Injection molding of PLA cutlery
PLA餐具的注塑成型

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Background背景

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.

一次性塑料制品通常由两种塑料制成：聚丙烯（PP）和聚苯乙烯（PS）。尤其是塑料器皿，因为价格实惠和方便而备受推崇。然而，一旦这些餐具被食物污染，回收就变得格外困难。另一方面，由可堆肥塑料制成的食品服务器具和包装，如Ingeo ™ 聚乳酸（PLA），便于在堆肥过程中进行处理，从而为传统塑料基材料的回收提供了一种可行的替代方案。所有可堆肥的塑料制品与食物垃圾一起可投入同一个垃圾箱，从而简化了食物垃圾从垃圾填埋场转移到堆肥的过程。然而，对于制造商而言，聚乳酸是一种热塑性材料，有其独特的挑战。本文从制造商的角度出发，探讨聚乳酸基化合物的注塑成型与聚苯乙烯和聚丙烯的成型的对比，特别是Natur-Tec改良后的Ingeo™聚乳酸餐具与聚苯乙烯或聚丙烯餐具的性能对比。

Comparison of thermal properties热性能比较

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.

为了了解材料的成型过程和性能，首先了解材料的热性能是很重要的。表1总结了聚乳酸、聚苯乙烯和聚丙烯的热性能。

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.

商用级无规则聚苯乙烯是一种无定形材料，即结晶度为0%，因此不具有熔点。该PS的玻璃化转变温度（Tg）为100℃（根据分子量的不同，在89至102℃之间）。玻璃化转变温度是聚合物的重要热性能，是聚合物（非晶区）随着温度的升高从坚硬的玻璃状材料转变为柔软的橡胶状材料的温度区域。硬塑料，如聚苯乙烯，使用温度远低于其玻璃化转变温度，即在其玻璃态。PS的Tg远远高于室温，因此PS可与高达90℃的热食品一起使用而不软化。

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.

另一方面，PP的Tg为0°C，与PS相比，PP在室温下更为柔软。这是市面上常见的区别PP餐具和PS餐具的方法。PP餐具容易弯曲且比较柔韧，而PS餐具则非常坚硬。聚丙烯和聚乳酸都是半结晶聚合物，熔点在160℃范围内。尽管具有相似的熔点，但PLA与PP并不相同，PLA具有与PP相似的高熔点和与PS相似的高于室温的Tg。这使得聚乳酸餐具，在室温下呈刚性或玻璃状。然而，当温度高于55℃的Tg时，PLA餐具开始软化，很难在高温应用中使用。尽管PLA是一种半结晶聚合物，但其结晶速率比PP慢得多。因此，用冷模制造的PLA零件基本上是非晶态的。PP食品器皿可用于热食品应用，因为其“结晶度”低得多，结晶速度更快，在5-10秒内结晶度便可达到30-70%[1]。当PP零件高于其Tg时，非晶区软化，但用以维持其形态结构的晶体有助于保持其形态，直到达到熔点。这个原理同样适用于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.

图1通过测量储能模量（刚度）关于温度的函数，清楚地说明了三种材料之间的这些差异。PS（橙色曲线）在低于100°C时保持其刚度，高于100°C时则会变形。非晶态Ingeo 2003D PLA（绿色曲线）遵循相同的趋势，直到其在55℃左右达到Tg，然后发生变形。如前所述，PP是一种半结晶材料，硬度（棕色曲线）缓慢下降，直到达到140°C的熔化温度。结晶PLA（Ingeo 3100HP–蓝色曲线）在室温下是刚性的，类似于PS，在大约60°C时刚度降低。然而，PLA的结晶区将结构固定在一起，防止产品变形，直到达到155℃的熔点。从棕色（PP）和蓝色（Ingeo 3100HP-PLA）曲线可以看出，这与PP的行为非常相似。因此，在PLA中增加结晶性有助于提高其在可堆肥食品应用中的耐热性。当然，在耐久的、不可堆肥的PLA应用中，还有其他提高耐热性的方法。

Molding and crystallization of PLA聚乳酸的成型与结晶

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:

从以上讨论可以看出，结晶是提高可堆肥食品用具产品耐高温性能的有效途径。有两种方法可以在可堆肥产品中形成结晶度，总结如下：

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.

a）单步工艺或模内退火：

通过改变模具温度来提高成型零件的性能，对传统塑料的结晶进行了实践和研究[3]。这一方式同样适用于PLA，在PLA中，结晶过程是在模具中进行的，方法是将模具加热到特定的PLA结晶温度，通常在100-130°C范围内。结晶速率受聚乳酸中D-成分的影响。D成分含量越低，结晶速率越快[4]。这对于成型过程特别重要，因为它直接影响模具中的循环时间。Ingeo 3100HP PLA餐具的循环时间约为30-45秒，具体取决于模具设计、流道系统和加热通道。因此，这种方法是目前较为昂贵的PLA零件结晶方法，因为在模具中结晶的循环时间远高于PP或PS的5-10秒。模内退火工艺的主要优点是可以充分利用成型设备的能力，而且工艺设置简单。此外，与下一节中描述的后退火处理工艺相比，零件的翘曲最小。

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.

b）两步工艺或后退火处理：
这是目前最流行的结晶聚乳酸的方法，特别是用于餐具。在第一步中，餐具在冷模中成型，然后在第二步中，餐具在设定为PLA结晶温度的对流烤箱中退火[5]。其优点是可以利用冷模的快速循环时间，在第一步中制备出几乎无定形的零件，使成型成本大大降低。后退火处理的缺点是（i）只有在适当的烤箱或自动化设备上进行前期投资后，才能充分利用其成型能力（ii）如果不能实现自动化的话，则可能为劳动密集型；（iii）由于材料在高于其Tg时会松弛，因此零件翘曲是一个取决于餐具几何结构的问题。

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

Natur-Tec改良的Ingeo-PLA复合材料餐具的性能

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.

Natur-Tec ™ 已经推出了一种双组分树脂解决方案，BF3002HT，由一种高度填充、冲击修正的基于Ingeo-PLA的母料组成，可以在注塑成型时与原始的Ingeo-PLA混合。目前市场上有竞争力的填充聚乳酸化合物不使用母料法，通常使用100%的复合树脂来成型餐具。Natur-Tec双组分解决方案的一个关键优势是，用于成型的树脂只有50%经历两次热处理，这有助于保持分子量，因此，与使用100%全复合树脂制造的零件相比，为最终零件提供了更好的机械强度。

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

性能测试方法：没有标准化的定量测试方法来比较各种餐具，除了军用规格中描述的方法最多是半定量的[6]。因此，为了量化餐具的刚度/柔韧性和在热水中的性能，Natur-Tec开发了两个内部测试，使用标准Instron设备进行拉伸/压缩测试

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.

刚度测试：在刚度测试中，把餐具柄夹在Instron的上部钳臂中，垂直向下推，直到刀柄弯曲或折断。

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.

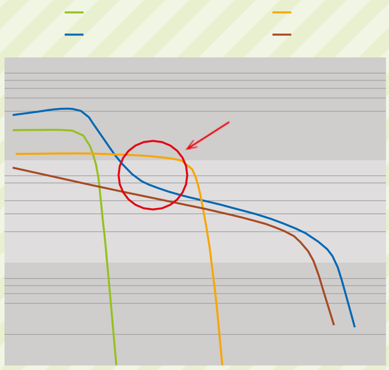
热水测试：在模拟热流体性能的热水测试中，餐具在80至90°C的控制温度下浸入热水中20秒，然后在垂直方向上被压缩。

	Glass transition temperature, 玻璃化转变温度，T_g, °C	Melting temperature 熔化温度, T_m, °C	% Crystallinity 结晶度百分比	Crystallization rate 结晶速率
PS	100	NA	0	NA
PP	0	140 – 170	30 – 70	Fast 快
PLA	55	160	30 – 50	Slow 慢

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]

图1:Ingeo 2003D聚乳酸、聚苯乙烯、聚丙烯和结晶Ingeo 3100HP PLA的储能模量（刚度）随温度的变化[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.

这两项测试都测量了打破/弯曲餐具所需的力（压缩载荷），以及餐具断裂前压缩的距离。根据设计和材料性能，，力与距离曲线下的面积提供了每个餐具的韧性（断裂时吸收的能量）。

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.

采用Natur-Tec BF3002HT树脂制造的餐具，在机械强度、热水耐受力和翘曲度等性能指标方面与市场上销售的标准PS和PP餐具进行了对比。PS餐具为基准的餐具在重量和长度上与Natur-Tec餐具相似，而PP餐具稍小，重量较轻。

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.

刚度性能数据：图2（a）和（b）显示了刚度测试的结果。图2（a）显示，PS和PLA在室温下都是刚性和强度更高的材料，与PP餐具相比，需要更大的力来断裂/变形。图2（a）还显示，与PP或Natur-Tec餐具相比，PS更脆，断裂更快。值得注意的是，Natur-Tec改良的Ingeo-PLA餐具在变形前没有断裂，并承受了更多的外力（约2千克力）。PP餐具也没有断裂，但在0.5kg的力作用下变形。这在图2（b）中很容易看出对比（其中比较了韧性或断裂吸收的总能量）。与PS和PP刀具相比，Natur-Tec餐具有更高的韧性。

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.

热水性能：图3（a）和（b）显示了热水测试的结果，在80°C和90°C两种温度下测量了使餐具变形的力。还记录了施加力后形状的变化。如图3（a）所示，PS餐具是低温下最坚硬的餐具。在90°C的高温下，由于接近PS的Tg，PS餐具开始软化，从而使其变形的力显著下降–图3（b）。如图所示，PS餐具在热水中压缩后变形，而Natur-Tec（和PP）餐具由于仍然具有弹性，因此保持其形状。

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 %.

后退火处理中的翘曲：在后退火步骤中餐具的翘曲往往是影响整体成品率和单件成本的主要问题。因此，研究了模压餐具的翘曲变形与Natur-Tec双组分树脂体系中母料用量的关系。勺子的翘曲是通过手柄长度和勺碗宽度的变化来测量的。所有零件在对流炉中的退火条件保持不变。图4显示了勺碗宽度的变化。研究发现，随着高填充母料比例的增加，餐具的翘曲度降低。当母料填充比例为50%时，翘曲度稳定在2%左右。所有被测餐具样品的结晶度为40-50%。

Summary总结

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

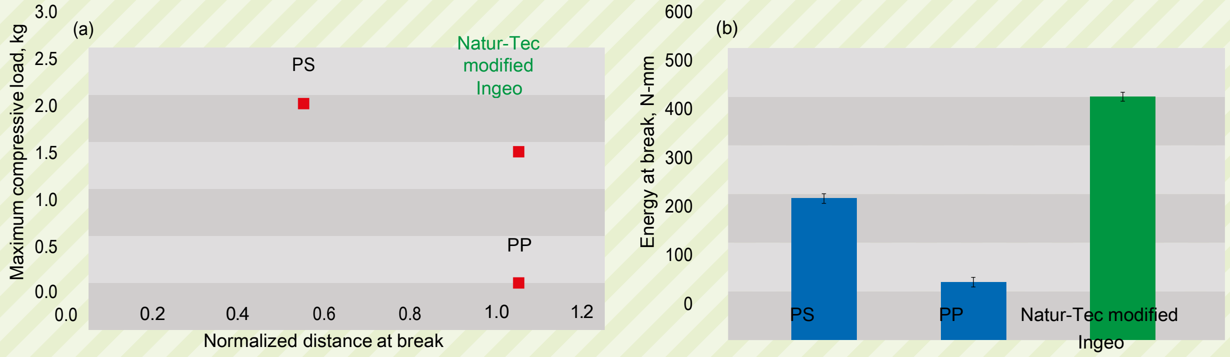
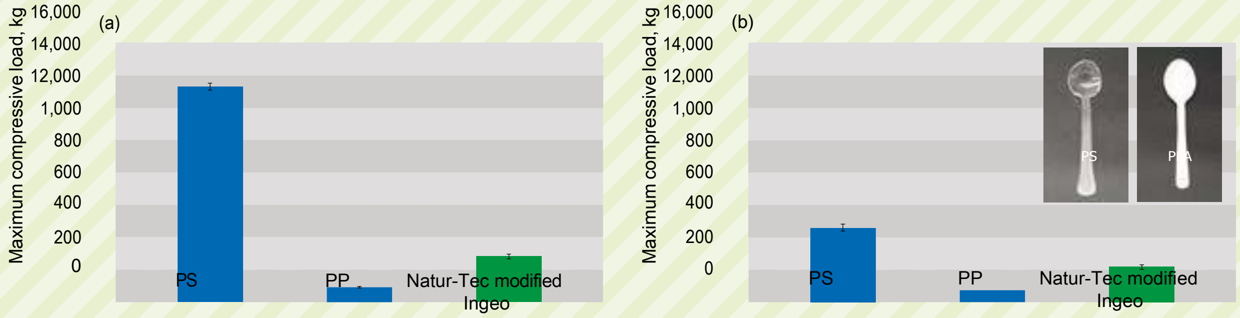


Figure 3: Hot water performance of spoon made with PS, PP and Natur-Tec's modified Ingeo PLA (a) at 80 °C and (b) at 90 °C



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.

PLA是一种半结晶聚合物，Tg为55°C，因此在室温下与PS一样表现为玻璃状聚合物，但是在使用温度高于55°C时，PLA餐具会变形，无法使用。在PLA中增加结晶度可允许其在高达90°C的条件下使用，因为结晶域将结构固定在一起并防止变形。结晶PLA餐具在较高的温度下具有较好的柔韧度，如同PP餐具一样。

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.

Natur-Tec改良的Ingeo-PLA复合材料制作的餐具比同等重量的PS餐具具有更好的韧性。当母料填充比例从15%增加到50%时，后退火处理餐具的翘曲度显著降低。与传统的填充聚乳酸化合物相比，双组分Natur-Tec树脂方案有助于保持分子量，并提供更好的机械性能。

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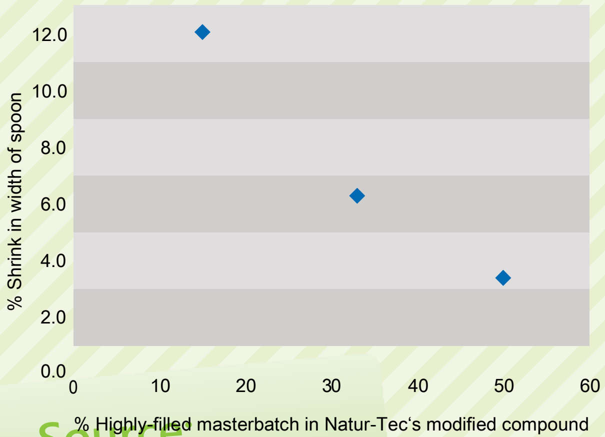
Figure 4: Warpage of spoon as measured by decrease in width of spoon-cup for cutlery made with different levels of masterbatch blended with virgin Ingeo PLA

图4：勺子的翘曲度，通过勺碗宽度的减小来测量，勺子是由不同填充比例的母料与原始Ingeo PLA混合制成的



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