

**THIS IS THE PEER REVIEWED VERSION OF
THE FOLLOWING ARTICLE:**

Felice De Santis, Roberto Pantani

“MELT COMPOUNDING OF POLY(LACTIC ACID) AND TALC: ASSESSMENT OF MATERIAL BEHAVIOR DURING
PROCESSING AND RESULTING CRYSTALLIZATION”

Journal of Polymer Research

Volume 22, Issue 12, 1 December 2015, Article number 242, Pages 1-9

DOI: 10.1007/s10965-015-0885-1

WHICH HAS BEEN PUBLISHED IN FINAL FORM AT
<https://link.springer.com/article/10.1007%2Fs10965-015-0885-1>

THIS ARTICLE MAY BE USED ONLY FOR NON-COMMERCIAL PURPOSES

Melt compounding of Poly(Lactic Acid) and talc: assessment of material behavior during processing and resulting crystallization

Felice De Santis, Roberto Pantani*

Department of Industrial Engineering, University of Salerno, 84084 Fisciano (SA), Italy

Felice De Santis
University of Salerno
Department of Industrial Engineering
Via Giovanni Paolo II, 132 - 84084 - Fisciano (SA) Italy E-mail: fedesantis@unisa.it
Phone: +39 089 96 4013

Abstract

The influence of talc incorporation by melt compounding on a commercial grade of poly (lactic acid) (PLA), and the choice of the optimal compounding conditions were investigated. Two types of talc, having micrometric and submicrometric distribution, were adopted. Since the compounding itself has a dramatic influence on the properties of PLA, a study was carried out aimed at assessing the effect of processing on this resin and choosing the most suitable processing conditions. It was found that the incorporation of talc increases the viscosity during the compounding and helps the stability of the viscosity during the mixing. Furthermore the talc, acting as a nucleating agent, enhances crystallization kinetics, so that crystallization half time can be reduced by one order of magnitude with respect to the pure PLA processed in the same way.

Keywords

Poly(Lactic Acid); talc; melt compounding; crystallization kinetics

1. Introduction

Poly lactide or poly(lactic acid) (PLA) is a thermoplastic aliphatic polyester obtained by ring-opening polymerization of lactide derived from the fermentation of sugar feed stocks such as corn. Recent development of the continuous process of production of this resin has lowered the price of polylactide to the point where it is now competitive with other degradable polymers and potentially competitive with petroleum derived plastics [1, 2].

PLA has found applications in the medical and packaging fields due to its promising mechanical properties, its potential for biodegradability and biocompatibility [3-8].

Its biocompatibility and bioresorbability had made it a suitable choice for applications such as drug delivery systems [9], sutures, blood vessels, etc [10]. Recent work has shown the efficacy of using electrospun PLA/silk–gelatin fibers as tubular scaffolds to support cell growth [11].

The academic attention on PLA is increased in the last ten years, and biomaterials are experiencing an even stronger growth. In particular performing the query in the Web Of Science search engine (<https://webofknowledge.com>: Thomson Reuters database indexing the scientific journals) of these topics, produces 20000 and 15000 published items in the last 20 years, about biomaterials and PLA respectively.

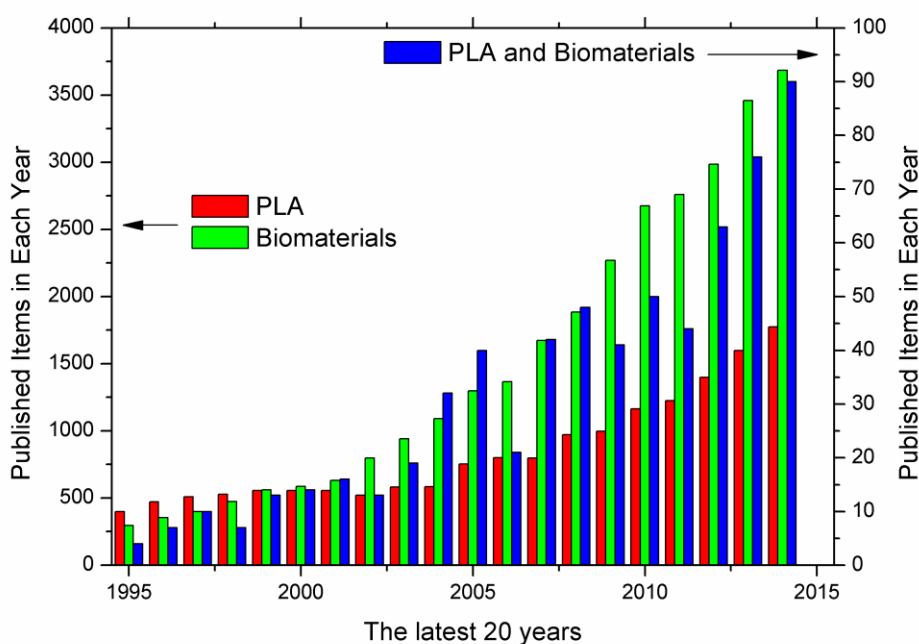


Figure 1. The articles published in the latest 20 years, on the topics “PLA”, “Biomaterials” on the left axis, on the topic “PLA” AND “Biomaterials” on the right axis.

Therefore, as shown in Figure 1, looking for both topics in Web Of Science database the result reveals a similar increasing trend, with 90 papers during 2014 in this more specific target.

The main drawbacks of PLA are related to its “slow” crystallization kinetics [10], if it is compared to the most common polymers like polypropylene or polyethylene, the processing window, limited by thermomechanical degradation [12], and last but not the least the mechanical properties when the parts are heated or exposed to humidity [13, 14].

To overcome some of these problems, in general, several additives to polymeric materials can be adopted: plasticizers, lubricants, pigments and coloring agents, expanders, and in particular nucleating agents [15, 16].

The addition of a nucleating agent generally increases the stiffness of the material, and reduces the cycle time of molding because of the effect on the rate of crystallization.

Some studies have been carried out for improving the crystallization rate of PLA by mixing it with nucleating agents such as talc [1, 17-19]. Shakoor and Thomas [11] found that talc acted as a nucleating agent and increased the crystallinity of the PLA with significant improvement in Young's modulus of the composites with increasing talc addition. Liu et al. [20] found that the melting blending led to homogeneous distribution of the inorganic filler within the PLA matrix but could decrease the molecular weight of PLA. In processing, on adding small percentage of talc to PLA it was possible to obtain foamed parts with a much better morphology, both with physical [21] and chemical blowing agents [22]. Moreover, as far as the specific use of talc is concerned in biomaterials, according to Najmunnisa et al. [21], talc is known to increase the production of endostatins which may have an anti-angiogenic effect. Thus, there is strong motivation for this study of the preparation and characterization of PLA composites containing talc [23].

In this work the effect of the compounding of PLA with two types of talc, having micrometric and submicrometric distribution, is investigated. In particular the mechanical behavior with melt compounding and the crystallization kinetics with different percentage of nucleating agent will be explored.

2. Materials and Methods

2.1 Polylactic acid

The polylactic acid (PLA), supplied by NatureWorks LLC (USA), is a commercial grade tradename, PLA 2002D [24], comprising D% comonomer of up to $4.25 \pm 0.55\%$ [25-27].

PLA 2002D is specifically designed for extrusion/thermoforming applications, with a melt flow index equal to 6. The weight average molecular weight and polydispersity are 215×10^3 g/mol and 1.9 [28], respectively.

The Mettler DSC 822 instrument differential scanning calorimeter was employed to detect melting temperature (T_m), and glass transition temperature (T_g) of PLA 2002D, 58°C and 153°C respectively [29, 15].

The pellets were predried at 60°C for 24 h in a vacuum oven, before any characterization or processing, to prevent degradation [30]. The crystallization kinetics and nucleation of the neat resin were previously investigated [29], from the molten and glassy state.

2.2 Talc

Talc is a natural material, a mineral composed of hydrated magnesium silicate with the chemical formula $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. In loose form, it is the widely used substance known as talc powder.

The main characteristics of talc are:

- It is naturally hydrophobic and organophilic
- It is inert and resist very well to acids and alkalis
- It is the softest mineral in the world
- It is a good electric and thermal insulator
- It is neither inflammable nor explosive

Thanks to these characteristics, talc is a mineral of choice in many industrial uses.

The talc powder was kindly supplied by IMI Fabi S.p.A. (Milan, Italy) in highly pure and highly lamellar grades, even at the finest particle size distributions. Two talc powders, with the same chemical composition [31] showed in Table 1, with grade names HTP1 and HTPultra5 were used in this work, with particle size distribution having a median diameter, D_{50} , of $1.88 \mu\text{m}$ and $0.65 \mu\text{m}$, respectively.

Table 1. Talc Chemical Analysis - Atomic Absorption Spectrometry [31]

SiO ₂	61.0 %
MgO	32.0 %
CaO	0.2 %
Fe ₂ O ₃	0.4 %
Al ₂ O ₃	0.4 %
Loss on Ignition at 1050 °C	6.0 %

2.3 The melt compounding

PLA and talc were mixed by melt compounding in a counter-rotating twin-screw microcompounder (HAAKE MiniLab II Micro Compounder, by Thermo Scientific) with an integrated backflow channel, as shown in Figure 2. Thanks to the backflow channel and the bypass valve, it is possible to define the residence time. The materials were mixed at 180 °C and 100 rpm, resulting in volumetric flow rate of 80 cm³/min.

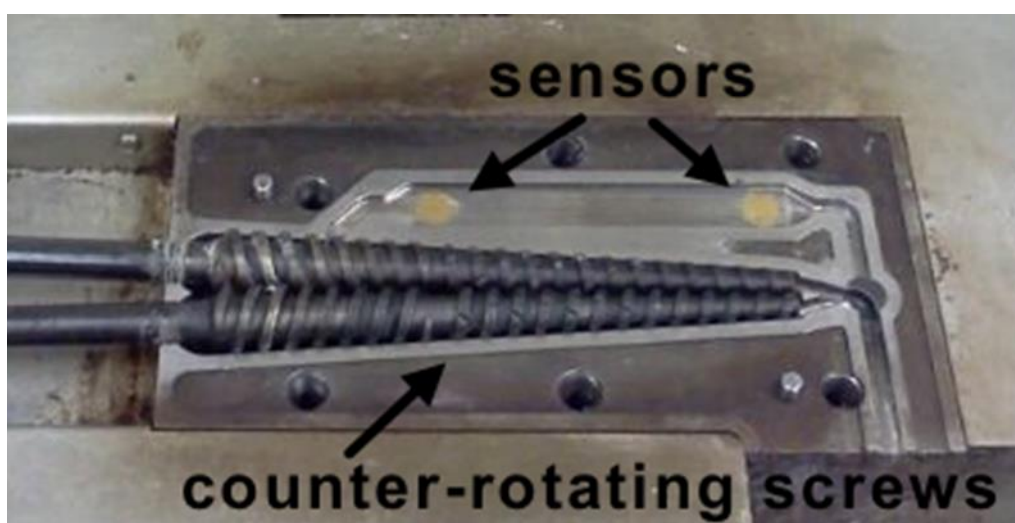


Figure 2. Detail of HAAKE MiniLab II Micro Compounder.

The microcompounder can monitor torque, pressure in the backflow channel, by the sensors shown in Figure 2. Thus, apparent viscosity can be monitored and it can be used to characterize the material during mixing.

Extruded ribbon samples of PLA were produced with backflow time of 0 min (without backflow), 5 min, 10 min, 30 min, 60 min, and 360 min, in order to determine the effect of processing condition. The extrusion for each residence time condition is repeated three times, to check reproducibility.

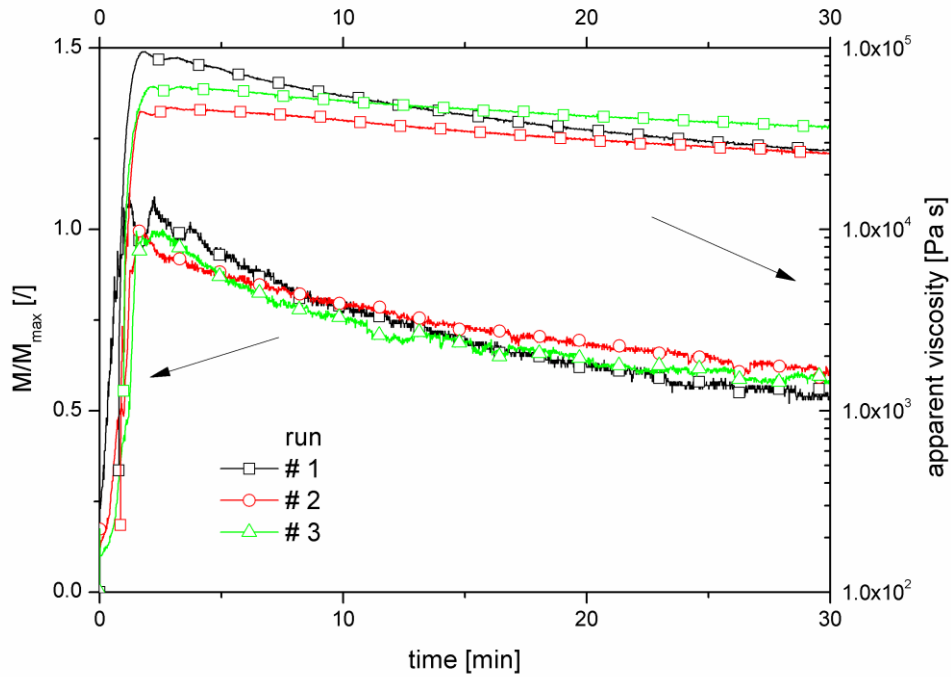


Figure 3. Normalized torque and apparent viscosity monitoring during the tests with 30 min of backflow time, for the neat PLA.

As shown in Figure 3, with a maximum torque M_{\max} of about 2 N m, during 30 minutes the torque reduces of about 40%, revealing a thermomechanical degradation. Also the apparent viscosity, calculated from pressure drop in the backflow channel, is reported in Figure 3. It follows a similar decreasing trend, and the three repeated runs show a reproducibility within a factor of 2.

A backflow of 10 min minimizes results in acceptable value of viscosity reduction and thus of PLA degradation [32].

Similar tests were performed, mixing the PLA with 1%, 3% and 10% of talc (as percentage by weight, wt%).

As an example the measured torque during the mixing of PLA with 1% of HTP1 and HTPultra5 talc are shown in Figure 4 and in Figure 5, respectively.

For both the composite materials the trend is similar to the neat PLA, but the talc improves the reproducibility of the tests, probably because it preserves the PLA matrix from degradation. The apparent viscosity of the materials with talc, measured in the backflow channel during the mixing, is always slightly higher than the PLA.

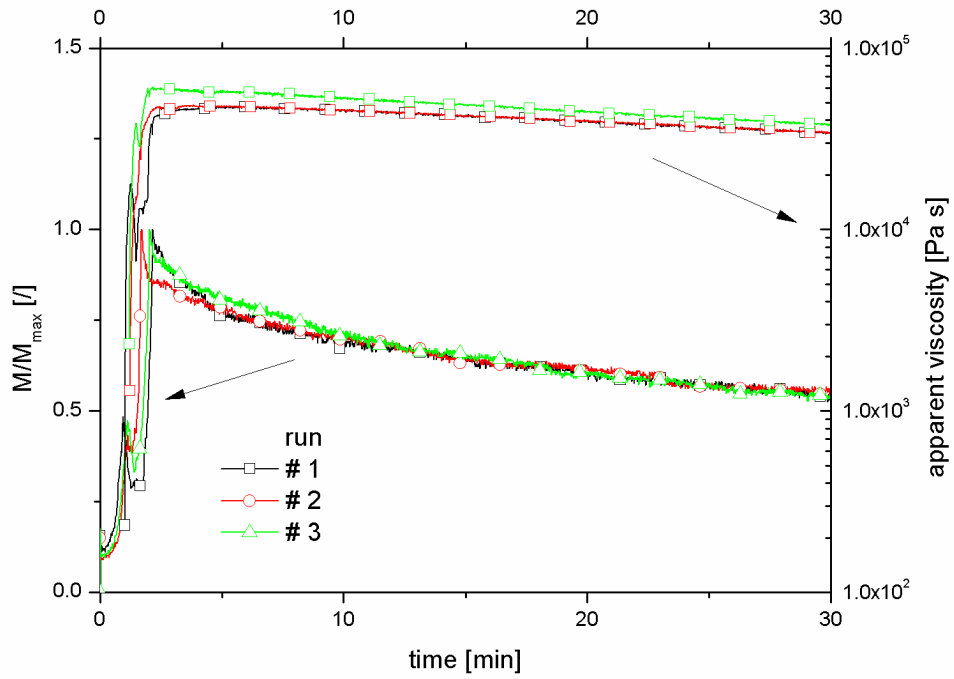


Figure 4. Normalized torque and apparent viscosity monitoring during the test with 30 min of backflow time, for PLA+ 1% HTP1 talc.

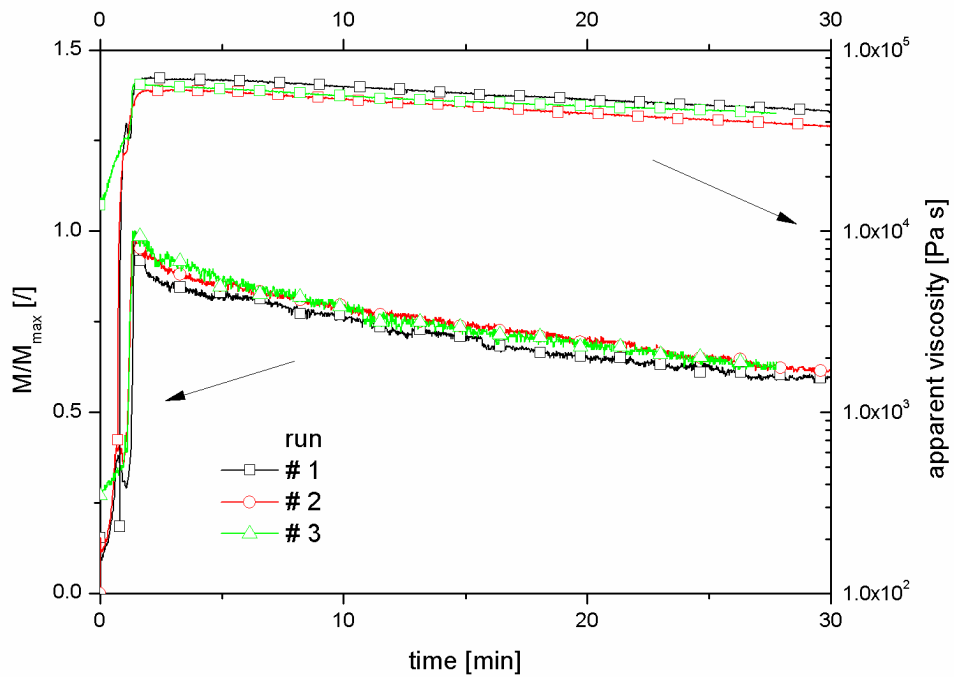


Figure 5. Normalized torque and apparent viscosity monitoring during the test with 30 min of backflow time, for PLA+ 1%HTPultra5 talc

2.4 Injection molding

As the microcompounder, the injection molding machine, Haake MiniJet II by Thermo Scientific, is not a conventional processing device. It has a pneumatic piston that pushes the material from the hot cylinder to the mold for the production of test specimens from as little as few grams. All processing parameters such as temperature (separate for injection cylinder and mold), injection pressure and duration, and post-pressure can be controlled. Strict management of the post-pressure during sample creation enables optimum compensation for material shrinkage due to the cooling of the sample.



Figure 6. Dog bone mold, for mechanical test samples.

In Table 2 the processing conditions adopted to obtain dog bone bars for tensile characterization (type IV according to standard ASTM D638, with thickness equal to 3mm), using the mold shown in Figure 6, are summarized.

Table 2. Processing conditions for the injection molding of dog-bone shaped tensile bars

Injection pressure [bar]	600
Holding pressure [bar]	200
Injection time [s]	30
Holding time [s]	5
Injection temperature [°C]	200
Mold temperature [°C]	30

2.5 Mechanical analysis

The tensile tests were performed with ATS Faar TC 1000 dynamometer at room temperature, with a traction velocity of 10 mm/min. From recorded data of engineering stress-strain the elasticity modulus, in the linear part, is calculated, with at least 5 dog-bone shaped tensile bars for each sample obtained by injection molding of neat and compounded material.

2.6 Differential scanning calorimetry (DSC)

A differential scanning calorimeter DSC 822TM from Mettler Toledo Inc. was used for determination and measurement of the transition behavior of PLA. The calibration of the temperature was performed with the onset extrapolated temperature of the melting transition of indium (156.6 °C, calibration standard, purity > 99.999 %). The samples with a weight of about 10 mg were placed into an aluminum pan and hermetically sealed. All the experiments were conducted in nitrogen (flow rate 50 mL/min), in order to prevent thermo-oxidative degradation.

The melting behavior of the materials was investigated, heating the sample from 25 °C to 200 °C.

In order to study melt isothermal crystallization, the sample was then cooled from 200 °C directly to isothermal test temperature (crystallization temperature), with a cooling rate of 10 K/min [29].

Because of the slow crystallization rate of neat PLA, the results of the isothermal step at 110 °C from the molten state show that crystallization develops on time scale of the order of 10⁴ s [29]. In the case of lower or higher temperature during isothermal test the heat flow plot is almost flat.

The uncertainty related to these tests, for example in the choice of the correct baseline, was got around by performing several tests at the same temperature with increasing isothermal crystallization times, analyzing the subsequent melting by heating up at 10 K/min the partially crystallized sample. This procedure, previously reported [29], is obviously time consuming, and at each isothermal temperature the time is increased until crystallization at that temperature is complete. This protocol overcomes the problems related to the slow crystallization of this material increasing significantly the confidence to the experimental data, as explained in the results.

3 Results and Discussion

3.1 Characterization of molded samples

The results of the tensile tests on dog-bone shaped molded samples of PLA at room temperature are shown in Figure 7 as function of the processing time.

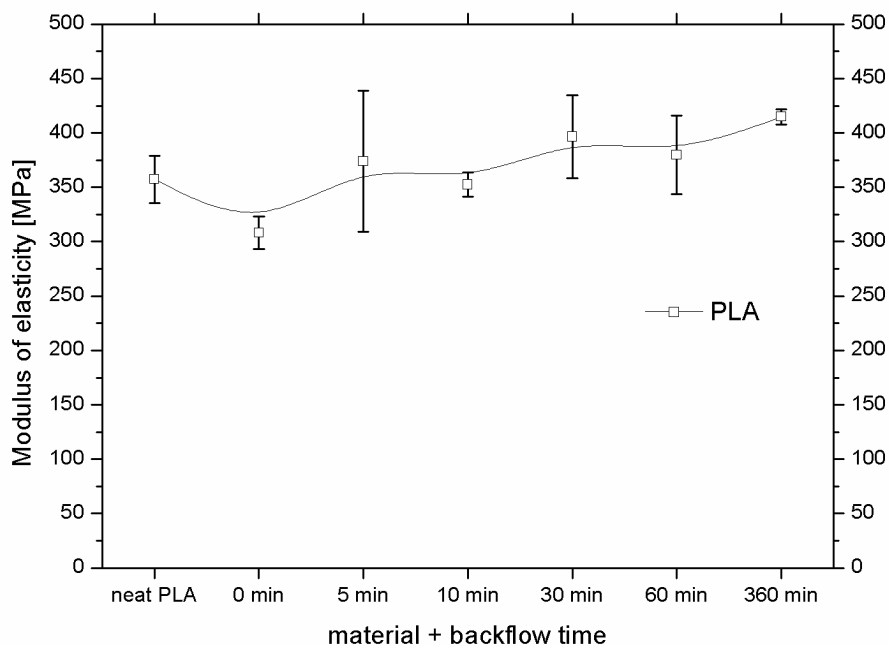


Figure 7. Modulus of elasticity, for neat and compounded PLA.

The mechanical properties, namely the modulus, do not exhibit significant changes, it is possible to observe just a slight growth in the elasticity modulus with the compounding time, in Figure 7 possibly due to the thermomechanical degradation which reduces the molecular weight of the material and increases its stiffness.

3.2 Crystallization kinetics

In order to evaluate the kinetic behavior, all the isothermal tests, performed from partial to complete crystallization, or rather the subsequent melting peaks were analyzed, as shown in Figure 8 for the isothermal test at 110 °C, from the molten state of compounded PLA without backflow. Time integration of the melting peaks, obtained during heating ramps performed at 10 K/min after isothermal crystallization, allows to evaluate indirectly the enthalpy associated to each crystallization time.

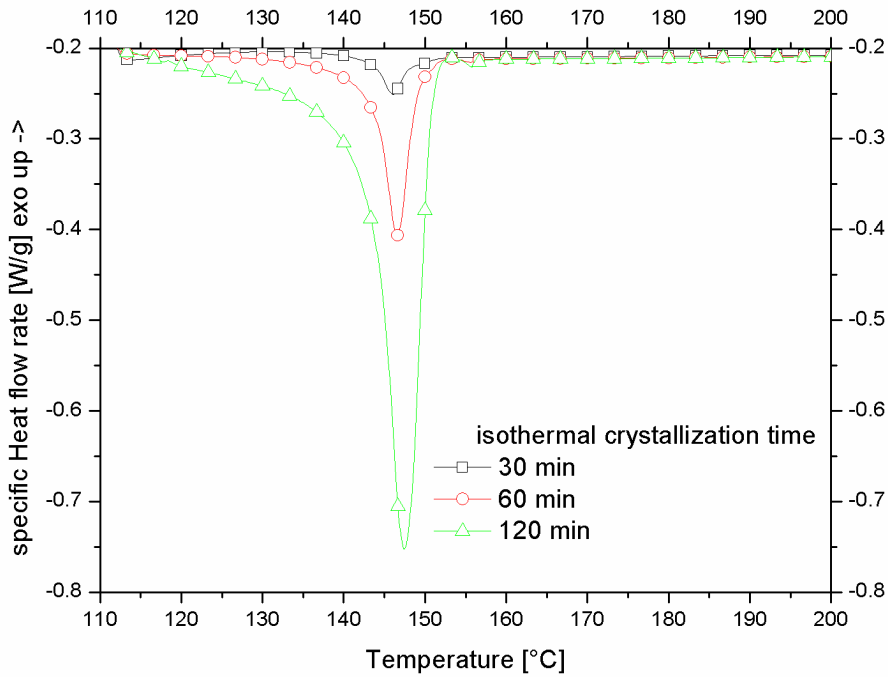


Figure 8. Melting peaks, from the molten state of compounded PLA without backflow, following crystallization at 110 °C changing isothermal crystallization time.

The result of these calculations are shown in Figure 9, for crystallizations at 110 °C of neat PLA. At this temperature the maximum crystallization rate is reached in the neat material, without compounding or processing, from the molten state [29].

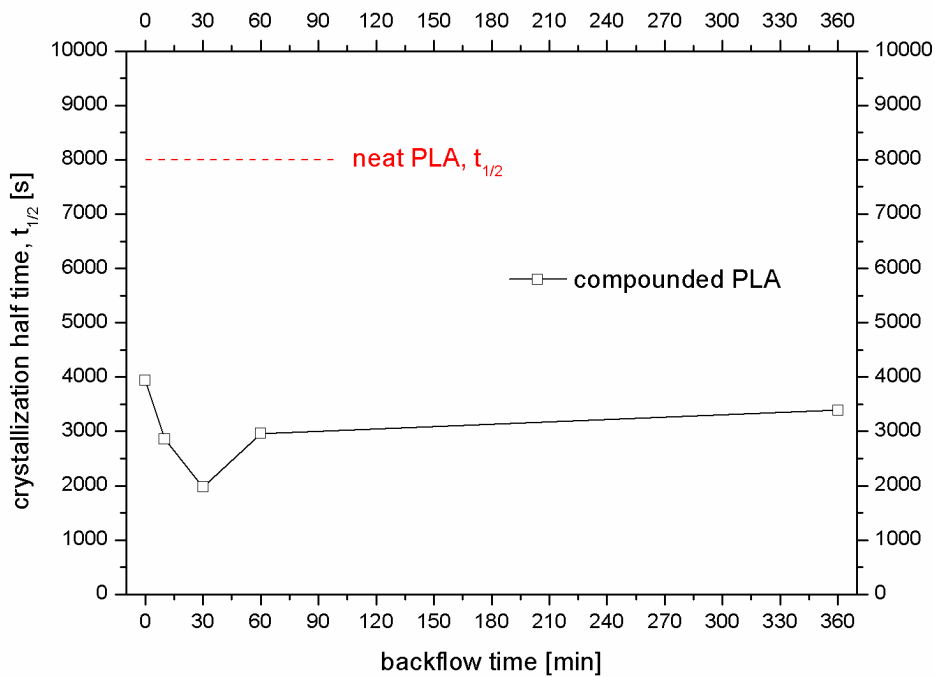


Figure 9. Crystallization half time, $t_{1/2}$, from the molten state of compounded PLA, following crystallization at 110 °C changing isothermal crystallization time. The crystallization half time of the same neat resin is also reported, from [29].

The crystallization kinetics is faster just for the effect of the compounding: even without backflow the crystallization half time is halved. But with the backflow time of 30 minutes, a minimum in crystallization half time is observed, so that this condition seems to be the best to improve crystallization kinetics.

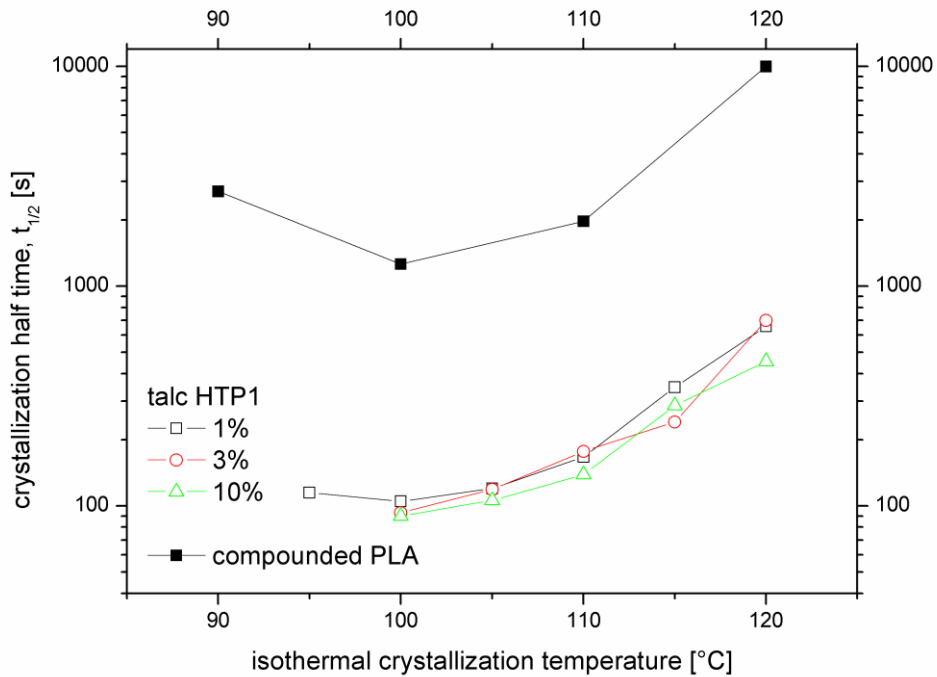


Figure 10. Crystallization half time, $t_{1/2}$, from the molten state of compounded PLA and with different percentage of HTP1 talc, with a backflow of 30 minutes.

The crystallization half times at each temperature, as reported in Figure 10, were evaluated for PLA compounded with different percentages of HTP1 talc. The crystallization half time has a similar trend for all the explored amount of talc, so that it seems that already at 1% it saturates its nucleating effect. On the other hand, the comparison with compounded PLA without talc, reported in Figure 9 at 110 °C, shows that the talc can decrease one order of magnitude the crystallization half time.

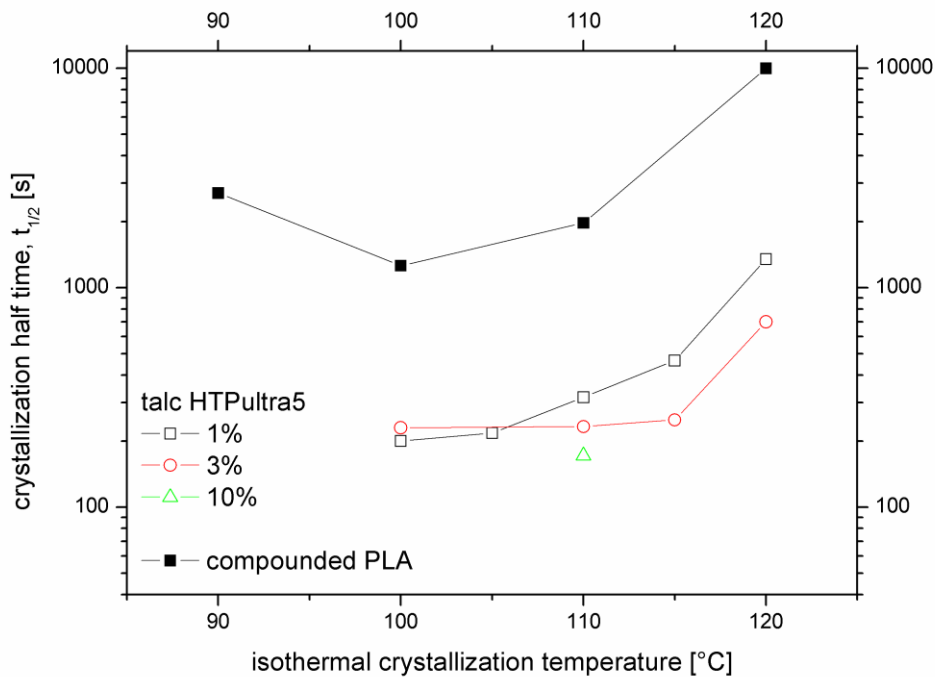


Figure 11. Crystallization half time, $t_{1/2}$, from the molten state of compounded PLA and with different percentage of HTPultra5 talc, with a backflow of 30 minutes.

The crystallization half time at each temperature, as reported in Figure 11, were evaluated for PLA compounded with different percentage of HTPultra5 talc, checking, if possible, the coherence with crystallization peak during isothermal step. The result shown in Figure 11 is similar to the HTP1 talc, and the comparison with compounded PLA, without talc reported in Figure 9 at 110 °C, shows that also the submicrometric talc has an effect of one order of magnitude on the crystallization kinetics.

Finally, among the three compounded materials, the one with 1% of talc seems to be the most promising: with the minimum quantity talc the enthalpy observed during isothermal solidification or subsequent melting is almost constant but the crystallization kinetics is faster comparing with the compounded PLA at 110 °C, as summarized in Figure 12. Furthermore the torque observed during the mixing is more regular.

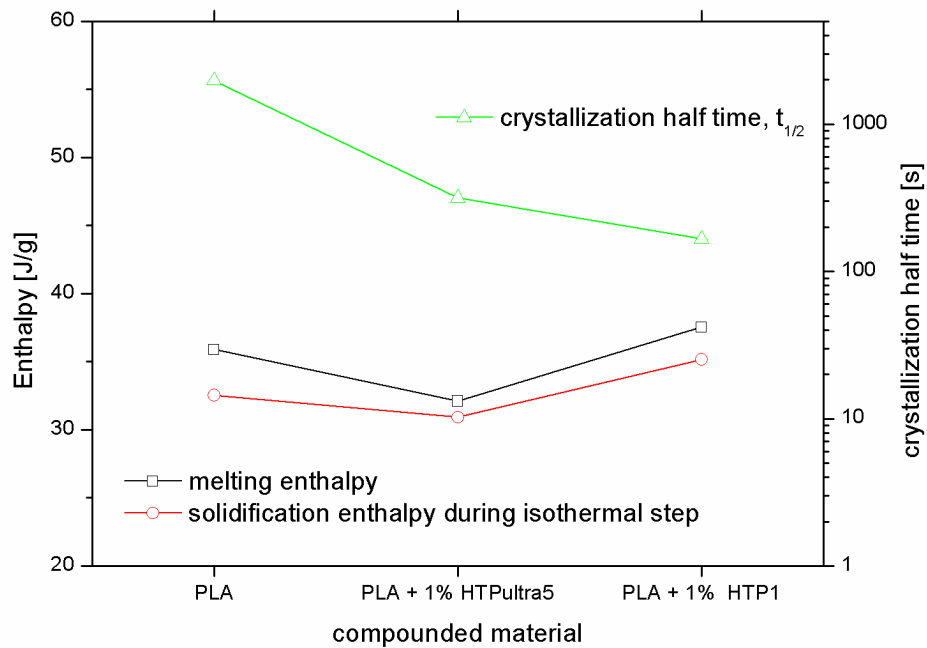


Figure 12. Enthalpy, on the right axis, observed during isothermal solidification at 110 °C or subsequent melting, and crystallization half time at 110 °C, on the left axis, for materials compounded with backflow time of 30 min.

The behavior of the two kinds of talc is very similar: the micrometric talc, HTP1 shows a slightly stronger effect on crystallization rate than submicrometric talc, HTPultra5, as shown in Figure 12 where the effects on crystallization half time of the addition of 1% of talc are reported. Probably, the particles of HTPultra tend to form agglomerates during the compounding, thus reducing the nucleating effect.

In dispersive mixing, a solid component needs to be broken down, but breakdown only occurs after a certain minimum stress (yield stress) has been exceeded. This is true if considering a mixture composed by a polymer (in molten phase) and a filler (in powder form, uncompacted). For fine and ultrafine talc, it is practically necessary to consider only compacted powder and in case of compacted talc the dispersion can be a critical issue, when a small amount of powder is added (the case of nucleating agent, for example).

Conclusions

In this work, the influence of melt compounding and incorporation of talc on a commercial grade of poly(lactic acid) was studied. The neat material was mixed, for different backflow times, to monitor the effect of processing on this resin. The apparent viscosity of the PLA decreases with compounding time, as the material is subject to thermo mechanical degradation. The elastic modulus of neat PLA, was measured on injection molded dog shape tensile bars. The elastic modulus slightly increases with compounding time, probably because of the molecular weight reduction due to degradation. Concerning the incorporation of talc, it was found that it increases the viscosity measured during the compounding but it also enhances the stability of the material viscosity during the mixing. Furthermore the talc, acting as a nucleating agent, has a strong effect on crystallization kinetics, so that by adding 1% of micrometric talc crystallization half time reduces of one order of magnitude with respect to the pure PLA processed in the same way.

Acknowledgments

Imi Fabi S.p.A. (Milan, Italy) is kindly acknowledged for the supply of the talc raw materials.

The authors wish to thank Carlos Eduardo Ferreira Gonçalves and Frederico Martins Gonçalves, from University of Minho in Guimarães, Portugal, for carrying out part of the experiments during their Erasmus project at University of Salerno.

References

1. Kolstad JJ. Crystallization kinetics of poly (L-lactide-co-meso-lactide). *Journal of applied polymer science*. 1996;62(7):1079-91.
2. Soroudi A, Jakubowicz I. Recycling of bioplastics, their blends and biocomposites: A review. *European Polymer Journal*. 2013;49(10):2839-58.
3. Bergsma J, Rozema F, Bos R, Boering G, De Bruijn W, Pennings A. In vivo degradation and biocompatibility study of in vitro pre-degraded as-polymerized polylactide particles. *Biomaterials*. 1995;16(4):267-74.
4. Suuronen R, Pohjonen T, Hietanen J, Lindqvist C. A 5-year in vitro and in vivo study of the biodegradation of polylactide plates. *Journal of Oral and Maxillofacial Surgery*. 1998;56(5):604-14.
5. Ignjatovic N, Uskokovic D. Synthesis and application of hydroxyapatite/polylactide composite biomaterial. *Applied Surface Science*. 2004;238(1):314-9.
6. Gupta A, Kumar V. New emerging trends in synthetic biodegradable polymers–Polylactide: A critique. *European Polymer Journal*. 2007;43(10):4053-74.
7. Singh S, Ray SS. Polylactide based nanostructured Biomaterials and their applications. *Journal of Nanoscience and Nanotechnology*. 2007;7(8):2596-615.
8. De Santis F, Gorrasi G, Pantani R. A spectroscopic approach to assess transport properties of water vapor in PLA. *Polymer Testing*. 2015;44:15-22.
9. Concilio S, Iannelli P, Sessa L, Olivieri R, Porta A, De Santis F et al. Biodegradable antimicrobial films based on poly(lactic acid) matrices and active azo compounds. *Journal of applied polymer science*. 2015;132(33). doi:10.1002/App.42357.
10. Saeidlou S, Huneault MA, Li H, Park CB. Poly (lactic acid) crystallization. *Progress in Polymer Science*. 2012;37(12):1657-77.
11. Shakoor A, Thomas NL. Talc as a nucleating agent and reinforcing filler in poly (lactic acid) composites. *Polymer Engineering & Science*. 2014;54(1):64-70.
12. Lim L-T, Auras R, Rubino M. Processing technologies for poly (lactic acid). *Progress in Polymer Science*. 2008;33(8):820-52.
13. Garlotta D. A literature review of poly (lactic acid). *Journal of Polymers and the Environment*. 2001;9(2):63-84.
14. De Santis F, Volpe V, Pantani R. Effect of molding conditions on crystallization kinetics and mechanical properties of Poly(lactic acid). Submitted. 2015.
15. Raquez J-M, Habibi Y, Murariu M, Dubois P. Polylactide (PLA)-based nanocomposites. *Progress in Polymer Science*. 2013;38(10):1504-42.
16. Gahleitner M, Grein C, Kheirandish S, Wolfschwenger J. Nucleation of polypropylene homo-and copolymers. *International Polymer Processing*. 2011;26(1):2-20.

17. Ke T, Sun X. Melting behavior and crystallization kinetics of starch and poly (lactic acid) composites. *Journal of applied polymer science*. 2003;89(5):1203-10.
18. Battagazzore D, Bocchini S, Frache A. Crystallization kinetics of poly (lactic acid)-talc composites. *Express Polymer Letters*. 2011;5(10):849-58.
19. Russo P, Acierno D, Vignali A, Lavorgna M. Poly (lactic acid)-based systems filled with talc microparticles: Thermal, structural, and morphological issues. *Polymer Composites*. 2014;35(6):1093-103. doi:10.1002/pc.22757.
20. Liu X, Wang T, Chow LC, Yang M, Mitchell JW. Effects of inorganic fillers on the thermal and mechanical properties of poly (lactic acid). *International Journal of Polymer Science*. 2014. doi:10.1155/2014/827028.
21. Pantani R, Volpe V, Titomanlio G. Foam injection molding of poly (lactic acid) with environmentally friendly physical blowing agents. *Journal of Materials Processing Technology*. 2014;214(12):3098-107.
22. Bergeret A, Benezet JC. Natural fibre-reinforced biofoams. *International Journal of Polymer Science*. 2011;2011.
23. Monticelli O, Bocchini S, Gardella L, Cavallo D, Cebe P, Germelli G. Impact of synthetic talc on PLLA electrospun fibers. *European Polymer Journal*. 2013;49(9):2572-83.
24. Polymer 2002D. In: Data Sheet Available from: Natureworks LLC. 2005.
25. Huneault MA, Li H. Morphology and properties of compatibilized polylactide/thermoplastic starch blends. *Polymer*. 2007;48(1):270-80.
26. Li H, Huneault MA, editors. Nucleation and Crystallisation of PLA. Proceedings. Society of Plastics Engineers Annual Technical Conference (ANTEC 2007): Plastics Encounter@ ANTEC 2007; 2007.
27. Othman N, Jazrawi B, Mehrkhodavandi P, Hatzikiriakos SG. Wall slip and melt fracture of poly (lactides). *Rheologica acta*. 2012;51(4):357-69.
28. Gorrasi G, Pantani R. Effect of PLA grades and morphologies on hydrolytic degradation at composting temperature: Assessment of structural modification and kinetic parameters. *Polymer Degradation and Stability*. 2013;98(5):1006-14.
29. De Santis F, Pantani R, Titomanlio G. Nucleation and crystallization kinetics of poly (lactic acid). *Thermochimica Acta*. 2011;522(1):128-34.
30. Pantani R, De Santis F, Sorrentino A, De Maio F, Titomanlio G. Crystallization kinetics of virgin and processed poly (lactic acid). *Polymer Degradation and Stability*. 2010;95(7):1148-59.
31. HTP1 and HTPultra5. In: Data Sheet Available from: IMI Fabi S.p.A. 2008.
32. Speranza V, De Meo A, Pantani R. Thermal and hydrolytic degradation kinetics of PLA in the molten state. *Polymer Degradation and Stability*. 2014;100:37-41. doi:DOI 10.1016/j.polymdegradstab.2013.12.031.