Injection molding of PLA cutlery

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Background

Disposable plastic items are typically made out of two types of plastics: polypropylene (PP) and polystyrene (PS). Plastic utensils, in particular, are highly regarded for the affordability and convenience. However, once these utensils are contaminated with food, recycling them becomes challenging. On the other hand, food service-ware and packaging made from compostable plastics, such as Ingeo™ Poly(lactic) acid (PLA), allow for easy disposal in composting, and thereby provide a viable alternative to recycling of conventional plastic-based materials. There is no need to clean the item as you would for high-quality conventional recycling. All compostable plastic products go into one bin together with the food waste, thereby making it simpler to facilitate diversion of food waste from landfill to composting. However, for manufacturers, PLA is a thermoplastic material that comes with its own unique challenges. This article examines from a manufacturer's perspective, how the injection molding of PLA-based compounds compares with molding of PS and PP, and in particular, how the performance of cutlery made from Natur-Tec's modified Ingeo PLA compares with cutlery made from PS or PP.

Comparison of thermal properties

In order to understand molding behavior and performance of a material, it is important to first understand its thermal properties. Table 1, summarizes the thermal properties of PLA, PS and PP.

Commercial grade, atactic PS is an amorphous material, i.e. has 0 % crystallinity, and as such it does not have a melting point. The glass transition temperature (T_g) of this PS is 100 °C (89 to 102 °C depending on the molecular weight). The glass transition temperature is an important thermal property of any polymer, and is the temperature region where the (amorphous region of) polymer transitions from a hard, glassy material to a soft, rubbery material as temperature increases. Hard plastics, such as PS, are used well below their T_g or in their glassy state. The T_g of PS is well above room temperature, and as such PS can be used with hot foods up to 90 °C without softening.

PP, on the other hand, has a T_g of 0 °C and is a more flexible polymer as compared to PS at room temperature. This is a common way to distinguish PP cutlery from PS cutlery in the market. PP cutlery tends to be bendable or pliable, whereas PS cutlery tends to be stiff and hard. PP and PLA are both semi-crystalline polymers with a melting point in the range of 160 °C. Despite having a similar melting point, PLA is different from PP. PLA has a high melting point similar to that of PP, and a T_g above room temperature similar to that of PS. This makes PLA cutlery, rigid or glassy at room temperature. However, above its T_g of 55 °C, PLA cutlery starts to soften and is difficult to use in high temperature applications. Although it is a semi-crystalline polymer, PLA has a much slower crystallization rate as compared to PP. Therefore, PLA parts made with a cold mold are essentially amorphous. PP food service ware is usable in hot food applications inspite of its much lower T_g because of its "*crystallinity*" and faster rate of crystallization – achieve a crystallinity of 30 – 70 % in 5 – 10 seconds [1]. When a PP part is above its T_g, the amorphous regions soften, but the crystals which contribute to the morphological structure help the part in maintaining form until its melting point is reached. This same principle can be applied to PLA.

Figure 1, clearly demonstrates these differences among the three materials by measuring storage modulus (stiffness) as a function of temperature. PS (orange curve) maintains its stiffness until 100 °C, above which it deforms. Amorphous Ingeo 2003D PLA (green curve) follows the same trend until it reaches its T_g around 55 °C, after which it deforms. As discussed earlier, PP is a semi-crystalline material and slowly decreases in stiffness (brown curve) until it reaches its melting temperature of 140 °C. Crystallized PLA (Ingeo 3100HP – blue curve) is rigid at room temperature, similar to PS, and decreases in stiffness at approximately 60 °C. However, the crystalline domains of PLA hold the structure together and prevent the product from deformation till its melting point of 155 °C is reached. This is very similar to PP behavior as can be seen from the brown (PP) and blue (Ingeo 3100HP PLA) curves. Thus, developing crystallinity in PLA helps increase resistance to heat in compostable foodservice ware applications. There are, of course, other ways to improve heat resistance in durable, non-compostable PLA applications.

Molding and crystallization of PLA

From the above discussions, it is clear that crystallization is an efficacious way to improve high-heat performance in compostable food service ware products. There are two methods in which one can develop crystallinity in a compostable part as summarized below:

a) *One-Step Process or In-mold annealing*:
Crystallization of a part by changing the mold temperature to improve performance of the molded part has been practiced and studied for traditional plastics [3]. The same can be applied to PLA, where crystallization is carried out in the mold itself by heating the mold to the crystallization temperature of the specific PLA grade, typically in the range of 100 – 130 °C. Crystallization rate is affected by the D-content present in the PLA. Lower the D-content, faster

is the crystallization rate [4]. This is particularly important for a molding process as it directly affects the cycle times in the mold. Cycle times for an Ingeo 3100HP PLA based cutlery is on the order 30 – 45 seconds depending on the mold design, runner system and heating channels. Therefore, this method is, currently a more expensive way of crystallizing a PLA part, as the cycle times to crystallize in the mold are much higher than those for PP or PS that are only 5 – 10 seconds. The main advantage of an in-mold annealing process is that one can utilize the full capacity of the molding equipment, and the process set-up is straightforward. Additionally, the warpage of the part is minimal as compared to a post-annealing process described in the next section.

b) *Two-Step Process or Post-annealing*:
This is currently the most popular way of crystallizing PLA, especially for cutlery. The cutlery is molded in step one in a cold mold, followed by step two in which the cutlery is annealed in a convection oven set at the PLA crystallization temperature [5]. The advantage is one can get benefit from the faster cycle times of the cold mold to make almost amorphous parts in step one and keep the molding cost much lower. The disadvantages of the post-annealing method are (i) molding capacity can only be fully utilized with an upfront investment in suitable ovens or automation (ii) it can be labor intensive if not automated, and (iii) part warpage is an issue depending upon the geometry of the cutlery, as the material relaxes when reheated above its T_g.

Performance of cutlery made with Natur-Tec's modified Ingeo PLA compound

Natur-Tec™ has launched a 2-part resin solution, BF3002HT, consisting of a highly-filled, impact-modified Ingeo PLA based masterbatch, that can be blended with virgin Ingeo PLA at the time of injection molding. Competitive filled-PLA compounds that are currently available in the market do not use the masterbatch approach and typically use 100 % of the compounded resin for molding cutlery. A key advantage of the Natur-Tec 2-part solution is that only 50 % of the resin used for molding goes through two heat histories, which in turn, helps in maintaining the molecular weight, and therefore provide improved mechanical strength for the final part, as compared to a part manufactured with the 100 % fully-compounded resin.

Performance Test Methods: There is no standardized quantitative test method to compare various cutleries, other than a military specification describing a method that is at best semi-quantitative [6]. As a result, to quantify the stiffness/flexibility of a cutlery and performance in hot water, Natur-Tec developed two in-house tests with standard Instron equipment used for tensile/compressive testing

1. Rigidity Test: In the rigidity test, the handle of a cutlery piece was clamped to the upper jaw of the Instron and pushed down vertically until it was bent or broken.

2. Hot Water Test: In the hot water test, which simulates performance in hot fluids, the cutlery was immersed in hot water at controlled temperature between 80 and 90 °C for 20 seconds before it was compressed in the vertical direction.

	Glass transition temperature, T_g, °C	Melting temperature, T_m, °C	% Crystallinity	Crystallization rate
PS	100	NA	0	NA
PP	0	140 – 170	30 – 70	Fast
PLA	55	160	30 – 50	Slow

Table 1: Typical thermal properties of PLA, PS and PP

Figure 1: Change in storage modulus (stiffness) as a function of temperature for Ingeo 2003D PLA, polystyrene, polypropylene and crystallized Ingeo 3100HP PLA [2]

Both tests measured the force (compressive load) to break/bend a cutlery, and how much distance is compressed before the cutlery failed. The area under the curve of force vs. distance provided the toughness (energy absorbed at break) of each cutlery based on design and material performance.

Cutlery made using Natur-Tec BF3002HT resin, was benchmarked against standard PS and PP cutlery sold in the market, for performance metrics such as mechanical strength, hot water resistance and warpage. The PS cutlery benchmarked was similar in weight and length as the Natur-Tec cutlery, whereas the PP cutlery was slightly smaller and lower in weight.

Rigidity Performance Data: Figures 2(a) and (b) show results obtained from the Rigidity test. Figure 2(a) shows that both PS and PLA are rigid and stronger materials at room temperature and need a higher force to break/deform as compared to the PP cutlery. Figure 2(a) also shows that PS is more brittle and breaks sooner, as compared to the PP or Natur-Tec cutlery. It is noteworthy that Natur-Tec's modified Ingeo PLA cutlery did not break and withstood more of the applied force before deforming (about 2 kg force). PP cutlery also did not break but it deformed when the applied force was only) 0.5 kg. This is evident in figure 2(b), where toughness or total energy absorbed to break was compared. Natur-Tec cutlery exhibits higher toughness as compared to both PS and PP cutlery.

Performance in Hot Water: Figure 3(a) and (b) show results obtained from a Hot Water test where force to deform a cutlery was measured at two temperatures: 80 °C and 90 °C. Any changes in shape after the force was applied were also noted. The PS cutlery was the most rigid cutlery at the lower temperature as shown in figure 3(a). At higher temperatures of 90°C, closer to the T_g of PS, the PS cutlery begins to soften and consequently the force to deform it dropped significantly – figure 3(b). Also PS cutlery deformed after being compressed in hot water as shown in picture, while Natur-Tec's (and the PP) cutlery retained its shape as they were still flexible.

Warpage in Post-Annealing: Warpage of the cutlery during the post-annealing step tends to be a major issue that affects overall yield and therefore the per-piece cost. As a result, warpage of the molded cutlery was studied as a function of masterbatch amount used in Natur-Tec's 2-part resin system. Warpage for the spoon was measured as changes in the length of the handle, and the width of the spoon bowl. The annealing conditions used were maintained the same for all parts in a convection oven. Figure 4 shows change in width of spoon-bowl. It was found that as the percentage of highly filled masterbatch was increased, the warpage of the cutlery decreased. Warpage plateaued out at approximately 2 % at a masterbatch loading level of 50 %. The crystallinity of all the cutlery samples tested was 40 – 50 %.

Summary

PLA is a semi-crystalline polymer with T_g of 55 °C and therefore behaves as a glassy polymer at room temperature like PS, At However at use temperatures above 55 °C, PLA cutlery will deform and will not be usable. Developing crystallinity in PLA allows use of PLA upto 90 °C because the crystalline domains hold the structure together and prevent deformation. Crystallized PLA cutlery tends to be flexible like PP cutlery at higher

Figure 2: (a) Stiffness comparison of spoon made with PS, PP and Natur-Tec's modified Ingeo PLA; (b) Toughness comparison of spoon made with PS, PP and Natur-Tec's modified Ingeo PLA

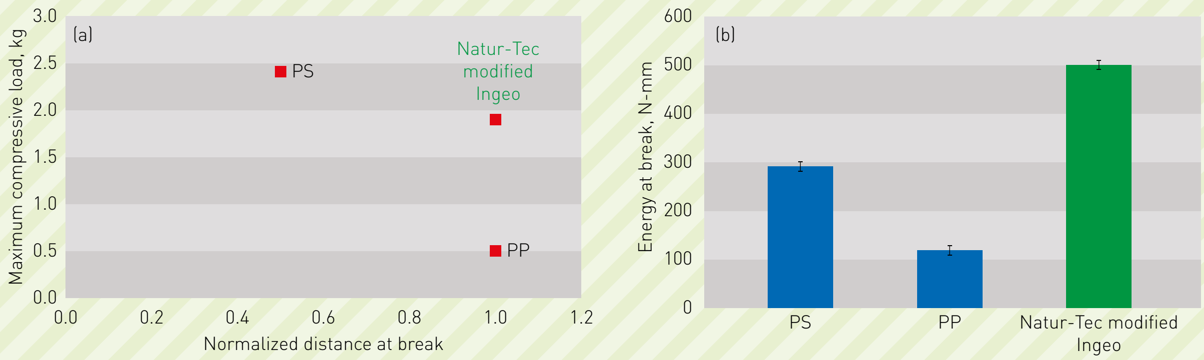
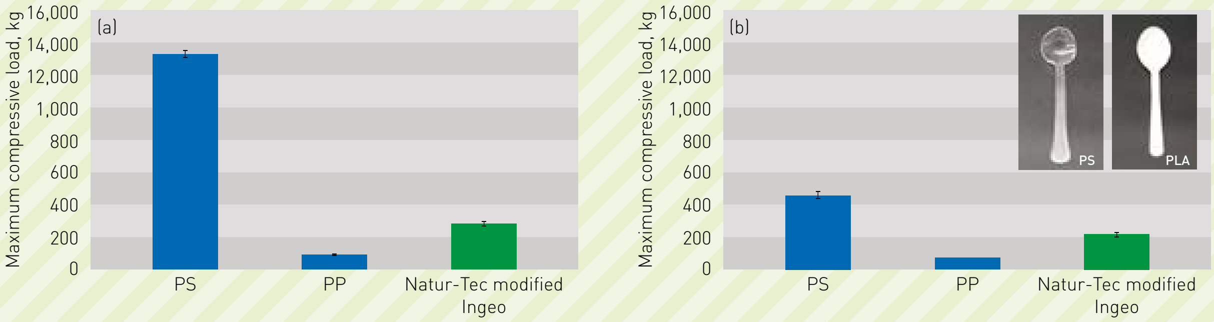


Figure 3: Hot water performance of spoon made with PS, PP and Natur-Tec's modified Ingeo PLA (a) at 80 °C and (b) at 90 °C



temperatures. Crystallization can be carried out in two ways: (1) as in-mold annealing where part is crystallized in a heated mold at 100 – 130°C and (2) as post-annealing where part is molded with a cold mold and then crystallized in a second step in an oven.

Cutlery made with Natur-Tec's modified Ingeo PLA compound has better toughness than PS cutlery of the same weight. Warpage, in post-annealed cutlery, is significantly reduced as the masterbatch is increased from 15 % to 50 %. The 2-part Natur-Tec resin solution helps retain molecular weight, and provides better mechanical performance as compared to a traditional filled-PLA compound.

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Figure 4: Warpage of spoon as measured by decrease in width of spoon-cup for cutlery made with different levels of masterbatch blended with virgin Ingeo PLA