

DEVELOPMENT OF HEAT RESISTANT BIODEGRADABLE POLYMER MADE FROM PLA

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Abstract

In our research we have investigated the effectiveness of various additives as potential nucleating agents for renewable resource based biodegradable polymer Poly(lactic acid) (PLA). These were Talc ($Mg_3Si_4O_{10}(OH)_2$), Titanium-dioxide (TiO_2), Aerosil (SiO_2), Chalk powder ($CaCO_3$) and also Poly(ethylene glycol) (PEG) was used as a plasticizer. Our goal was to develop a semi-crystalline, PLA based biodegradable polymer for injection moulding purposes, where significant crystallinity develops during processing. Besides the analysis of the effect of various additives as nucleating agents, the dimensional stability of the final product was also investigated. We have demonstrated that by using adequate nucleating agents, plasticizers, and special injection moulding technology, injection moulded PLA products with more than 120°C of heat resistance can be produced.

1 Introduction

Nowadays, due to increasing environmental consciousness, biomass based (biobased) and biodegradable polymers (or biopolymers) gain more and more attention. The main goal is to exchange ordinary, petrol based plastics with biopolymers typically in short term applications where the long-term stability of petrol based plastics is unnecessary. Moreover, due to the fact that biopolymers can be synthesised totally from renewable resources (biomass), and they are biodegradable, so thus they can be fit into the life cycle of nature, making these materials the material of sustainable development [1].

One of the most promising materials for making biopolymers is starch. Starch containing agricultural plants like maize (corn), wheat, potato, rice, pea are produced all over the World in high amounts making it an abundance. Moreover, the renewing time of these agricultural plants is typically less than a year, which makes them very productive. In the 1980's much scientific work was made in order to make starch processable with conventional plastic processing equipments based on the already well known processing of starch by the food industry. As a result, thermoplastic starch (TPS) was developed [2], however, its drawbacks like low mechanical properties, high water absorption, water solubility, changing mechanical properties in time (ageing), high shrinkage shortly highlighted that it will be difficult to commercialise this material. Again high amount of research was done to eliminate the

drawbacks of TPS like compounding it with natural fibres to make biocomposites [3], it only found the way of commercialisation by compounding with another biodegradable polymer, the petrol based Poly(ϵ -caprolactone) (PCL). Nowadays, the TPS/PCL blends are commercialised under the trade name Mater-Bi from Novamont (Italy).

Another possible way to utilise starch is its fermentation in the presence of sugar. During this process, lactic acid can be made, which can be polymerised into Poly(lactic acid) (PLA) [4]. PLA has excellent mechanical properties (high strength and stiffness), low shrinkage, can be easily processed by using conventional plastic processing equipments like extrusion, injection moulding, thermoforming, blow moulding, and also has the capability to degrade in industrial compost. Its degradation begins with hydrolysis at elevated (above 60°C) temperatures, and the generated oligomer lactic acid can be processed into non toxic materials like humus, water, carbon-dioxide (and methane in anaerobic conditions) by the help of the natural degradation action of bacteria and fungi [5]. The fact that PLA is a fully renewable resource based polymer with high mechanical properties and the capability to biodegrade in compost make PLA one of the most promising biopolymers of all. Lots of PLA products are already commercialised like injection moulded cutleries, flower pots, toothbrush handles, office utensils, thermoformed cups, trays, plates, blow moulded bottles, extruded sheets. However, PLA also has drawbacks which in contempt of the initial success still retard its wide industrial and commercial usage. These main drawbacks are the somewhat high price, the low heat deflection temperature (HDT) and its slow crystallisation kinetics. The price of one kg of PLA is around 1.9 Euro in 2012, which is the price of an engineering plastic, at the same time, this price is expected to decrease due to the increasing PLA production and usage. Another main drawback is the low HDT value, since around the glass transition temperature (T_g) of PLA its high stiffness dramatically drops. Unfortunately, in many applications, this temperature is quickly reached for example in a coffee cup. It would be advantageous to use semi-crystalline PLA products which have much higher HDT value due to the crystalline structure, however, due to high cooling rates and the last discussed drawback, the slow crystallisation kinetics of PLA, the semi-crystalline PLA pellets typically become amorphous PLA products during injection moulding.

A possible way to increase HDT value is the incorporation of highly effective nucleating agents to increase crystallinity. Since injection moulding is a commonly used technology in the industry according to its productiveness, making it the best technology to widely commercialise PLA products, but it also has very high cooling rates, thus it is rather difficult to induce PLA to crystallise during processing. The effect of nucleating agents like Talc [6-8] TBC8-eb (p-tert-butylcalix(8)arene ethylbenzene) [9], Ethylene-Bis-Stearamide (EBS) [7], CaCO₃, TiO₂, BaSO₄ [10], or Starch was analysed. It was found that Talc and TBC8-eb are highly effective nucleating agents, they increased crystallisation rate, while BaSO₄, TiO₂, CaCO₃, EBS and starch was found to be less effective. In most publications [6], [8-10] only isothermal crystallisation was analysed, the non-isothermal is much lower [7], [11] although during injection moulding the crystallisation conditions are typically non-isothermal. Although Talc was found to be highly effective, it is very difficult to produce significant crystallinity during injection moulding only by adding Talc due to very high cooling rates. Harris et al. [7] analysed the non-isothermal crystallisation of 2wt% Talc content PLA by injection moulding it into high temperature mould (110°C). It was found that by using high cycle times, the part crystallised during cooling which resulted in a 30°C higher HDT value compared to low mould temperature injection moulding. Plasticizers like Poly(ethylene

glycol) (PEG) [12], Oligomer lactic acid (OLA), or citrate esters [13] were also found to be effective in enhancing the mobility of molecular chains, thus increasing crystallisation rate. The synergistic effect of nucleating agents and plasticizers were also analysed including PEG and Talc [11] by injection moulding the PEG and Talc content PLA into hot mould (80°C). It was found that PEG and Talc have synergistic effect in increasing the crystallisation rate, but significant crystallinity can only be developed by using high cycle times. Several different nucleating agents were tested however, most papers deal only with the isothermal and in fewer cases the non-isothermal crystallisation of single nucleating agents, but the number of the papers dealing with injection moulding of PLA containing both plasticizers and nucleating agents into high temperature mould to analyse the non-isothermal crystallisation is limited.

In this paper our goal was to analyse the synergistic effect of several potential natural additives as nucleating agents and both plasticizers at the same time on the crystallisation kinetics of PLA. The injection moulding technology parameters, especially the effect of mould temperature on the heat stability of the nucleated and plasticized PLA products was also determined.

2 Materials and methods

Injection moulding grade PLA type 3051D (D-Lactide content is about 4%) was purchased from NatureWorks (Blair, NE). It was dried at 120°C for 4 hours prior to extrusion and injection moulding to prevent any degradation due to remaining moisture content. Poly(ethylene glycol) (PEG1500) was obtained from Molar Chemicals Ltd. (Hungary), Talc (Mg₃Si₄O₁₀(OH)₂) and Titanium-dioxide (TiO₂) was purchased from Novia Ltd. (Hungary), while Chalk powder (CaCO₃) was obtained from Omya Hungaria Ltd. (Hungary) and Aerosil (SiO₂) was purchased from Novochem Ltd. (Hungary). The purchased materials were dry blended in various ratios and then extruded by using a LabTech Scientific twin screw extruder (screw diameter = 26 mm, L/D = 40) equipped with a 2 mm hole diameter die. The composition and the abbreviation of the produced materials can be seen in Table 1.

Abbreviation	Plasticizer content	Additive type and content
PLA	-	-
PLA/PEG	10 wt% PEG	-
PLA/Ti	10 wt% PEG	10 wt% Titanium-dioxide
PLA/Mg	10 wt% PEG	10 wt% Talc
PLA/Ca	10 wt% PEG	10 wt% Chalk powder
PLA/Si	10 wt% PEG	10 wt% Aerosil

Table 1. The composition of the produced PLA based filled materials

A temperature profile of 175-180-185-190°C was used from the hopper to the die with a screw rotational speed of 30 rpm. The extrudates were pelletized and crystallised at 120°C for 2 hours prior to injection moulding to prevent pellet sticking problems described in our previous research [14]. 80x80 mm area, 2 mm thick flat specimens were injection moulded by using an Arburg Allrounder 370S 700-250 injection moulding machine equipped with a diameter 30 mm, L/D = 25 screw. The injection pressure varied according to material compositions. The holding pressure and time was set for 600 bar and 20 s respectively while the cooling time was 30 s. Various mould temperatures of 20°C and 80°C were used to

analyse the effect of cooling rate on the crystallisation of PLA based filled materials during processing.

The Differential Scanning Calorimetry (DSC) analyses were performed on 4-6 mg samples by using DSC Q2000 TA Instruments. The samples for the DSC were taken out from the injection moulded specimens. A heating/cooling/heating cycle was used from 0 to 180°C at 10°C/min heating and cooling rate and at the highest cooling rate as possible with the Q2000 TA DSC which is 50°C/min. The latter was used to simulate high cooling rates during injection moulding, however it is known that during the injection moulding process, 100-500°C/min cooling rates are common, but cooling rate of course highly depends on the mould temperature and the thickness of the part as well. The crystallinity of the samples was calculated by the melting enthalpy value of 100% crystalline PLLA (93,0 J/g) [6].

The dimensional stability of the injection moulded specimens was analysed by placing them into a heated oven and measuring the dimensional changes caused by heat with a digital calliper. The oven was heated at 100°C for one hour, and the specimens were placed on a flat surface to avoid any deformation caused by own weight deflection.

Finally the heat resistance of the specimens was tested by placing them into a heated oven in a cantilever beam, so that only one side of the specimens was fixed. The deflection of the specimens was analysed during increasing heat.

3 Results and discussion

The DSC measurements were performed by cutting a small part from the middle of the injection moulded specimens according to the flow length and cross section. The cooling curves are plotted in Figure 1.

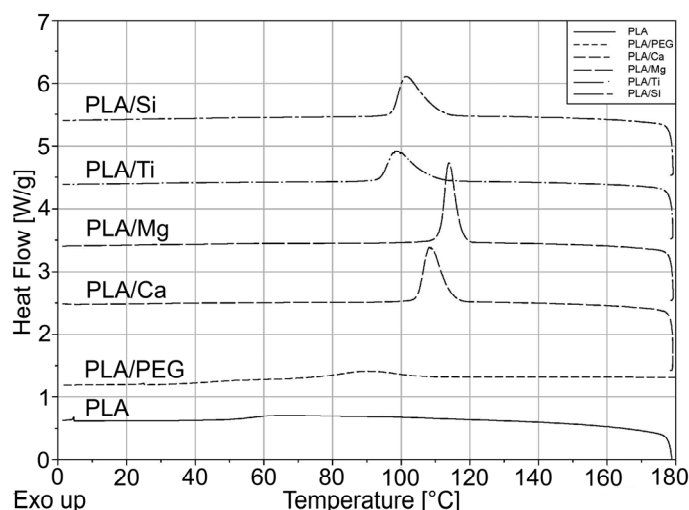


Figure 1. Cooling DSC curves (10°C/min)

On the cooling curves registered at a cooling rate of 10°C/min it can be seen that PLA did not crystallise, while the PLA/PEG compound had very slow crystallization rate and the PLA

compound containing PEG and additives had much higher crystallization rate. The evaluation of thermal properties can be seen in Table 2.

Material type	Crystallization peak temperature [°C]	Crystallization enthalpy [J/g]	Enthalpy of fusion [J/g]	Crystallisation rate [W/g]
PLA	-	-	-	-
PLA/PEG	90.3	18.37	42.37	0.09
PLA/Ti	98.6	34.99	35.11	0.46
PLA/Mg	113.9	39.49	38.45	1.23
PLA/Ca	108.3	41.32	40.07	0.83
PLA/Si	101.4	40.65	40.75	0.59

Table 2. Thermal properties obtained by 10°C/min cooling rate

Crystallisation rate was calculated by the height of the crystallisation peaks. Of course it is in good correlation with crystallisation peak temperature; the higher the peak temperature, the higher the crystallisation rate is. Crystallisation peak temperature is generally used to qualify the nucleation ability; the higher this peak temperature is, the better the nucleation ability is, thus Talc and PEG found to have the best nucleation from the analysed additives. Furthermore it can be seen in Table 3 that the crystallisation enthalpy and the enthalpy of fusion for the next heating cycle according to the PLA/Ti, PLA/Mg, PLA/Ca and PLA/Si materials is almost the same, which means crystallinity reached its maximum value during cooling, thus, all of the analysed additives proved to have good nucleation ability when used together with PEG. However, this can be only stated for low cooling rate (10°C/min), thus higher cooling rate was used (50°C/min) to simulate conditions similar to injection moulding (Figure 2.).

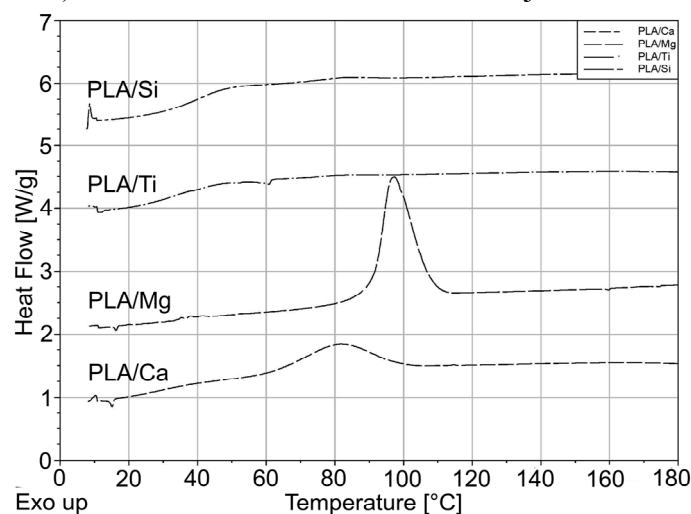


Figure 2. Cooling DSC curves (50°C/min)

It can be stated that Aerosil and Titanium-dioxide did not have enough nucleation ability to develop significant crystallinity by using high cooling rate, while Chalk powder only developed minor crystallinity. At the same time Talc was found to be still very effective, thus crystallinity reached its maximum value by using both Talc and PEG despite of the high cooling rate. The flake shaped structure of Talc was much found to be more effective in nucleation than the spherical shaped additives.

The dimensional stability of the injection moulded specimens (injection moulded by using 20°C mould temperature) was analysed at 100°C. It was found that all of the specimens had

high deformation caused by cold crystallisation and thus the change in specific volume except for the PLA/Mg specimen (Figure 3.). All of the specimens were amorphous prior to dimensional stability test as it was checked with DSC, so all of them became soft at 100°C, but Talc retarded deformation.

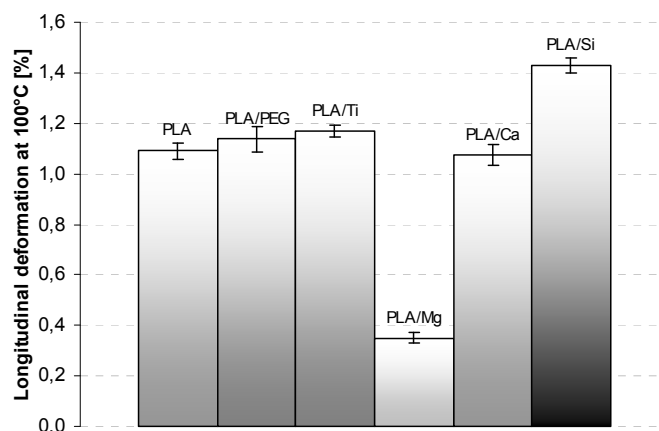


Figure 3. Longitudinal deformation of the specimens at 100°C

The low deformation of the PLA/Mg could be explained by the geometry of the filler; the flake shaped Talc particles appeared to be advantageous again in retarding the deformation more than the other, spherical shaped fillers. The flake shaped additives have also a high surface to volume ratio like synthetic fibres, which makes them useful for example in lowering the shrinkage or retarding deformation.

According to the DSC and dimensional stability results, the PLA/Mg material was selected for further testing by injection moulding it into high temperature mould (80°C) to develop semi-crystalline PLA during processing. Proper demoulding was only possible with at least 300 s of cooling time to develop enough crystallinity accordingly, enough stiffness for the part. The DSC analysis showed that significantly higher crystallinity developed by using high mould temperature compared to low mould temperature (Table 3.), however the crystallinity of the specimen was still far from the theoretical maximum reached previously by using low cooling rate DSC measurements (around 40-45%).

Material type	Cold crystallization enthalpy [J/g]	Enthalpy of fusion [J/g]	Crystallinity [%]
PLA/Mg-20°C (injection moulded at 20°C)	28.82	41.20	13.3
PLA/Mg-80°C (injection moulded at 80°C)	22.02	42.26	21.8

Table 3. Thermal properties of PLA/Mg materials injection moulded into 20°C and 80°C temperature mould

Finally, the heat resistant property of PLA (without additives) and PLA/Mg-80°C samples were tested (Figure 4-6.) by using a cantilever beam and registering the deflection visually.



Figure 4. Deflection of the PLA (middle) and PLA/Mg-80°C specimens (left and right) at 60°C

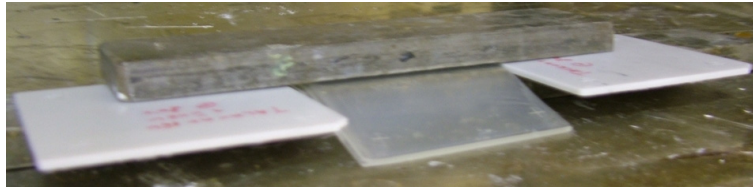


Figure 5. Deflection of the PLA (middle) and PLA/Mg-80°C specimens (left and right) at 90°C



Figure 6. Deflection of the PLA (middle) and PLA/Mg-80°C specimens (left and right) at 120°C

It is found that during the heat stability tests, the pure PLA specimens highly deformed and became opaque according to cold crystallisation, at the same time for the PLA/Mg-80°C there was no deformation and deflection observed. During heating the PLA/Mg-80°C specimens also cold crystallised due to its not complete crystallinity (Table 3.) but the synergistic effect of the already developed semi-crystalline molecular structure (developed during injection moulding) and the deformation retardant property of Talc was enough to avoid any deformation and deflection which finally made the specimen heat resistant. However, the high injection moulding cycle time due to the high cooling (crystallisation) time seems to be difficult to overcome, and additives with much more efficient nucleation ability has to be found.

4 Conclusions

In our work, we analysed the synergistic effect of various additives as nucleating agents and Poly(ethylene glycol) PEG on the crystallisation of renewable resource based, biodegradable polymer Poly(lactic acid) (PLA). The selected additives for nucleating agents were Talc ($Mg_3Si_4O_{10}(OH)_2$), Titanium-dioxide (TiO_2), Chalk powder ($CaCO_3$) and Aerosil (SiO_2). It was found that by using additives along with PEG, all of the selected additives had nucleation effect in order of Talc>Chalk powder>Aerosil>Titanium-dioxide. Talc was also found to be an effective nucleating agent along with PEG when higher cooling rates are used, which is applied especially during injection moulding. It was also determined that Talc effectively retarded deformation caused by specific volume changes due to cold crystallisation while the other investigated additives were not so effective. This effect was related to the flake shape, thus the high surface to volume ratio of Talc. An injection moulding technique was used with high mould temperature (80°C) and high cooling (crystallisation) time (300 s) to induce Talc and PEG containing PLA to crystallise during processing. We have demonstrated that by using Talc, along with PEG, and special injection moulding technology heat resistant PLA products can be injection moulded. The heat resistant capability was found to be partially due

to its crystallinity and partially due to the deformation retarding capability of Talc. However, it seems to be difficult to overcome the high injection moulding cycle times required to induce crystallisation and thus to produce stiff PLA products for proper demoulding.

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