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Thermal and mechanical analysis of injection moulded Poly(Lactic Acid) filled with Poly(Ethylene Glycol) and talc

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Abstract

In our research, the effect of talc particle size was analysed on the thermal and mechanical properties of renewable resource based, biodegradable polymer Poly(Lactic Acid) (PLA). Various talc particles with an average particle size of 24 μm, 1.9 μm, and 0.7 μm were blend mixed with PLA in 10 and 20 mass% containing no or an additional 10 mass% of Poly(Ethylene Glycol) (PEG) to increase molecular chain mobility. It was demonstrated that with decreasing talc particle size, its nucleation ability increased as well as all of the investigated mechanical properties of the compounds, however, in case of compounds containing PEG, this tendency was the opposite according to Charpy impact strength results. The talc with the best nucleating ability was selected and a full factorial design of experiment was made to optimise the talc and PEG content and to investigate their cross-effect in the 1-3-5-10-15 mass% additive content range. Finally, the effect of mould temperature and cooling time was analysed on the crystallinity and heat deflection temperature of the final injection moulded parts.

Keywords

Injection moulding, talc, particle size, Poly(Lactic Acid), nucleating agent

1. Introduction

In the 21st century, renewable resource based and inherently biodegradable polymers gain more and more attention. This increasing interest can be related to two exceptional properties of these polymers. Firstly, these polymers can be fully synthetized from renewable resources, for example from agricultural products lowering the crude-oil dependency of plastics. Secondly, these polymers can undergo biological degradation in suitable environment like in industrial compost into non-toxic materials like humus, water, carbon-dioxide, which is also an important aspect to decrease waste management problems caused by low life cycle packaging applications of mass-plastics [1].

One of the most important renewable resources to produce biodegradable polymers is starch. Starch is a polysaccharide which can be found in abundant amounts all over the Globe since it is the major component of the widely grown agricultural plants like corn (maize), wheat, rice. Starch can be fermented in the presence of sugar into lactic acid, which can be further processed by polycondensation into Poly(Lactic Acid) (PLA). PLA can also be produced from the polymerisation of the dimer of lactic acid called lactide. Two isomers of lactic acid can be distinguished, namely L-lactic acid and D-lactic acid, thus three types of lactides are available, namely L-lactide, D-lactide and L-D-lactide (Meso-lactide). The abbreviation PLA is regarded as the copolymer of L-, and D-lactic acid, in most cases being L-lactic acid as the main component, but when PLA is made entirely from L-, or D-lactic acid, it is referred as PLLA and PDLA respectively. PLA is a thermoplastic polymer which can be easily processed by conventional plastic processing equipments, has good mechanical properties, low processing shrinkage, reasonable price, it is capable of undergoing degradation in compost, and it is the most promising biodegradable polymer at the moment [2]. PLA is already commercialised as the material of cutleries, cups, food containers, flower pots, etc. and it is currently widening applications like in medical devices [3], however, most applications of PLA are still related to the packaging industry despite its good mechanical properties. According to its mechanical properties, PLA is an engineering plastic with high strength (~60 MPa) and high stiffness (~3 GPa), but its low heat deflection temperate (*HDT*) at around 55°C caused by its low glass transition temperature (T_g) still retards its usage as the material of high performance engineering parts. Although PLA with low D-lactide content is a semi-crystalline polymer and a typical semi-crystalline material has higher *HDT* than T_g, due to its crystalline content, but according to the very slow crystallisation of PLA, during most thermoplastic processing technologies, where the material is rapidly cooled from melt to form a product, the PLA products become practically amorphous and thus transparent. At the same time above T_g, PLA intensively cold-crystallises and reaches a crystalline ratio of around 50-55%, which ensures its *HDT* of around 120°C, however, when increasing temperature, softening and distortion of a PLA product takes place first, only followed by the cold crystallisation, thus it is not possible to post-anneal PLA products to increase *HDT* without major distortion.

To truly increase the *HDT* of PLA, it can be reinforced with natural fibres [4-13] and/or it can be compounded with nucleating agents [14-25]. The theory to increase *HDT* by incorporating natural fibres according to PLA products is that the fibres can increase the modulus of PLA, especially in the critical 50-80°C range around and above T_g. Accordingly, if it is possible to keep the storage modulus as high as possible and to keep the shape of the PLA product by avoiding major deformation in this temperature range, then the storage modulus of PLA will increase due to cold crystallisation ensuring high *HDT*. Another possible solution to increase *HDT* is to compound PLA with nucleating agents. In this case, high *HDT* is expected due to the developed crystallinity caused by enhanced crystallisation upon cooling from melt. By reinforcing PLA with fibres, both methods are present due to the nucleating ability of some fibres. However, another problem is that to be able to commercialise PLA products economical, highly productive, accurate, low cycle time processing technology must be used like injection moulding with high cooling rates, thus it is complicated to develop high crystalline content for PLA even with highly effective nucleating agents. Moreover, the length of the fibres used for reinforcing PLA is also highly reduced to a typical range of 0.2-0.4 mm during injection moulding, which decreases the maximum obtainable modulus and *HDT* increasing effect of the fibres.

Much research has been made to reinforce PLA with typically natural plant fibres [4-13] or even with glass [26] or basalt [27] fibres to make PLA based biocomposites suitable for high temperature engineering applications. By incorporating natural plant fibres to PLA in order to increase *HDT* it is critical to form strong connection between the fibres and the matrix. The adequate stiffness and length of reinforcing fibres is also important, which will help retarding the high stiffness loss of amorphous PLA products above T_g. Despite the significant amount of research, the increase of *HDT* is only a few times reported, which can be related to the low modulus of plant fibres. At the same time the fibres not only increase the modulus of the PLA, but the nucleating effect of microcellulose [10, 11] and nanocellulose [12, 13] fibre derivates was also demonstrated, however, significant crystallinity was only proved to develop at low cooling rates as 2°C min^{-1} [13], 5°C min^{-1} [10], 10°C min^{-1} [11, 12] by using differential scanning calorimetry (DSC) tests. By using fibres with much higher stiffness like glass [26] and basalt fibres [27] the *HDT* was still only increased by 9°C and 5°C respectively. Basalt fibres seem to have much better nucleating ability than cellulose fibres, and it was possible to fully crystallise PLA during cooling rates at 10°C min^{-1} above 20 mass% (m%) of silane treated basalt fibres, however, during injection moulding, only half of the achievable crystallinity of PLA developed, which is still remarkable, but again it was not enough for significant increase in *HDT*, only the dimensional stability of the injection moulded products were highly improved [27].

In the literature, the effect of numerous organic and inorganic materials were tested as potential nucleating agents like talc [14-16], talc along with Poly(Ethylene Glycol) (PEG) [17] TBC8-eb (p-tert-butylcalix(8)arene ethylebenzene) [18], Ethylene-Bis-Stearamide (EBS) [15], $CaCO_3$, TiO_2, $BaSO_4$ [19], native starch [16], microcellulose-, [10, 11] and nanocellulose derivatives [12, 13], orotic acid [20], hydrazide compounds [21], ethylenebis(12-hydroxystearylamide) (EBHSA) [21], layered metal phosphonates [22], multiwall carbon nanotubes [23] and PLA stereocomplex [24]. Talc was even tested for its effect on photooxidation of PLA [28]. Most of these results were also summarised in a recently published review paper according to PLA nucleation [25].

It was found that talc, talc along with PEG, TBC8-eb, orotic acid, hydrazide compound, layered metal phosphonates, EBHSA and PLA stereocomplex are highly effective nucleating agents for PLA, while $BaSO_4$, TiO_2, $CaCO_3$, EBS, cellulose derivatives, native starch, and multiwall carbon nanotubes were found to be less effective. The nucleation ability of the various materials can be compared by using the crystallisation temperature upon cooling from melt (Table 1.).

The nucleating agents with better nucleating ability are represented by higher crystallisation temperature, however, it is hard to compare the results due to various types of PLA used (due to the high variance in crystallisation property according to D-lactide content), various nucleating agent content and various measuring conditions (cooling rate). Although talc was found to be less but still effective nucleating agent compared to orotic acid, hydrazide compound or PLA stereocomplex, but it is apparent that talc is far the most available and cheapest of all. However by using talc alone, it is still very difficult to produce significant crystallinity and thus high *HDT* during injection moulding due to very high cooling rates. There are two ways to further enhance crystallinity: First, lower cooling rate can be used by injecting the melt of PLA into hot moulds. In this way, not only the cooling rate decreases, but at the same time the part can also be annealed in the mould. Harris et al. [15] analysed the non-isothermal crystallisation of 2m% talc content PLA by injection moulding it into 110°C hot mould. It was found that the part highly crystallised during cooling which resulted in a 30°C higher *HDT* compared to 25°C cold mould injection moulding, but high cycle time had to be used for significant crystallinity to develop. The second option is to use plasticizers like Poly(Ethylene Glycol) (PEG) [29] together with talc to enhance molecular chain mobility. In some cases, the combining of these two methods are also analysed by injection moulding PEG and talc content PLA into hot mould (80°C) [17]. Li and Huneault demonstrated that PEG and talc have synergistic effect in increasing the crystallisation rate, but significant crystallinity still can only be developed by using high cycle times.

According to the literature the combined usage of PEG and talc seems to be an excellent choice for enhancing crystallisation to produce high *HDT* injection moulded PLA parts for engineering applications at a reasonable price. Despite the significant amount of research, there was a lack of information in the literature according to the effect of talc particle size, to the optimal talc and PEG additive content and finally to the optimal cooling time for injection moulding talc and PEG filled PLA into hot mould. Thus, in this paper our goal was to: 1. Analyse the effect of talc particle size on the mechanical and thermal properties of PLA nucleated with talc and plasticized with PEG. 2. Make a full factorial design of experiment to optimise talc and PEG additive content and analyse their cross-effect. 3. Investigate the effect of mould temperature and cooling time on the crystallinity and *HDT* on the talc and PEG filled, injection moulded PLA parts.

2. Experimental

2.1. Materials

Injection moulding grade PLA type AI1001 from eSUN (Shenzen, China) was used for the research with a D-lactide content of 4%. AI1001 has a density of 1.24 g cm^{-3}, a glass transition temperature of 62°C, a melting temperature of 162°C and a melt flow index of 10 g 10^{-1} min^{-1} (2.16 kg, 190°C). Three different talc particles were purchased with a mean value of 24.4 μm (from Qualchem Ltd., Hungary), 1.9 μm (type HTP1 from IMI Fabi Ltd., Italy) and 0.65 μm (type HTPultra5 from IMI Fabi Ltd., Italy). Poly(ethylene glycol) (PEG) was obtained from Molar Chemicals Ltd. (Hungary) with a molar mass of 1500 g mol^{-1}.

2.2. Preparation of the compounds

Prior to processing PLA was dried at 120°C for 6 hours while talc and PEG were used as received. The dried PLA pellets and the additives were dry blended and extruded into compounds by using a LabTech Scientific twin screw extruder (from Bangkok, Thailand) with a screw diameter of 26 mm, and an *L/D* ratio of 40. The temperature profile was 190-185-180-175°C from the die to the hopper, while the screw rotational speed was set to 20 rpm. 2 mm diameter rod shaped extrudate was produced, which was pelletized prior to injection moulding. The abbreviation of the produced compounds were PLA-xS(M or L)T-yP, where "x" represents the m% of talc used, "S", "M" and "L" represent the particle size of the talc particle as small, medium or large, "y" represents the m% of PEG used and finally letters "T" and "P" stand for talc and PEG respectively, thus for example PLA-5MT-10P represents a compound with 5m% of medium particle sized talc and 10m% of PEG. After extrusion, it was not necessary to anneal the compounds because all of them had enough crystallinity to avoid pellet sticking [30]. These compounds were injection moulded into ISO standard dumbbell, three-point bending and Charpy specimens with a cross section of 4x10 mm by using an Arburg Allrounder 370S 700-290 injection moulding machine (from Lossburg, Germany) equipped with a 30 mm diameter screw and an *L/D* ratio of 25. Injection rate of 50 cm^3 s^{-1}, holding pressure and time of 600 bars and 20 sec respectively, residual cooling time of 40 sec and melt temperature of 190°C was used. All parameters were fixed during production, only the temperature of the mould and the residual cooling time were varied in a test. According to this setup, continuous and fully automated injection moulding production of quality PLA specimens could be achieved.

2.3. Methods

The mechanical properties of the compounds were analysed by using tensile, three-point bending and Charpy tests. Tensile and three-point bending tests were performed by using a Zwick Z020 universal testing machine (from Ulm, Germany) equipped with a Zwick BZ 020/TN2S force measuring cell with a force limit of 20kN using a cross-head speed of 5 mm min^{-1}. The Charpy impact tests were performed on unnotched samples by using a Ceast Resil Impactor (from Torino, Italy) impact testing machine equipped with a 15 J impact energy hammer and a DAS8000 data collector unit. Tensile strength (σ_t/MPa), tensile modulus (E_t/GPa) and strain at maximum force (ε_t/%) were determined from the tensile test, flexural strength (σ_f/MPa), flexural modulus (E_f/GPa) were determined from the flexural tests, while Charpy impact strength (α_{cU}/kJ m^{-2}) was determined from the Charpy impact test. All of the tests were performed at room temperature at a relative humidity of 50 ± 10%.

Differential Scanning Calorimetry measurements were performed on a TA Instruments Q2000 type calorimeter (from New Castle, USA) by using 3-6 mg of samples taken from the injection moulded specimens. The samples were tested in non-isothermal mode (heat/cool/heat) from 0 to 180°C at a cooling rate of 10°C min^{-1} to determine glass transition temperature (T_g), cold crystallisation temperature (T_{cc}), enthalpy of cold-crystallisation (ΔH_{cc}), melting temperature (T_m), enthalpy of fusion (ΔH_m) from the heating scan and crystallisation temperature (T_c), enthalpy of crystallisation (ΔH_c) from the cooling scan. Crystallinity was calculated by using Equation (1):

$$X = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f \cdot (1-\alpha)} \cdot 100\,, \tag{1}$$

where X/% is the calculated crystallinity, ΔH_m/J g^{-1} and ΔH_{cc}/J g^{-1} is the enthalpy of fusion and the enthalpy of cold-crystallisation respectively, ΔH_f/J g^{-1} is the enthalpy of fusion for 100% crystalline PLA (93.0 J g^{-1} [14]) and α is the mass fraction of the sum of the additives (talc and PEG).

Besides the commonly used 10°C cooling rate, 50°C min^{-1} cooling rate was also used to somewhat simulate injection moulding conditions and to be able to easily classify the crystallisation ability of the compounds with the similar crystallisation temperature measured at 10°C min^{-1} cooling rate.

Dynamic Mechanical Analysis was performed on a TA Instruments type Q800 tester (from New Castle, USA) by using the injection moulded three-point bending specimens. Dual cantilever layout was used to be able to gain storage modulus information above glass transition temperature (T_g). A heating rate of 2°C min^{-1} was used from 0 to 160°C with a span length of 35 mm, an amplitude of 20 µm, and a frequency of 1 Hz.

Heat Deflection Temperature tests were performed by using a Ceast 6505/000 HDT analyser (from Torino, Italy). Injection moulded specimens with a cross-section of 4x10 mm were used in edgewise mode with a support distance of 100 mm. The specific load was set to 0.45 MPa and the heating rate to 2°C min^{-1}. The *HDT* was obtained when the deflection reached 0.33 mm.

Scanning electron microscopy was performed by using a JEOL JSM 6380LA type electron microscope on fracture surfaces of tensile specimens. The fracture surface of the specimens was sputtered with Au/Pd alloy prior to observation to avoid electrostatic charging. The instrument was operated using 15 kV.

2.4. Research plan

Our research to develop injection moulded high heat deflection temperature PLA products with reasonable cycle time consists of three separate steps. The first one was to analyse the effect of talc particle size on the mechanical and thermal properties of PLA to be able to choose the most suitable one. In this case 10m% and 20m% of talc and 0 and 10m% of PEG content compounds were produced with three different particle size talc particles, thus a total number of 12 compounds were examined.

In the second step, a full factorial research was accomplished to analyse the effect of the amount of talc and PEG on the thermal properties of PLA in order to choose the one with best nucleation properties presumably suitable for injection moulding high *HDT* products. In this case PLA based compounds with all possible linear combinations of 1, 3, 5, 10, 15 m% talc and 1, 3, 5, 10, 15 m% PEG content were produced, and thus a total number of 25 compounds were tested. The talc used in this test was the one with the best nucleation ability chosen from the previous test.

In the third and final step, the effect of moulding temperature was analysed on the compound developed in the previous steps to analyse whether it is possible to injection mould high *HDT* PLA products with low cycle times. The temperature of the mould was varied between 20°C and 90°C in 10°C intervals, and the possibility of producing deformation-free specimens was analysed while leaving the holding and residual cooling time strictly the same as it was for producing pure PLA specimens. Only the deformation-free samples were evaluated as acceptable ones ready for further testing. All of the specimens with the slightest deformation upon demoulding were rejected. The mechanical and thermal properties of the acceptable specimens were investigated to determine the applicability of the compound. Finally, the effect of residual cooling time was analysed to find out the possibilities of injection moulding high *HDT*, nucleated PLA with low and thus economic cycle time.

3. Results and discussion

3.1. Effect of talc particle size

To produce high *HDT* injection moulded parts from PLA, it is necessary to develop significant crystallinity during processing, which will retard the enormous storage modulus loss above T_g. Enhancing crystallisation can be achieved by using nucleating agents, and their efficiency can be easily determined by the higher the better crystallisation temperature upon cooling from melt. DSC measurements were performed at a cooling rate of 10°C min^{-1} and 50°C min^{-1} to investigate the effect of talc particle size on the crystallisation temperature (Fig. 1., Fig. 2.).

The results show that at a cooling rate of 10°C min^{-1} all of the samples fully crystallised during cooling, which is indicated by the absence of cold crystallisation in the second heating scan. At the same time, at 50°C

min^{-1} only the compounds containing both talc and PEG were able to fully crystallise, but the crystallisation of the compounds containing only talc was incomplete as indicated by the appearance of cold crystallisation in the second heating scan. According to the compounds containing only talc there was no significant increase found in the crystallisation temperature with increasing talc content. It was also found that the talc with the smaller particle size had significantly better nucleating ability and thus increased crystallisation temperature (Fig. 1.) especially when higher cooling rate (50°C min^{-1}) was used and PEG was also added to the compound (Fig. 2.).

At the same time there was no significant difference found in the nucleation effect of medium and small particle size talc particles, which may be explained by the relatively minor difference in the particle size of the medium (1.9 µm) and small (0.65 µm) particle size talc particles compared to the large particle size talc (24.4 µm). Finally, the compound with the highest additive content and with the smallest particle size talc was found to have the highest crystallisation temperature, namely 118.5°C and 108.2°C measured at 10°C min^{-1} and 50°C min^{-1} cooling rate respectively. The crystallinity of the injection moulded specimens was also calculated by using the first heating and the cooling scan (Table 2.) by Equation 1. The maximum possible crystallinity of the pure PLA was determined using very low (0.5°C min^{-1}) cooling rate.

According to 10m% talc and 10m% PEG and 20m% talc and 10m% PEG compounds the crystallinity increased as the effect of smaller talc particle size from 24.7% to 36.2% and from 36.3% to 43.3% respectively. The compound containing 20m% small particle size talc and 10m% PEG had the fastest crystallisation kinetics from the investigated compounds and thus enormous crystallinity developed during injection moulding into 20°C mould (43.3%), but it still was not enough to fully crystallise PLA and to reach its maximum possible crystallinity of 54.7%. It was also demonstrated that the additives not only influence crystallinity but also cold crystallisation temperature. Both talc and PEG decrease cold crystallisation temperature, and the smaller particle size talc was used, the higher the cold crystallisation decreasing effect was. At the same time it is likely that talc only reduces cold crystallisation temperature to a certain temperature around 80°C because by adding 10m% small particle size talc to a compound with a cold crystallisation temperature lower than 80°C like the 10m% small particle size talc and 10m% PEG, it has not further decreased but increased cold crystallisation temperature from 68.2°C to 81.7°C.

With an industrial point of view one of the most important aspects is how the additives influence the storage modulus of injection moulded PLA products directly due to the modulus of the additives or indirectly by affecting crystallinity and cold crystallisation. Unfortunately these two effects cannot be separated in most cases. In case of the compounds containing only talc as additive it can be stated that talc increased storage modulus as it was expected, and the smaller the used talc particle size was, the higher it increased the modulus, but again only minor differences were measured according to small and medium particle size talc (data not presented here). In the case of talc filled PLA compounds, the storage modulus difference can be mainly related to the talc particle size, because crystallinity of these compounds was practically the same around 18-22% (Table 2.).

The 10m% talc and 10m% PEG content compounds (Fig. 3.) became softer compared to the 10m% talc content compounds, thus the storage modulus measured at room temperature decreased, and moreover, as the effect of PEG, the cold crystallisation temperature further decreased. Although the crystallinity of the 10m% talc and 10m% PEG compounds increased from 24.7% to 36.2% with decreasing particle size, this crystallinity was still not enough to retard huge modulus loss above T_g.

Compared to the 10m% talc and 10m% PEG compounds, the 20m% talc and 10m% PEG compounds (Fig. 4.) had significantly higher cold crystallisation temperature as discussed before (but lower compared to 20m% talc content compounds), thus storage modulus began to increase due to cold crystallization at a higher temperature. According to this higher cold crystallization temperature and to the significantly higher crystallinity compared to other tested compounds, an almost constant storage modulus was found in the temperature range of 50-70°C for the 20m% talc and 10m% PEG content compounds. It was also found that the 10m% small talc and 10m% PEG compound had almost the same crystallinity as 20m% large talc and 10m% PEG, but for the former compound, the constant storage modulus range was absent due to lower cold crystallisation temperature. With decreasing talc particle size the storage modulus of the 20m% talc and 10m% PEG compounds highly increased especially in the critical temperature range of 50-70°C from 26 MPa to 146 MPa, which can be explained by the high crystallinity. Although the modulus loss above T_g was reduced with increasing crystallinity, but it was still not enough to completely avoid it. From the tested compounds the PLA-20ST-10P compound had the highest crystallinity and thus the lowest modulus loss above T_g. It is interesting to note, that only crystallinity values near the possible maximum (>40%) reduced the drop in modulus above T_g significantly, thus to develop high *HDT* compound based on PLA the goal is not to develop significant but the possible maximum crystallinity. According to the practical uses another important aspect is the mechanical properties of the compounds (Table 3.).

The tensile and flexural elasticity modulus of the compounds naturally increased with increasing talc, with decreasing talc particle size and without using PEG. According to the small and medium size talc there was significant difference found in the modulus values only when PEG was also added to the compound. The same tendency was observed for tensile and flexural strength values. Talc was found to have a minor reinforcing effect on PLA, what increased with decreasing particle size. According to the strain at maximum force, all of the measured values were in the range of 2-3% including the strain of the pure PLA, which means that the additives had only minor effect on the strain and the specimens have not become uselessly brittle. Next to the low *HDT*, the low impact strength is also one of the main drawbacks of PLA. By adding 10m% talc to PLA, the Charpy impact strength enormously increased from 23.0 to 67.7 kJ m^{-2} in the case of small particle size talc. Again it was demonstrated that it is favourable to use lower particle size talc, since the smaller the talc particle size was, the higher the impact strength increased. Interestingly, this tendency becomes the opposite, when PEG was also added to the compound, namely impact strength decreases from 44.3 and 47.8 kJ m^{-2} to 29.5 and 26.9 kJ m^{-2} according to 10m% large and 10m% small particle size talc and 20m% large and 20m% small particle size talc filled PLA with PEG content respectively. This behaviour was also analysed by using electron microscopy of the fracture surface of the tensile specimens (Fig. 5.).

As it can be seen there is strong adhesion between the two phases, and possibly due to the increased specific surface of the smaller particle size talc it increases impact strength more than large particle size talc. The impact strength increasing effect of the large particle size talc was also limited as huge agglomerated talc particles with a size of more than 50 µm were also observable. It was also found that ductile fracture surface developed when 20m% small particle size talc, or when talc and PEG both were used. This ductile surface is represented by crazing and resulted in increased impact strength, however, the tendency found when PEG was added to the compound (decreasing impact strength with decreasing talc particle size) could not be simply correlated to the type of fracture, and thus it was not possible to explain this behaviour only by the SEM micrographs. A possible explanation for this opposite tendency with the compounds containing PEG is that the critical length of the talc particles may increase due to lower adhesion between a plasticized matrix and the particles. This increased critical particle length of the talc particles may cause the smaller sized talc particles not to increase impact strength, but still the talc particles with higher length were able to do so.

3.2. Effect of talc and Poly(ethylene Glycol) content

After it was demonstrated that it is favourable to use small particle size talc to promote heterogeneous nucleation and PEG to promote homogeneous nucleation at the same time to significantly increase total crystallinity, the cross-effect of heterogeneous and homogeneous nucleation caused by talc and PEG and the optimal content of these two additives were analysed. This was performed by using a full factorial design of experiment in the range of 1-3-5-10-15m% additive content by using the crystallisation peak temperature of the compounds as a widely used indicator for the effectiveness of nucleation. The design of experiment was split into four to be able to independently analyse the effect and cross-effect of low (1-3-5m%) and high (5-10-15m%) additive content on the crystallisation peak temperature measured at low (10°C min^{-1}) and at high (50°C min^{-1}) cooling rates. The *B-coefficients* were determined as the indicator of the extent of the nucleation ability of the additives (talc, PEG) and their cross-effect (talc x PEG) (Fig. 6.).

As it can be seen on Fig. 6. low talc and PEG content had significant effect on crystallisation temperature, but their cross-effect was insignificant according to low cooling rate, while at high cooling rate neither their cross-effect, nor the effect of the additives itself was significant. This can be obviously explained by the high cooling rate, which highly reduced the crystallisation temperature increasing effect of the additives. For the higher additive content both talc and PEG had significant effect in case of both cooling rates, which suggests that the effect of high cooling rate can be compensated by using higher additive content. At the same time, their cross-effect was statistically insignificant. For a certain PEG content crystallisation temperature increases with increasing talc content, but for higher PEG content crystallisation temperature only increases in the same rate with increasing talc content. No cross or synergistic nucleation effect was found between these two additives related to homogenous and heterogeneous nucleation on the crystallisation temperature, which means to increase crystallisation temperature the more the better rule is valid according to the additive content and no optimal content exists in the investigated additive content range. Even though these two additives were not found to have synergistic effect on nucleation and thus on the beginning of crystallisation, but they still have synergistic effect on the final crystallinity as Li and Huneault [17] stated, because PEG not only promotes homogenous nucleation but also crystallisation rate (nucleus growth) due to increased molecular chain mobility.

3.3. Effect of mould temperature and cycle time

PLA-20ST-10P compound was selected for the final investigations according to its highest crystallinity from the investigated compounds and the possibility of fully crystallizing during injection moulding into hot mould. This compound was injection moulded into different temperature mould between 20°C (cold) to 90°C (hot) to analyse the effect of mould temperature on crystallinity. When injecting nucleated PLA into hot mould, crystallinity is expected to develop due to both crystallisation from melt during cooling and due to annealing the PLA product in the hot mould. Naturally, to be able to develop highly crystalline PLA product which can be injection moulded with low cycle time, it is advantageous that the nucleated PLA could reach as high crystallinity as possible during cooling from melt, without the need of further increasing crystallinity of the PLA product within the mould by using annealing, which will increase cycle time. It is also very important to select the optimal mould temperature: when injection moulding nucleated PLA into cold mould, high crystallinity may not develop due to high cooling rate, but the cycle time will be low and the parts will be stiff enough for proper demoulding. On the contrary, when nucleated PLA is injected into hot mould, higher crystallinity will develop, but the parts will be much less stiff due to high demoulding temperature and the cycle time will be longer because crystallisation takes much time for PLA and only high crystallinity will ensure enough stiffness for the parts to be properly demoulded at the temperatures higher than T_g. In our research beyond the investigation of the effect of mould temperature, the effect of cycle time (residual cooling time) was also investigated, and the lowest possible cycle time to produce highly crystalline PLA products was determined. The storage modulus and crystallinity values of the specimens injection moulded by using PLA-20ST-10P compound into different mould temperature can be seen in Fig. 7.. By using 60 sec of total cooling time, 20°C, 30°C, 80°C and 90°C moulding temperature could be used to produce stiff enough, properly demoulded specimens, while between 30-80°C mould temperature demoulding problems occurred due to still soft specimens. As it can be seen by increasing mould temperature, crystallinity increased due to lower cooling rate. According to the results, for the 80°C and 90°C mould temperature, the cooling rate could be reduced so low compared to 20°C and 30°C mould temperature, that the injection moulded, nucleated PLA could reach the highest possible crystallinity.

Due to higher crystallinity of the specimens injection moulded into hot mould, the significant storage modulus loss could be avoided, which implies the higher *HDT* of this nucleated compound compared to neat PLA products. As it could be already observed in the storage modulus, the *HDT* highly increased with increasing moulding temperature from an average value of 37.9°C to 108.6°C according to the moulding temperature of 20°C and 90°C respectively. The low *HDT* (38°C) of the PLA-20ST-10P compound injection moulded into cold mould compared to neat PLA can be explained by the plasticizer content. Finally, it was also investigated that how much the cooling time and thus the cycle time can be reduced by keeping the high *HDT* of the product and to make the injection moulding of nucleated PLA more economical. By decreasing cooling time of a thermoplastic material processed by injection moulding, the temperature inside the part increases at ejection and when too low cooling time is applied, demoulding problems could occur due to still soft specimens. For nucleated PLA, in case of hot mould, the cooling time is not only used to cool the part but it can also be considered as an in-mould annealing time. In the case when too low cooling time was chosen, the nucleated PLA products will still be soft not due to high moulding temperature, but due to low crystallinity caused by low in-mould annealing time. Nevertheless, it may be possible to shorten the cooling time, thus the nucleated PLA products will not reach the possible maximum crystallinity during injection moulding, but enough for proper demoulding and during the cooling of the ejected product outside the mould it may finish crystallisation. As in the previous test 90°C mould temperature had the most significant effect on HDT, thus this temperature was investigated for decreasing cycle time. It was possible to decrease the 60 sec of total cooling time by 15 sec, while the *HDT* of the specimen only slightly decreased from an average value of 108.6°C to 105.5°C.

By further decreasing the total cooling time demoulding problems occurred due to still soft specimens with most likely low crystallinity. At the same time comparing the results to the literature, it can be stated that it was possible to further decrease the cycle time of the injection moulded, nucleated, high HDT PLA in case of 90°C mould temperature. For example for talc filled PLA Harris and Lee [15] reached a cycle time of around 3 minutes, while for talc and PEG filled PLA injected into hot mould Li and Huneault [17] reached a cycle time of around 1 minute. It is also to be noted that Harris and Lee [15] used a PLA with 1.4% of D-Lactide content, and Li and Huneault [17] used a PLA with 2% of D-Lactide content, which can be crystallised more easily due to the lower D-Lactide content PLA compared to the PLA used in this paper with 4% D-Lactide content. This type of PLA was used to analyse the modification possibilities of a common PLA with reasonable price. Nevertheless, it was proved that it is possible injection mould high HDT nucleated PLA with a more reasonable cycle time. However, this cycle time is of course highly dependent on the geometry of the product (wall thickness, geometrical stiffness) and the construction of the mould (cold or hot runner system).

4. Conclusion

In our research, the effect of talc particle size, talc and Poly(ethylene Glycol) (PEG) content, their cross-effect and the effect of mould temperature was analysed on the thermal, thermo-mechanical, and mechnical properties of Poly(Lactic Acid) (PLA). Talc particles with three different particle sizes were used (24.4 μm, 1.9 μm, 0.65 μm) to produce talc and PEG filled PLA specimens by using twin-screw extrusion and injection moulding.

It was demonstrated by using differential scanning calorimetry that by decreasing talc particle size its nucleating effect increased especially when higher cooling rates were applied (50°C min^{-1}) and PEG was also added to the compound. In case of the compound containing 20m% talc and 10m% PEG crystallisation temperature increased from 101.9°C to 108.2°C by decreasing talc particle size from 24.4 μm to 0.65 μm. This compound with the smallest particle size talc reached a very significant crystallinity of 43.3% during injection moulding into 20°C temperature mould, however, the possible maximum crystalline ratio of the PLA material used (54.7%) still could not develop. Significant crystallinity highly reduced storage modulus loss above glass transition temperature (T_g) compared to the other investigated compounds, however, this storage modulus loss was still very significant despite to the high crystalline ratio of 43.3%. For the mechanical properties, it can be stated that the smaller the talc particle size was, the more it increased tensile and flexural modulus. The 1.9 μm and 0.65 μm particle size talc even had minor reinforcing effect. By adding PEG to the compound naturally both modulus and strength values highly decreased. As for the Charpy impact strength a special phenomenon was observed as by decreasing talc particle size, the impact strength increased in the case of compounds containing only talc reaching an impressive value of 63.9 kJ m^{-2}, which was represented by ductile fracture surfaces observed by using scanning electron microscope, while with decreasing talc particle size the impact strength decreased when PEG was also added to the compound.

In the second step of our investigations a full factorial design of experiment was made according to 1-3-5-10-15m% small particle size talc and PEG content to analyse the synergistic effect of heterogeneous and homogenous nucleation caused by talc and PEG respectively. It was demonstrated that both talc and PEG content are significant in increasing crystallisation temperature, which is a widely used indicator of the effectiveness of nucleation, however, this effect of the additives becomes more and more insignificant with increasing cooling rate. Surprisingly it was proved that the nucleation cross-effect of talc and PEG is statistically insignificant, thus to increase crystallisation temperature the more the better rule is valid according to talc and PEG content.

Finally the effect of mould temperature and cooling time was analysed on the crystalline ratio and heat deflection temperature (*HDT*) of the 20m% small particle size talc and 10m% PEG filled PLA. It was demonstrated that by increasing mould temperature the *HDT* of the specimen could be increased significantly from 37.9°C to 108.6°C according to 20°C and 90°C mould temperature respectively, which can be related to the higher crystalline ratio caused by the lower cooling rate of the high temperature mould. It was also proved that it is possible to decrease total cooling time and thus cycle time to make the injection moulding of nucleated PLA more economical. For the 90°C mould temperature it was possible to decrease the total cooling time of 60 sec by 15 sec, while the *HDT* of the part only slightly decreased from and average value of 108.6°C to 105.5°C.

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Tables:

Table 1 Crystallisation temperature of PLA nucleated with various materials

PLA used	Nucleating agent	DSC cooling rate/°C min^{-1}	Temperature of crystallisation T_c/°C	Reference
3051D, NatureWorks, 4% D-lactide content	15wt% Talc	10	89	[13]
3001D, NatureWorks, 1.4% D-lactide content	20wt% Talc	10	113	[14]
4032D, NatureWorks, 2% D-lactide content	1wt% Talc + 10wt% PEG(3350)	20	105	[16]
Jiu Ding Company, PLLA	1wt% TBC8-eb	5	134	[17]
3001D, NatureWorks, 1.4% D-lactide content	2wt% EBS	10	97	[14]
3051D, NatureWorks, 4% D-lactide content	0.5wt% $BaSO_4$; $CaCO_3$; TiO_2	10	No sharp crystallisation	[18]
Lacea H-100, Mitsui Chemicals, D-lactide content not shown	10wt% Microfibrillated cellulose	5	103	[9]
4032D, NatureWorks, 2% D-lactide content	2.5wt% Cellulose nanofibre	2	103	[12]
Biomer Company, PLLA	0.3wt% Orotic acid	10	124	[19]
Producer not shown, 0.6% D-lactide content	1wt% Hydrazide compound	20	131	[20]
Producer not shown, 0.6% D-lactide content	1wt% EBHSA	20	110	[20]
4032D, NatureWorks, 2% D-lactide content	2wt% zinc phenyl-phosphonate	10	123	[21]
5051X, Cargill Dow, PLLA	0.08 wt% Multiwall carbon nanotube	10	88	[22]
Unitika Co., PLLA	10wt% PDLA	1	135	[23]

Table 2 Crystallinity of the injection moulded compounds measured at 10°C min^{-1} heating and cooling rate

Compound	T_{cc}/°C	T_m/°C	ΔH_m/J g^{-1}	ΔH_{cc}/J g^{-1}	X/%
PLA (0.5°Cmin^{-1} cooling rate)	106.3	165.8	50.9	-	54.7
PLA-10LT	94.7	163.1	37.5	21.9	18.6
PLA-10MT	93.1	162.7	38.9	21.2	21.1
PLA-10ST	92.0	162.9	39.9	22.1	21.3
PLA-20LT	93.0	162.8	34.1	19.8	19.3
PLA-20MT	89.9	162.3	35.3	19.3	21.4
PLA-20ST	88.8	162.5	36.4	19.7	22.5
PLA-10LT-10P	74.3	161.7	38.9	20.5	24.7
PLA-10MT-10P	69.4	162.1	38.7	17.2	28.9
PLA-10ST-10P	68.2	162.2	45.5	18.6	36.2
PLA-20LT-10P	86.0	161.3	33.8	10.1	36.3
PLA-20MT-10P	84.6	161.3	33.4	8.5	38.2
PLA-20ST-10P	81.7	161.6	33.9	5.7	43.3

Table 3 Mechanical properties of the compounds

Compound	Tensile properties			Flexural properties		Charpy
	σ_t/MPa	E_t/GPa	ε_t/%	σ_f/MPa	E_f/GPa	α_{cU}/kJ m^{-2}
PLA	64.5 ± 0.3	2.97 ± 0.03	2.93 ± 0.06	101.5 ± 1.3	3.29 ± 0.02	23.0 ± 1.5
PLA-10LT	59.6 ± 0.2	3.37 ± 0.05	2.69 ± 0.11	98.3 ± 0.7	3.93 ± 0.05	37.3 ± 1.8
PLA-10MT	63.4 ± 0.2	3.98 ± 0.02	2.50 ± 0.02	103.5 ± 0.3	4.81 ± 0.01	54.8 ± 1.6
PLA-10ST	63.7 ± 0.3	3.93 ± 0.02	2.67 ± 0.06	104.3 ± 0.3	4.87 ± 0.03	67.7 ± 3.3
PLA-20LT	57.3 ± 0.2	4.01 ± 0.10	2.34 ± 0.01	97.0 ± 0.8	4.91 ± 0.06	30.5 ± 1.0
PLA-20MT	65.2 ± 0.5	4.93 ± 0.15	2.36 ± 0.11	109.4 ± 0.5	6.85 ± 0.06	39.5 ± 1.5
PLA-20ST	66.8 ± 0.6	4.89 ± 0.09	2.34 ± 0.11	109.9 ± 1.5	6.59 ± 0.08	39.7 ± 2.8
PLA-10LT-10P	28.0 ± 0.4	1.97 ± 0.05	2.79 ± 0.05	46.4 ± 0.2	2.03 ± 0.03	44.3 ± 1.7
PLA-10MT-10P	31.0 ± 0.6	2.39 ± 0.03	2.60 ± 0.11	55.3 ± 0.6	2.93 ± 0.05	33.9 ± 1.7
PLA-10ST-10P	38.2 ± 1.2	2.86 ± 0.09	2.23 ± 0.07	60.0 ± 0.3	3.32 ± 0.06	29.5 ± 1.4
PLA-20LT-10P	20.1 ± 2.4	1.71 ± 0.19	2.69 ± 0.07	40.0 ± 2.5	2.17 ± 0.11	47.8 ± 1.7
PLA-20MT-10P	28.4 ± 0.3	2.71 ± 0.03	2.28 ± 0.20	42.7 ± 3.2	2.65 ± 0.21	31.8 ± 2.1
PLA-20ST-10P	32.3 ± 1.9	2.97 ± 0.16	2.44 ± 0.18	52.5 ± 3.5	3.42 ± 0.22	26.9 ± 1.3

Figures:

Fig. 1 Cooling scan of compounds with small and large talc particle size measured at 10°C min^{-1}

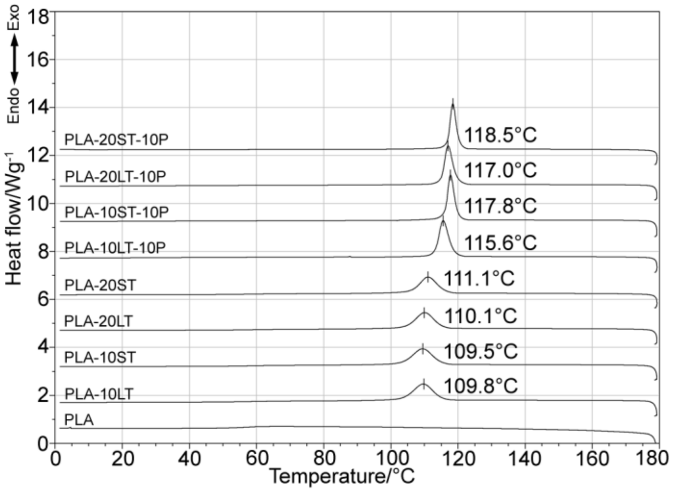

Fig. 2 Cooling scan of compounds with small and large talc particle size measured at 50°C min^{-1}

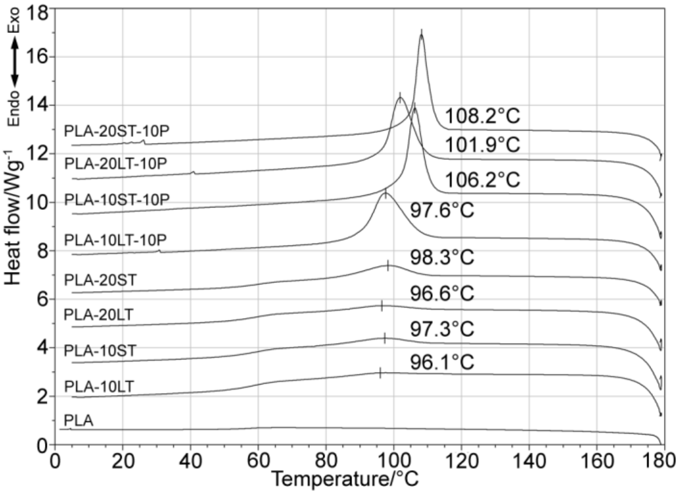

Fig. 3 Storage modulus of the compounds with 10m% talc and 10m% PEG content

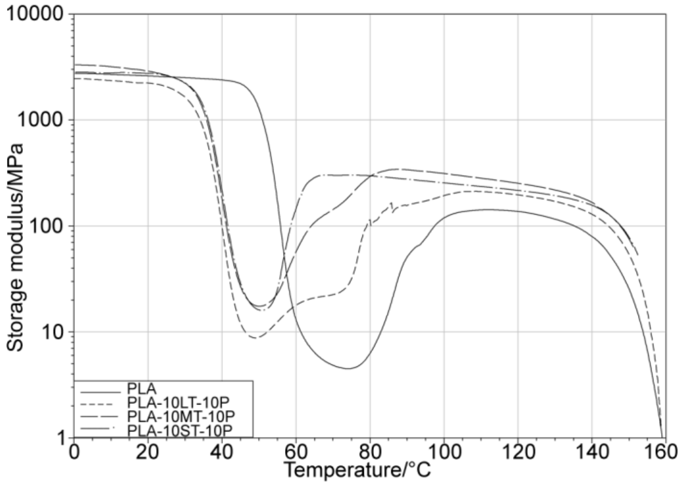

Fig. 4 Storage modulus of the compounds with 20m% talc and 10m% PEG content

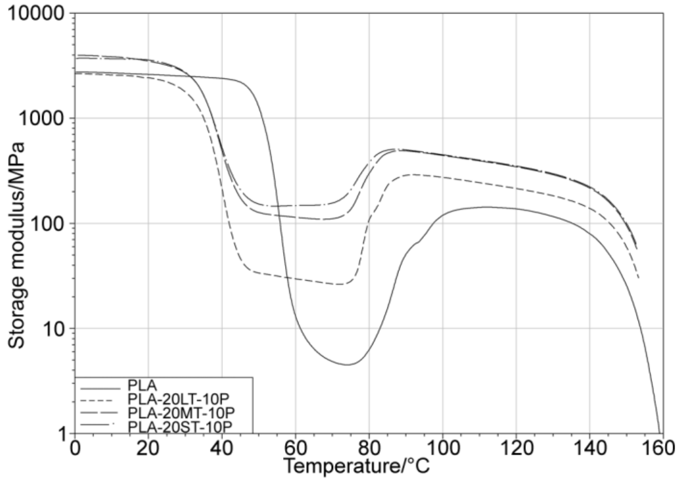

Fig. 5 Fracture surface of 20m% talc filled PLA tensile specimens (a-c) and 20m% talc and PEG filled PLA tensile specimens (d-f) (from left to right: large, medium, small talc particle size)

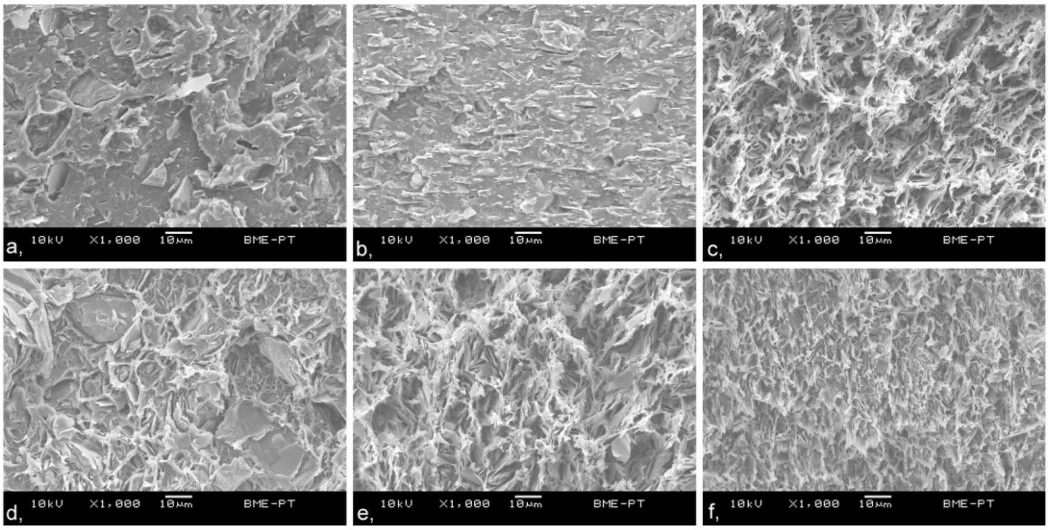

Fig. 6 B-coefficients of compounds containing 1-3-5m% talc and PEG cooled at 10°C min^{-1} (a) and 50°C min^{-1} (b); 5-10-15m% talc and PEG cooled at 10°C min^{-1} (c) and 50°C min^{-1} (d)

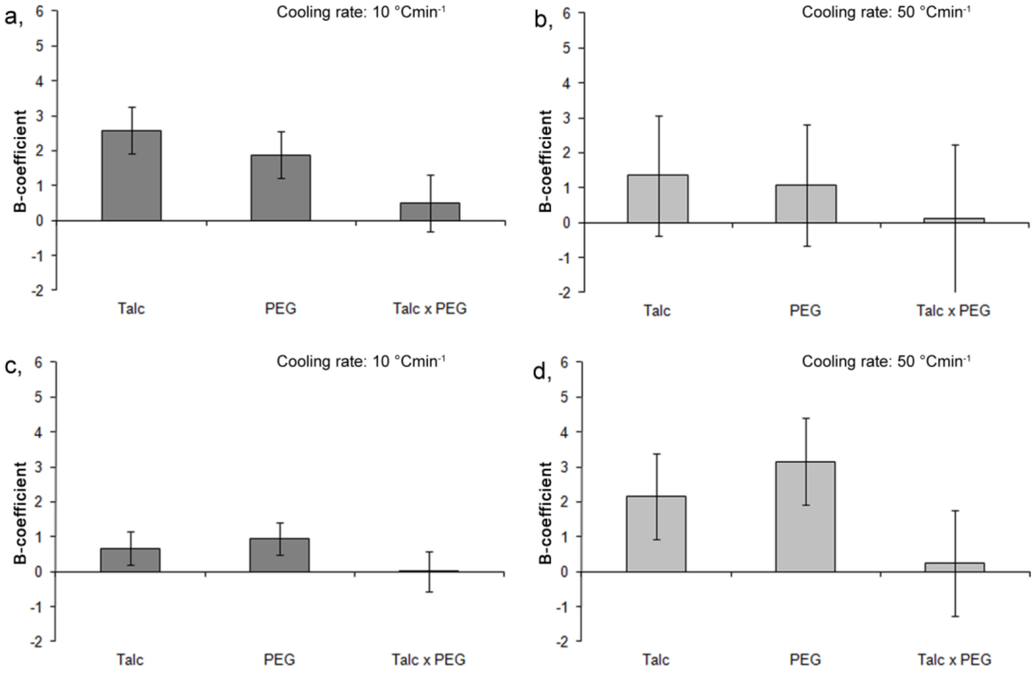

Fig. 7 **S**torage modulus of the PLA-20ST-10P compound injection moulded into different temperature mould