

# Novel Green Polymer Composites: Major Enhancements in the Crystallization Kinetics of Poly(lactic acid) and Mechanical Properties of Polypropylene Created via Solid-State Shear Pulverization

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## ABSTRACT

Hybrids of poly(lactic acid) (PLA) or polypropylene (PP) with microcrystalline cellulose (MCC) were created using a novel, continuous, and industrially scalable process called solid-state shear pulverization (SSSP), which exposes polymers to high shear and compressive forces near ambient temperature. For the PLA composite, this was followed with melt processing (MP) with added polyethylene glycol (PEG). We demonstrate a synergistic effect of MCC and PEG in enhancing the crystallization kinetics of PLA. For example, we were able to successfully injection mold a highly crystalline (~ 35 %) commercial bottle cap in 33 sec, which as far as we know, is the highest level of crystallinity obtained at this cycle time. Neat PLA took over 10 min to reach similar crystallinity levels. Additionally, an SSSP processed 80/20 wt% PP/MCC composite was successfully injection molded into a bottle cap, which showed excellent MCC dispersion and stiffness, while maintaining of the “living hinge” character of PP.

**Keywords:** polypropylene, poly(lactic acid), cellulose, solid-state shear pulverization, physical properties

## 1 INTRODUCTION

### 1.1 Issues with Poly(lactic acid)

Poly(lactic acid) has attracted much attention recently because it has numerous beneficial properties: (1) it can be obtained from renewable agricultural sources such as corn, sugar, and milk byproducts [1,2]; (2) it is recyclable and exhibits biocompatibility, which leads to a reduction in municipal landfill volumes [3,4]; (3) it is relatively cheaper than other biodegradable polymers and commercially available; (4) its production consumes quantities of carbon dioxide [5]; and (5) it has high stiffness and strength, which are comparable to polystyrene. There has also been a significant push in recent years from several European countries and even cities in the United States to implement biodegradable and compostable materials [6]. In particular, several state and local governments are enacting restrictions

or outright bans on polystyrene and non-renewable containers. In addition, a number of government bodies, especially in Europe, are considering taxing non-renewable packaging.

Technological applications of PLA, however, have been limited because of its low thermal stability and toughness and its low crystallinity in the as-processed state. The low thermal stability is a significant issue often encountered with biodegradable plastics because processing of these materials above the melt temperature,  $T_m$ , leads to polymer degradation and large molecular weight reduction, which negatively impacts the mechanical properties [7]. The low toughness is another major issue with PLA which limits its use in the packaging industry where the material must exhibit ductile rather than brittle behavior. Lastly, the low crystallinity of PLA impacts its use in high temperature applications. Only the crystalline PLA phase can confer useful mechanical properties above the low glass transition temperature,  $T_g$ , of PLA, which is ~ 60 °C. The low crystallinity is associated with the grudgingly slow crystallization rate of PLA. This makes application in processes such as injection molding impractical, where the cycle times are extremely fast (20-30 sec) and the desired product is semi-crystalline rather than amorphous PLA. Figures 1a and 1b show an amorphous and a semi-crystalline PLA cup, respectively, upon the addition of boiling water. The PLA cup in figure 1b was annealed at 110 °C for 10 min in order to induce a high level of crystallinity in the sample. This annealing time was required to ensure that distortion did not occur following the addition of boiling water. From figures 1a and 1b, it is evident that inducing a high level of crystallinity during processing is necessary to produce PLA parts that can be used in high temperature applications.

Overcoming these technological challenges associated with PLA will lead to considerable opportunities to develop novel and advanced biobased and biodegradable products, especially for high temperature applications.



Figure 1: Image of poly(lactic acid) cups with a) low level and b) high level of crystallinity following the addition of boiling water. The highly crystalline cup was annealed at 110 °C for 10 min in order to induce a high level of crystallinity, thereby preventing distortion in the cup at high temperatures.

## 1.2 Issues with Polypropylene

Interest in using polymers as replacements for other materials such as metals, wood, and ceramics has increased significantly over the last few decades [8]. This is due to advantages that polymers offer over conventional materials, including ease of processing, productivity, and cost reduction [9]. One polymer that has gained much interest as a replacement material is PP. The reason being is that unlike most conventional polymer, PP has a favorable combination of low cost, good processability, and a great balance of physical and mechanical properties. Nevertheless, in order to meet the high demands on strength and stiffness for many applications in aerospace, automotive, microelectronics, infrastructure and construction, medical, and chemical industries, PP must be reinforced with filler materials [8,10].

The use of conventional fillers such as glass or carbon fibers has received much academic and commercial attention [11]. Although excellent mechanical properties have been achieved, life cycle assessment does not yield favorable results for these reinforced composites due to limited recyclability and high energy requirements of their end-of-life processes [12-15]. Over the past decade, there has been a trend toward environmentally-friendly composite systems, which focus on the use of natural fibers as alternatives to glass fibers. The reason being is that many of these fibers are derived from renewable resources [16], and have excellent physical properties. A great example of a natural and “green” filler with great mechanical properties

is cellulose. This material is readily available for use as a filler in composites and has been heavily researched [16,17].

The macroscopic properties of composite materials reinforced with micro-sized fillers are determined by several factors, such as the characteristics of each component, its composition, the geometry of the filler, the filler/filler and filler/matrix interactions, the filler dispersion and, in some cases, the modification of the characteristics of the matrix itself [18]. Of these factors, the potential property improvement of any composite material depends greatly on the degree of dispersion and the degree of interaction/adhesion between the matrix and reinforcing phase [19,20]. Using fillers with large surface area is one method for obtaining better interaction between the matrix and reinforcement agent. Fillers with high aspect ratios lead to better mechanical properties, heat resistance, and dimensional stability [21]. However, effective dispersion of the filler is still a major challenge.

## 1.3 Solid-State Shear Pulverization

In order to overcome the issues associated with the grudgingly slow crystallization of PLA and low strength and stiffness of PP, we utilize a novel and continuous approach known as SSSP to effectively disperse MCC in these polymeric materials. The MCC particles act as nucleating agents in PLA and reinforcement particles in PP. The SSSP process employs a modified twin-screw extruder from Berstorff (screw diameter = 25 mm, length/diameter = 26.5) (figure 1). Ref 22-37 give a more detailed description of the SSSP process. A key difference between the SSSP apparatus used in this research and conventional twin-screw extruders is that the SSSP apparatus is maintained at a temperature below  $T_g$  and/or  $T_m$  of the polymer through a circulating cooling system set at 20 °F (-7 °C) around the pulverizer barrels. This allows for repeated fragmentation and fusion steps in the solid state without the limitations of thermodynamics, viscosity, and degradation often encountered in melt processing of polymers. Solid-state shear pulverization also eliminates the use of hazardous solvents, which is a major requirement in achieving sustainability and promoting green chemistry.

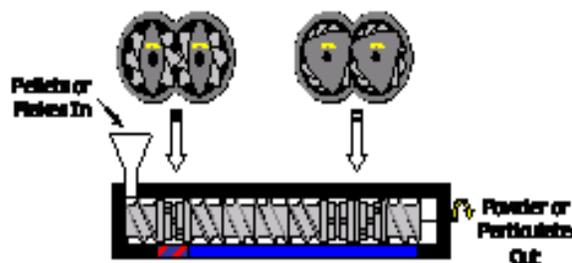


Figure 2: Schematic of SSSP apparatus

## 2 MATERIALS

Poly(lactic acid) was generously donated by Prof. John Dorgan from the Colorado School of Mines. The thermoforming grade, linear PLA material (96/4 L/D ratio) was produced by Cargill-Dow Polymers (now NatureWorks) with a weight-average molecular weight of  $M_w = 95,000$  g/mol and a number average molecular weight of  $M_n = 56,000$  g/mol, as determined by gel permeation chromatography (GPC) using universal calibration. Polypropylene (ATOFINA 3270, MFI = 2.0 g/10 min) was supplied by Total Petrochemical. Microcrystalline cellulose (Lattice® NT100) was kindly donated by FMC Biopolymer. Polyethylene glycol (Carbowax™ 3350) was purchased from Dow Chemical in powdered form. All materials were used as-received.

## 3 RESULTS AND DISCUSSION

### 3.1 Poly(lactic acid)

Differential scanning calorimetry (DSC) reveals no exothermic crystallization peak in the cooling scan (10 °C/min) of neat PLA, indicating that neat PLA does not crystallize when cooled from the melt state (figure 3a). In contrast, the sample made by addition of 1 wt% MCC to PLA via SSSP followed by MP with 10 wt% PEG reached the maximum achievable crystallinity of PLA (40-45%) at cooling rates of not only 10 °C/min but greater than 100 °C/min (figure 3b). The enhanced crystallization kinetics led to extremely fast cycle times needed to injection mold highly crystalline PLA parts. Shown in figures 4a and 4b are a 89/1/10 wt% PLA/MCC/PEG injection molded cap, produced in a cycle time of 33 seconds, before and after the addition of boiling water, respectively. It is evident from figure 4a that the cap ejected cleanly (no distortion in the part) from the hot mold, indicating the development of a high level of crystallinity. From DSC, the part was ~ 35% crystalline, which, as far as we know, is the highest level of crystallinity obtained at this cycle time. Figure 4b shows that this level of crystallinity prevents distortion in the part when placed in hot water for several minutes, thus demonstrating its use for high temperature applications.

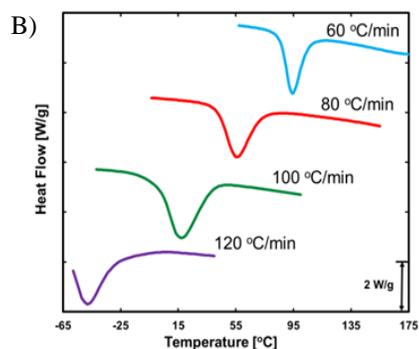
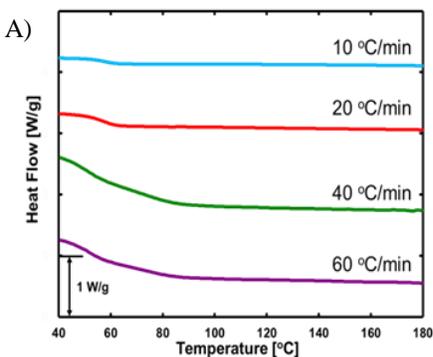


Figure 3: Nonisothermal crystallization curves for a) as-received PLA pellet and b) 89/1/10wt% PLA/MCC/PEG composite made by SSSP followed by melt-processing. Data were obtained via DSC by heating samples from -60 °C to 200 °C and then cooling to -60 °C at various rates, and repeating the heating and cooling cycle, with data taken during the second cooling cycle

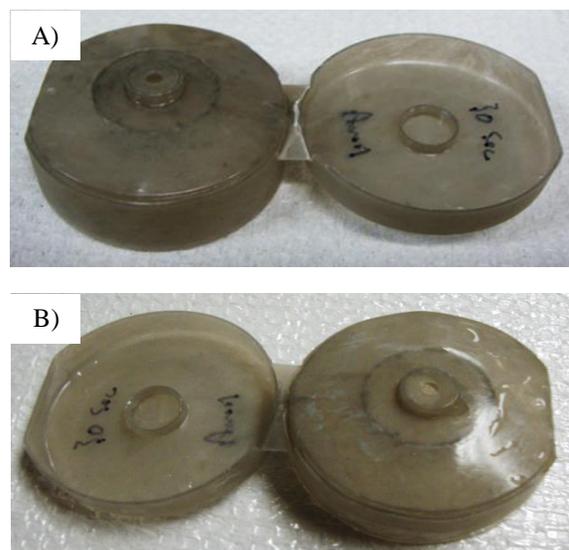


Figure 4: Injection molded 89/1/10 wt% PLA/MCC/PEG caps a) before and b) after the addition of boiling water. Total cycle time was ~ 33 sec.

### 3.2 Polypropylene

Recently, it was shown that the addition of MCC to PP via SSSP can greatly enhance the mechanical properties. Walker found that the well-dispersed fibers increased the tensile strength of PP by 60% and 100%, with the addition of 5 and 20 wt% MCC, respectively [37]. Such materials could be useful in real-world applications. One such application is a bottle cap with thinner walls while maintaining a high stiffness. Essentially, the ultimate goal is to reduce the amount of non-degradable PP needed to make the part, but still have similar functionality as a part with thicker walls. Shown in figures 5a and 5b is neat PP and a SSSP processed 80/20 wt% PP/MCC composite bottle cap, respectively. The cap shown in figure 5b is the

first demonstration of an injection molded product from SSSP processed materials. There have been attempts of making this same part by only melt-processing cellulose and PP directly in the injection molding apparatus, but this led to unusable parts. Here, we demonstrate the following advantages of the SSSP processed caps:

- Excellent dispersion of MCC
- Major increase in stiffness for the PP/MCC cap as compared to cap made from neat PP
- Maintains of the “living hinge” character of PP even at high MCC contents
- Lowered processing temperature and pressures
- No odor development from degradation of cellulose paraticles

Overall, this study demonstrates that SSSP processing with biodegradable fillers may provide a green solution to the challenges associated with PLA and PP and that sustainable engineering of polymers can be synonymous with property improvement.

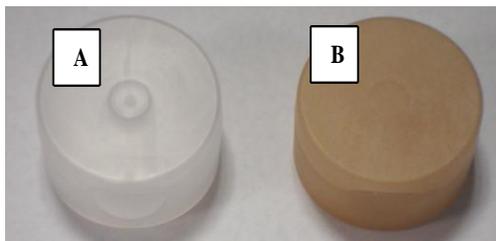


Figure 5: Injection molded a) neat PP and b) 80/20 wt% PP/MCC bottle caps

#### 4 REFERENCES

- Holland and Tighe, “Biodegradable Polymers,” Academic Press, London, 1<sup>st</sup> Ed., p. 101-165, 1992.
- D.J. Sawyer, *Macromol. Symp.* 201, 271, 2003.
- R.E. Drumright, P.R. Gruber and D.E. Henton, *Adv. Mater.* 12, 1841, 2000.
- B. Braun, J.R. Dorgan and D.M. Knauss, *J. Polym. Env.* 14, 49-58, 2006.
- J.R. Dorgan, H.J. Lehermeier, L.I. Palade and J. Cicero, *Macromol. Symp.* 175, 55, 2001.
- G. Instone, “Making Sense of Sustainable Packaging.” Produce Merchandising, [www.produceretailer.com/](http://www.produceretailer.com/)
- H.W. McCormick, F.M. Brower and L. Kim, *J. Polym. Sci.* 39, 87, 1959.
- N.J. Capiati and R.S. Porter, *J. Mater. Sci.* 10:1671. doi: 10.10007/BF00554928.
- D.N. Saheb and J.P. Jog, *Adv. Polym. Techn.* 18, 351 1999.
- N.M. Barkoula, T. Peijs, T. Schimanski and J. Loos, *Polym. Comp.* 26, 114, 2005.
- K.P. Matabola, A.R. De Vries, F.S. Moolman, and A.S. Luyt, *J. Mat. Sci.* 44, 6213, 2009.
- K. Banik, T.N. Abraham and J. Karger-Kocsis, *Macromolecular Mat. Eng.* 292, 1, 2007.
- J. Loos, T. Schimanski, J. Hofman, T. Peijs and P.J. Lemstra, *Polymer*, 42, 3827, 2001.
- Z. Xiadong, L. Qunfang, D. Gance, *Polym. Compos.* 10, 299, 2002.
- V.G. Reyes and W.J. Cantwell, *Compos. Sci. Techn.* 60, 1085, 2000.
- L. Suryanegara, A.N. Nakagaito and H. Yano, *Compos. Sci. and Techn.* 69, 1187, 2009.
- A.K. Bledzki, A. Jazkiewicz and D. Scherzer, *Compos.: Part A*, 40, 404, 2009.
- Pukanszky and Fekete, “Mineral Fillers in Thermoplastics I,” Springer, New York, 1<sup>st</sup> Ed., p. 109-139, 1999.
- G.I Williams and R.P. Wool, *Appl. Comp. Mat.* 7, 421, 2000.
- Wallenberger and Weston “Natural Fibers, Plastics and Composites,” Norwell: Kluwer Academic Press, 1<sup>st</sup> Ed., p. 149-165, 2004.
- A. Paul and S. Thomas, *J. Appl. Polym. Sci.* 63, 247, 1997.
- C. Pierre, A. Flores, K. Wakabayashi, and J.M. Torkelson, *Soc. Plast. Eng. ANTEC*, 66, 2082, 2008.
- A.H. Lebovitz, K. Khait, and J.M. Torkelson, *Polymer*, 44, 199, 2003.
- Y. Tao, J. Kim, and J.M. Torkelson, *Polymer*, 47, 6773, 2006.
- M. Diop and J.M. Torkelson, *Soc. Plast. Eng. ANTEC*, accepted 2012.
- K. Khait and J.M. Torkelson, *Polym.-Plast. Technol.* 38, 445, 1999.
- M. Ganglani, J.M. Torkelson, S.H. Carr, and K. Khait, *J. Appl. Polym. Sci.* 80, 671, 2001.
- K. Wakabayashi, Y. Tao, A.H. Lebovitz, and J.M. Torkelson, *Soc. Plast. Eng. ANTEC*, 65, 1528, 2007.
- K. Wakabayashi, C. Pierre, D.A. Dikin, R.S. Ruoff, T. Ramanathan, L.C. Brinson, and J.M. Torkelson, *Macromolecules*, 41, 1905, 2008.
- J. Masuda and J.M. Torkelson, *Macromolecules*, 41, 5974, 2008.
- K. Wakabayashi, P.J. Brunner, J. Masuda, S.A. Hewlett, and J.M. Torkelson, *Polymer*, 51, 5525, 2010.
- P.J. Brunner and J.M. Torkelson, *Soc. Plast. Eng. ANTEC*, accepted 2012.
- K. Khait and S.H. Carr, *Soc. Plast. Eng. ANTEC*, 55, 3086, 1997.
- K. Khait and S.H. Carr, *Soc. Plast. Eng. ANTEC*, 56, 2533, 1998.
- P.J. Brunner, J.T. Clark., J.M. Torkelson, and K. Wakabayashi, accepted to *Polym. Eng. Sci.* 2012. Available online DOI 10.1002/pen.23115.
- K. Khait and S.H. Carr, “Solid-State Shear Pulverization: A New Polymer Processing and Powder Technology,” Technomic Publ. Co., Lancaster, 2001.
- P.J. Brunner, A.M. Flores, J.R. Dorgan and J.M. Torkelson, *PMSE Preprints*, 101, 1584, 2009.