Effect of crystalline forms (alpha ' and alpha) of poly(lactic acid) on its mechanical, thermo-mechanical, heat deflection temperature and creep properties

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Effect of crystalline forms (α' and α) of Poly(lactic acid) on its mechanical, thermo-mechanical, heat deflection temperature and creep properties

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Abstract

In this paper the effect of crystallinity and crystalline forms (ratio of the less ordered α' and the more ordered α crystalline forms) of injection moulded Poly(Lactic Acid) (PLA) was analysed on the mechanical, thermo-mechanical, Heat Deflection Temperature (HDT) and creep properties. The injection moulded PLA specimens were post-production annealed in a heat chamber at 80°C crystallization temperature (T_c) for 0-60 minutes to develop various crystallinity as well as at 80-140°C T_c for one hour to develop various ratios of α' and α crystal forms with the possible maximum crystallinity. It was demonstrated that not only crystallinity, but also the ratio of the crystalline forms of α' and α significantly influences the application-wise properties like storage modulus and thus HDT as well as tensile, flexural, impact properties and finally creep characteristics. In most cases better properties (higher HDT, storage modulus, mechanical properties, and creep resistance) could be reached by increasing the α to α' crystalline form ratio in the PLA specimens.

Keywords

1. Introduction

Nowadays, the renewable resource based and inherently biodegradable polymers (or biopolymers in short) are gaining more and more attention, since they are believed to partially replace petrol based plastics in the future and solve or at least moderate waste management problems caused by the accumulation of low life cycle plastic products mainly used in the packaging industry [1-4]. Due to these two extraordinary properties, namely the renewable resource based and biodegradable feature, the biopolymers could be inserted into the life cycle of nature, which makes them and their usage very attractive. Currently, the most promising renewable resource (starch) based and inherently biodegradable polymer is Poly(Lactic Acid) (PLA) [5-8]. PLA is a thermoplastic, aliphatic, semi-crystalline polyester with excellent strength (~65 MPa of tensile strength) and modulus (~ 3 GPa of tensile modulus), but with unfortunately low impact strength (notched and unnotched Charpy impact strength of 3 kJ/m^2 and 23 kJ/m^2 respectively) and low heat deflection temperature (HDT, ~55°C). Due to its easy process-ability and reasonable price, PLA has already been commercialized and thus can be found on the market in most cases as the material of cups, cutleries, office utensils, flower pots, yoghurt cans, bottles (for still water), etc. It can also be physically or chemically foamed for loose-fill packaging [9], moreover, it has also already entered the medical industry as biocompatible and bio-absorbable implants [10-12] and by reinforcing it with various natural fibres like plant based cellulose [13-16] or mineral fibres [17, 18], it may very likely have engineering applications as well.

According to its crystalline structure, PLA can be crystallized into three crystalline forms, namely α, β and γ [19-24]. The most common and stable polymorph is α form (orthorhombic unit cell), which is developed when PLA is crystallized from melt or from solution [20, 21]. On the contrary, β form (trigonal unit cell) could be obtained by applying high drawing and high temperature conditions to the α form [22, 23], while γ form (orthorhombic unit cell) could be developed by epitaxial crystallization on hexa-methylbenzene substrate [24]. Most research concentrated on investigating the α crystal form since this type is developed during usual melt processing of PLA, thus from the processing point of view, this one has the most practical significance. However, unfortunately PLA has very slow crystallisation kinetics, meaning that it could only crystallize into the α crystalline form when cooled at a very low cooling rate (~1-2°C/min) from melt [25] otherwise by applying higher cooling rates, the usage of various nucleating agents [26-36] is necessary to induce crystallization. Accordingly, by using the typical melt processing technologies like extrusion or injection moulding, it is especially challenging to develop significant crystallinity due to the very high cooling rate generally applied to achieve low cycle time and thus economical production. Thus, the produced PLA parts have usually low crystallinity (only a few percent), high clarity and are practically amorphous. At the same time, α crystalline form could not only be developed by slow cooling from melt (or by using nucleating agents) but also in solid state during cold-crystallization by heating the (mostly amorphous) PLA product above glass transition temperature (T$_g$). In our previous publication [37] the thermo-mechanical properties of injection moulded PLA specimens cold-crystallized at 80°C for various times was analysed and found that the storage modulus loss above T$_g$ typical to amorphous polymers could be effectively reduced and thus the HDT could be increased significantly by increasing crystallinity. Moreover, it was also reported [38-40] that PLA could not only crystallize into α crystalline form from melt (or during cold-crystallization), but also into a less ordered or disordered crystal named α', which has the same conformation, but

a loose packing manner and lower density compared to the more ordered α crystal form. It is also suggested that α' phase is only a metaphase rather than a stable phase like α.

The crystal structure of the α' and α phases, their development as well as the effect of crystallization temperature (T_c), crystallization time (t_c) and molecular weight (M_w) on the melting behaviour of PLA has been investigated by many authors [41-46] by using Differential Scanning Calorimetry (DSC), Wide Angle X-Ray Diffraction (WAXD) and Fourier Transformation Infrared Spectroscopy (FTIR) techniques. According to the current knowledge, the development of α and α' is dependent on the T_c. When PLA is crystallized below 100°C or above 120°C, entirely the less ordered α' or the more ordered α form is developed respectively. On the contrary, when PLA is crystallized between 100°C and 120°C, the mixture of α' and α form is generated and the higher the T_c, the higher the α to α' ratio . According to the melting process, it was found that PLA shows a multiple melting behaviour depending on the T_c and thus on the α' and α crystal form content. When T_c was below 100°C, then a small exothermic peak appeared just before melting, which could be related to the α' to α phase transition, followed by the melting of the newly developed α phase. The small exothermic peak just before melting, which corresponds to the transition of the less ordered α' into the more ordered α was found not to be a melt-recrystallization process, but a solid phase transition without melting of the α' phase. On the contrary, when T_c was between 100°C and 120°C, this small exothermic peak disappears and an additional melting endotherm appears thus the melting process becomes bimodal. The height of the newly appeared endothermic peak increases with increasing T_c and both endotherms are considered to relate with the melting of the α phase. Subsequently, the lower temperature endotherm is related to the synchronous melting of the original α form crystals and to the α' to α crystalline phase transition, this case not in solid state, but in a melt-recrystallization process while the higher temperature endotherm is related to the melting of the crystals formed during the α' to α crystalline phase transition. Finally, when T_c was above 120°C, only one melting endothermic peak appeared entirely related to the melting of the α phase.

As it was demonstrated, many authors investigated the effect of T_c on the multiple melting behaviour of PLA and thus the ratio of α' and α crystal forms has been widely studied, but according to our best knowledge, there is not a single paper dealing with the effect of T_c and thus the ratio of α' and α crystal forms on the mechanical, thermo-mechanical, HDT and creep properties of injection moulded PLA products despite of the significance of these properties in reference to application. Inducing cold-crystallisation as a post-production thermal treatment (annealing) on injection moulded PLA parts may have low practical significance at first sight, since the initially amorphous PLA parts will somewhat distort due to the drop in modulus (entering rubbery state) and to the release of internal (processing) stresses [37]. However, by using this technique to control crystallinity and crystalline order (ratio of α' and α), firstly their effect on various application-wise properties could be determined and secondly, the result could be used in practice to set optimal processing parameters, especially optimal mould temperature analogously to the investigated T_c to produce injection moulded, in-mould-annealed PLA parts with the desired crystallinity and crystal order. Note, that in the case when the mould temperature is higher than the T_g of PLA, nucleating agents are generally used to decrease in-mould-annealing (crystallizing) time and thus cycle time to a reasonable and economical level. In a recently published paper, Yang et al. [47] investigated the mechanical, thermo-mechanical and creep properties of nucleated and annealed, compression moulded PLA specimens, however, only one T_c was applied for annealing (110°C), thus the effect of crystallinity was truly investigated, but the influence of the ratio of α' and α crystal forms by using multiple T_cs has not been examined yet.

Accordingly, in our work injection moulded PLA products were post-production thermal treated (annealed or cold-crystallized) at various T_cs ranging from 80°C to 140°C to be able to control both crystallinity as well as crystalline order (ratio of α' and α) and their effect on the mechanical, thermo-mechanical, HDT and creep properties was investigated.

2. Experimental

2.1. Materials

Injection moulding grade PLA type 3001D from NatureWorks (Minnetonka, MN, USA) was used for the research with a D-Lactide content of 1.4%. 3001D PLA has a density of 1.24 g/cm³, a T_g range of 55-60°C, a melting temperature range of 170-190°C and a melt flow index of 22 g/10min (at 210°C, with 2.16 kg load).

2.2. Material preparation and processing

PLA was dried at 80°C for 6 hours prior to processing remove the residual moisture to avoid hydrolitical degradation during processing. ISO standard dumbbell shape specimens with a cross-section of 4x10 mm were injection moulded with an Arburg Allrounder 370S 700-290 injection moulding machine (Lossburg, Germany) equipped with a diameter 30 mm, L/D = 25 screw. Injection rate of 50 cm³/s, holding pressure of 600 bars, holding time of 20 sec, residual cooling time of 40 sec, melt and mould temperature of 190°C and 25°C was used respectively. The dumbbell shaped specimens were post-production annealed in a heat chamber type TYFSF WGL 45B (Huanghua, China) at 80°C T_c for 0-60 minutes to develop various crystallinity as well as at 80-90-100-110-120-130-140°C T_c for one hour to develop various ratios of α' and α crystal forms with the possible maximum crystallinity.

2.3. Methods

Differential Scanning Calorimetry measurements were performed on a TA Instruments Q2000 type calorimeter (New Castle, USA) by using 3-6 mg of samples taken from the middle of the cross-section of the injection moulded specimens. Firstly, the samples were taken from unannealed injection moulded specimens and isothermal measurements were performed to determine necessary annealing times. Secondly, after annealing the injection moulded specimens for various times or at various temperatures, the samples were investigated in non-isothermal mode (heat/cool/heat) from 0 to 200°C at a heating/cooling rate of 5°C/min to determine glass transition temperature (T_g), cold crystallisation temperature (T_{cc}), enthalpy of cold-crystallisation (ΔH_{cc}), melting temperature (T_m), and enthalpy of fusion (ΔH_m). Crystallinity was calculated from the first heating scan of the injection moulded specimens by using Equation (1):

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

where X [%] is the calculated crystallinity, ΔH_m [J/g] and ΔH_{cc} [J/g] is the enthalpy of fusion and the enthalpy of cold-crystallisation respectively, ΔH_f [J/g] is the enthalpy of fusion for 100% crystalline PLA (93.0 J/g) [30].

Heat Deflection Temperature measurements were performed on a Ceast HV3 type HDT (Torino, Italy) measuring equipment according to ISO 75 standard. HDT B type measurements were carried out in flatwise mode with a loading stress of 0.45 MPa, heating rate of 2°C/min (120°C/hour) and with a span length of 64 mm.

The mechanical properties of the annealed and unannealed PLA specimens were analysed by using tensile, flexural and Charpy tests. The tensile and the flexural tests were performed by using a Zwick Z020 universal testing machine (Ulm, Germany) equipped with a Zwick BZ 020/TN2S force measuring cell with a force limit of 20kN and by using a crosshead speed of 5 mm/min. The Charpy impact tests were performed on unnotched samples by using a Ceast Resil Impactor (Torino, Italy) impact testing machine equipped with a 15 J impact energy hammer and a DAS8000 data collector unit. All of the tests were performed at room temperature at a relative humidity of 50 ± 10 %.

Dynamic Mechanical Analysis was performed on a TA Instruments type Q800 tester (New Castle, USA) by using the injection moulded specimens. Dual cantilever layout was used to be able to gain storage modulus information above T_g. A heating rate of 2°C/min was used from 0 to 180°C with a span length of 35 mm, an amplitude of 20 μm and a frequency of 1 Hz.

The creep tests were performed by using a Zwick Z005 universal testing machine equipped with a 5kN load cell. First, the tensile strength of the PLA specimens was determined by using force controlled tensile testing. A load rate of 20 N/s was used and 20 specimens were tested. Afterwards 5, 7.5, 10, 12.5, 15, 20, 25, 30, 35, 40, 50, 60, 65, 70, 75, 80, 85, 90 and 95% of the determined maximum force value was used as static loading force for the creep tests. These are named as load "levels" (for instance 30% load level) since it is a dimensionless quantity. 20 N/s load rate was applied until the force reached the given static loading level and kept it for one hour. Two specimens were used for each loading level if the specimens did not break until the one hour creep test, and 5 specimens were used if they were broken during the creep test. All of the measurements were performed at room temperature (23 ± 1°C) and at a relative humidity of 50 ± 10%. Finally, by using the load-time equivalence principle, master curves were constructed.

Wide-angle X-ray diffraction was used to determine the crystal forms with a Philips model PW 3710 based PW 1050 Bragg-Brentano parafocusing goniometer using CuK_α radiation.

Scanning electron microscopy (SEM) was performed by using a Jeol JSM 6380LA type electron microscope. The fracture surfaces of the tensile specimens were used for the observations. Au/Pd alloy was sputtered onto the surface prior to observation to avoid electrostatic charging.

3. Results and discussion

After annealing the injection moulded PLA specimens at various T_cs (from 80°C to 140°C for one hour), their DSC measurement was performed to determine the crystallinity and more importantly, the crystalline order of α' and α belong to each applied T_c (Fig. 1).
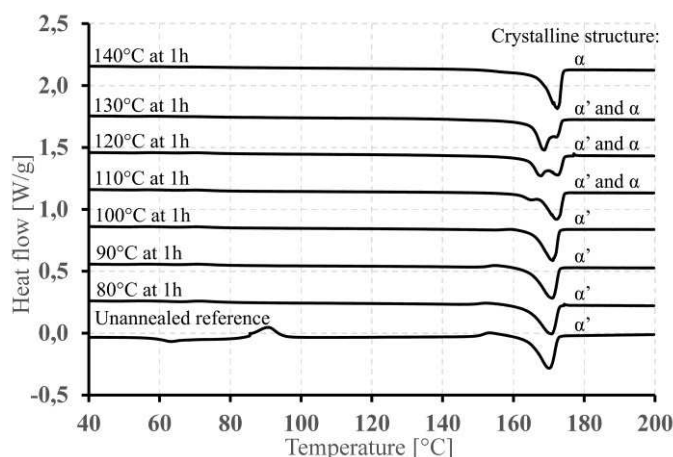
Fig. 1. DSC curves (first heating scan) of PLA annealed at various T_cs from 80°C to 140°C for one hour

In every case, the first heating scan was analysed, since it characterizes the crystalline structure developed during annealing. On the DSC curve of the unannealed, reference PLA specimen, the T_g was observable around 60-65°C, while there was still significant cold-crystallization found between 80-100°C (cold-crystallization peak at 91°C) representing the unfinished crystallization of the reference specimens during injection moulding due to high cooling rate and slow crystallisation kinetics of PLA. Moreover, just before melting, between 147°C-160°C (peak temperature at 153°C) an exothermic peak was visible indicating the α' to α phase transition in solid state, followed by the melting of the newly formed α crystal form between 160°C-174°C (melting temperature peak at 170°C). The exothermic peak before melting suggests that only the disordered α' crystal form developed during cold-crystallization due to the relatively low cold-crystallization peak temperature at 91°C. When the DSC curve of the annealed specimens was examined, the cold-crystallization was found to be absent meaning that the crystallization was completed during the one hour annealing process for all annealing temperatures. In case of the DSC curve of the specimen annealed at 80°C, the exothermic peak before melting could still be found representing that only the disordered α' developed during the annealing process. The same was also found for the specimens annealed at 90°C and at 100°C, but the exothermic peak of the α' to α phase transition shifted to higher temperatures (still below melting). On the contrary, when the specimens were annealed at 110°C, 120°C and 130°C, a double melting peak was found and the exothermic peak before melting was absent. This means that these specimens had both the disordered α' and the more ordered α crystal content, since the first melting peak represents the simultaneous melting of the α crystal form developed during annealing and the recrystallization of the α' to α crystal form, while the second melting peak represents the melting of the α crystal form developed in the recrystallization process. Another important finding is that by increasing T_c, the peak related to the lower temperature became increasingly dominant meaning that more α and less α' crystal form developed in the specimens. Finally, when the specimen was annealed at 140°C, only one melting peak was found without the exothermic peak before melting, meaning that the crystal form developed during annealing was entirely the more ordered α form. As a short summary of the effect of T_c on the crystal forms, it was found that entirely α', both α' and α, and entirely α crystal structure developed when the specimens were annealed at or below 100°C, between 110°C-130°C, and at or above 140°C respectively. These finding were also verified by WAXD measurements (Fig. 2).
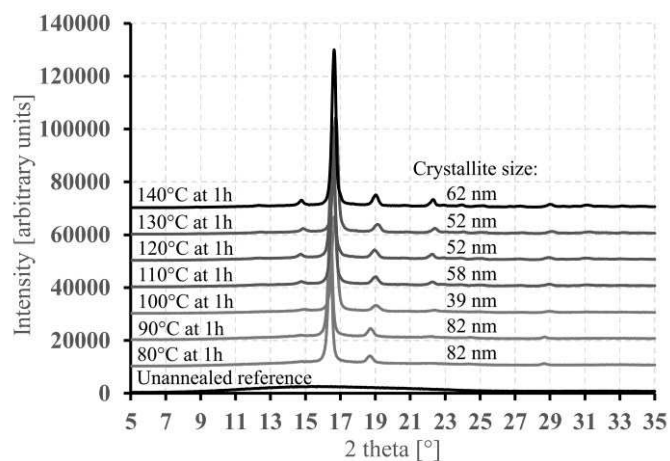
Fig. 2. WAXD spectra of annealed PLA at various T_cs from 80°C to 140°C for one hour

For the specimen annealed at 80°C, and thus having only disordered α' crystal form, only two dominant peaks were observable at 16.4° and at 18.7°, but by increasing annealing temperature up to 140°C and thus inducing the development of the more ordered α crystal form, two new peaks appeared and became also dominant at 14.8° and at 22.3°, while the original peaks at 16.4° and 18.7° shifted to 16.6° and 19.0° respectively. After determining the crystal forms belong to each T_c, first the effect of annealing time and thus crystallinity was investigated on the HDT followed by the examination of the effect of T_c and thus crystal forms on the same property. Accordingly, PLA specimens were annealed at 80°C for various amount of time, and both crystallinity and HDT was measured (Fig. 3). Note that in this case, the crystal form was entirely the less ordered α' as measured previously by DSC.
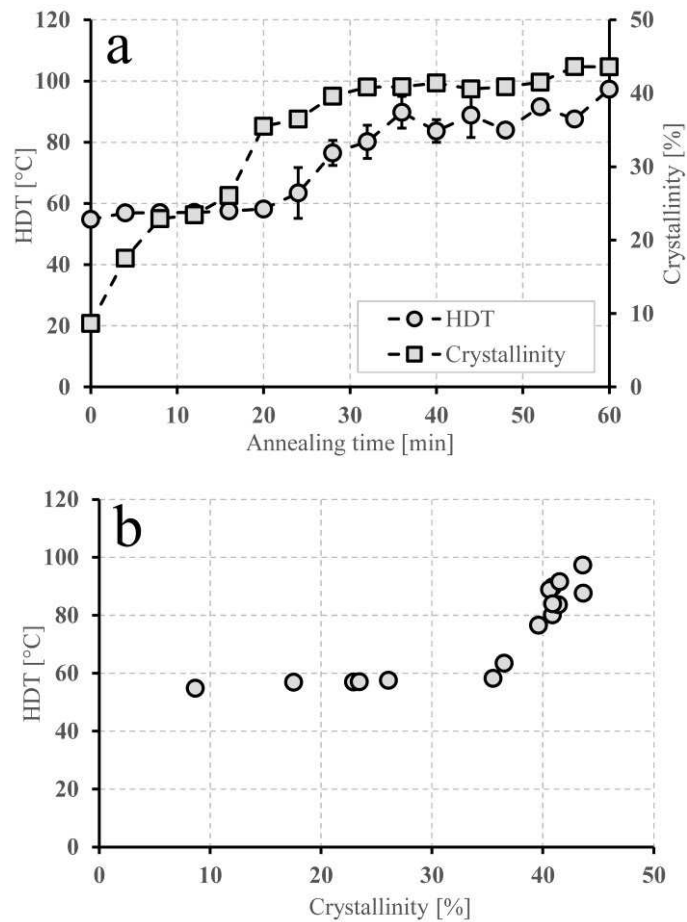
Fig. 3. Heat deflection temperature of PLA annealed at 80°C as a function of annealing time (a) and crystallinity (b)

As it can be observed, even the unannealed, injection moulded PLA specimen reached a crystallinity of 8.7%, which could be the effect of the low (1.4%) D-Lactide content of the chosen PLA and thus its relatively fast crystallization kinetics compared to other, higher D-Lactide content PLA grades. By increasing annealing time and thus crystallinity, there was only minor improvement in HDT from 55°C to 58°C even up to a relatively significant crystallinity of 35%. On the contrary, above 35% of crystallinity up to the measured maximum level of 44%, HDT started to increase significantly, namely it practically linearly increased from 58°C to 97°C. After determining the effect of crystallinity and the α' less ordered crystal form on the HDT, the effect of T_c and thus crystal forms (ratio of α' and α) was investigated on the same property (Fig. 4).
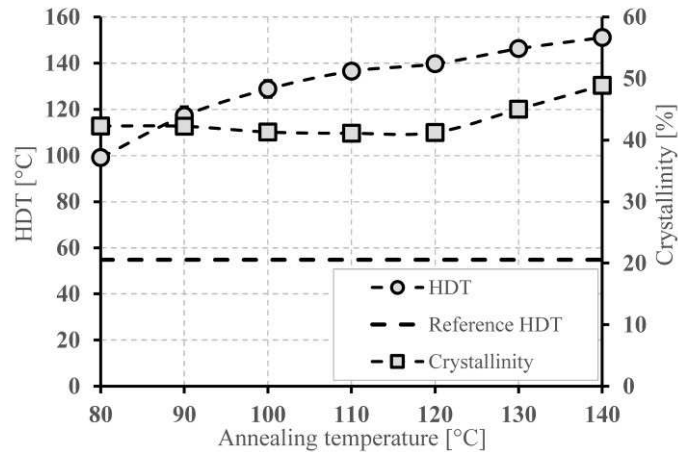
Fig. 4. Heat deflection temperature of the PLA specimens annealed at various temperatures for one hour. Dashed horizontal line represents the heat deflection temperature of the reference (unannealed) PLA

As it was previously demonstrated, by increasing T_c (annealing temperature), the crystal form of PLA more and more shifted from entirely α' to entirely α. Accordingly, the T_c is an excellent indicator to distinguish the effect of various crystal structure. Interestingly, it was found that the crystallinity was practically the same for the specimens annealed between 80°C and 120°C (40-42%), still the HDT highly increased from 97°C up to 140°C. Since in this T_c region, there was no significant difference in crystallinity, accordingly this very significant HDT increasing effect must have been the influence of crystal structure and thus α' gradually developing into α crystal form by increasing annealing temperature. At the same time, the DSC results only partially confirm this phenomenon, since the specimens annealed above 100°C truly had more and more α crystal form content, but the PLA specimens annealed between 80-100°C all had the same crystal structure (entirely α') and thus the HDT results should have been the same in this region instead it increased from 97°C to 129°C. The most likely explanation is that in the 80-100°C T_c range the crystal structure was truly the same less ordered α', but it already became denser (closer packing and thus lower lattice spacing) by increasing T_c, at the same time it still has not developed into the more ordered α. This explanation is confirmed by the results of Zhang et al. [42] since the authors demonstrated the decrease in lattice spacing and therefore the closer chain packing within the same α' crystal form by increasing T_c, however, this degree of ordering was still much lower compared to the α crystalline form. By further increasing T_c above 100°C up to 120°C, in this case the increase in HDT from 129°C to 140°C could be directly related to the appearance and increasing amount of the more ordered α crystal form and its much lower lattice spacing compared to α' crystal form. Finally, by increasing the T_c above 120°C, HDT could still be improved from 140°C up to 151°C, but in this case not only the increasing α to α' ratio could have caused this effect, but also the crystallinity was found to increase from 41% to 49%. When Fig. 3/b is completed with the HDT results from the annealed specimens at various T_cs, it is even more observable, that not only crystallinity but crystal structure and thus the ratio of α to α' also play an essential role on the HDT of the specimens (Fig. 5).
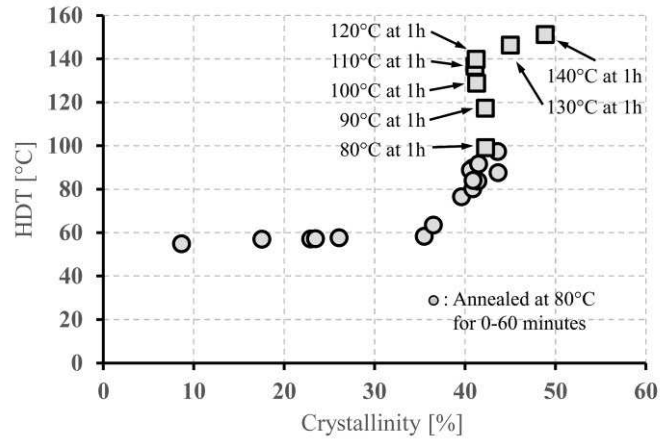
Fig. 5. Heat deflection temperature and crystallinity relationship for PLA annealed at 80°C for various amount of time and at various temperatures from 80°C to 140°C for one hour

Since the HDT of the specimens is in direct correlation with the storage modulus, accordingly, the DMA measurement of the specimens was performed for deeper understanding (Fig. 6). The lowest modulus corresponding to the performed HDT B measurement (0.34 mm allowed deflection under 0.45 MPa stress in bending mode with 4x10 mm cross section and 64 mm span length,) was calculated as 255 MPa and was also represented in the figure as a dashed line.
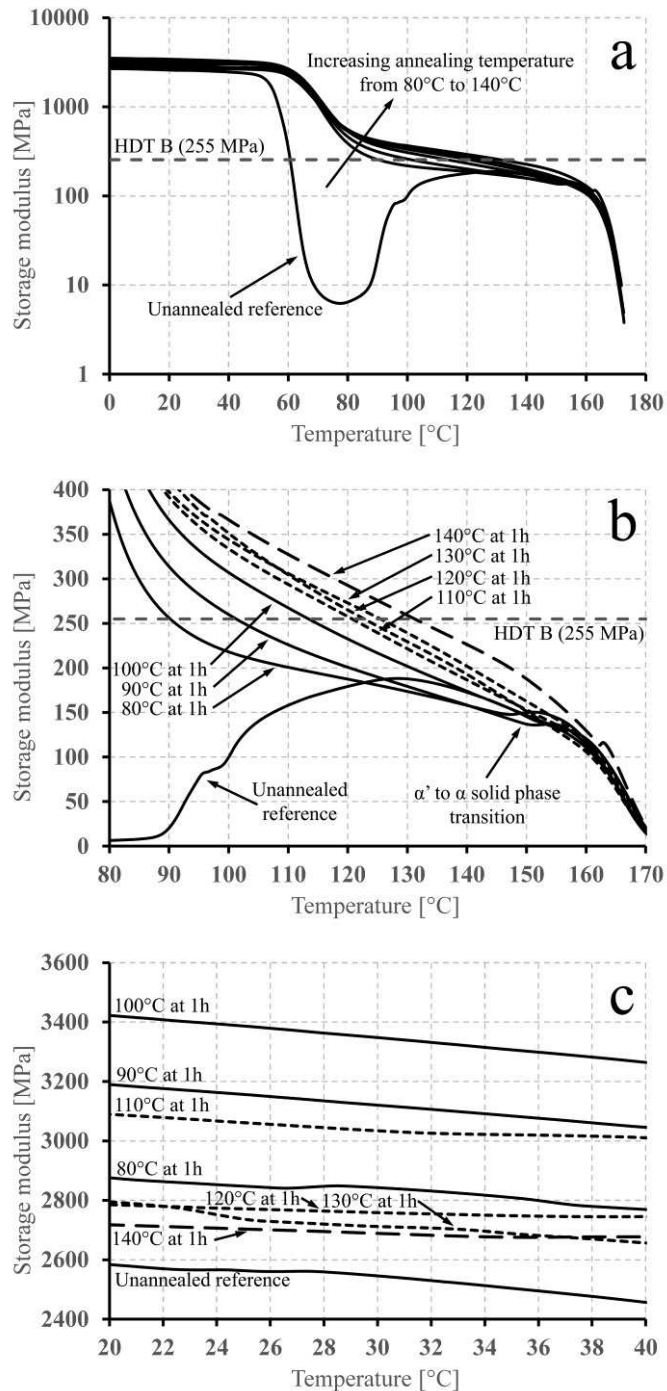
Fig. 6. Storage modulus of the unannealed and at various temperatures from 80°C to 140°C for one hour annealed PLA in 0-180°C (a), 80-170°C (b) and 20-40°C (c) temperature range. Dashed line represents the lowest modulus corresponding to the HDT B measurement

In the case of unannealed PLA specimen, the storage modulus was found to be 2570 MPa at 23°C, while by reaching T_g, due to the low crystallinity, it entered rubbery state and thus its storage modulus dropped significantly to 6 MPa at 78°C. By further increasing temperature, the modulus started to increase as an effect of cold-crystallization (180 MPa at 120°C) and by approaching melt temperature around 160°C, the modulus finally dropped. In case of all annealed specimens, the drop in the modulus just above T_g was significantly reduced due to the crystalline structure that retarded the micro-brown movement of the polymer chains. Moreover, in the case

of specimens annealed between 80-100°C and thus having entirely α' crystal form, just before the final drop in modulus due to the approaching melt temperature, a very small increase or more likely plateau could also be observed representing the α' to α solid phase transition (Fig. 6/b). On the contrary, on the storage modulus curve of the specimens annealed at or above 110°C this plateau was absent since the α' to α transition took place as a part of the melting process not able to investigate by DMA. It was also found that the modulus values were influenced by the applied T_c for annealing and thus the ratio of α and α' crystal forms as suggested by the HDT measurement results. The higher the T_c was applied for annealing, the higher the modulus values were in the 80-140°C temperature range, typically, where the HDT value of semi-crystalline PLA is expected. Accordingly, the temperatures corresponding to the 255 MPa storage modulus vales obtained from the DMA results were found to be in high correlation with the HDT results, however, the temperatures obtained from the DMA results were always 10-15°C lower compared to HDT values most likely due to the differences in measurement conditions. Interestingly, if the modulus values between 20-40°C are analysed (Fig. 6/c), it was found that the effect of T_c was not as obvious as in the 80-140°C temperature range. Namely, it was found that by increasing T_c from 80 to 100°C first the modulus values increased when the crystal form was entirely α', at the same time, above 100°C of T_c, and thus by increasing α content, the modulus started to decrease (Fig. 7).
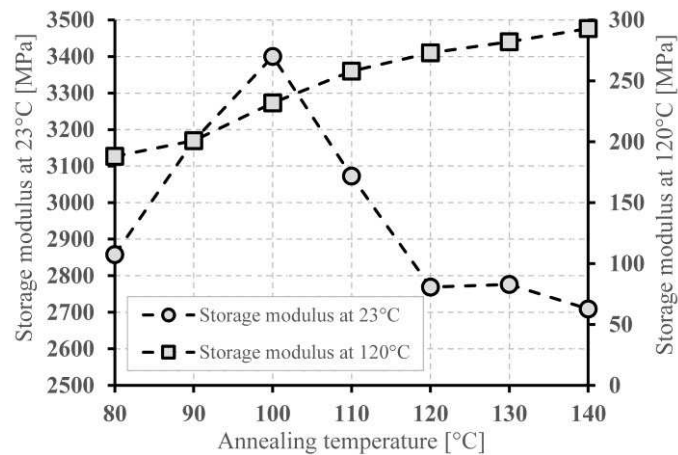

Fig. 7. Storage modulus measuread at 23°C and at 120°C of the PLA specimens annealed at various temperatures for one hour

The mechanical properties were also investigated (Fig. 8) and it was found that the annealing process increased both tensile and flexural modulus from their original value of 3.24 GPa and 3.21 GPa even up to 3.64 GPa and 4.19 GPa respectively. Please note that in most cases the standard deviation was so low, that the error bars were overlapped by the dots representing the experimental points.
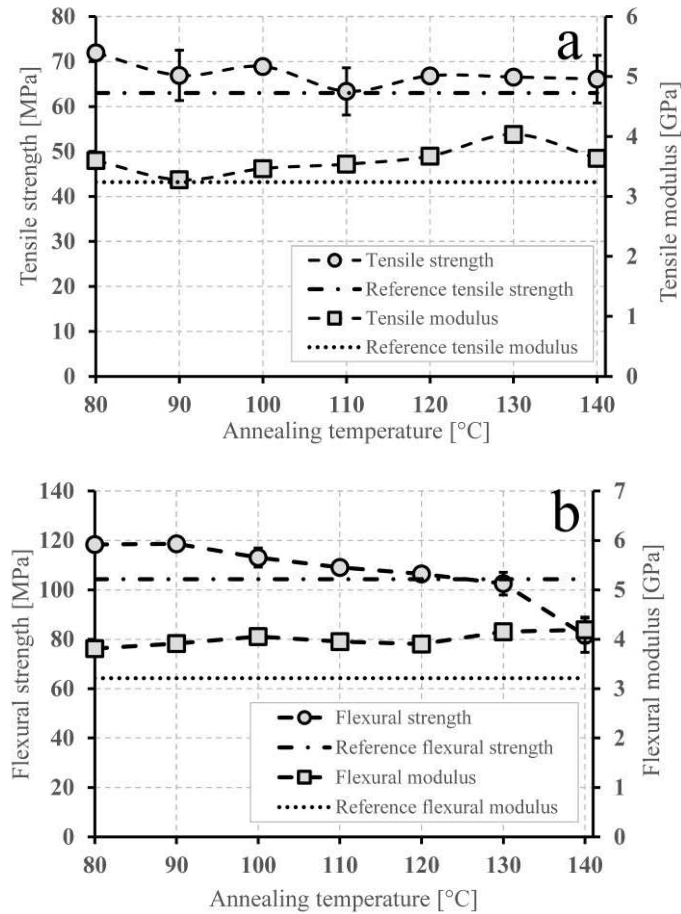
Fig. 8. Tensile (a) and flexural (b) properties of PLA annealed at various T_cs for one hour

Moreover, both tensile and flexural modulus values increased with increasing T_c, thus the maximum modulus values were in both cases reached when the crystal structure was entirely the more ordered α crystal form and the applied T_c was 140°C. In case of tensile and flexural strength it was also found that annealing increased both mechanical properties from their original value of 63.0 MPa and 104.3 MPa even up to 71.9 MPa and 118.3 MPa respectively. On the contrary, in this case the maximum values were reached in both cases when the lowest T_c was applied (80°C) and by further increasing T_c, both strength values decreased. In case of flexural strength, it even decreased below the strength of the unannealed PLA specimen. The decrease of the strength values could be explained not by the different crystal forms, but by a possible thermal degradation at elevated temperatures. This assumption is strengthened when the Charpy impact strength results are investigated (Fig. 9).
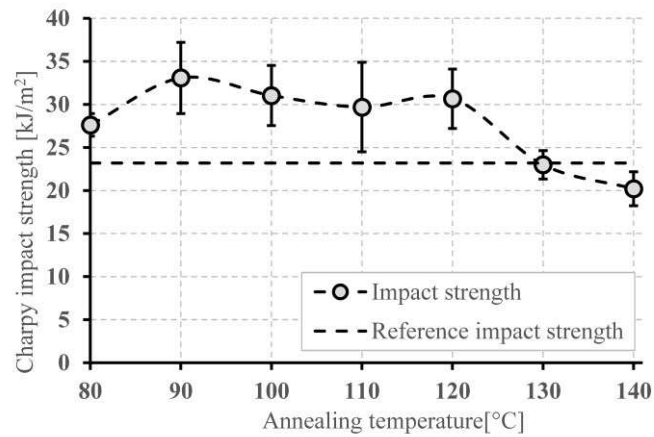
Fig. 9. Charpy impact strength of PLA annealed at various T_cs for one hour

Again, it was found that the Charpy impact strength of the specimens increased from 23.2 kJ/m^2 even up to 33.1 kJ/m^2 by using annealing (at 90°C). Impact strength was practically constant in the 90-120°C T_c region, however, it monotonously decreased by further increasing the T_c above 120°C. At 140°C of T_c, the impact strength (20.2 kJ/m^2) even decreased below the impact strength of the unannealed PLA specimen, which could be most likely the effect of a possible thermal degradation at elevated temperature. The fracture surface of the specimens was also investigated by SEM (Fig. 10).
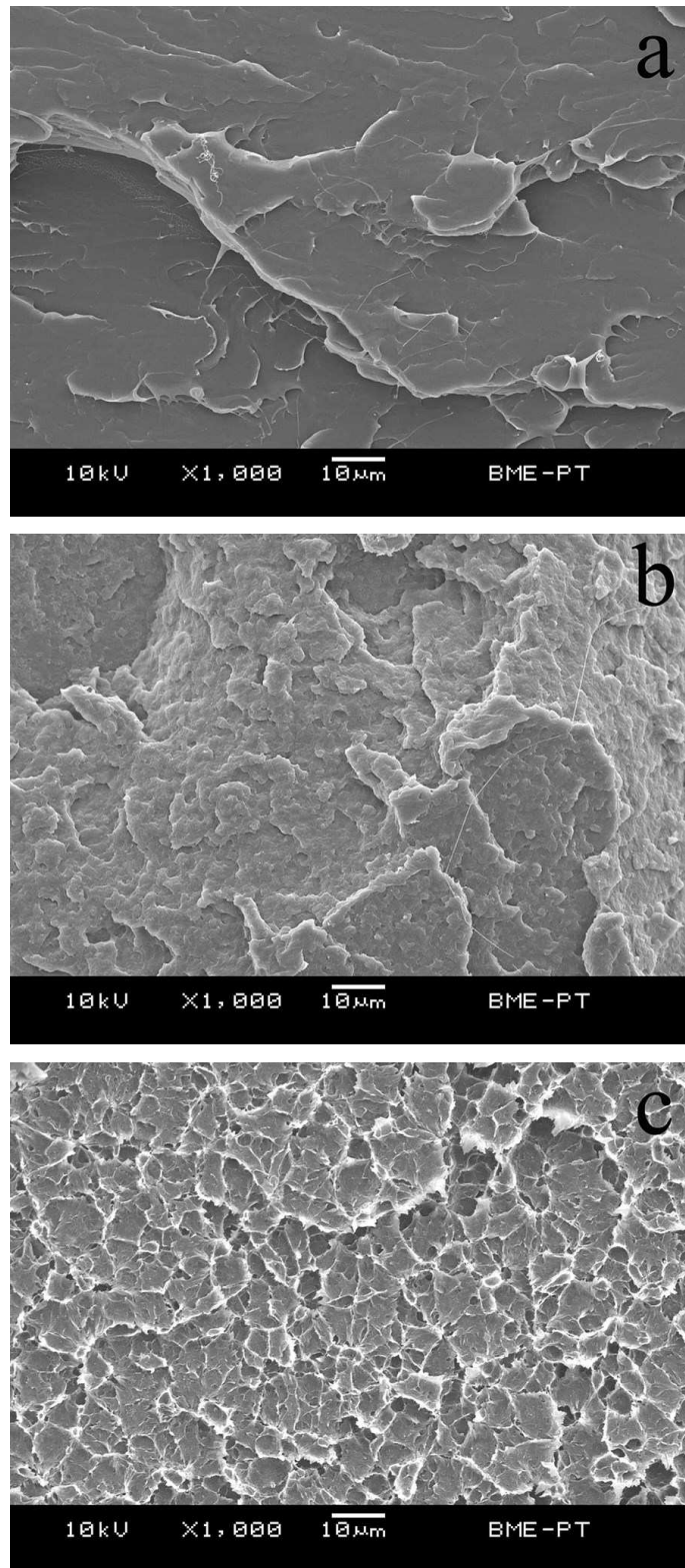
Fig. 10. Typical fracture surfaces of the unannealed (a) and annealed (b) PLA, latter with crazed areas (c)

It was found that the unannealed PLA had a typical very brittle fracture surface represented by sharp edges, while at every annealing temperature investigated, much more ductile surface was found with more structured surface. In case of annealed specimens, in every case very ductile areas were also found with highly

crazed surfaces (Fig. 10/c) explaining the higher impact strength caused by the annealing process. Moreover, there was no visible major difference in the fracture surfaces of the specimens annealed at various temperatures, thus these three micrographs very well represent the typical fracture surfaces found.

Finally, the creep of the unannealed and annealed PLA specimens was also investigated (Fig. 11) as another very important property related to the application of PLA products.
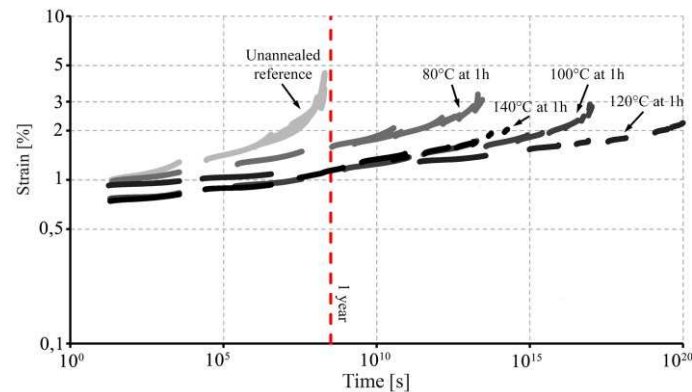

Fig. 11. Creep mastercurves of PLA unannealed and annealed PLA at various T_cs

As it can be observed on the creep mastercurves, the unannealed PLA had the highest creep represented by the highest elongation due to its low crystallinity of 8.7%, at the same time, by using annealing and thus increasing crystallinity creep could be highly moderated. Accordingly, in the case of PLA annealed at 80°C creep could be effectively reduced to 1.5% elongation at one year by increasing crystallinity from 8.7% to 42.3% compared to the unannealed PLA that already broke within the same creep time. Moreover, not only crystallinity, but again T_c and thus the developed crystal form (α to α' ratio) also highly influenced creep characteristics. Namely, by increasing T_c from 80°C to 100°C, creep was further reduced to 1.1% of elongation at one year and time to failure increased even though both specimens had entirely α' crystal form content. As it was previously already demonstrated, despite of the entirely α' crystal form developed when the T_c was between 80-100°C, the increase of T_c still decreased lattice spacing which affected among others HDT or storage modulus and in this case creep characteristics. Moreover, when 120°C of T_c was applied, the PLA had both α' and α crystal form content thus the appearance of the more ordered α form further decreased creep (1.0% elongation at one year) and increased time to failure. Interestingly, the PLA annealed at 120°C showed higher initial elongation despite of the partial α crystal form content compared to the PLA annealed at 100°C having entirely α' crystal form content. At the same time, the PLA annealed at 120°C had obviously lower increase in elongation in time and also higher time to failure. These results that the PLA annealed at 120°C had higher initial elongation compared to the PLA annealed at 100°C was found to be in correlation with the storage modulus results, suggesting that the α crystal form was softer compared to the α' at 23°C, at the same time, the α crystal form more effectively reduced creep elongation than α' crystal form. Finally, when the PLA was annealed at 140°C, it only contained the more ordered α crystal form, thus the highest reduction in creep was expected, but unfortunately, its creep increased to a similar level as the PLA annealed at 100°C and having entirely α' crystal form. This effect was previously demonstrated in the decreasing flexural and impact strength values and explained by a possible thermal degradation at this elevated temperature.

4. Conclusion

In our research, the effect of crystallinity and crystalline forms (ratio of the less ordered α' and the more ordered α crystalline forms) of injection moulded Poly(Lactic Acid) (PLA) was analysed on the mechanical, thermo-mechanical, Heat Deflection Temperature (HDT) and creep properties. To be able to develop the desired crystalline structure, the injection moulded PLA specimens were post-production annealed in a heat chamber at 80°C crystallization temperature (T_c) for 0-60 minutes to develop various crystallinity as well as at 80-140°C T_c for one hour to develop various ratios of α' and α crystal forms with the possible maximum crystallinity. According to the Differential Scanning Calorimetry (DSC) results, the crystalline structure of annealed PLA was investigated as a function of T_c and it was found that entirely α', both α' and α, and entirely α crystal structure developed when the specimens were annealed at or below 100°C, between 110°C-130°C, and at or above 140°C respectively. When PLA was annealed at 80°C for various times, to develop various crystalline ratios, it was pointed that until 35% of crystallinity there was only minor improvement in HDT from 55°C to 58°C, at the same time above 35% up to the maximum crystallinity level of 44% the HDT practically linearly increased from 58°C to 97°C. Moreover, when the effect of T_c (80-140°C annealing for 1 hour) was investigated, it was demonstrated that despite of the practically same crystallinity reached, the HDT could be further improved from 97°C even up to 151°C which could be explained by the gradual change in crystal structure from the less ordered α' to the more ordered α crystal form. These finding were in correlation with the Dynamic Mechanical Analysis (DMA) results, since the higher the T_c was applied, the more ordered crystalline structure developed and the higher the storage modulus was in the 80-140°C temperature region. The mechanical properties were also examined (tensile, flexural, impact properties) and it was found that by annealing PLA, 14% and 13% improvement was found in tensile and flexural strength, as well as 12% and 30% in tensile and flexural modulus respectively and even 43% in impact strength values, however, the too high T_c caused strength values to drop probably due to some extent of thermal degradation. Nevertheless, the improvement in impact strength values were validated by Scanning Electron Microscopy (SEM) observations where more ductile fracture surface and even crazed areas were found compared to the typical brittle fracture surface of unannealed PLA represented by sharp edges. Finally, the creep of PLA specimens annealed at various T_cs was examined and it was found that again not only crystallinity highly reduced creep, but also crystalline order significantly affected creep characteristics, namely, the α crystal form more effectively reduced creep elongation and increased time to failure than the α' crystal form.

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