

Talc filled PLA

Micronized talc:
a functional filler
for PLA nucleation



The limited service temperature of standard PLA is narrowing the application opportunities in many disposable items (i.e. hot beverages cups) as well as in durable applications where service temperature is a relevant property. In general, for semi-crystalline polymers, by increasing the degree of crystallinity it is possible to improve the service temperature. Because of the limited crystallization kinetic of PLA, such polymer is not able to crystallise during standard shaping processes (such as in injection moulding). The usage of nucleating agent improves the crystallization speed, allowing PLA to enhance its properties.

Highly micronized talc is a common nucleator for many semi-crystalline polymers (the most common one is polypropylene) and some properties of micronized talc as nucleator for PLA were investigated.

Talc is a natural mineral and it can be identified as an hydrated magnesium sheet silicate. Talc is ranked as the softest mineral (Mohs scale) and it is hydrophobic and chemically inert. Thanks to its platy structure, talc is able to improve mechanical performances of polymers, offering quite high specific surface to better interact with the polymer. Because of its affinity with polymers, talc surface is a perfect substrate for crystal growth.

Experimental

Concerning PLA, the ability of different talc grades to enhance crystallization in such polymer was measured. The basic evaluation performed on PLA was related to differential scanning calorimeter (DSC) experiments. DSC is an easy method to evaluate crystallization, recording the exothermic peak, typically observed during cooling experiment for most of semi-crystalline polymers. But when the crystallization process is very slow, polymer chain structure re-organization can take place during further melting experiment.

With reference to neat PLA, once the polymer is in molten state and the previous thermal history completely erased, if cooled under controlled conditions (10°C/min), the crystallization doesn't take place. By melting the sample still under same controlled conditions, it is possible to record an exothermic peak at approximately 110°C, showing the PLA crystallization (Fig. 1).

In this experimental evaluation, three different talc grades were considered: talc HTP1c (highly micronized talc), talc HTPUltra5c (ultrafine talc) and talc NTT05 (high performance talc). By modifying PLA with minor amounts of micronized talc, it is possible to improve the crystallization behaviour, allowing modified PLA to achieve crystallization under cooling conditions. Two different talc loading rates were evaluated: 1% and 5%, by weight. Modification was performed by dispersing talc in PLA via a 25mm twin screw extruder, feeding talc upstream together with resin; also neat PLA was extruded, as a reference for the process conditions.

Table 1: half crystallization time for PLA modified with talc at different isothermal holding temperatures

	$t_{1/2}$ @ 90°C [s]	$t_{1/2}$ @ 100°C [s]	$t_{1/2}$ @ 110°C [s]
Neat PLA	596	222	268
PLA + 1% HTP1c	107	59	63
PLA + 5% HTP1c	<20	25	48

In Fig. 2 it is possible to see the different DSC patterns for talc modified PLA at 1% talc HTP1c loading. In general all the three samples of talc gave same results in terms of crystallization temperature. By increasing the talc loading (5%), a higher crystallization temperature is recorded with no specific distinctions between the three talc samples. Talc loading plays a major role in PLA nucleation rather than the talc fineness.

A relevant experiment, in order to better understand the crystallization conditions of talc modified PLA, is related to isothermal crystallization. Only talc HTP1c was considered as PLA modifier in this experiment. In DSC, the samples were heated up to 200°C at 10°C/min, held 5 min at 200°C and cooled rapidly (at 100°C/min) down to the testing temperature, holding the specimen at testing temperature for a certain time, until crystallization takes place. Time was recorded and it quantifies the crystallization kinetic. Crystallization occurs at a temperature higher than glass transition temperature (Tg) because below Tg, molecular mobility is virtually zero, with no possibility of chain folding. PLA Tg is in the range of 60-70°C and experiments were performed from 90 to 110°C as testing (hold) temperature for the isothermal crystallization on PLA modified with talc HTP1c at both 1% and 5% loading.

In this experiment, the presence of talc significantly reduces the time to crystallization (generally expressed as time to achieve 50% of crystallization, $t_{1/2}$) allowing nucleated PLA to achieve crystallinity in a more reasonable time for practical process purposes. In Fig. 3, the behaviour of PLA modification with talc HTP1c at both 1% and 5% loading is shown. For each type of modification, three different temperatures were investigated. In table 1, the $t_{1/2}$ values are summarized. The behaviour of the other two talc grades is basically similar to HTP1c. Talc loading plays a relevant role in shortening $t_{1/2}$.

Based on such experiments, it appears that moulded PLA items must be kept at relatively high temperature for a certain time to develop the expected degree of crystallinity. Such process can be performed either from the melt or from quenched state, with a visible impact on production costs. The presence of a talc (as nucleator) in the resin helps to shorten such time improving the productivity. The reduction of crystallization time is also driven by the talc concentration. The minimum crystallization time is recorded at 100°C.

Fig. 1: DSC curves of neat PLA

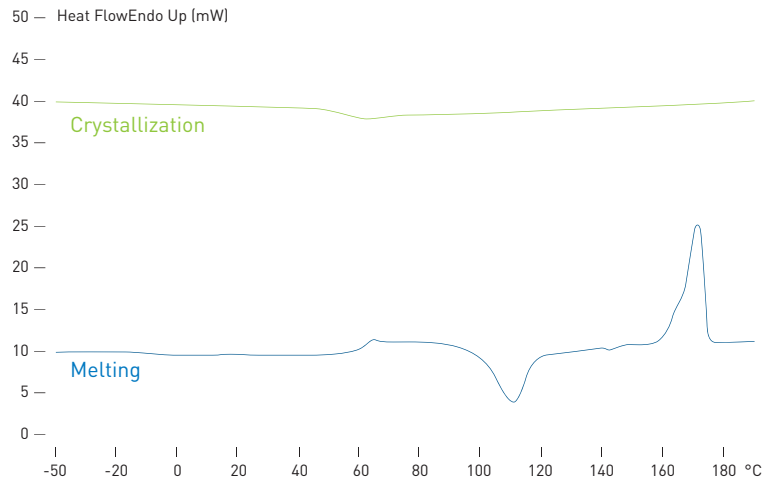


Fig. 2: DSC crystallization curves of talc modified PLA

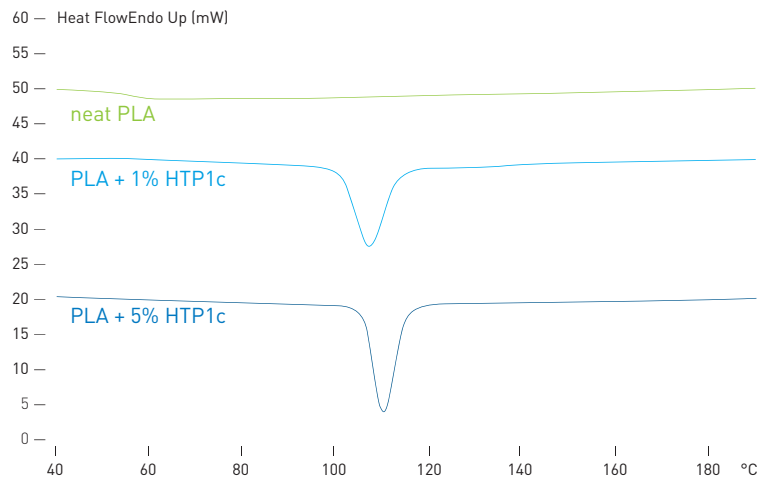
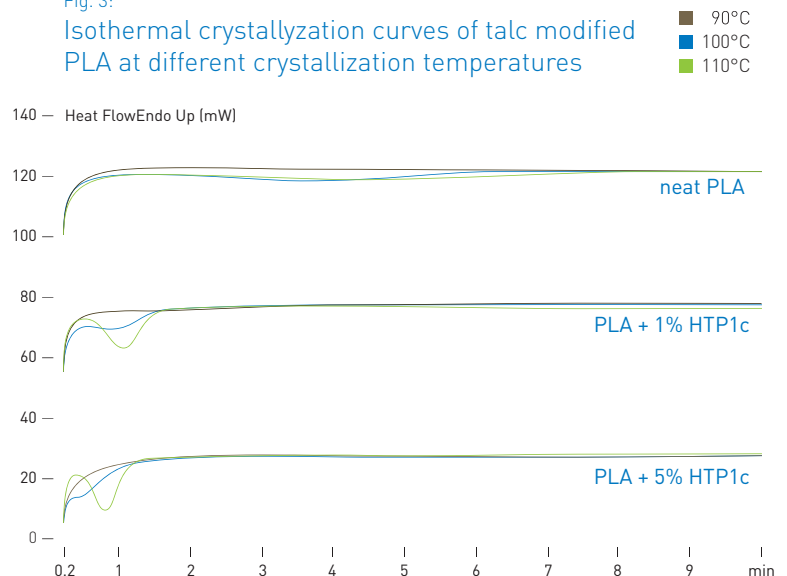


Fig. 3: Isothermal crystallization curves of talc modified PLA at different crystallization temperatures



Impact notched 1% 5%

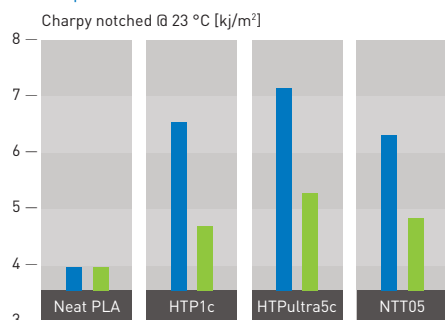


Fig. 5: Charpy notched (according to ISO 179/1eA) of PLA modified with different loadings of micronized talc. Specimens were annealed 3h@110°C before testing

HDT A (@ 1.82 MPa) 1% 5%

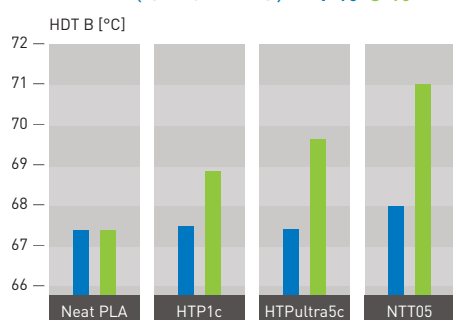


Fig. 6: Heat Distortion Temperature (HDT A 1.82 MPa (according to ISO 75) of PLA modified with different loadings of micronized talc. Specimens were annealed 3h@110°C before testing

Stiffness 1% 5%

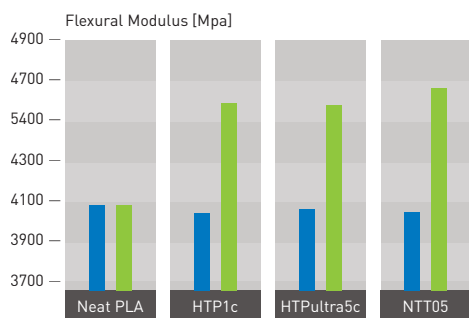


Fig. 4: Flexural modulus (according to ISO 178) of PLA modified with different loadings of micronized talc. Specimens were annealed 3h @110°C before testing



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For nucleation process the type of talc plays a minor role, while for both mechanical and thermal performances the situation is different and the three considered talc grades gave peculiar set of properties.

In order to have comparable data, all specimens were injected by holding the mould at 30°C, to quench the molten polymer. In such condition, the crystallization didn't take place in the mould. Specimens were annealed in oven at 110°C per 3 hours to post crystallize PLA.

In terms of stiffness, the flexural modulus behaviour is shown in Fig. 4. The modification with 1% of talc didn't affect PLA rigidity, while 5% talc loading recorded a visible improvement, up to 15% for talc NTT05 modification. Thanks to its platy structure, talc is able to improve PLA rigidity. Stiffness enhancement is generally linear with talc loading, but higher loading rates than 5% have not been investigated in this experimental work.

The presence of a nucleator let the impact resistance improve versus the neat resin, because of better organized polymer structure. All the samples containing talc gave higher impact resistance than reference (Fig. 5). 1% talc loading is enough to record a significant improving in impact resistance. Ultrafine talc sample (HTPultra5c) shows better results thanks to its very tight particle size distribution.

Concerning the evaluation of the service temperature, Heat Distortion Temperature (HDT) has been considered. HDT is the temperature at which a specimen, under a three point bending experiment at a specific load conditions, records a deflection of 0.25mm; it gives an easy indication about the service temperature.

In Figure 6, HDT A (@ 1.82 MPa) data are listed. 1% talc modification doesn't improve HDT of PLA, while the 5% talc modification offers a visible variation in service temperature. The modification with a high performing talc such as NTT05 allows to record a significant variation in HDT temperature versus the same loading of a highly micronized talc as HTP1c.

Conclusions

To allow PLA utilization in applications where service temperature plays the major role, the addition of highly micronized talc represents a good methodology for improving its thermal and mechanical properties, making such composites more interesting for technical applications. The incorporation of talc significantly accelerates the crystallization of PLA.

From the experimental evidences, it appears that a small amount of talc (1%) is enough to achieve crystallization during molten PLA cooling process. In order to record a better kinetic in crystallization process, a higher talc amount has to be considered (5% loading), in combination with a relatively high mould temperature.

The modification of PLA with talc allows to achieve higher rigidity (without compromising the impact resistance) and, thanks to the nucleation, better service temperature.

In order to achieve reliable results in PLA modification, it is necessary to use micronized talc characterized by high degree in purity, by tight particle size distribution and by high lamellarity such as the three talc products examined in this experimental work. In particular, the right selection of talc becomes very important when relatively high talc loadings are considered (i.e. 5%) and the other mechanical properties can be significantly affected by the type of talc.

To summarize, for a cost-effective PLA modification, talc HTP1 offers the most attractive set of properties, while for outstanding final mechanical properties, talc NTT05 can record the best-in-class properties still remaining, in terms of costs, as an extender for PLA. □