Modified Calcium Carbonate opens new opportunities for the use of PLA

Polylactic Acid (PLA) is one of the fastest growing biobased polymers on the market. Processors have tried to use Calcium Carbonate to improve properties and the cost structure, as is common in conventional polymers. Omya gained experience showing that conventional Calcium Carbonate can lead to the degradation of PLA and PLA / PBAT blends used in products such as cups, trays, lids and bags. Omya followed market demand to develop a new type of Calcium Carbonate that does not cause PLA degradation.

Introduction

PLA is a bio-polyester which degrades when processed with moisture due to hydrolysis. Calcium Carbonate is by nature a somewhat hygroscopic material and carries a certain amount of moisture on its surface and in its crystal structures.

In 1952, Omya launched the first surface-treated Calcium Carbonate with reduced moisture adsorption. Today it is common to use surface-treated calcium carbonate in all types of polymer applications to prevent processing problems and surface defects on the final products. The most common surface treatment materials are based on fatty acids, such as stearic acid. With such a treatment, a good reduction of the moisture uptake on the Calcium Carbonate can be observed, but it ultimately causes hydrolysis in PLA.

With the development of Omya Smartfill® technology, the situation has changed. It is now possible to add 40 % or more of Calcium Carbonate in films, sheets or injection molded parts without causing significant hydrolysis while improving important properties such as elongation, stiffness and impact.

Product Evaluation

Melt flow rate is considered a good indicator of polymer chains degradation: As PLA degradation increases, it is expected that the melt flow rate of the polymer or compound would increase too.

Table 2 shows the difference between conventionally treated Omyacarb® 1T and Omya Smartfill after preparing a 40 % Calcium Carbonate compound with Natureworks Ingeo™ 2003D. The compounding line is a continuous kneader without vacuum degassing and only pre-dried PLA was used. The results show that using a conventional Calcium Carbonate, such as Omyacarb 1T, MFR increased significantly, which means that important polymer degradation has taken place during processing. In contrast, Omya Smartfill does not show signs of degradation and kept the melt flow on the same level as virgin PLA.

A more common technology for processing PLA is twin-screw compounding with the ability to extract water by vacuum degassing. Table 3 shows that in these processing conditions, the melt flow rate increase with Omyacarb 1T was more limited but still not satisfactory. The use of Omya Smartfill led again to a significantly lower MFR and matched the viscosity of unfilled PLA.

Omya Smartfill does not require pre-drying or venting when compounding

To test the effect of Calcium Carbonate on PLA properties, a 300mm working width laboratory casting line was used to make 800 µm PLA sheets with different Calcium Carbonate loadings.

Fig 1 and Fig 2 show the same typical property changes Calcium Carbonate provides in PLA as expected with Calcium Carbonate addition in conventional thermoplastic polymers. Yield strength decreases, and stiffness increases with increasing Calcium Carbonate concentration.

After sheet production, part of it was cut into small pieces to check the extent of degradation. This was done after the second heat history through MFR measurement (Fig 3). The results clearly show that Omya Smartfill does not cause additional PLA degradation, whereas Omyacarb 1T causes heavy degradation, which can make polymer processing difficult.

In many polymers, the elongation at break is reduced due to the addition of mineral additives. Surprisingly Omya Smartfill added to PLA boosts the ultimate elongation. Fig 4 shows a strong increase in elongation at break achieved when adding Omya Smartfill with a maximum at around 20 % addition but even at 40 % addition elongation is far higher than for virgin PLA. This proves that Omya Smartfill increases stiffness and elasticity simultaneously and allows a processor to achieve high filler levels with superior mechanical properties. This effect can be seen also when adding Omyacarb 1T but to a much less extent, which could be related to degradation.

Similar injection molding tests show comparable improvements and an increased impact strength on top, but there are additional benefits that contribute to overall cost savings when using 40 % Omya Smartfill, including:

- 12 % lower specific heat capacity
- 78 % higher thermal conductivity
- 60 % higher thermal diffusivity
- 89 % opacity at 30 % filler level without the use of titanium dioxide

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Physical properties help to increase productivity. When using Omya Smartfill in thermoforming or injection molding, less energy is needed for heating and cooling and lower cycle times can be achieved.

Omya Smartfill is always the right choice when conventional Calcium Carbonate causes polymer degradation due to hydrolysis. It is EU 10/2011 and FDA approved for food contact, it meets composting requirements and has passed the ecotoxicity test. The material is supplied as a powder and needs to be pre-dispersed in a compound before being used on conventional single screw extrusion lines.

Omya recently received an Innovator Award from the Sustainable Packaging Coalition (SPC) as a member of PepsiCo's Supply Chain Partnership to deliver a new biobased film package to market. The outcome of a Partnership Innovator Award was one of a select few entries chosen for advancing the state of sustainable packaging. NatureWorks, Danimer Scientific, Berry Global, Johnson-Bryce and PepsiCo also received an award.

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Table 1: Moisture adsorption of common calcium carbonate grades and Omya Smartfill 55 - OM (mg/g, upon relative humidity change from 10% rH to 85 % rH at 23 °C)

Calcium Carbonate	Moisture Adsorption
Conventional un-treated	1580 ppm
Conventional treated	750 ppm
Omya Smartfill 55-OM	390 ppm

Table 2: MFR (210°C/ 2.16kg [g/10min]) (without degassing)

	MFR
100% PLA Ingeo 2003D	6
60% PLA + 40% Omyacarb 1T	49
60% PLA + 40% Omya Smartfill	5

Table 3: MFR (210°C/ 2.16kg [g/10min]) (with degassing)

	MFR
100% PLA Ingeo 2003D	6
60% PLA + 40% Omyacarb 1T	25
60% PLA + 40% Omya Smartfill	6

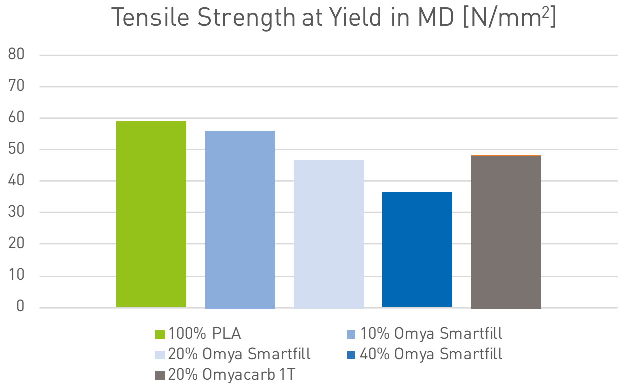

Fig 1

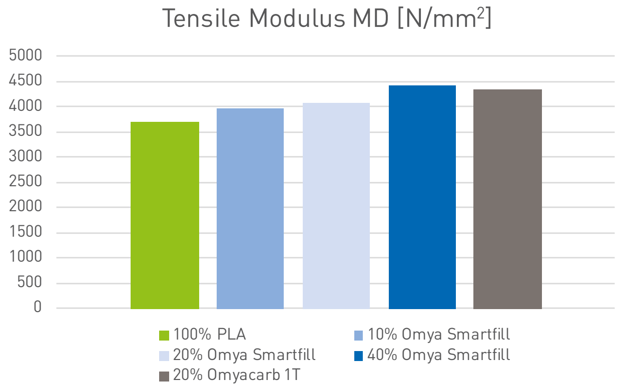

Fig 2

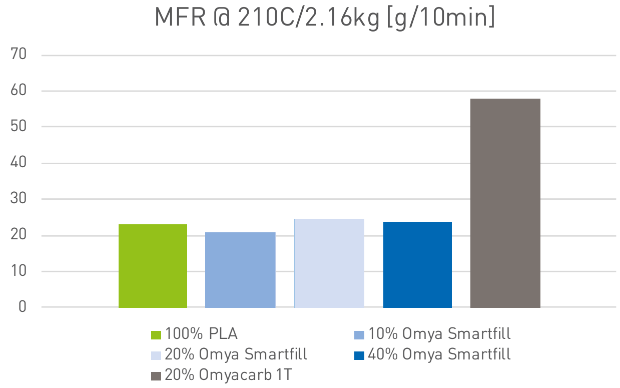

Fig 3: MFR after sheet production

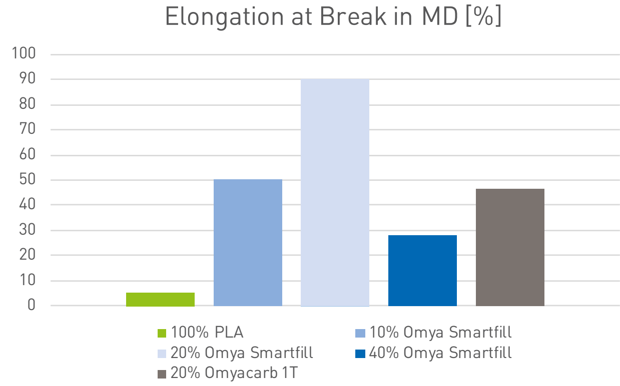

Fig 4: Impact of calcium carbonate to elasticity