphous sheets were annealed at 100 °C for 1 h. To attain samples with various crystallinities, the amorphous sheets at a fiber content of 10 wt% were annealed at 80 °C for different lengths of time. To evaluate the potential of MFC and nucleant in accelerating the injection molding cycle of PLA: PLA, phenylphosphonic acid zinc (PPA-Zn), and MFC at a fiber content of 10 wt% were mixed in an organic solvent followed by oven drying. The dry mixture were injection molded into different temperature mold and were kept in the mold for different lengths of time to obtain samples with various crystallinities.

The mechanical properties were studied by tensile test. The thermal properties were evaluated by TMA and DMA. The degree of crystallization was investigated by X-ray diffraction and differential scanning calorimetry.

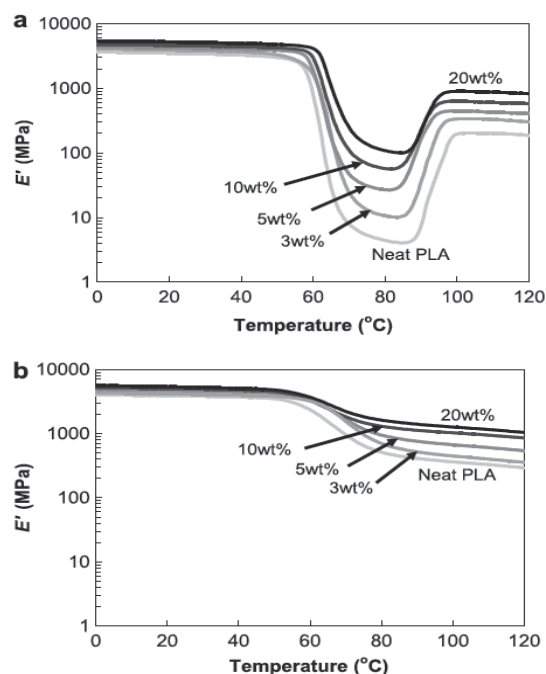


Fig. 1. Effect of MFC contents (wt%) on the temperature dependency of the storage modulus under (a) amorphous and (b) crystallized states

The deforming behavior of composites was performed by a cantilever beam test in a forced convection oven. Rectangular samples were clamped at one end as cantilevers and subjected to a temperature of 110 °C for 3 h.

Results and Discussion

Fig. 1 shows the effect of MFC reinforcement on the storage modulus of PLA in amorphous and fully crystallized states. In the amorphous state, the addition of MFC at a fiber content of 20 wt% improved the modulus of neat PLA by 50% from 3508 MPa to 5223 MPa at 20 °C (glassy state), and interestingly, by 27 times from 4 MPa to 109 MPa at 80 °C (rubbery state) [1].

Figure 2 shows the cantilever beam test of PLA and PLA/MFC 10 wt% composites with different degrees of crystallinity. The composite (Xc: 17%) did not show downward deformation during heating at 110 °C for 3 h. On the other hand, the amorphous composite (Xc: 0%) exhibited the highest downward deformation, which gradually decreased as the crystallinity increased up to 9%. The addition of fiber restricted the mobility of the polymer chains, and the presence of the crystalline structure of PLA also acted as a physical crosslinking, decreasing the mobility of the PLA amorphous regions, and as a result increasing the composite's stiffness [2].

Figure 3 shows samples shapes when ejected from the mold after holding at 95 °C for 10 s. Only the PLA/PPA-Zn/MFC composite could be obtained without distortion, while neat PLA and the PLA/PPA-Zn and PLA/MFC composites were all deformed. This result shows the advantage of MFC-reinforced PLA/PPA-Zn composite: although the composite was partially crystallized, it was easily demolded in a short time without distortion [3].

From these results, it was concluded that reinforcement with cellulose nanofibers made possible to manufacture high heat resistance and high strength the PLA semi-structural parts at similar molding cycles of PP. In the future, to apply this finding in industrial applications, a further experiment is needed to avoid the using of solvent method in the preparation of nanocomposites

References

- [1] Suryanegara L, A.N. Nakagaito, and H. Yano, "The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites," *Compos Sci Technol*, vol. 69, no. 7-8, pp. 1187-1192, 2009.
- [2] Suryanegara L, A.N. Nakagaito, and H. Yano, "Thermo-mechanical properties of microfibrillated cellulose-reinforced partially crystallized PLA composites," *Cellulose*, vol. 17, no. 4, pp. 771-778, 2010.
- [3] Suryanegara L, H. Okumura, A.N. Nakagaito and H. Yano, "The synergetic effect of phenylphosphonic acid zinc and microfibrillated cellulose on the injection molding cycle time of PLA composites," *Cellulose*, vol. 18, no. 3, pp. 689-698, 2011.

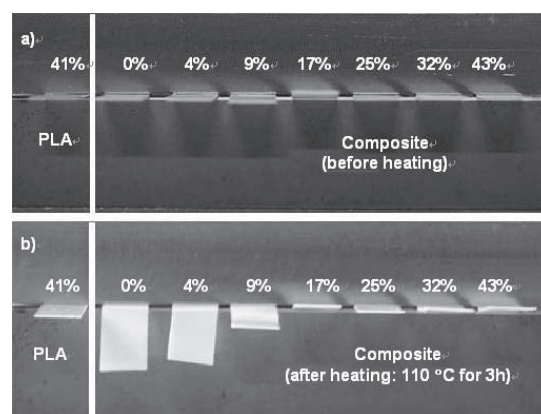


Figure 2. Cantilever beam test of PLA and PLA/MFC 10 wt% composites with different degrees of crystallinity at 110 °C for 3 h

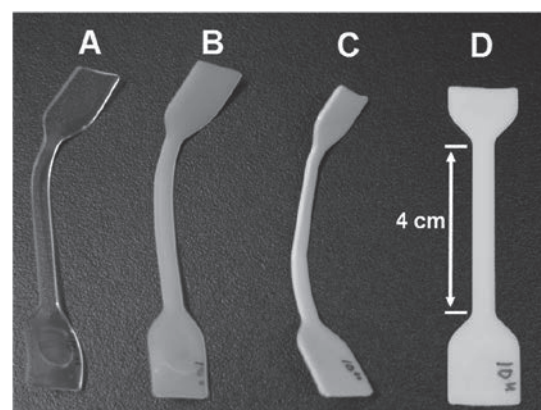


Figure 3. Samples shapes when ejected from the mold after holding at 95 °C for 10 s: a Neat PLA, b PLA/PPA-Zn, c PLA/MFC, d PLA/PPA-Zn/MFC