**Isothermal cold crystallization kinetics and properties of thermoformed poly(lactic acid) composite films**

Anongnat Somwangthanaroj1,2,\*, Chutimar Deetuam1, Chavakorn Samthong1, Suphattra Choksriwichit1

*1 Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand; 2 Special Task Force of Activating Research (STAR) in Novel Technology for Food Packaging and Control of Shelf Life, Chulalongkorn University, Bangkok 10330, Thailand*

*\*Corresponding author: anongnat.s@chula.ac.th*

**Highlights**

* Effects of fillers and silane surface functionalization were investigated.
* Faster cold crystallization of PLA with the presence of fillers was observed.
* Talc is the most effective nucleating agent for PLA.

**1. Introduction**

Biodegradable polymers have gained great attention as eco-friendly alternatives to conventional plastics derived from fossil fuels. Poly(lactic acid) (PLA) is the most well-known biodegradable thermoplastic that has been extensively used for diverse applications, such as household appliances, automobile interiors, tissue engineering, drug delivery, and food packaging materials [1, 2] because of its unique properties including biodegradability, biocompatibility, high transparency, and high tensile strength (75 MPa) and modulus (3.2 GPa) [3, 4]. Nevertheless, PLA has some weaknesses including brittleness with elongation at break less than 4%, poor melt strength, poor thermal stability, and low gas barrier properties. Further, PLA is also known as a slow crystallizing polymer; this leads to a very long injection moulding cycle time during the cooling step, and the end-use products have low crystallinity, which strongly affects its optical, thermal, and mechanical properties [5]. Accordingly, slow crystallization behaviour of PLA should be improved for potentially being used in the industrial applications as it deserves. In this work, the effect of the addition of talc, CaCO3, and cassava starch at various contents on the morphology, mechanical and thermal properties, and isothermal cold crystallization kinetics of PLA composites is examined.

**2. Methods**

The isothermal cold crystallization kinetics is investigated by fitting the experimental data from differential scanning calorimetry (DSC) with a theoretical Avrami model. The study on annealing effect under cold crystallization on the thermal and tensile properties is performed by comparing cast films with thermoforming films. Eventually, surface treatment of talc with vinyltriethoxysilane (VTES) and 3−aminopropyltriethoxysilane (APTES) is also performed to examine the silanization effect on the properties of PLA composites in comparison with the untreated system. Tensile properties including tensile strength, elongation at break, Young’s modulus, and tensile toughness of cast films and thermoforming films of neat PLA and PLA composites were measured at room temperature using a universal testing machine (Intron model 5567, USA) in accordance with ASTM D882.

**3. Results and discussion**

The Avrami model was employed to study the isothermal cold crystallization kinetics by DSC. Dynamic DSC results revealed that incorporation of filler can facilitate the cold crystallization of PLA. The highest isothermal cold crystallization rate constant *k* and the shortest crystallization half time *t*1/2 were achieved for the PLA/talc composites under isothermal temperature of 100 oC, implying that talc was the most effective nucleating agent for PLA in this study. After annealing the cast films under isothermal cold crystallization condition to induce the orientation of PLA chains, the thermoforming films had higher degree of crystallinity as well as improved tensile strength and Young’s modulus. The successful grafting of silane coupling agent onto the talc surface was confirmed by FTIR measurement and it was noticed that films with the silanization of talc surface with APTES showed the fastest cold crystallization rate. Therefore, the strong interfacial adhesion in the PLA composites containing APTES treated talc resulted in less debonded talc particles from the cryofractured surfaces and an enhancement of tensile properties.



**Figure 1.** Relative degree of crystallinity *X*c of neat PLA and its composite cast films containing 5 vol% untreated fillers at *T*iso = 100 oC. Inserted horizontal line is *X*c = 50%.

**4. Conclusions**

The effects of three different fillers and silane surface functionalization on morphology, thermal and tensile properties of the poly(lactic acid) (PLA) composites were comparatively examined. The surface functionalization of talc particles by silanization reveals higher tensile strength as well as faster cold crystallization rate, which is attributed to the enhanced interfacial interaction between PLA chains and talc particles. Therefore, it can be summarized from our work that cold crystallization behaviour of the polymer composites depends not only on inherent nucleating ability of filler, but also the surface functionality of the filler particles.

**References**

[1] Arrieta, M. P.; López, J.; Hernández, A.; Rayón, E. *Eur. Polym. J.* **2014,** *50*, 255.

[2] Samthong, C.; Seemork, P.; Nobukawa, S.; Yamaguchi, M.; Praserthdam, P.; Somwangthanaroj, A. *J. Appl. Polym. Sci.* **2015,** *132*, 41415.

[3] Huang, T.; Yamaguchi, M. *J. Appl. Polym. Sci.* **2017,** *134*, 44960.

[4] Deetuam, C.; Samthong, C.; Pratumpol, P.; Somwangthanaroj, A. *Iran. Polym. J.* **2017,** *26*, 615.

[5] Auras, R.; Lim, L. T.; Selke, S. E. M.; Tsuji, H. In Poly(lactic acid): Synthesis, Structures, Properties, Processing, and Applications; John Wiley & Sons Inc.: New Jersey, **2011**.