MASTER

Stereocomplexation of poly(L-lactide)/poly(D-lactide)
Exploring the (combined) effects of PMMA and shear

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Master thesis report

Stereocomplexation of poly(L-lactide)/poly(D-lactide): Exploring the (combined) effects of PMMA and shear

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Abstract

This research addresses the topic of stereocomplex (SC) crystallisation in the polymer poly(lactic acid) (PLA). PLA is biodegradable, compostable, producible from renewable resources, and non-toxic to the human body and the environment. Unfortunately PLA also has a poor heat resistance, a low melting point, and a poor hydrolysis stability compared to currently used engineering plastics. These properties can be improved by utilizing SC crystallisation between enantiomeric poly(l-lactide) (PLLA) and poly(d-lactide) (PDLA). The goal of this project is to investigate how SC crystallisation in PLLA/PDLA mixtures can be optimized using polymethylmethacrylaat (PMMA) and shear. To gain more insight in how the crystallisation process and temperature, PMMA content and applied shear effect the crystallisation of SC-PLA, systematic fundamental research is done on these aspects both separately and combined. This research was done making use of differential scanning calorimetry (DSC) and oscillatory time sweep measurements in a rheometer. These tests show that adding PMMA up to 30wt% increases the SC crystallinity, but also increases the crystallisation time. When adding shear it is seen that with increasing shear rate and shear time SC crystallinity becomes higher. Adding shear also decreases crystallisation time, where shear rate has a bigger effect on this than shear time. These two effects do not influence each other with regards to the crystallisation time. However the effects of PMMA and shear enhance each other with regards to SC crystallinity, since with increasing shear the effect of the PMMA on the SC crystallinity increases.

Contents

Abbreviations and Symbols

Abbreviations

DSC	Differential scanning calorimetry
HC	Homocrystallite
HMw	High molecular weight
Mw	Molecular weight
PDLA	Poly(D-lactide)
PLA	Poly(lactic acid)
PLLA	Poly(L-lactide)
PMMA	Polymethylmethacrylaat
POM	Polarised optical microscopy
SC	Stereocomplex
WAXD	Wide-angle X-ray diffraction
wt%	Weight percentage

List of symbols

G'	Storage modulus	$[Pa]$
G''	Loss modulus	$[Pa]$
ΔH	Enthalpy	$[J/g]$
k	Crystallisation rate constant	$[-]$
n	Avrami exponent	$[-]$
T_c	Crystallisation temperature	$[^{\circ}C]$
T_g	Glass transition temperature	$[^{\circ}C]$
T_m	Melt temperature	$[^{\circ}C]$
t_0	Crystallisation start time	$[s]$
$t_{1/2}$	Crystallisation half time	$[s]$
X	Crystallinity	$[\%]$
Wi	Weissenberg number	$[-]$
$\dot{\gamma}$	Shear rate	$[s^{-1}]$
τ	Relaxation time	$[s]$
ω	Frequency	$[rad/s]$

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Introduction

1.1 Background and motivation

The polymer poly(lactic acid) (PLA) is biodegradable, compostable, producible from renewable resources, and nontoxic to the human body and the environment [26]. All these qualities make that it has gained a lot of interest over the past few decades. Especially with the current environmental issues due to the increasing amount of plastic waste such as the pollution of tap water, increased flood damage for cities, and damage in the ocean wild life, it would be of great help if PLA could replace more widely used polymers which put a strain on the environment [7, 10, 31].

PLA is currently almost exclusively used for short-time commodity applications [7]. This is because PLA has a poor heat resistance, a low melting point, and a poor hydrolysis stability compared to currently used engineering plastics [7]. A good way to improve these properties in PLA is to utilize stereocomplexation (SC) between enantiomeric poly(l-lactide) (PLLA) and poly(d-lactide) (PDLA). Whereas the melting temperature of either pure PLLA or PDLA is approximately 170-180°C, for PLLA/PDLA stereocomplex crystals this is approximately 220-230°C [7, 26]. Besides the higher melting temperature PLLA and PDLA chains have a denser packing and stronger intermolecular hydrogen bonds and bipolar interactions. This leads to enhanced properties, such as hydrolysis resistance, thermal stability, mechanical strength, and heat resistance, in SC-PLA [7].

To maximally exploit the possibilities of SC-PLA, a lot of research is focused on producing PLA with a high SC content. Below a certain molecular weight (Mw) for the PLLA and PDLA only SC crystals can form and the homocrystallisation (HC) of PLLA and PDLA is suppressed [7, 26]. However the commercially available PLLA and PDLA have a Mw above this threshold which is also necessary for good mechanical properties and processability. For high Mw PLLA/PDLA blends there have been quite some studies which succeeded in creating SC-PLA with exclusively SC crystals. Unfortunately most of these processes required very specific, tedious and complicated procedures which makes them unsuitable for commercial use [7]. The general focus for SC-PLA research at the moment is to use more widely used production processes to create SC-PLA with a high SC content or which contains exclusively SC crystals.

1.2 Problem definition

As stated above regular PLA does not have the best mechanical properties. This study will focus on different methods to enhance SC crystallisation.

Two different methods will be used to attempt to enhance the SC formation. It is demonstrated in literature that both adding polymethylmethacrylate (PMMA) and applying shear can enhance the formation of SC crystals [2, 9, 20, 28, 29, 27]. To gain more insight in how the crystallisation process and temperature, PMMA content and applied shear effect the crystallisation of SC-PLA, systematic fundamental research will be done on these aspects both separately and combined.

The main question this research aims to answer is: how can stereocomplex crystallisation in PLLA/PDLA mixtures be optimized, using PMMA and shear? In this research there will also be information gathered on the three following sub-questions. How does the crystallisation procedure influence the crystallisation process and SC content? How does PMMA influence the crystallisation kinetics and crystallinity of PLLA/PDLA mixtures? How does shear influence the crystallisation kinetics and crystallinity of PMMA/PLLA/PDLA mixtures?

Literature survey

2.1 Stereocomplex crystallisation

2.1.1 Theory

PLA has two optically active types with opposite configurations, poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA), see Figure 2.1a. Both configurations can crystallise into homocrystallites (HC) which have relatively weak bonds and thus a relatively poor heat resistance, a low melting point, and poor hydrolysis stability compared to currently used engineering plastics [7, 8]. However, when PLLA and PDLA are blended together much stronger interactions between both configurations occur, and they can crystallise into stereocomplex crystallites (SC). This is due to the fact that SC crystallites have an opposite helical direction and thus can be packed side-by-side more tightly and make stronger bonds [8]. An example of such a SC structure is shown in Figure 2.1b.

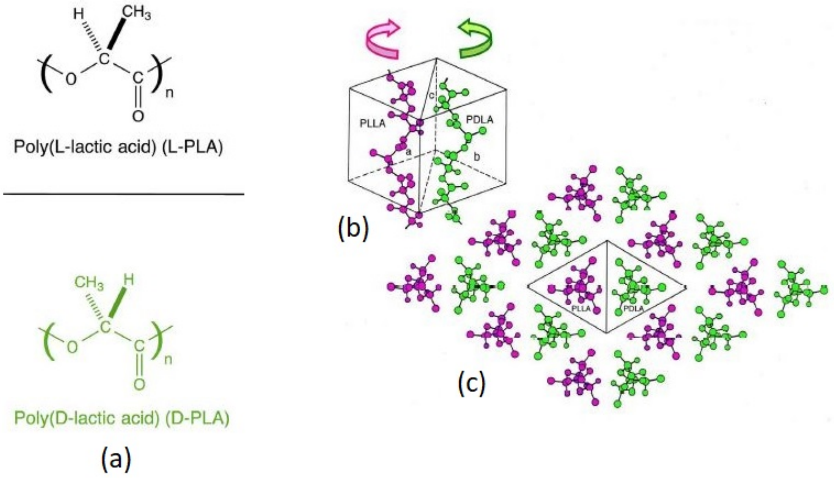


Figure 2.1: (a) Molecular structure of PLLA and PDLA. (b) Molecular arrangement and helical direction of PLA chains in the stereocomplex crystal structure of PLLA and PDLA. (c) The projection of the stereocomplex crystal structure of PLLA and PDLA on the plane normal to the chain axis. The arrows indicate the relative directions of the PLA helices [8].

2.1.2 State of the art

Ever since it was discovered that SC crystallites could provide a solution for the low melting temperature, poor heat resistance and low hydrolysis stability many studies have been done on the crystallisation behaviour, crystal structure and properties of SC-PLA.

In 2017, Bai et al. [7] reviewed the current state of the art of processing technologies for SC-PLA based on linear high molecular weight (HMW) PLAs. Since PLLA and PDLA form SC in a 1:1 ratio, this 1:1 ratio of PLLA/PDLA is necessary to achieve full SC crystallisation, which is confirmed by multiple studies. However, even though a 1:1 ratio of PLLA/PDLA in theory could contain only SC crystallites, HC and SC crystallites will most likely coexist in SC-PLA due to HC crystallites having a lower kinetic barrier and the SC acting as a nucleation agent for HC crystallites. Molecular weight (Mw) and fabrication route are the two most important factors in HC and SC formation. Solution blending and a low Mw appears to be favourable for SC formation. Tsuji et al. [6, 5] determined a threshold Mw of 6×10^3 and 4×10^4 g/mol for melt blending and solution blending respectively below which only SC crystallites are formed. Unfortunately both values are lower than the Mw of most commercially available PLLA and PDLA. So regardless of the production method when using commercially available PLLA and PDLA there will always be both HC and SC formed when processing these materials. A study of Tsuji et al. [5] also showed that within the range of commercially available PLLA and PDLA there will most likely be no significant difference in SC formation for PLLA/PDLA with equal Mw or with different Mw.

A broad study on the effects of the isothermal crystallisation temperature and the difference between melt and cold crystallisation has been executed by Boa et al. [21]. They looked at the effect of the above parameters on the crystallisation half time and the degree of crystallinity for both HC and SC crystallites. In this study the PLLA/PDLA mixture is solution blended in a 1:1 ratio. Making use of differential scanning calorimetry (DSC) measurements they heated a sample to 270°C for 2 minutes to erase the thermal history. For melt crystallisation the sample was cooled with a rate of 60°C/min to the isothermal crystallisation temperature. For cold crystallisation the sample was quenched, after erasing the thermal history, and than heated to the isothermal crystallisation temperature with a rate of 200°C/min. For both crystallisation processes they kept the sample at the isothermal crystallisation temperature for one hour. After these crystallisation protocols the samples are analysed both by using DSC and heating the sample to 270°C with a rate of 10°C/min and by using wide-angle X-ray diffraction (WAXD) to determine the crystallinities of both HC and SC crystallites. The results of this study are summarized in Table 2.1. Some conclusions can be drawn from Table 2.1. First, cold crystallisation is overall significantly faster than melt crystallisation. Second, cold crystallisation gives a higher SC content than melt crystallisation. Both of these observations can be explained by looking into the mechanisms which occur during melt and cold crystallisation. For both processes it is expected that during the cooling/heating to the isothermal crystallisation temperature a certain number of nuclei are formed whose number could depend on the heating/cooling rate. In the case of melt crystallisation SC nuclei are formed first due to the lower melting temperature of HC crystals. These SC nuclei can act as heterogeneous nucleation sites for HC crystallisation and homogeneous nucleation sites for SC crystallisation. This results in a competition balance between HC and SC crystallisation on the SC nucleation sites. For the cold crystallisation process the nuclei formed during heating consist of both HC and SC nuclei. This results in a more easy HC and SC regularisation and growth, which leads to a faster crystallisation. The fact that the SC crystallisation in this case is hardly disturbed, due to the presence of both HC and SC nuclei, allows for a higher SC crystallinity. Furthermore at a temperature of 170°C and above only SC crystallites can be formed, which is due to the fact that these crystallisation temperatures are above the melting temperature of HC crystallites. At temperatures of 180°C and above no more exothermal peaks were observed for melt crystallisation during DSC, so the crystallisation could not be measured, if it even occurred. Due to the faster crystallisation and the higher SC crystallinity cold crystallisation is favoured over melt crystallisation for creating SC rich products. Unfortunately a lot of widely used processing methods process the materials in a molten or softened state, after which it cools, crystallises and hardens. This is more comparable to the melt crystallisation process used by Boa et al. [21].

Another method of producing SC crystallites is by recrystallising HC crystallites into SC crystallites [30, 32]. One method of doing this is with a two-step crystallisation process. Where the material is first crystallised in a temperature range below the melting temperature of HC crystallites and afterwards heated to a temperature between the melting temperature of HC and SC crystallites, leading to only the HC crystallites melting and recrystallising into SC crystallites. Important to know for this method of creating SC crystallites is the fact that there are two types of HC crystallites, α and α' [25, 12]. These two types of HC crystallites differ in the fact that α' is the disordered version of α, and forms significantly smaller crystallites. For plain PLLA/PDLA mixtures cho et al. [25] determined that below a crystallisation temperature of 100°C only α'-HC is formed and above 120°C only α-HC is formed. In the range of 100 to 120°C both types occur.

The fact that α'-HC forms at lower crystallisation temperatures is due to the lower chain mobility at lower crystallisation temperatures. A noteworthy observation Zhang et al. [12] made was that α'-HC transitions into α-HC when heated to a temperature of 160°C. The recrystallisation process from HC to SC crystalls is something which will also be tested during the present research. Furthermore it is important to also look into how these recrystallisation results are affected by the addition op PMMA.

Table 2.1: Crystallisation of PLLA/PDLA, in a 1:1 ratio, under different conditions. Mw PLLA is 2.1×10^5 g/mol, Mw PDLA is 1×10^5 g/mol [21].

	Melt			Cold		
T [°C]	$t_{1/2}$ [min.]	X_{HC} [%]	X_{SC} [%]	$t_{1/2}$ [min.]	X_{HC} [%]	X_{SC} [%]
90	9.4	41	0	4.8	42	0
100	4.9	37	2.5	1.8	45	3
110	8.6	32	5	1.4	33	13
120	13.6	28	7.5	1	33	16
130	8.7	31.5	10	1.2	23	12.5
140	10.9	34	9	2.2	26	19
150	23	27	17	6	18	22
160	14.4	3	12	0.97	17.5	20
170	31.9	0	13	1.4	0	27
180	-	-	-	2	0	33
190	-	-	-	3.6	0	35
200	-	-	-	12.2	0	37

2.2 PMMA enhanced crystallisation

2.2.1 Theory

Studies have shown a good miscibility between PMMA and SC-PLA [17], and adding PMMA to PLLA/PDLA mixtures has a positive effect on the formation of SC crystallites [2, 20, 27]. PMMA has a high glass transition temperature (Tg), thus PMMA/PLA blends have a higher Tg than pure PLA. This increase in Tg leads to a lower chain mobility in the blends [17]. PMMA is also an amorphous polymer, so when mixed with PLA the PMMA causes a dilution effect of the PLA at the crystal growth front during crystallisation. These two factors combined suppress the HC crystallisation, leading to a higher SC content after crystallisation [17].

2.2.2 State of the art

Boa et al. [20] looked at the effects of adding PMMA to a 1:1 ratio PLLA/PDLA material on the SC formation during isothermal melt crystallisation. This was done with DSC experiments in which the samples were heated to 270°C for two minutes, to erase the thermal history, then cooled to the crystallisation temperature at a rate of 50°C/min, and kept at that temperature for one hour. After this procedure the samples were quenched and analysed using WAXD to determine the HC and SC crystallinity. The results are shown in Figure 2.2. What is interesting to see is that different combinations of thermal conditions and sample composition can yield the same crystallinity. Both PLA with 25 wt% PMMA crystallised at 160°C and PLA with 50 wt% PMMA crystallised at 120°C result in the same amount of HC and SC crystallites. This is beneficial because it gives more options for processing procedures which can potentially create SC rich materials and products. Another noteworthy observation is that the highest SC content and the highest overall crystallinity come from different conditions. The highest SC content comes from either of the two conditions mentioned above, but the highest overall crystallinity comes from the PLA containing 10 wt% PMMA crystallised at 140°C or 120°C. It is possible to recrystallise

HC crystallites to SC crystallites when heating PLA to a temperature between the melting temperatures of HC and SC crystallites. It might therefore be possible to obtain an even higher SC content when after melt crystallisation with the parameters for the highest overall crystallinity a second crystallisation is applied to recrystallise the HC crystals to SC crystals. An additional advantage of the different procedures which show potential to reach similar results is the fact that comparable results can be achieved with a lower PMMA content. If less additives are needed the advantages of pure PLA are also less compromised. What stands out most in these results, but has not been mentioned so far, is that the SC content increases with increasing temperature and PMMA content except for PLA with 50 wt% PMMA (above 120°C). This indicates that the range between 25 and 50 wt% most likely contains an optimal wt% after which the addition of more PMMA hinders the SC crystallisation at high temperatures.

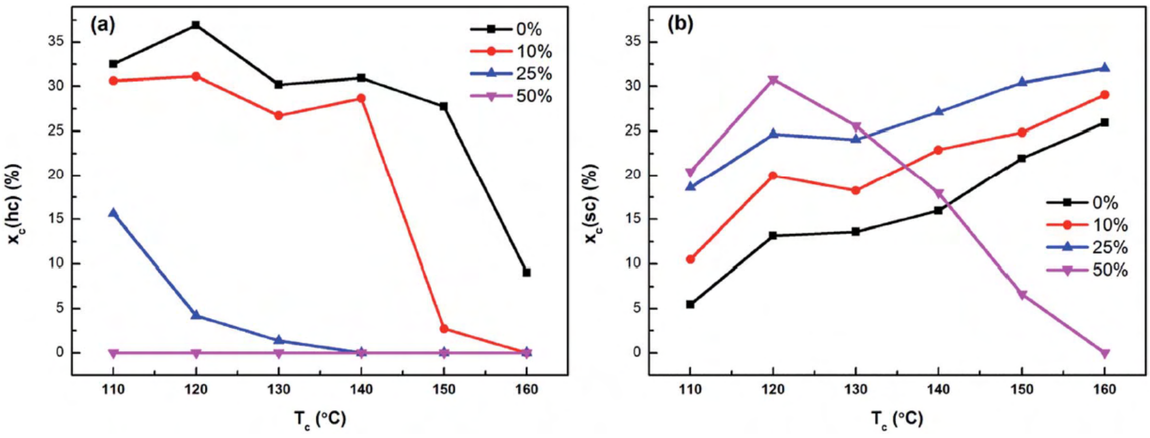


Figure 2.2: (a) HC and (b) SC crystallinity of PLA with different wt% PMMA after isothermal melt crystallisation at different temperatures [20].

Samuel et al. [2] gave more insight in the effects of PMMA within the range of 20-50 wt%, here the ratio of PLLA/PDLA was 1:1. After melt blending the PLLA/PDLA/PMMA for 10 min at 230°C, the samples where tested with DSC. The crystallisation temperature and enthalpy of both the HC and SC crystallites, and the melt temperature of the SC crystallites were determined in non-isothermal experiments. This was done by first heating the samples to 230°C at a rate of 10°C/min to erase the thermal history, then cooling to -40°C at a rate of 10°C/min, and then heating again to 230°C at a rate of 10°C/min. The results for the melt temperature of SC crystallites were gathered during the second heating scan, all the other results where from the cooling scan. The results are shown in Table 2.2. There are no results for HC above 20 wt% PMMA, because for this cooling pattern there were no HC crystallites found. This is because the addition of PMMA restrains HC formation. This effect has also been reported in PMMA/PLLA blends [3]. For the SC crystallites both the crystallisation temperature and the melt temperature go down with increasing PMMA content. For the enthalpy, which is an indicator for the amount of SC crystallites, an increase is seen with increasing PMMA content up to 40 wt%. For PLLA/PDLA with 50 wt% PMMA the enthalpy goes down again which is in accordance with the results from Boa at al. [20] presented above. One note to make regarding these results is that the enthalpy shown here is normalised to the amount of PLLA/PDLA present in the sample. This means that the absolute amount of SC crystallites in the whole sample can be lower even though a higher enthalpy is shown in these results. The absolute values for the enthalpy given in Table 2.2 are not stated in the article [2], but computed using the relative value for the enthalpy and the wt%.

The results of Igushi et al. [27], shown in Table 2.3, give a good visualisation of the difference between the absolute SC content and the SC content normalised to the amount of PLA, for different mixing ratios between PLLA, PDLA and PMMA. The samples used in this research were melt blended at 190°C, next they were compression molded into films at a temperature of 190°C, afterwards the samples were annealed at 130°C for 1, 12 and 24h. The results shown in Table 2.3 were gathered through DSC tests where the samples were heated from 20°C to 255°C with a heating rate of 20°C/min. These results show that with increasing amounts of PMMA the SC formation in the PLA is enhanced. Unfortunately with higher amounts of PMMA the PMMA more or less dilutes the high SC-PLA so the overall material has approximately the same amount of SC as material with a lower PMMA content. The utilization of different thermal protocols to enhance the overall SC content, for instance the two step crystallisation mentioned in section 2.2, has not been reported yet in combination with PMMA.

Table 2.2: Effect of PMMA on crystallisation during cooling for 1:1 PLLA/PDLA. [2]. Absolute enthalpy was not mentioned in the the paper, but computed using the normalised enthalpy and the known wt% PMMA.

PMMA [wt%]	$T_{c,HC}$ [$°C$]	$\Delta H_{c,HC}$ [$\frac{J}{g_{PLA}}$]	$T_{c,SC}$ [$°C$]	$\Delta H_{c,SC,norm}$ [$\frac{J}{g_{PLA}}$]	$\Delta H_{c,SC,abs}$ [$\frac{J}{g_{sample}}$]	$T_{m,SC}$ [$°C$]
0	131.9	32	190.3	17	17	220.1
20	103.0	4	183.5	22	17.6	218.4
30			183.3	29	20.3	217.8
40			179.4	34	20.4	216.8
50			165.7	26	13	215.1

Table 2.3: Comparison between the absolute SC crystallinity and normalised SC crystallinity for different ratios PLLA:PDLA:PMMA [27].

(PLLA/PDLA/PMMA) wt%	X_{SC} % Absolute	X_{SC} % Normalised to amount of PLA
90/10/0	11.4	11.4
70/10/20	12.1	15.1
50/10/40	13.3	22.2
30/10/60	16.0	40.0
80/20/0	22.2	22.2
60/20/20	22.1	27.6
40/20/20	23.5	39.2
20/20/60	23.9	59.8

2.3 Shear-induced crystallisation

2.3.1 Theory

Shear-induced crystallisation is a well know phenomenon within polymer science, and is not exclusive for PLA [4, 11, 24]. When shear is applied on a melt the amorphous and entangled chains are being oriented and stretched, leading to more contact area and interactions between the chains, and thus enhancing the crystallisation. This phenomenon can also be observed in PLA [33]. Without any shear the PLA chains in PLLA/PDLA melts are in the coiled state and entangled with each other, this limits the stereoselective interactions between PLLA and PDLA chains. In this case the interactions only take place on the surface of the PLA coils where PLLA and PDLA can come in contact with each other. When a shear flow is applied both the PLLA en PDLA chains will go to an oriented state instead of a random coil state. In the oriented PLA chains more carbonyl groups are exposed and the chances of interacting with each other increase. This is beneficial for the stereoselective interactions between PLLA and PDLA and thus enhances the formation of SC nuclei. Next to this the stereoselective interactions between PLLA and PDLA might also cause a cross-linking network in PLLA/PDLA melts. This cross-linked network could magnify the effect of shear due to its long relaxation time [33].

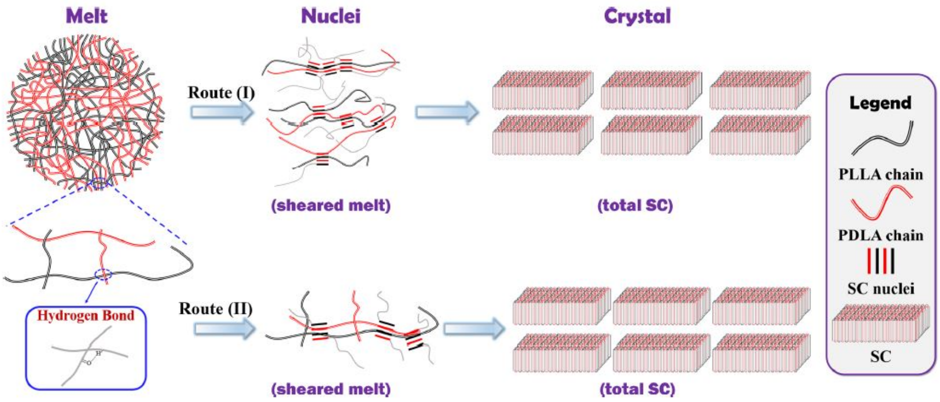


Figure 2.3: Schematics of the crystallisation process of PLLA/PDLA melts under shear [33].

2.3.2 State of the art

Bai et al. [9] looked at how shear time, shear rate and PLLA/PDLA ratio affect the SC crystallisation. This was done by solution blending the PLLA/PDLA mixture. During both polarized optical microscopy (POM) and rheometry tests the samples were heated to 200°C for 5 minutes to erase thermal history. Then the samples where cooled to 160°C with a cooling rate of 30°C/min for the POM tests and 15°C/min for the rheometry tests. As soon as the samples reached 160°C a step shear was applied at different rates and for different shear times. Afterwards the samples were isothermally crystallized at 160°C. The shear times were in the range of 0 to 40 s, the shear rates in the range of 0 to 20 s^{-1}, and the wt% of PDLA ranged from 0 to 10. They found that a longer shear time, higher shear rate, and higher PDLA concentration all resulted in a higher nucleation density. However none of these parameters affected the crystal growth rate. A higher shear rate also shortens the impingement time. A higher wt% PDLA was also responsible for faster crystallisation. For all the different parameters in these ranges no shish-kebab structures were found during crystallisation.

The effect of shear rate and crystallisation temperature on the crystallisation of both SC and HC was studied by Song et al. [28]. Here 1:1 PLLA/PDLA mixtures were heated to 230°C for 3 min and then cooled to the crystallisation temperature at a rate of 30°C/min after which a shear pulse was applied for 5 s. The shear rates ranged from 0 to 180 s^{-1} and the crystallisation temperatures used were 150, 160 and 180°C. In-situ WAXD was used to follow the crystallisation of the samples. Figure 2.4 shows the results at the end of crystallisation. There are no results for the HC crystals at a temperature of 180°C since this is above the melting temperature of HC crystallites. The results show that for both the overall crystallinity and the SC crystallinity it holds that the higher the shear rate, the higher the crystallinity. For the overall crystallinity it is also shown that a lower crystallisation temperature results in a higher crystallinity. This is due to the temperature range being in the same range as the melting temperature of HC crystallites. Thus a small increase in temperature can lead to more HC crystallites melting, thereby reducing the overall crystallinity. In the SC graph it is visible that at a crystallisation temperature of 160°C, the shear has more influence on the crystallisation than at a temperature of 180°C. Song et al. [28] also looked at the nucleation density using POM and the crystallisation half time ($t_{1/2}$) for shear rates in the range of 0 to 100 s^{-1}. The conclusions were that for both SC and HC crystallites the nucleation density increases with increasing shear rate, and $t_{1/2}$ reduces for both a higher shear rate and a lower crystallisation temperature for both HC and SC crystallites.

In another research Song et al. [29] looked at the shear enhanced SC formation. Here solution blended PLLA/PDLA with a 1:1 ratio were heated to 230°C for 3 minutes to erase the thermal history. Next the sample was cooled at 30°C/min until the desired shear temperature was reached after which the sample was cooled at 5°C/min to room temperature. The moment the sample reached 2.5°C above the desired shear temperature a shear pulse was applied for 5 s. Three different shear rates where tested: 50, 100 and 178 s^{-1}. Both the effect of shear rate and shear temperature on crystallinity have been studied, the results are shown in Figure 2.5 and 2.6 respectively. These results show that crystallisation of SC crystallites is greatly enhanced by high shear rates and low shear temperatures, resulting in a higher final SC crystallinity after cooling. Figure 2.5 shows that the SC content significantly increases for a shear rate of 178 s^{-1}. However, due to the increased SC content the formation of HC is significantly hindered by the restricted mobility of the polymer chains, leading to a comparable overall crystallinity for all shear rates. The same restricted mobility can be seen for low temperature in Figure 2.6. Here the lowest temperature of 150°C has the highest SC content, but also the lowest overall crystallinity due to the limited formation of HC.

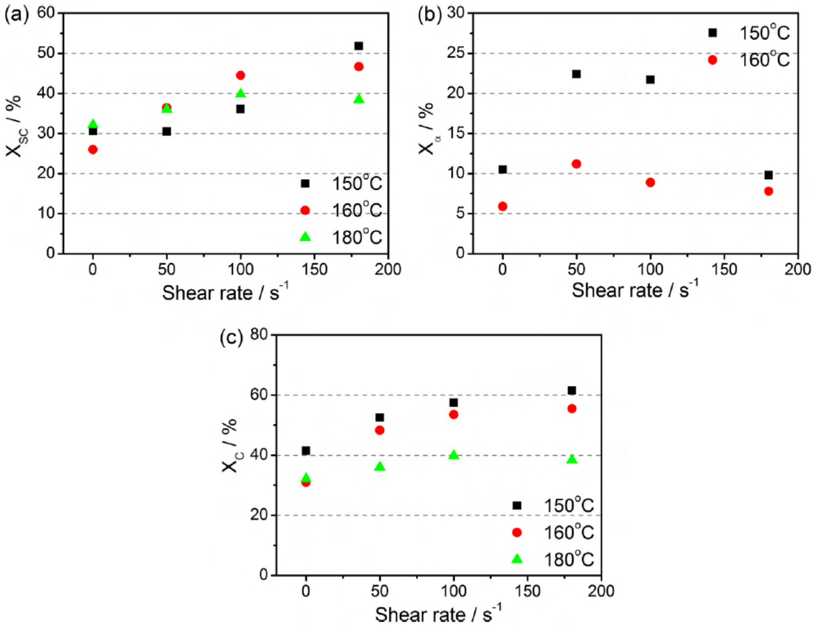


Figure 2.4: The phase contents of (a) SC and (b) α-HC and (c) overall crystallinity of PLLA/PDLA versus shear rate after isothermal crystallisation at different temperatures [28].

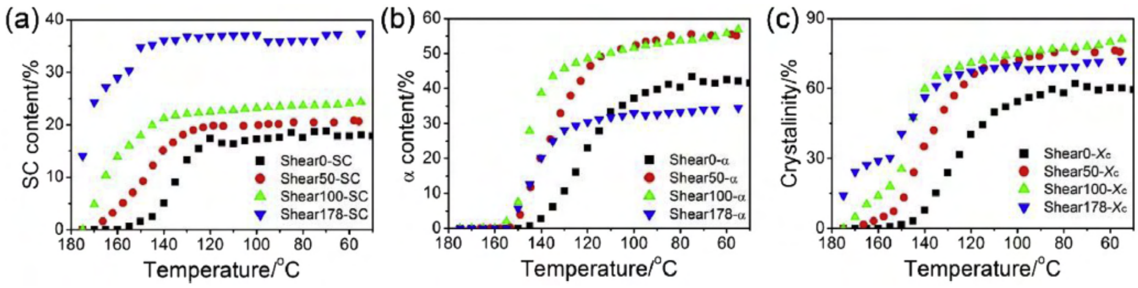


Figure 2.5: The phase contents of (a) SC, (b) α-HC, and (c) overall crystallinity of PLLA/PDLA versus temperature during non-isothermal crystallisation after shear at 175°C for different shear rates [29].

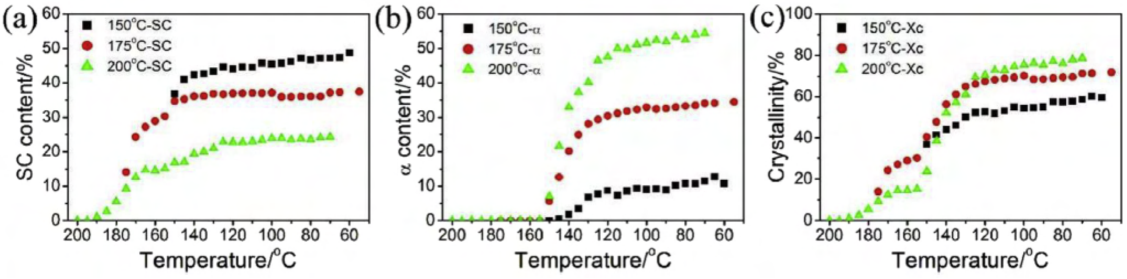


Figure 2.6: The phase contents of (a) SC, (b) α-HC, and (c) overall crystallinity of PLLA/PDLA versus temperature during non-isothermal crystallisation after shear with a shear rate of 178 s^{-1} for different shear temperatures [29].

Xie et al. [15] looked into the effects of crystallisation temperature on shear induced shish-kebab structures in SC-PLA. The samples used were 1:1 PLLA/PDLA mixtures, and were sheared for 1 s with a shear rate of 100 s^{-1}. The shear was applied when the samples reached the crystallisation temperature after being heated to erase the thermal history. The used crystallisation temperatures were 150, 165, and 180°C. For the different temperatures the sizes of the shish, the structural basis of the shish, and the structure of the lamellae were analyzed. The results from this analysis are schematically shown in Figure 2.7. It can be seen that above the melting temperature of HC crystallites ($T_{m,HC}$) the lamellae consist out of only SC crystallites, whereas below $T_{m,HC}$ the lamellae consist of both HC and SC crystallites. Furthermore both the shish itself and the extended chain bundles in the center of the shish have a larger diameter for lower temperatures. There has not been any research done so far on the combined effects of PMMA and shear on the SC crystallisation.

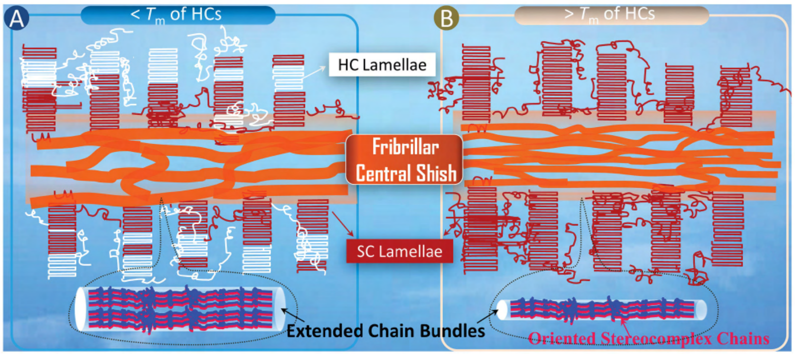


Figure 2.7: Schematic overview of shear induced shish-kebab structures of SC-PLA at different temperatures (shear time is 1 s, shear rate is 100 s^{-1}) [15].

Material and methods

3.1 Materials and sample preparation

PLLA (Luminy® L130) and PDLA (Luminy® D120) both with Mw = 115 kg/mol were received from Corbion (Gorichem, the Netherlands). The PMMA (Acryrex® CM-205) was received from Chimei (Tainan City, Taiwan). To prepare the materials for testing equal parts PLLA and PDLA were melt blended together in a DSM Xplore mini extruder with various concentrations of PMMA at a temperature of 240°C and 100 rpm. The addition of the materials took approximately 1.5 min each, after which everything was mixed together for another 6 to 7 minutes. Afterwards the materials are compression molded into flat disks, which are used for both rheology and DSC tests. This was done in a Fontijne Holland TP400 table press. First the plates and material were heated for 4 minutes without any pressure at a temperature of 230°C. Next, with 5 small increments of applying and releasing pressure, the pressure is build up to 50 kN which is then put on the material for 1 minute. The disks made for rheology tests have a diameter of 25 mm and a thickness of 1 mm. The disks used to make the DSC samples have a diameter of 25 mm and a thickness of 0.5 mm. From these disks the DSC samples were made by punching smaller disks with a diameter of 3 mm, thickness of 0.5 mm and a weight of around 6-8 mg . Before testing the samples are dried at 70°C for a minimum of 2 hours, and afterwards they are stored in a vacuum oven at 35°C to keep them dry. All samples are tested maximum 3 weeks after making, since after this time the samples show inconsistent results compared to the results when used before this time. The wt% PMMA in all samples ranges from 0 to 40.

3.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) tests are used for a general thermal analysis of the materials. This gives characteristic temperatures such as glass transition temperature, crystallisation temperature, melting temperature, and whether or not HC and SC crystallites are present. All DSC tests are executed on a Mettler Toledo DSC823e, under a nitrogen gas flow of 50 mL/min.

3.2.1 Isothermal melt crystallisation

The combined effect of different crystallisation temperatures and the addition of PMMA will be investigated, making use of DSC. This is done to expand on the research of Boa et al. [20] with different amounts of PMMA and by looking at the crystallisation times and kinetics. The applied temperature protocol for the DSC tests can be seen in Figure 3.1. The sample is first heated to 270°C for 2 minutes to erase the thermal history, then a temperature step is applied to the isothermal crystallisation temperature, after which it is heated again with a rate of 10°C/min to 270°C to monitor the melting behaviour after crystallisation. The sample is kept long enough at the crystallisation temperature to fully crystallise. The crystallisation temperature ranges from 110 to 160°C. These tests provide two curves, a crystallisation curve and a melting curve, as shown in Figure 3.2. The area under the peaks can be determined by integration and represents the crystallisation or melting enthalpy (ΔH). The higher the absolute value of ΔH, the higher the crystallinity. The melting peaks at 160 to 180°C and 200 to 235°C are the melting of the HC and the SC crystallites respectively. Furthermore the crystallisation curve can also be used to determine the crystallisation time.

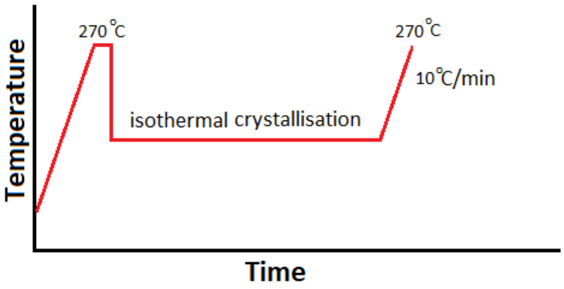
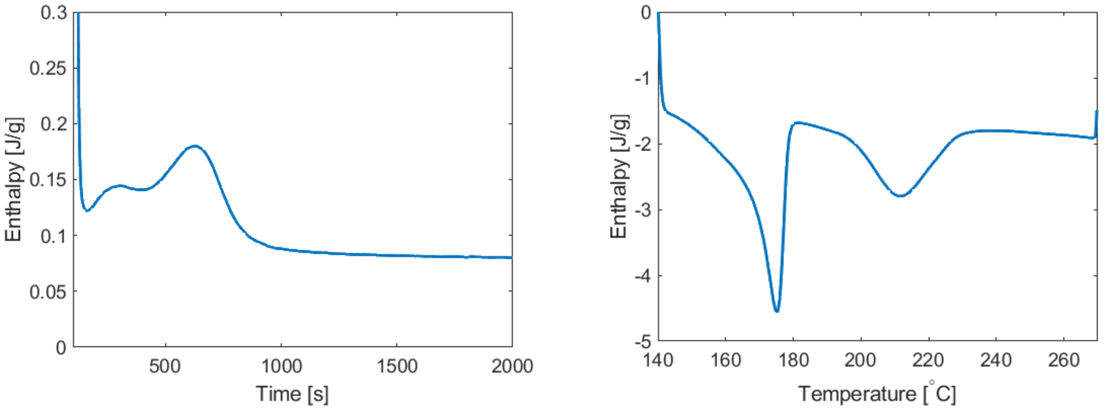


Figure 3.1: Schematics of the temperature protocol applied for the isothermal melt crystallisation.



(a) Isothermal crystallisation curve

(b) Melting curve

Figure 3.2: Crystallisation and melting curve of a 1:1 PLLA/PDLA mixture isothermally crystallised at 140°C.

For some samples the crystallisation already started before the machine response to the temperature step was fully done. To be able to take into account the machine response time a baseline experiment has been done where the same protocol was applied to a pure PMMA sample, which does not crystallise. This baseline was then fitted at the beginning and the end of the crystallisation curve, see Figure 3.3. This baseline experiment was only done at one temperature since a change in temperature only shifted the curves slightly horizontally which can be accounted for by fitting the baseline at the start of the crystallisation.

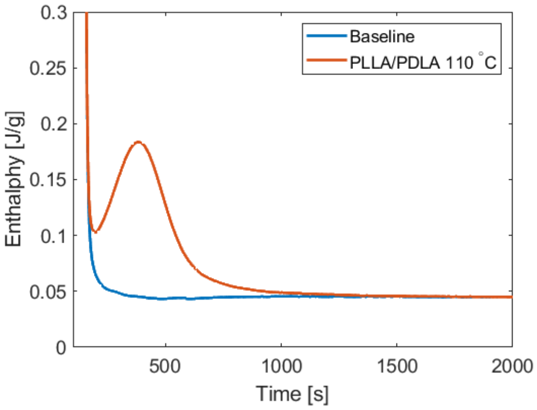


Figure 3.3: Crystallisation curve of a 1:1 PLLA/PDLA mixture isothermally crystallised at 110°C and baseline for determination of crystallisation enthalpy and time.

This baseline correction was used to determine the crystallisation enthalpy ΔH, crystallisation time, relative crystallinity, start of the crystallisation t_0, crystallisation half time $t_{1/2}$, and the Avrami constants. The crystallisation enthalpy is determined by calculating the area between the curve and the baseline. The relative crystallinity is then determined by equation 3.1:

$$X_t = \frac{\Delta H_t}{\Delta H_{tot}} \tag{3.1}$$

where X_t is the relative crystallinity, ΔH_t the enthalpy at time t and ΔH_{tot} the total enthalpy at the end of crystallisation. The crystallisation start time, t_0, is the time t where the baseline and crystallisation curve start to deviate and is calculated as the lowest value for t where $\Delta H_{crystallisation} - \Delta H_{baseline} > 0.01$. The crystallisation half time, $t_{1/2}$, is determined as the time where X_t equals $0.5 + t_0$. The Avrami equation, as described in equation 3.2, can be used to describe the isothermal crystallisation kinetics [16, 21, 17]:

$$1 - X_t = exp(-kt^n) \tag{3.2}$$

where X_t is the relative crystallinity, n is the Avrami exponent which is usually an integer between 1 and 4, k is the overall crystallisation rate constant, and t is the crystallisation time. Equation 3.2 can, with the use of logarithmic properties, be rewritten to equation 3.3[16, 21, 17]:

$$log(-ln(1 - X_t)) = nlog(t) + log(k) \tag{3.3}$$

Using this equation the constants n and k can be determined by a linear fitting of $log(-ln(1-X_t))$ versus $log(t)$.

To analyse the melting curves it is beneficial to look at the shape of the melting curve. To see whether or not the crystallisation protocol or addition PMMA effects the melting temperatures or the shapes of the peaks. Furthermore to look at the crystallinity of the samples after crystallisation the enthalpy, ΔH, of the melting curves can be determined. To do this in a consistent way a straight line is fitted through the end of the curves and the area between the fitted line and the melting curves is assumed to be ΔH, see Figure 3.4. If the melting enthalpy for only the HC or SC melting peak can be determined the HC and SC crystallinity can be calculated as well. This can be done by dividing the measured ΔH of the HC or SC melting peak by the melting enthalpy of pure HC or SC crystals which is equal to 98 J/g and 146 J/g respectively [18, 19].

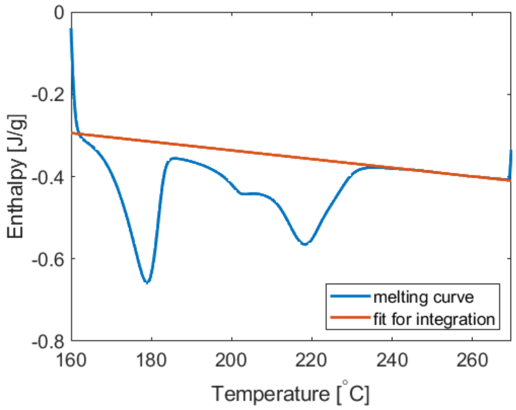


Figure 3.4: Melting enthalpy of a 1:1 PLLA/PDLA mixture with 10 wt% PMMA after isothermal crystallisation at 160°C.

3.2.2 Two step crystallisation

As stated in Chapter 2 the influence of PMMA and the influence of different temperature protocols on HC to SC recrystallisation has not been reported in literature yet. The protocol for these DSC tests can be seen in Figure 3.5. Here the sample is heated to 250°C for two minutes to erase the thermal history, next it is cooled with a rate of 60°C/min to the isothermal melt crystallisation temperature, ranging from 80°C to 140°C, and kept there till fully crystallised. Then for the recrystallisation the sample is heated with a rate of 150°C/min to the second isothermal cold crystallisation temperature, ranging from 190°C to 220°C. Lastly the material is heated at a rate of 10°C/min to obtain a heating curve to determine the melting enthalpy. The enthalpy during the recrystallisation is very low and thus no useful crystallisation curve can be obtained for this recrystallisation step. For these steps the melting enthalpy of the last heating curve is used as an indicator for the SC crystallinity after recrystallisation. In order to get more insight in the crystallisation as a function of time the protocol is repeated with a varying time for the recrystallisation step. During the heating curve the crystallites start to melt fast leading to the melting curves not always having a clear plateau before the melting peak. To keep a consistent way of determining the melting enthalpy a line is fitted through the plateau at the end of the curve, and everything below this line is assumed to be melting enthalpy, see Figure 3.6.

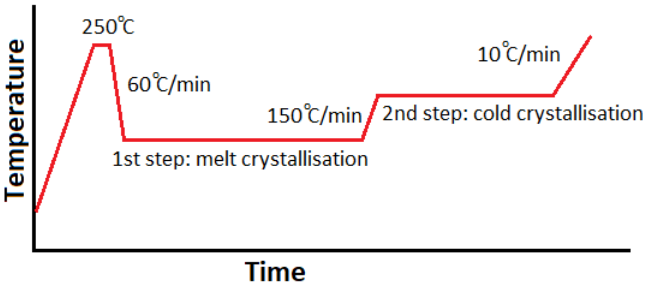


Figure 3.5: Schematics of the temperature protocol applied for the two step crystallisation.

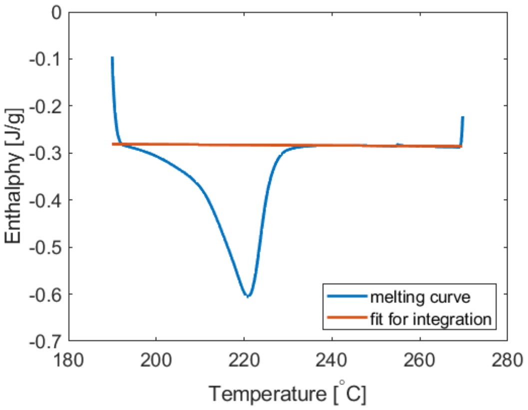


Figure 3.6: Melting curve of a 1:1 PLLA/PDLA mixture isothermally crystallised at 100°C for 30 min, recrystallised at 190°C for 30 min and the fitted line is used as the baseline to determine the melting enthalpy.

3.3 Rheometry

3.3.1 Critical shear rate

The last part of this research aims at gaining more insight in the shear induced crystallisation of PLLA/PDLA mixtures, and its effect in combination with adding PMMA. Shear induced crystallisation only occurs when polymer chains are oriented due to an applied shear. The chains can only be oriented when the shear rate is fast enough in relation to the relaxation time of the material. If this is not the case the polymer flows upon applying shear instead of being orientated and stretched. This relation is expressed by the Weissenberg number:

$$Wi = \frac{elastic \quad forces}{viscous \quad forces} = \dot{\gamma}\tau \tag{3.4}$$

where $\dot{\gamma}$ is the shear rate and τ the relaxation time. For any shear induced crystallisation to occur the Weissenberg number (Wi) needs to be larger than one [1, 11]. The longest relaxation time, the reptation relaxation time, can be determined using equation 3.5:

$$\tau_{rep} = \frac{1}{\omega_L} \tag{3.5}$$

where ω_L is the frequency of the intersection point of the tangents of the storage modulus (G') and loss modulus (G") at low frequencies, where the tangent for G' has a slope of 2 and the tangent of G" has a slope of 1. This intersection point can be determined using the results of a frequency sweep. Combining equations 3.4, 3.5 and the fact that Wi needs to be lager than 1, the critical shear rate can be determined as:

$$\begin{gathered} Wi = \dot{\gamma}\tau_{rep} > 1 \\ \tfrac{\dot{\gamma}}{\omega_L} > 1 \\ \dot{\gamma} > \omega_L \\ \dot{\gamma_c} = \omega_L \end{gathered} \tag{3.6}$$

Frequency sweeps have been done for PMMA/PLLA in different ratios and at different temperatures. These tests were executed on an Anton Paar rotational rheometer. For these frequency sweeps the strain was set at 1% and the frequency range was 0.01 to 100 Hz, the dynamic moduli G' and G" were measured. As explained above these results were used to determine the critical shear rate $\dot{\gamma_c}$ as defined in Equation 3.6. For a more in dept explanation on Wi, τ_{rep}, ω_L, and how exactly these frequency sweep results are analysed see the preparation phase report in Appendix B.1. An overview of the determined critical shear rates for all measured materials and temperatures is given in Table 3.1. These results are used to determine a measurement range for the shear rates in which it is expected to see shear-induced crystallisation.

Table 3.1: Critical shear rates for different PLLA/PMMA ratios and temperatures.

wt% PMMA Temperature [°C]	10	20	30	40
170	13	8.5	4.5	1.6
180	35	16.5	7	4.5
190	50	34	14	6
200	72	50	25	11
210	96	85	39	25
220	160	141	63	43

3.3.2 Shear-induced crystallisation

To see if and how the addition of PMMA and applying shear effects the crystallisation of PLA as well as the interaction of the two, oscillatory time sweeps have been executed. These tests are performed on an Anthon Paar rheometer with a temperature controlled convection oven that is flushed with nitrogen gas. During these tests G' and G" of the material are measured as a function of time. This gives insight in the crystallisation of the material as a function of time. For these time sweeps the oscillatory angular frequency was set to 1 rad/s and an amplitude of 0.1% was chosen. The applied temperature protocol and shear during these tests can be seen in Figure 3.7. The sample is first heated to 250°C for 2 minutes to erase the thermal history, and then the sample is cooled to the crystallisation temperature of 160°C with a cooling rate of 15°C/min. As soon as the temperature of 160°C is reached a shear pulse is applied after which the oscillatory time sweep is started. After the sample is fully crystallised the sample is heated again to 250°C to also follow the melting of the crystals. In order to prevent the sample from starting to crystallise during the cooling from 250°C to the crystallisation temperature of 160°C this cooling is done as fast as possible. The cooling of the machine itself is not linear, it needs some time to start the cooling and the cooling also slows down when approaching the target temperature to prevent an undershoot. In order to speed up the start of the cooling and to reach the maximum cooling rate as fast as possible the oven is opened and a small fan is aimed at the sample at the start of the cooling. The fan is taken away and the oven is closed again when the temperature reaches 210°C. This way the cooling starts significantly faster, and by closing the oven at this moment there is little to no overshoot. This method however does cause a slight inconsistencies in the temperature profile due to the manual opening and closing of the oven. Figure 3.8 shows the temperature profile of different tests from the start of the cooling until 15 minutes into the crystallisation, after 6 minutes the shear is applied and the oscillatory time sweep is started. Figure 3.8 also shows that in general the temperature profile for the cooling stays consistent. From the moment the shear is applied the temperature stays within +/- 1°C from the set crystallisation temperature.

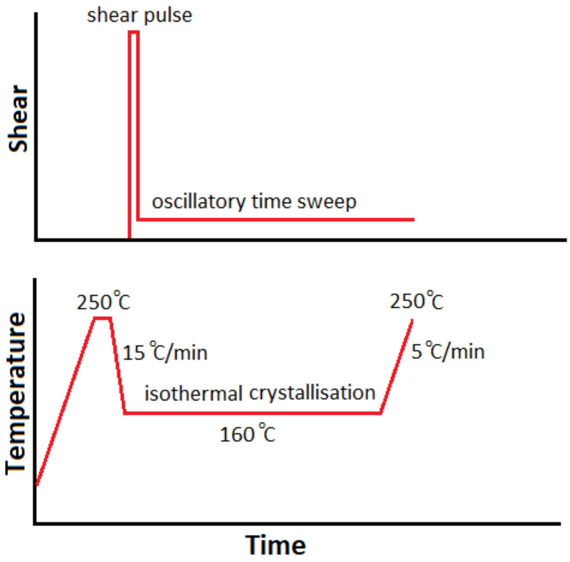
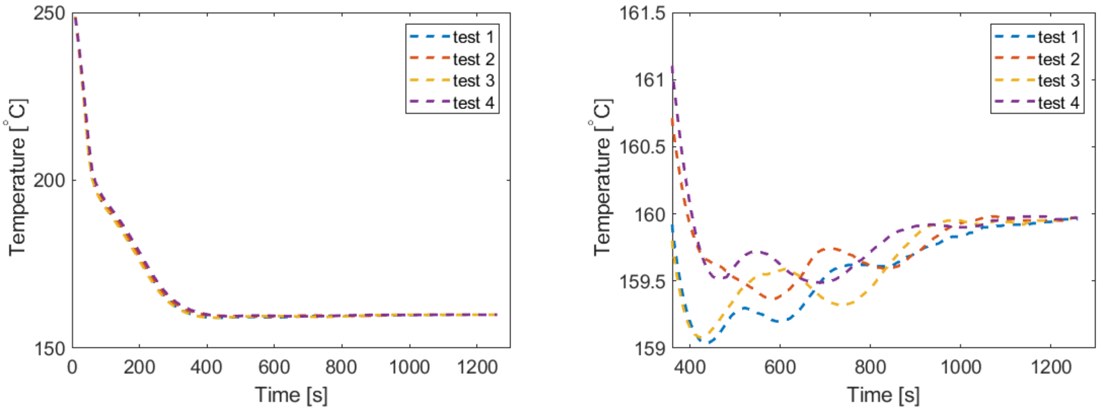


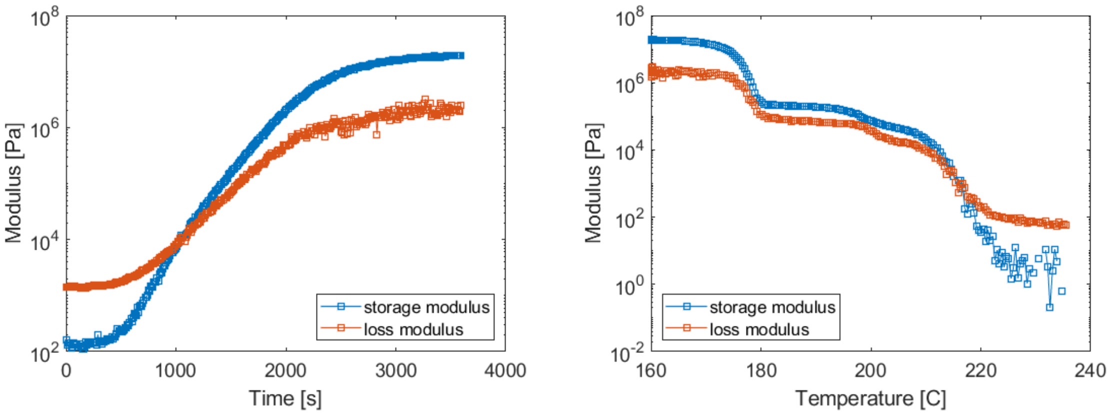
Figure 3.7: Schematics of the temperature and shear protocol applied for the oscillatory time sweeps.



(a) Full temperature profile during cooling (b) Temperature profile first 15 min of crystallisation

Figure 3.8: (a) Full temperature profile for the cooling during the rheometry tests (b) Temperature profile for the first 15 minutes of crystallisation during the rheometry tests

Using this method two sets of tests are performed for samples with a PMMA content of 0, 10 and 30 wt%. One set where the shear time was kept constant at 1 s and the shear rate ranged between 0 and 50 s^{-1}, and one set where the shear rate was kept constant at 10 s^{-1} and the shear times ranged between 0 and 10 s. These tests provide curves for G' and G" as a function of time. An example of these curves for the crystallisation and melting of a plain PLLA/PDLA sample can be seen in Figure 3.9. The G' refers to the elastic modulus, and reflects the elastic behavior of a material when deformed. The higher G', the more solid like and stiffer the material behaves. The G" refers to the viscous modulus, which reflects the flow behaviour of a material while it is deformed. The higher G" the higher the viscosity of the material and the harder it is for the material to flow. If G" is larger than G' the material is in a more liquid like state, if G' is larger than G" the material is in a more solid like state. When analysing these curves G' is used as an indicator for the relative crystallinity of the material. The cross over point is used as a reference to compare crystallisation speeds similar to how $t_{1/2}$ is used in the analysis of the DSC results. For the melting curves the melting of the crystals leads to a drop in modulus. So a steep tangent down would compare to a sharp melting peak in the enthalpy results of the DSC tests. A two step crystallisation protocol as applied in the DSC tests mentioned in Section 3.2.2 is not applied combined with shear. The reason for this is that the isothermal melt crystallisation temperature for the rheometry tests needed to be 160°C. This will be discussed in the next chapter, applying a second crystallisation step afterwards would lead to some tests taking more than a day each. This was logistically not possible and could lead to other unwanted side effects in the results such as thermal degradation.



(a) Storage and loss modulus during crystallisation

(b) Storage and loss modulus during melting

Figure 3.9: (a) Storage modulus (G’) and loss modulus (G”) of a 1:1 PLLA/PDLA mixture during isothermal crystallisation at 160°C. (b) Storage modulus (G’) and loss modulus (G”) of a 1:1 PLLA/PDLA mixture during melting.

Result and discussion

4.1 Quiescent crystallisation

Before the results of the DSC tests as described in Chapter 3 are being discussed, it is important to look at the reproducibility, and the reliability and error of the results. The results for the melting curves of two tests with the same protocol are shown in Figure 4.1. The protocol here is the protocol for the two step crystallisation as shown in Figure 3.5, where the first crystallisation temperature is 100°C and the second crystallisation temperature is 210°C. Both tests were executed with samples from the same mixing batch. Both melting curves have the same shape, there is only a small difference for the height of the melting peak with one being slightly higher. However this difference is insignificant in comparison to the total area of the peak. This leads to the conclusion that even though there might be some small errors in the calculated enthalpy these errors will not significantly influence the results. All DSC test were performed with samples from the same mixing batch. All samples used for the isothermal crystallisation tests were from disks from the same compression mold batch. All samples used for the two step crystallisation were also from disks from the same compression mold batch.

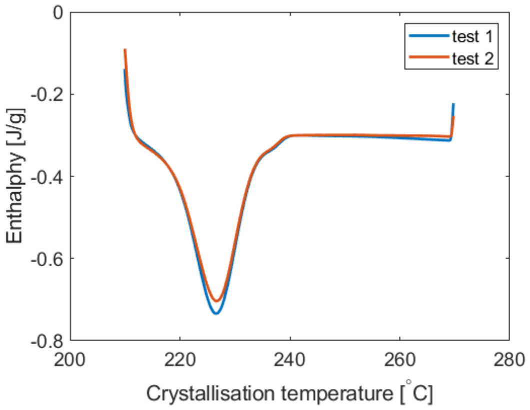
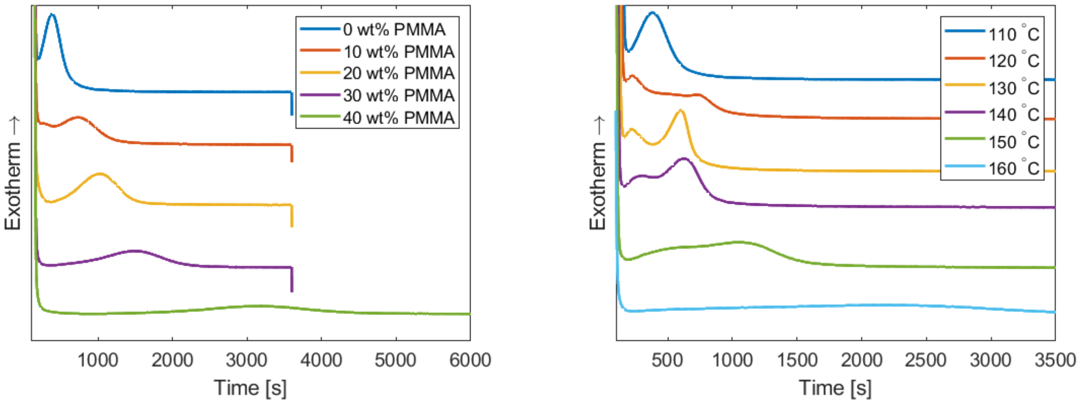


Figure 4.1: Melting curves of two samples of a 1:1 PLLA/PDLA mixture isothermally crystallised at 100°C for 30 min and recrystallised at 210°C for 30 min.

4.1.1 Isothermal melt crystallisation

A selection of the crystallisation peaks resulting from the isothermal melt crystallisation tests using DSC as discussed in Chapter 3 can be seen in Figure 4.2. Here the crystallisation curves for different amounts of PMMA at a crystallisation temperature of 110°C and for different crystallisation temperatures on plain PLA are shown. Similar graphs for different crystallisation temperatures and PMMA contents can be found in Appendix A.1. In Figure 4.2a it can be seen that with increasing PMMA content the crystallisation peak shifts to the right and becomes flatter and wider, indicating a slower crystallisation which also starts later. In Figure 4.2b it can be seen that with increasing temperature the crystallisation peaks again become flatter and wider indicating a slower crystallisation. Something else to notice is that in the crystallisation temperature range of 120°C to 150°C a double crystallisation peak can be seen. This double crystallisation peak could have multiple reasons. It could be the separation of HC and SC crystallisation, where the first peak would be the HC due to the fact that HC has a lower kinetic barrier [7]. However this is unlikely since in Figure 4.2a non of the curves show this double crystallisation peak even though both HC and SC are formed. A more likely reason would be, it indicating that after crystallisation of the material the crystals start to form a network [9, 33]. It could also mean that the crystallites start to impinge with each other and their growth could then be related to the subsidiary lamellae or to the thickening of lamellae [21].

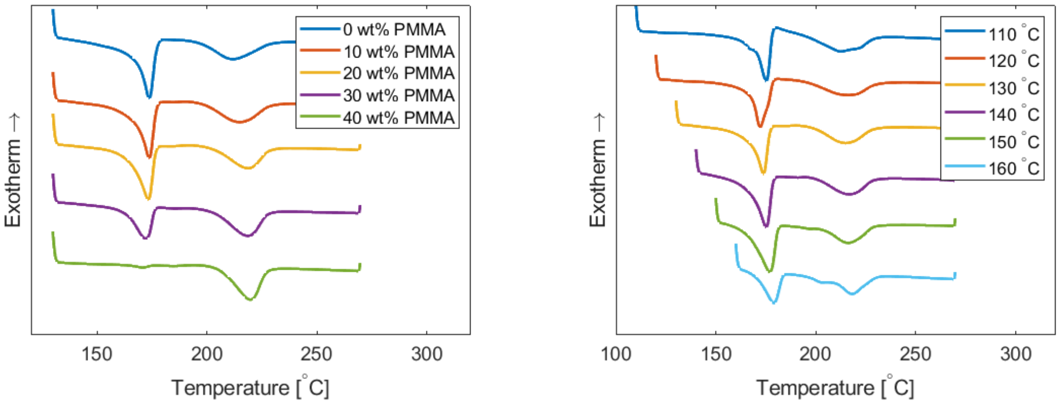


(a) Crystallisation temperature is 110°C

(b) 0 wt% PMMA

Figure 4.2: (a) Crystallisation curves of a 1:1 PLLA/PDLA mixture containing different wt% PMMA isothermally crystallised at 110°C. (b) Crystallisation curves of a 1:1 PLLA/PDLA mixture isothermally crystallised at different temperatures.

A selection of the melting peaks resulting from the isothermal melt crystallisation tests using DSC as discussed in Chapter 3 can be seen in Figure 4.3. Here the melting curves for PLA containing different amounts of PMMA at a crystallisation temperature of 130°C and for different crystallisation temperatures on PLA with 10wt% PMMA are shown. Similar graphs for different crystallisation temperatures and PMMA contents can be found in Appendix A.1. In both graphs of Figure 4.3 it can be seen that with increasing PMMA content and increasing crystallisation temperature the melting peak of HC crystals, 160 to 180°C, becomes smaller and the melting peak for SC crystals, 220 to 235°C, becomes larger. This indicates an increase in SC crystallinity with increasing PMMA content and increasing crystallisation temperature. An important note to make is that in Figure 4.3b it can be seen that for the lower crystallisation temperatures 110°C and 120° a small crystallisation peak occurs right after the HC melting peak. This could indicate either a recrystallisation of HC crystals to SC crystals, or further cold crystallisation of the material. This makes the SC content in the material higher before the SC starts melting, this leads to the SC melting peak for these graphs giving a slightly to high indication of SC content after isothermal crystallisation. The PMMA content does not seem to influence this occurrence of HC to SC recrystallisation during the heating curve after isothermal crystallisation at 110°C and 120°. Furthermore it can be seen in Figure 4.3b that for a crystallisation temperature of 150°C and 160°C the SC crystals start to show a double melting peak. All of these observations are in accordance with the findings of Boa et al [20]. As already discussed in Chapter 2 the increase in SC crystallinity and simultaneous decrease in HC crystallinity is due to the fact that the PMMA both increases the Tg of the material leading to a lower chain mobility, and diluting the PLA at the crystal growth fronts [17]. The occurrence of the double SC melting peaks at higher crystallisation temperatures could have multiple physical meanings. It could indicate that after crystallisation of the material the crystals start to form a network. One SC melting peak is thus the melting of the network and the other of the crystallites [9, 20, 22, 33]. It could also mean that the crystallites start to impinge with each other and their growth could then be related to the subsidiary lamellae or to the thickening of lamellae [21].



(a) Crystallisation temperature is 130°C

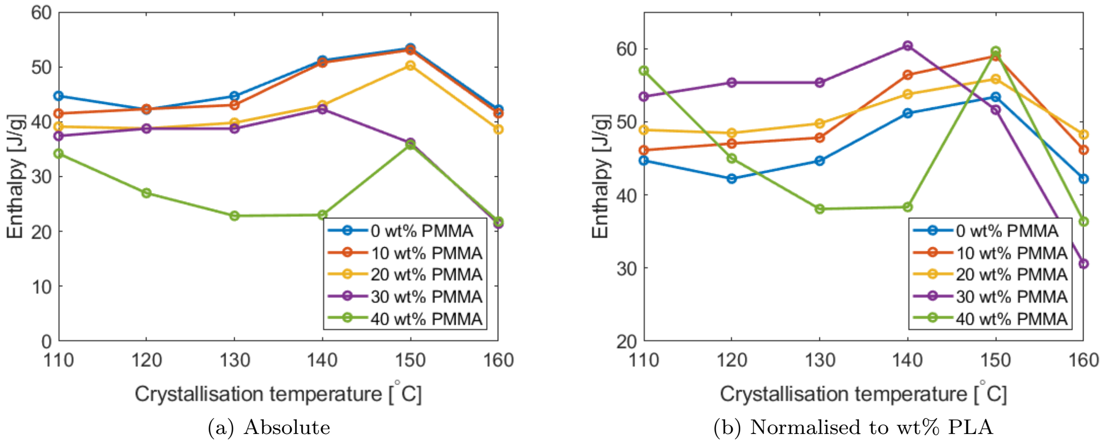
(b) 10 wt% PMMA

Figure 4.3: (a) Melting curves of a 1:1 PLLA/PDLA mixture containing different wt% PMMA isothermally crystallised at 130°C. (b) Melting curves of a 1:1 PLLA/PDLA mixture containing 10 wt% PMMA isothermally crystallised at different temperatures.

After performing the isothermal melt crystallisation tests using DSC as described in Chapter 3 the overall crystallinities of the fully crystallised samples are determined. This is done by calculating the melting enthalpy as discussed in the previous chapter. Since pure HC crystals have a different melting enthalpy than pure SC crystals the overall melting enthalpy cannot be converted to a crystallinity percentage for the material. The results for the overall melting enthalpy are shown in Figure 4.4. Both the absolute value for the enthalpy as measured as well as the enthalpy normalised to the amount of PLA are given. The normalised values represent the enthalpy relative to the amount of PLA in the sample, and are calculated using equation 4.1:

$$\Delta H_{norm} = \frac{\Delta H_{abs}}{1 - \frac{wt\%_{PMMA}}{100}} \tag{4.1}$$

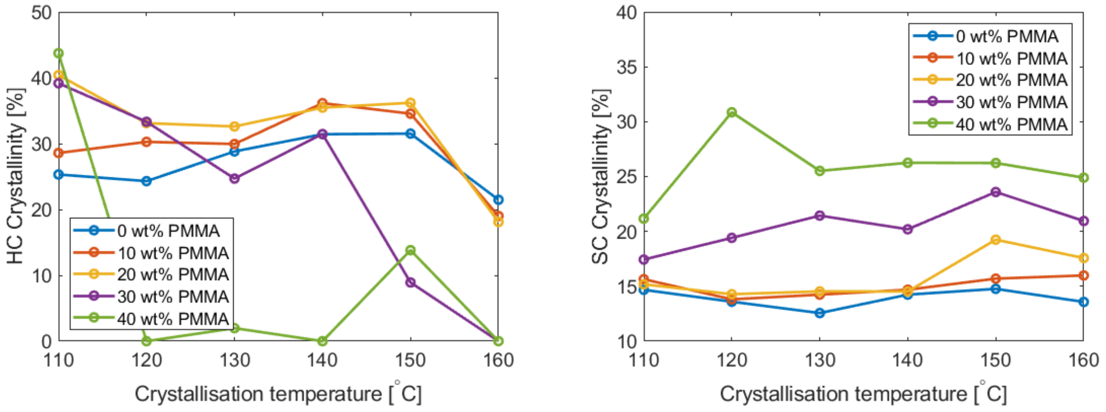
where ΔH_{norm} is the normalised enthalpy, ΔH_{abs} the absolute value for the enthalpy as measured, and $wt\%_{PMMA}$ is the amount of PMMA in the sample. In both graphs of Figure 4.4 it can be seen that with increasing crystallisation temperature the materials show a higher melting enthalpy, indicating a higher crystallinity. This is the case up to 150°C after which the melting enthalpy decreases for 160°C, which is in accordance with the results found by Boa et al. [20]. This could be due to the fact that from 160°C onward the melting temperature of HC crystals is approached and thus HC crystals can form significantly less, leading to a lower overall crystallinity. This general trend of increased enthalpy with increased crystallisation temperature seems to be not affected by the addition of PMMA up to 30 wt%. It can be concluded that somewhere between 30 and 40 wt% there is an amount of PMMA for which this increasing crystallinity with increasing crystallisation temperature is obstructed by the PMMA. In the results of Boa et al. [20] this was already visible for the mixtures with 25wt% and 50wt% PMMA. These tests have given more insight in the effect of PMMA for a PMMA content between 25wt% and 50wt% PMMA. When looking at Figure 4.4a the overall crystallinity of the complete material decreases with increasing wt% PMMA, even though Figure 4.4b shows that the crystallinity of the PLA in the material increases with increasing wt% PMMA. This shows the dilution effect with the addition of PMMA.



(a) Absolute (b) Normalised to wt% PLA

Figure 4.4: Melting enthalpy of a 1:1 PLLA/PDLA mixture with different wt% PMMA after isothermal crystallisation. (a) Absolute melting enthalpy. (b) Melting enthalpy normalised to the amount of PLA.

The results for the HC and SC crystallinity separately are shown in Figure 4.5, these results are normalised to the wt% PLA in the samples. The first important note to make with regards to these results is that for the higher crystallisation temperatures 150°C and 160°C in some melting graphs the HC and SC melting peak were not completely separable using the method described in Chapter 3, see Figure 3.4. In order to determine the HC and SC crystallinity for these graphs two separate straight lines were fitted to the graphs. One from the start of the graph to 180°C and one from 180°C to the end of the graph. The area between the first fitted line and the graph was determined as the HC melting enthalpy and the area between the second fitted line and the graph was determined as the SC melting enthalpy. This however leads to both the HC and SC crystallinity shown in Figure 4.5 being lower than they are in reality for high isothermal crystallisation temperatures. The second important note to make with regards to these results is that, as discussed above, for the lower isothermal crystallisation temperatures 110°C and 120°C a small crystallisation peak occurs during the heating of the sample after isothermal crystallisation. When analysing these curves using the method as described in Chapter 3 the fitted line has two intersection points, see Figures 4.6. Intersection point 1 is determined to be the point where the melting of HC crystals ends and the crystallisation during heating begins. Intersection point 2 is determined to be the point where the crystallisation during heating ends and the melting of SC crystals begins. In Figure 4.5 the HC crystallinity is determined using the enthalpy between the start of the graph and intersection point 1, the SC crystallinity is determined using the enthalpy between intersection point 2 and the end of the graph. This method leads to the SC crystallinity as shown in Figure 4.5 being higher than it is in reality for low isothermal crystallisation temperatures. Taking these notes into account the results of Figure 4.5a show that, for a PMMA content of 30wt% or more, both an increase in PMMA content and an increase in crystallisation temperature lead to a decrease in HC crystallinity. Figure 4.5b show that with increasing PMMA content the SC crystallinity increases. The results also show that with increasing isothermal crystallisation temperature the SC crystallinity seems to slightly increase. Both of these conclusions are in accordance with the results of Boa et al. [20].



(a) HC crystallinity

(b) SC crystallinity

Figure 4.5: (a) HC crystallinity and (b) SC crystallinity of a 1:1 PLLA/PDLA mixture with different wt% PMMA after isothermal crystallisation. Values are normalised to the wt% PLA present in the samples.

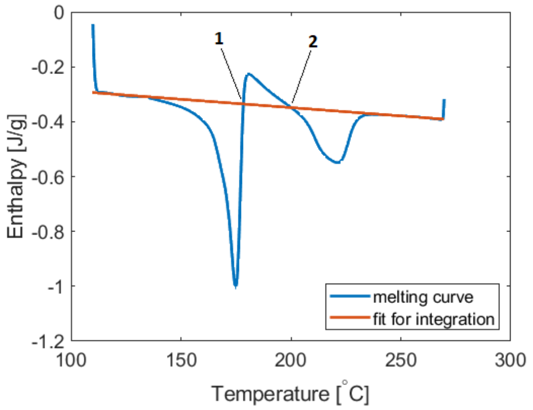
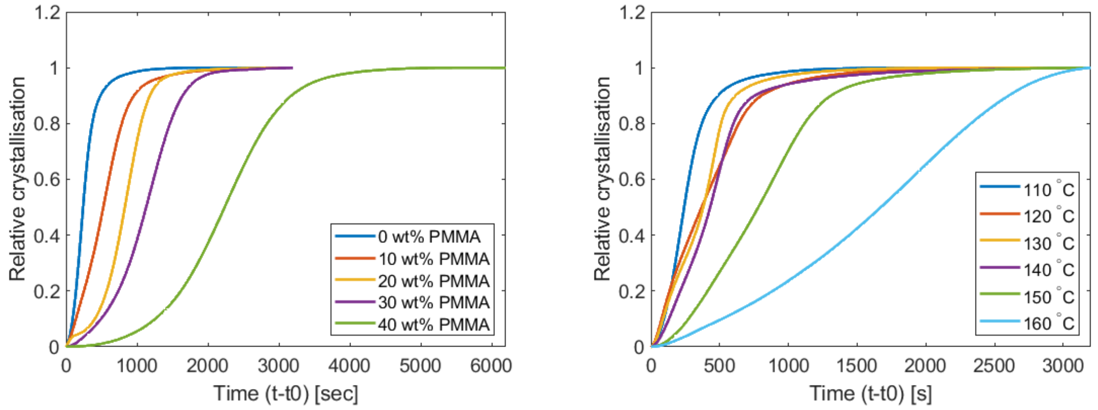


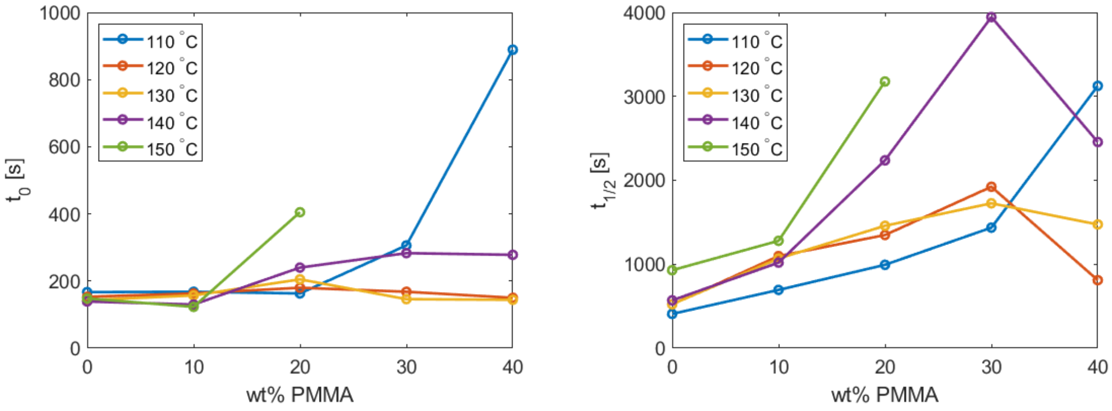
Figure 4.6: Melting curve of a 1:1 PLLA/PDLA mixture with 20wt% PMMA isothermally crystallised at 110°C and the fitted line to determine the melting enthalpy.

The results for the relative crystallisation as a function of time of these same isothermal melt crystallisation tests can be seen in Figure 4.7. Here the effects of the PMMA at a crystallisation temperature of 110°C and the effects of the crystallisation temperature on plain PLLA/PDLA mixtures are shown. The same graphs for different crystallisation temperatures and PMMA contents can be found in Appendix A.1. For all crystallisation temperatures and PMMA contents it can be seen that both with increasing wt% PMMA and increasing crystallisation temperature the crystallisation time goes up. These results are as expected since PMMA increases the Tg of the material leading to a lower chain mobility and a dilution effect at the crystal growth fronts [17], which suppresses the HC crystallisation. This suppression of crystallisation both favors SC crystals to form but also increases the crystallisation time. The crystallisation starting time, t_0, and the crystallisation half time, $t_{1/2}$, for all samples are shown in Figure 4.8. Here it can be seen that both an increase in temperature and in PMMA content have the most effect on $t_{1/2}$, and less so on t_0. Meaning both PMMA content and temperature do not make the crystallisation start all that much later but do significantly decrease the crystallisation rate. Another observation is that the addition of the PMMA does seem to increase the effect of temperature on both t_0 and $t_{1/2}$, at least up to a PMMA content of 30wt%.



(a) Crystallisation temperature is 110°C (b) WT% PMMA is 0

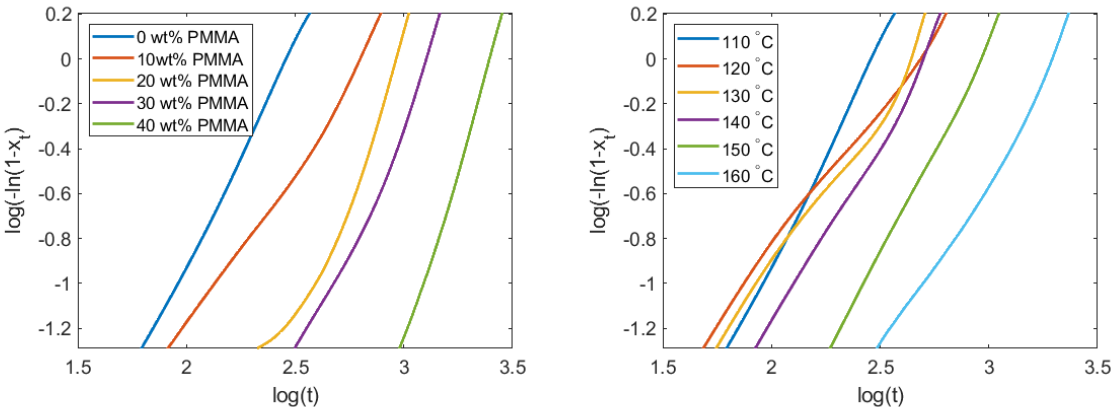
Figure 4.7: (a) Relative crystallisation of a 1:1 PLLA/PDLA mixture containing different wt% PMMA isothermally crystallised at 110°C. (b) Relative crystallinity of a 1:1 PLLA/PDLA mixture isothermally crystallised at different temperatures.



(a) Crystallisation starting time t_0 (b) Crystallisation half time $t_{1/2}$

Figure 4.8: (a) Crystallisation t_0 of a 1:1 PLLA/PDLA mixture with varying wt% of PMMA isothermally crystallised at different temperatures. (b) Crystallisation $t_{1/2}$ of a 1:1 PLLA/PDLA mixture with varying wt% of PMMA isothermally crystallised at different temperatures.

The Avrami plots of these isothermal melt crystallisation tests can be seen in Figure 4.9. Here the Avrami plots for a relative crystallinity range of 5 to 80% for different PMMA contents at a crystallisation temperature of 110°C, and for different crystallisation temperatures on plain PLLA/PDLA mixtures are shown. The same graphs for different crystallisation temperatures and PMMA contents can be found in Appendix A.1. In Figure 4.9 it can be seen that for increasing wt% and increasing temperature the graphs shift to the right. This indicates that with increasing PMMA content it takes longer to reach the same relative crystallinity, thus with increasing PMMA content the crystallisation becomes slower. This is in accordance with the previous results. In Figure 4.9b it can furthermore be seen that in the temperature range of 120-140 °C the Avrami plots do not show linear behaviour. This indicates an asymmetric exothermal peak [21, 16], which was also already visible in the crystallisation curves, see Figure 4.2b. Boa et al. [21] also found a range of crystallisation temperatures of 130 to 150°C in which the Avrami plots do not show a linear behaviour. The slight difference in temperature range between the results of Boa et al. and the present ones could be due to the different Mw of the materials used. As discussed in the previous chapter the Avrami plots are commonly used to determine the overall crystallisation rate constant k and exponent n. Figure 4.10 shows k as a function of the crystallisation temperature for PLLA/PDLA mixtures with different PMMA contents. Table 4.1 gives all the values for n. Both k and n are determined for a relative crystallinity range of 5 to 15%, this is the linear part of the plots where $log(-ln(1 - X_t))$ is between -1.3 and -0.8. When looking at Figure 4.10 in general a slight peak at 120°C can be seen, meaning that for all different amounts of PMMA content the overall crystallisation rate is the highest at a crystallisation temperature of 120°C. Figure 4.10 does not show a clear effect of PMMA on k. This is in contrast with the fact that for $t_{1/2}$ a clear decrease with increasing PMMA content was seen. This could be due to the fact that k is determined fitting linearly to only the first part of the Avrami plots, representing only the crystallisation up to a relative crystallinity of 15%. As previously mentioned in the temperature range of 120 to 150°C a double crystallisation peak occurs. These double crystallisation peaks make that the crystallisation rate changes during crystallisation. Crystallisation starts relatively fast as the first peak starts but then drops when going from the first to the second peak. This would lead to the fact that the values for k, determined relatively early in the crystallisation process, can show a different dependence on the amount of PMMA than $t_{1/2}$, which indicates the half way point of crystallisation. When looking at Table 4.1 almost all values for n are between 1 and 2. This indicates that the crystallisation growth is limited in dimension, which could mean that either the distribution of nucleation sites is non-random or the nucleation sites are saturated [13].



(a) Avrami plots for crystallisation at 110°C

(b) Avrami plots for plain PLLA/PDLA mixture

Figure 4.9: (a) Avrami plots of 1:1 PLLA/PDLA mixtures with different wt% of PMMA isothermally crystallised at 110°C. (b) Avrami plots of a 1:1 PLLA/PDLA mixtures isothermally crystallised at different temperatures.

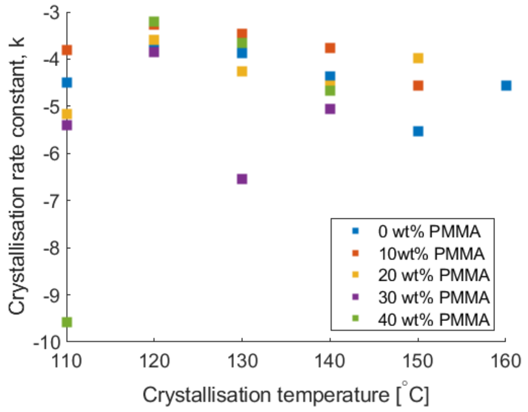


Figure 4.10: Crystallisation rate constant of a 1:1 PLLA/PDLA mixture with different wt% PMMA after isothermal crystallisation at different temperatures.

Table 4.1: Exponent n for the Avrami equation for crystallisation of a 1:1 PLLA/PDLA mixture with different wt% of PMMA isothermally crystallised at different temperatures.

Crys. temp [°C] PMMA [wt%]	110	120	130	140	150	160
0	1.8	1.5	1.5	1.6	1.9	1.3
10	1.3	1.1	1.2	1.4	1.6	
20	1.6	1	1.4	1.4	1.1	
30	1.6	1.1	2.2	1.5		
40	2.8	1	1.1	1.3		

4.1.2 Two step crystallisation

As discussed in Chapter 3 the DSC signal during the recrystallisation in the range 190°C to 220°C is to weak to obtain an isothermal crystallisation curve. This means that it is not possible to monitor the crystallisation as a function of time. A solution for this is to loop the experiment with in every loop a longer crystallisation time for the recrystallisation part while keeping the rest of the procedure the same. Since the thermal history is removed in between the different loops it should be possible to apply these loops on the same sample, at least until a form of thermal degradation occurs. To check this procedure, the protocol of Figure 3.5 is applied multiple times on the same sample with a constant crystallisation time for both crystallisation steps. This should lead to the same results for every loop. The results of these tests for different first crystallisation and melting temperatures, and a constant recrystallisation temperature of 190°C are shown in Figure 4.11. In these experiments the melting curve can only contain enthalpy changes due to the melting of SC crystals, this is because of the high temperature of the second crystallisation step. This also means that the melting enthalpy can be used to calculate the crystallinity of the material. The crystallinity is calculated by dividing the measured melting enthalpy by the melting enthalpy of pure SC crystals which is equal to 146 J/g [18, 19]. In Figure 4.11 it is seen that the crystallinity increases with every loop, even though the thermal history should be erased in between each curve. Lowering the melting temperature from 270°C to 250°C does influence the overall crystallinity but does not influence the effect observed when repeating the tests. This leads to the conclusion that the increased crystallinity for every repetition is not due to thermal degradation, since then the effect would become smaller for a lower melting temperature. This also leads to the conclusion that the effect is not due to melt memory since then the effect would become larger for a lower melting temperature. The cause of the effect is thus unknown so far.

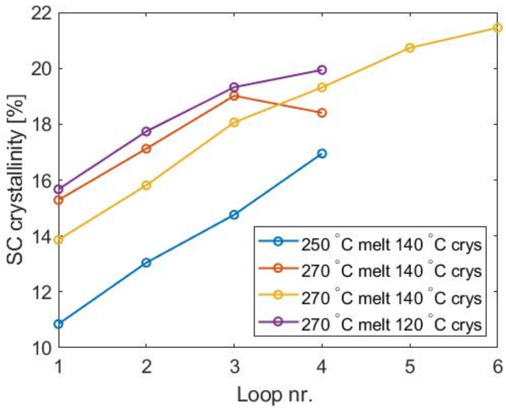
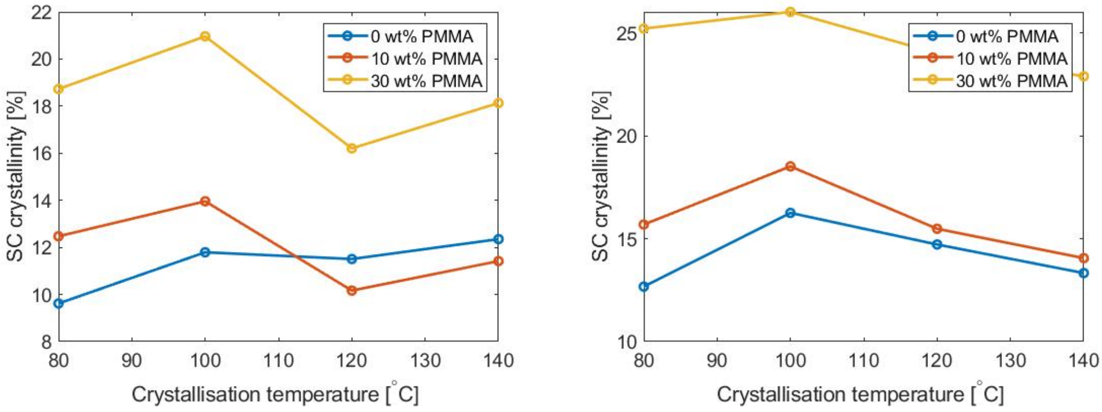


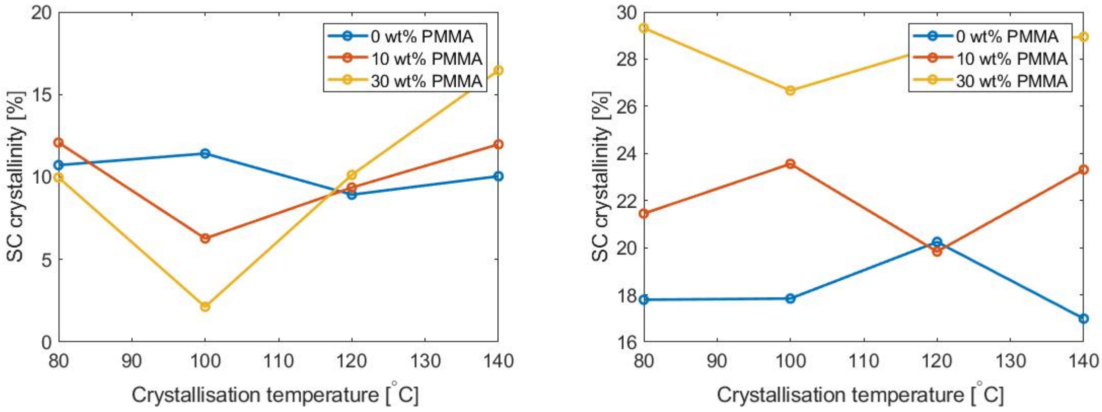
Figure 4.11: Crystallinity of 1:1 PLLA/PDLA mixtures after different repetitions of the same crystallisation and recrystallisation protocol, for different melting and crystallisation temperatures.

To avoid the above mentioned phenomenon to have an influence on the results the decision has been made to use a new sample for every test, so always only the first loop is measured. This limited the amount of tests possible to execute, and thus only two crystallisation times for the recrystallisation step have been selected namely, 1 minute and 30 minutes. The results of these tests can be found in Figures 4.12 and 4.13. They show the results per recrystallisation temperature and per wt% PMMA respectively. All results are normalised to the PLA amount present in the samples, the graphs containing the absolute values can be found in Appendix A.1. When looking at Figure 4.12 it can be seen that for lower recrystallisation temperatures an initial crystallisation temperature of 100°C seems optimal, Figure 4.12a-b. For a higher recrystallisation temperature a higher initial crystallisation temperature seems to give the highest crystallinity, Figure 4.12c-f. This effect also seems to be enhanced by the addition of PMMA. This would suggest that both pure α-HC crystals, which in plain PLLA/PDLA exclusively form for initial crystallisation temperatures of 120°C and above [25, 12], and pure α'-HC crystals, which in plain PLLA/PDLA exclusively form for initial crystallisation temperatures below 100°C, recrystallise easier for higher recrystallisation temperatures. When a mixture of both α-HC and α'-HC is present a lower recrystallisation temperature presumably leads to the highest SC crystallinity. However for these conclusions it is important to note that α'-HC forms at lower crystallisation temperatures due to the lower chain mobility at lower crystallisation temperatures. As mentioned before adding PMMA to PLLA/PDLA mixtures lowers the chain mobility which could influence the exact temperature ranges in which α-HC and α'-HC are formed. Next, for low recrystallisation temperatures the addition of PMMA gives a higher crystallinity for all initial crystallisation temperatures, Figure 4.12a-b, whereas for high recrystallisation temperatures the addition of PMMA is only beneficial at high initial crystallisation temperatures, Figure 4.12c-f. This leads to the conclusion that for higher recrystallisation temperatures PMMA obstructs the recrystallisation from α'-HC crystals to SC crystals, while increasing the recrystallisation from α-HC crystals to SC crystals. When looking at Figure 4.13 it can be seen that at lower recrystallisation temperatures the addition of PMMA increases the crystallinity more than at higher recrystallisation temperatures. This could be explained by the fact that PMMA increases the SC crystallinity by obstructing HC crystallisation. At higher recrystallisation temperatures HC crystals are certain to be completely molten, thus the PMMA has no HC crystallisation to obstruct. When PMMA is added in high amounts it could even obstruct the SC crystallisation due to the lowered chain mobility [17]. This can be seen by the fact that the sample containing 30wt% PMMA recrystallised at a temperature of 220°C has a lower crystallinity than the plain PLLA/PDLA sample. Furthermore for a recrystallisation time of 1 minute an increasing recrystallisation temperature leads to a decrease in crystallinity. This indicates that with increasing recrystallisation temperature the recrystallisation either starts later or is slower. This is in accordance with the previous results showing an increase in crystallisation time when increasing the crystallisation temperature. Looking at a crystallisation time of 30 minutes it appears that a recrystallisation temperature of 210°C gives overall the highest crystallinity. This is probably due to the fact that at this temperature is high enough for all the HC crystals to melt, while still being low enough to not cause any SC crystals or the formed network to melt.



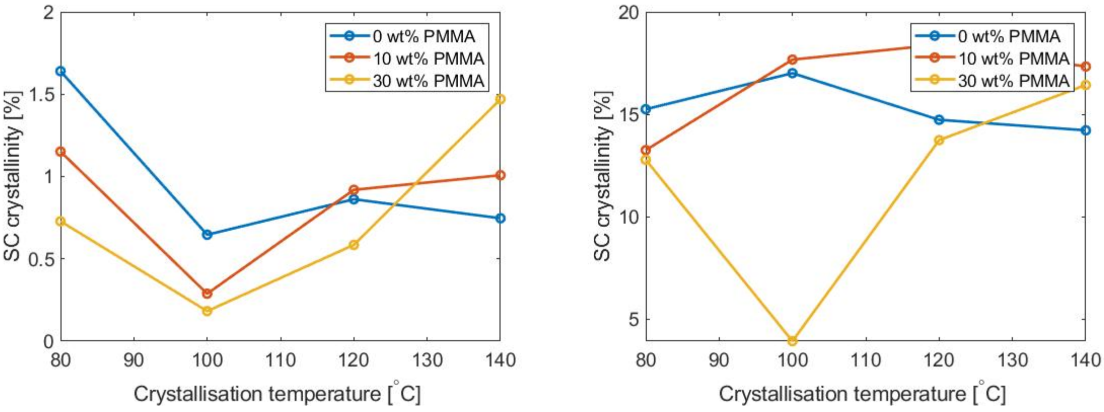
(a) Recrystallised at 190°C for 1 min

(b) Recrystallised at 190°C for 30 min



(c) Recrystallised at 210°C for 1 min

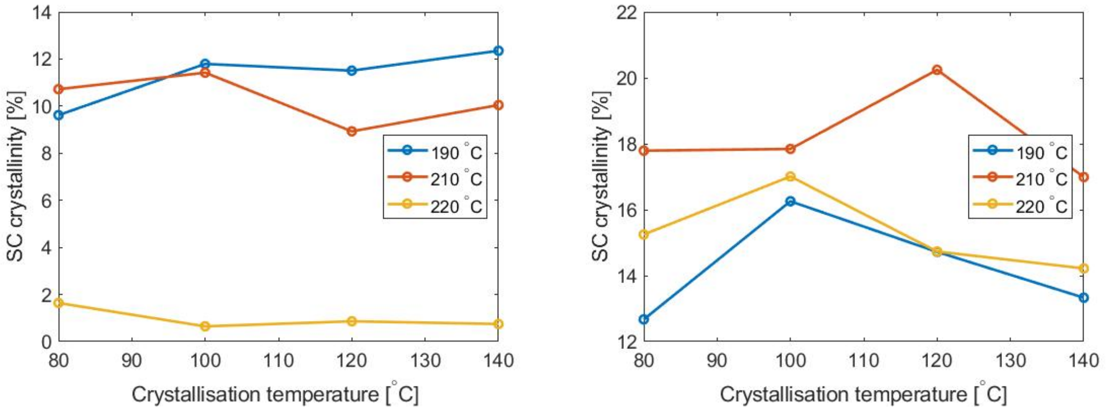
(d) Recrystallised at 210°C for 30 min



(e) Recrystallised at 220°C for 1 min

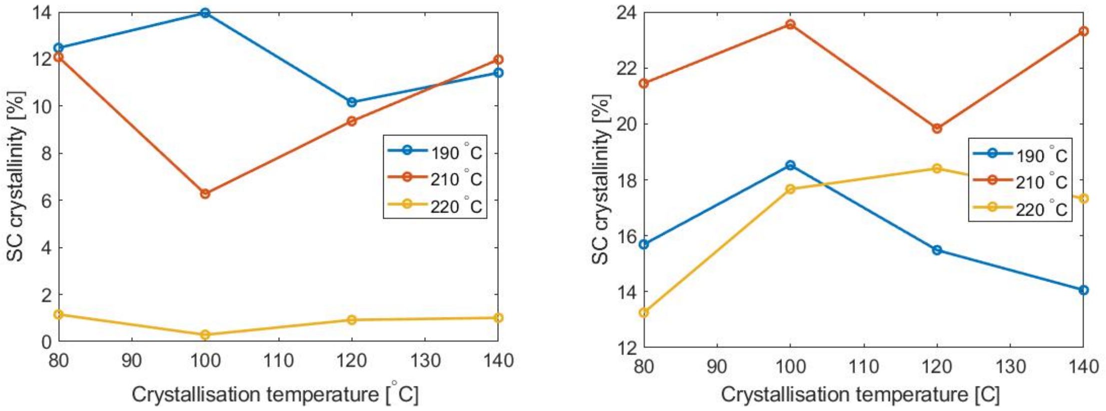
(f) Recrystallised at 220°C for 30 min

Figure 4.12: Crystallinity of a 1:1 PLLA/PDLA mixture containing different wt% PMMA, after crystallisation and recrystallisation at different temperatures. Shown per recrystallisation temperature. Values are normalised to the the wt% PLA present in the samples.



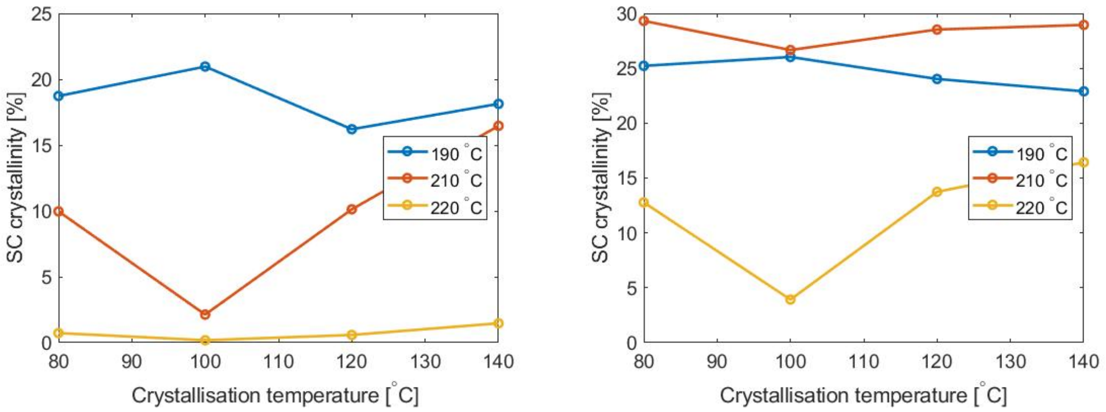
(a) 0wt% PMMA recrystallised for 1 min

(b) 0wt% PMMA recrystallised for 30 min



(c) 10wt% PMMA recrystallised for 1 min

(d) 10wt% PMMA recrystallised for 30 min



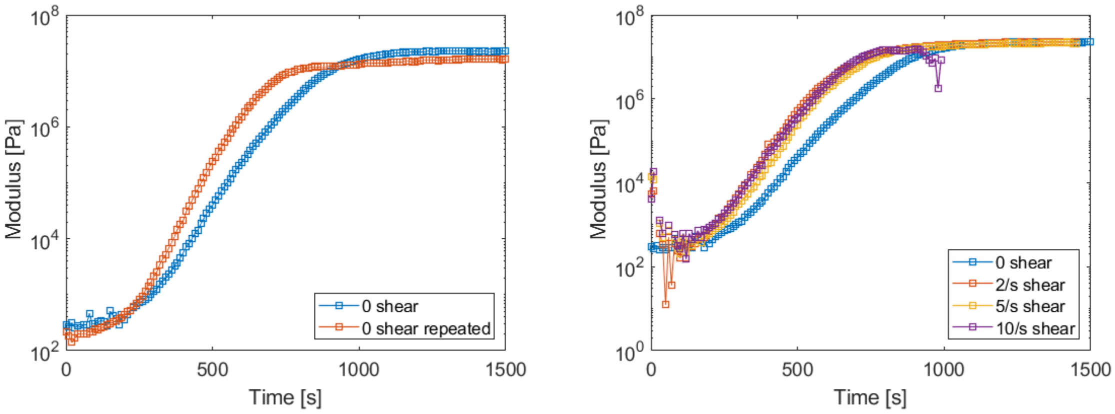
(e) 30wt% PMMA recrystallised for 1 min

(f) 30wt% PMMA recrystallised for 30 min

Figure 4.13: Crystallinity of a 1:1 PLLA/PDLA mixture containing different wt% PMMA, after crystallisation and recrystallisation at different temperatures. Shown per wt% PMMA. Values are normalised to the the wt% PLA present in the samples.

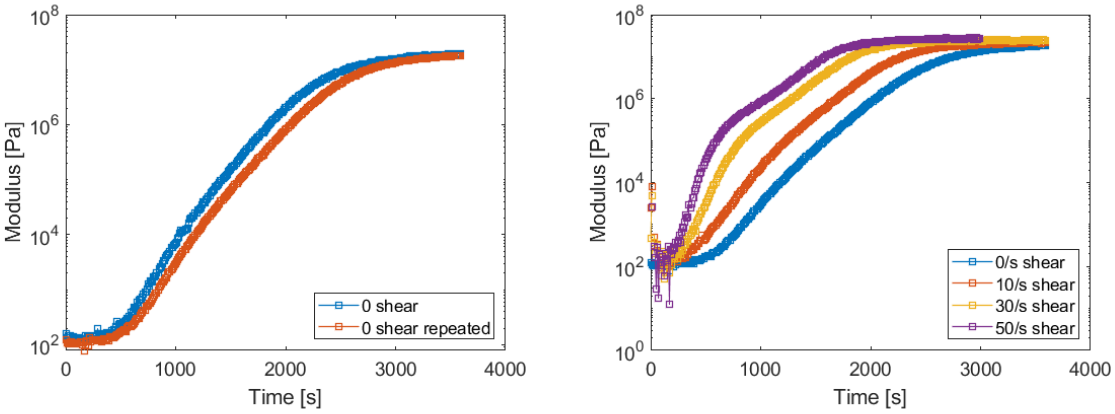
4.2 Flow-induced crystallisation

Ideally, the rheometry tests to look at the flow-induced crystallisation would be executed at a temperature within the same range of the DSC tests in order to make direct comparisons. However, when testing for an isothermal crystallisation temperature of 140° the crystallisation started immediately when shear was being applied, this meant that G' and G" could only be measured at the end of the crystallisation. In order to slow down the crystallisation to get the full curves for G' and G" the isothermal crystallisation temperature was increased to 150°. This did give full curves for G' and G" during crystallisation, the curves for G' can be seen in Figure 4.14b. However the difference between the curves is not significant when looking at the reproducibility, as seen in Figure 4.14. Here the deviation on the results with the same shear conditions is of the same order as the difference between results with different shear conditions. In order to obtain results where the difference between curves with different shear conditions is significantly larger than the deviation between repeated experiments with the same conditions, both the isothermal crystallisation temperature was increased to 160°, to increase the timescale of the experiment, and the shear range was increased to between 0 and 50 s^{-1} to enhance the shear rate effects. This gave results that showed effects that were significantly larger than the error, as can be seen in Figure 4.15 where both the reproducibility and a set of results are shown for plain PLA samples.



(a) Reproducibility (b) Results for different shear rates

Figure 4.14: G' of a 1:1 PLLA/PDLA mixture during isothermal crystallisation at 150°C. Different shear rates and shear times where applied at time t=0.



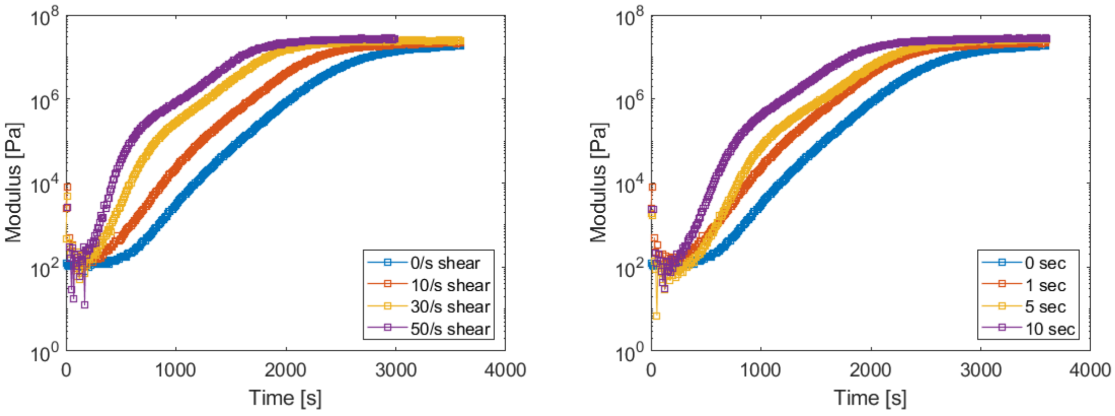
(a) Reproducibility (b) Results for different shear rates

Figure 4.15: G' of a 1:1 PLLA/PDLA mixture during isothermal crystallisation at 160°C. Different shear rates and shear times where applied at time t=0.

The results for G' during the crystallisation part of the oscillatory time sweep rheometry tests as described in Chapter 3 can be found in Figures 4.16, 4.17, and 4.18. In Figure 4.18 the graphs for the samples containing 30wt% PMMA are cropped to only show the first 100 minutes, to give a more clear overview of the influence of shear. The plots for 30wt% for full crystallisation can be found in Figure 4.19. When looking at Figures 4.16, 4.17, and 4.18 it can be seen that with either increasing shear rate or increasing shear time the crystallisation starts significantly sooner and happens faster. With increasing amount of PMMA the crystallisation takes a lot longer, which is in accordance with the results from the DSC tests, and literature since this is due to the fact that PMMA obstructs the HC crystallisation [17]. It can also be seen that with a higher strain, or PMMA content the crystallisation starts to separate into two crystallisation phases. This could have multiple physical meanings. It could indicate that after crystallisation of the material the crystals start to form a network which further increases G' [9, 33]. It could also mean that the crystallites start to impinge with each other and their growth could then be related to the subsidiary lamellae or to the thickening of lamellae [21]. Furthermore the shear seems to mostly increase the crystallisation rate of the first phase while having less to no effect on the second crystallisation phase. To make this more clear the derivative of the graph has been determined using Equation 4.2:

$$f' = \frac{\Delta G'}{\Delta t} \tag{4.2}$$

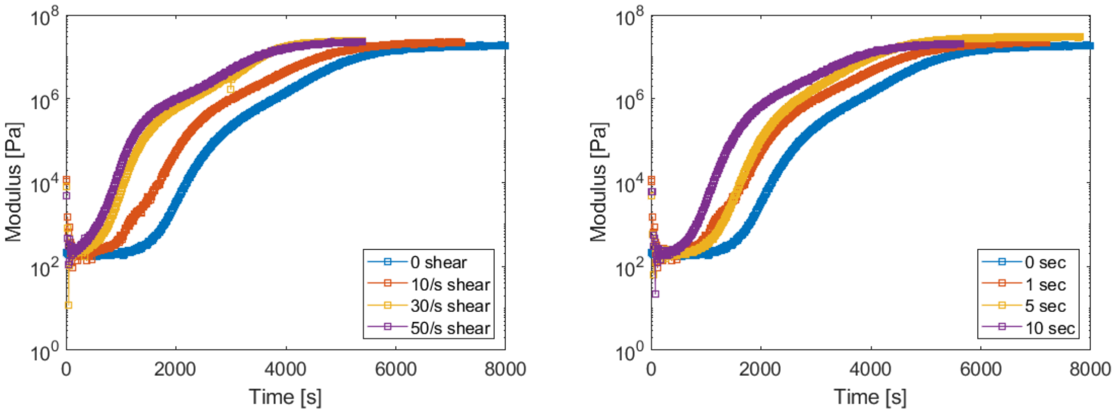
where f' is the derivative, $\Delta G'$ the difference in G' between two data points 60 seconds apart from each other and Δt the difference in time, so this is a constant of 60 seconds. The graphs for this derivative over time can be seen in Figure 4.20. In these graphs the first peak represents the derivative of the primary crystallisation. From the start of the plateau the derivative of the secondary crystallisation can be seen up until the derivative is 0 when the crystallisation is finished. These graphs show indeed that the primary crystallisation is most effected by shear, where an increase in shear rate leads to a higher value for the derivative of the primary crystallisation, and the maximum value is reached sooner. This indicates that both the crystallisation rate increases with increasing shear rate, as well as t_0 decreases with increasing shear rate. Furthermore Figure 4.20a-b shows that the derivative for the secondary crystallisation does not have a different value only a horizontal shift over time, which is due to the decrease in t_0 with increasing shear rate. For Figure 4.20c no difference for the secondary crystallisation can be seen. These observations lead to the conclusion that the shear indeed mostly effects the primary crystallisation, and less so the secondary crystallisation. This effect of shear on the crystallisation rate and on t_0 is due to the fact that the shear gives orientation to the chains leading to more surface contact between chains, which makes it easier for the chains to crystallise. This is in accordance with the literature discussed in chapter 2. Bai et al. [9] also saw a decrease in t_0 for increased shear in PLLA/PDLA mixtures without PMMA, and Song et al. [28] also saw a decrease in $t_{1/2}$ for increasing shear, implying a higher crystallisation rate with increasing shear in PLLA/PDLA mixtures without PMMA.



(a) fixed shear time of 1 s

(b) fixed shear rate of 10 s^{-1}

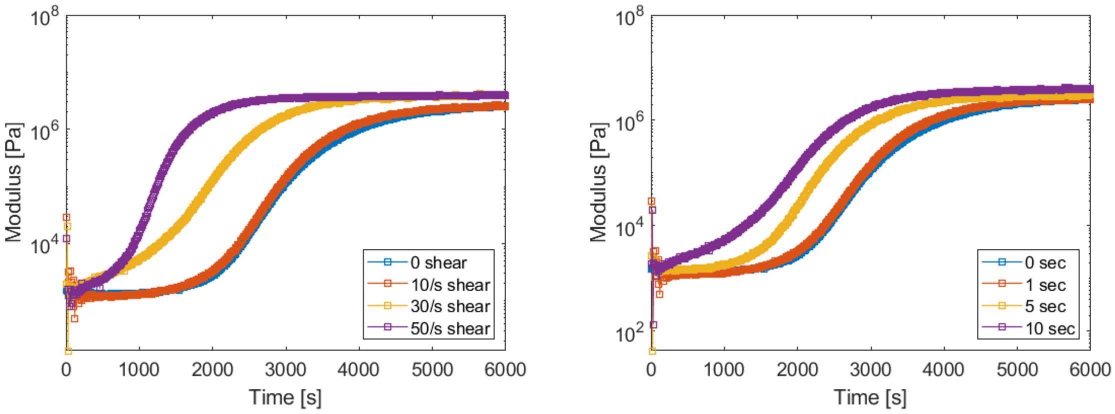
Figure 4.16: G' of a 1:1 PLLA/PDLA mixture during isothermal crystallisation at 160°C. Different shear rates and shear times where applied at time t=0.



(a) fixed shear time of 1 s

(b) fixed shear rate of 10 s^{-1}

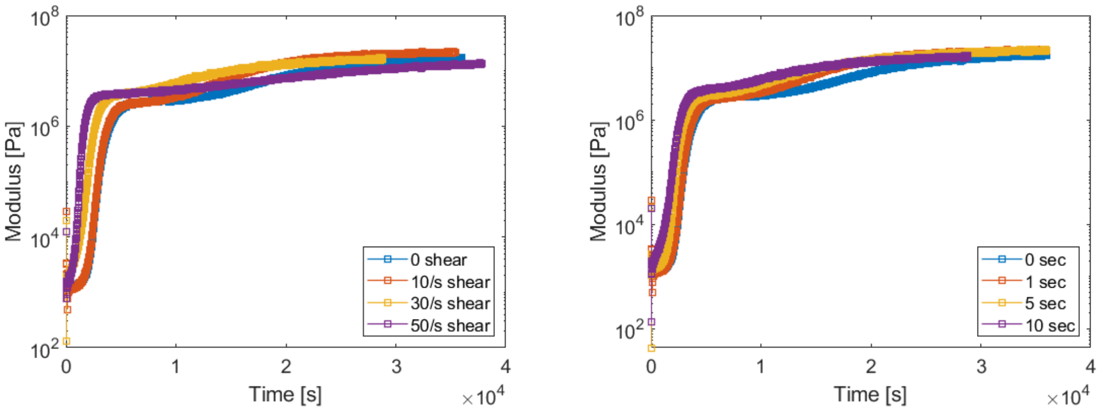
Figure 4.17: G' of a 1:1 PLLA/PDLA mixture containing 10wt% of PMMA during isothermal crystallisation at 160°C. Different shear rates and times where applied at time t=0.



(a) fixed shear time of 1s

(b) fixed shear rate of 10 s^{-1}

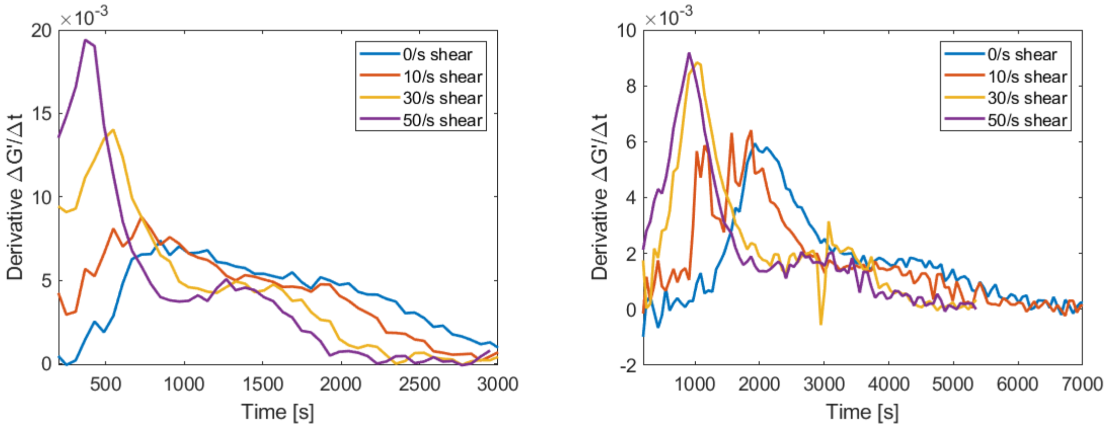
Figure 4.18: G' of a 1:1 PLLA/PDLA mixture containing 30 wt% of PMMA during isothermal crystallisation at 160°C. Different shear rates and times where applied at time t=0.



(a) Fixed shear time of 1s

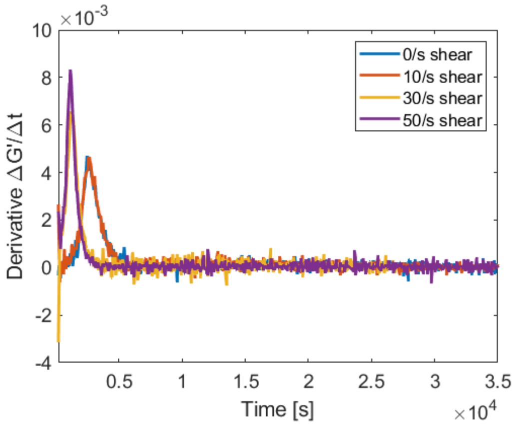
(b) Fixed shear rate of 10 s^{-1}

Figure 4.19: G' of a 1:1 PLLA/PDLA mixture containing 30wt% of PMMA during isothermal crystallisation at 160°C. Different shear rates and times where applied at time t=0.



(a) 0wt% for different shear rates

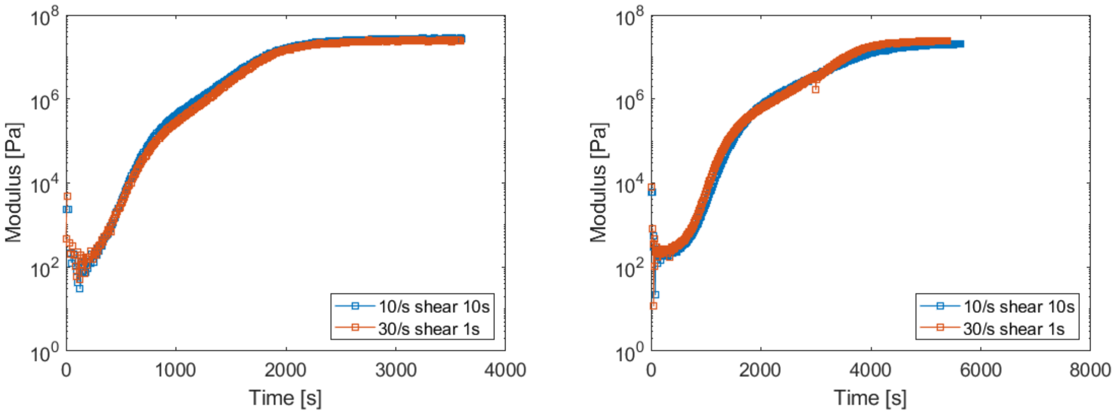
(b) 10wt% for different shear rates



(c) 30wt% for different shear rates

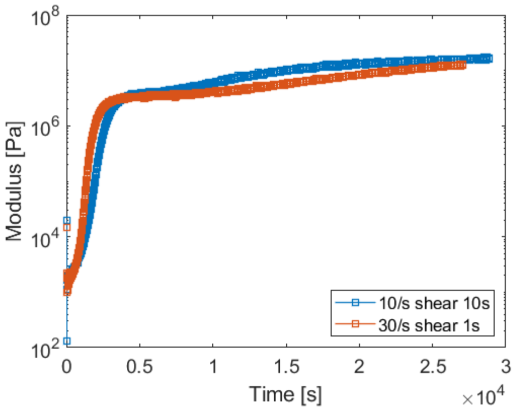
Figure 4.20: Slope of G' of a 1:1 PLLA/PDLA mixture with different PMMA contents during isothermal crystallisation at 160°C. Different shear rates were applied for 1 s at time t=0.

To see if shear rate en shear time have the same influence both were compared to each other. An interesting result from this comparison is shown in Figure 4.21, where it can be seen that a shear rate of 30 s^{-1} and shear time of 1 s gives the same results as a shear rate of 10 s^{-1} for 10 s for both plain PLA and PLA with 10wt% PMMA. Since the strain, defined as shear rate × shear time, for one is 30 while for the other being 100 it can be concluded that the shear rate in this case has a greater effect than the shear time. For PLA with 30wt% PMMA these two cases did not show the same results. Here a shear rate of 30 s^{-1} and shear time of 1 s gives an even larger effect than applying a shear rate of 10 s^{-1} for 10 s despite this being a larger strain. This difference in effect could be due to the fact that when shearing for longer time, even though the same strain is applied, the material might be able to partially relax during the application of the shear. This is in accordance with the observations of Bai et al. [9], who also found more influence of shear rate than shear time when looking into the crystallisation for plain PLLA/PDLA mixtures with different PLLA/PDLA ratios.



(a) 0wt% PMMA strain comparison

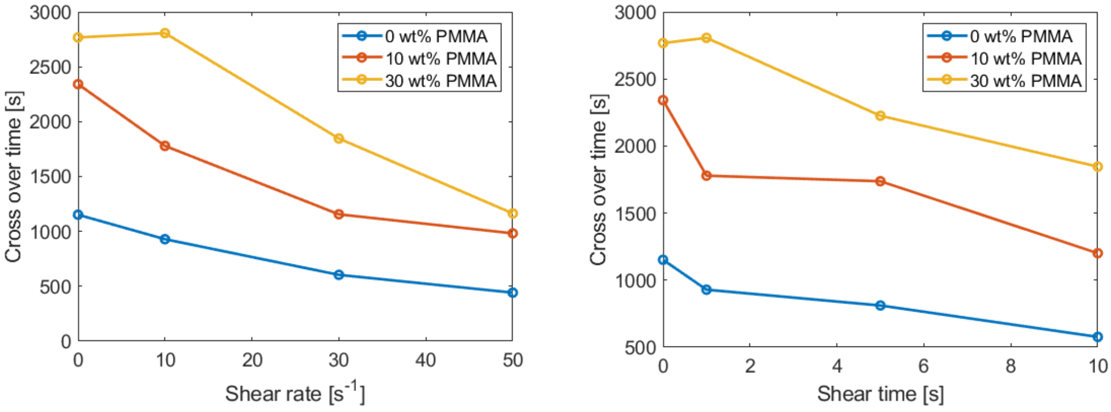
(b) 10wt% PMMA strain comparison



(c) 30wt% PMMA strain comparison

Figure 4.21: G' comparison between an applied shear with a shear rate of 30 s^{-1} for 1 s and an applied shear with a shear rate of 10 s^{-1} for 10 s during isothermal crystallisation at 160°C.

The cross over times between G' and G" have been plotted versus shear rate and shear time for different PMMA contents to get a better idea of how the addition of PMMA influences the shear effect during crystallisation, this can be seen in Figure 4.22. From these graphs it can be seen that the addition of PMMA increases the cross over time, as already concluded from previous results above as well as from the DSC experiments, where with increasing PMMA amount the $t_{1/2}$ also increased. Another interesting conclusion which can be drawn is that with increasing shear rate the influence of PMMA seems to become less, whereas for a varying shear time the PMMA influence seems to stay more or less constant.

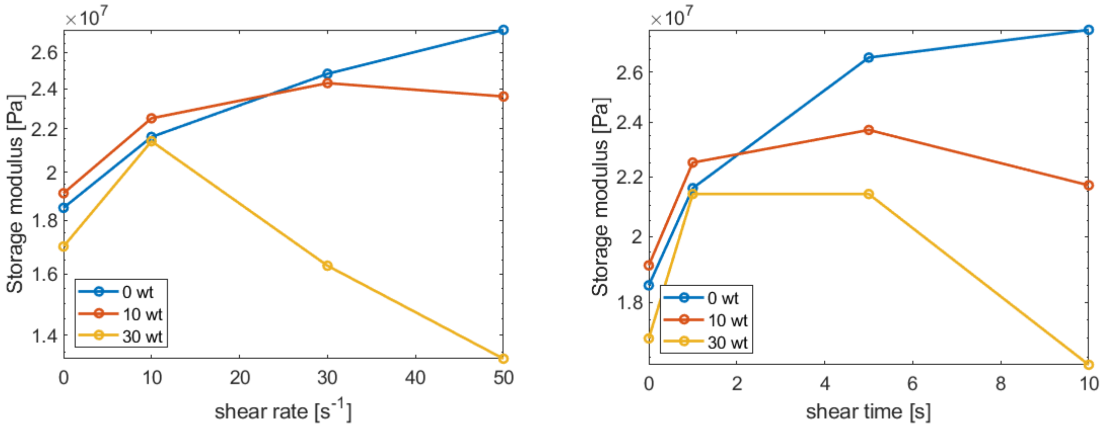


(a) Fixed shear time of 1 s

(b) Fixed shear rate of 10 s^{-1}

Figure 4.22: Cross over times of G' and G" for varying shear rates and times of a 1:1 PLLA/PDLA mixture containing different wt% of PMMA during isothermal crystallisation at 160°C.

In order to determine the effect of the applied shear and the PMMA content on the overall crystallinity in a quantitative manner, the value of G' at a temperature of 160°C is plotted against the shear rate and shear time for all the different PMMA contents in Figures 4.23. These graphs show that adding PMMA lowers the maximum G' for shear rates above 10 s^{-1} and shear times above 1 s. This effect becomes larger for increasing shear rate or shear time. This lower maximum G' could be due to either a lower overall crystallinity of the material, since the PMMA limits the HC formation, or it could be due to the fact that the chains are more oriented and thus have fewer cross links, since more cross linking also increases G' [23]. The fact that the drop becomes larger with increasing shear and the fact that the results for the overall crystallisation from the DSC tests in Figure 4.4a show a lower overall crystallisation when the values are not normalised to the amount of PLA, it is likely that this drop comes from a combination of both the chains being more oriented and a lower overall crystallisation. The fact that the effect of the shear on this drop is enhanced by the addition of PMMA might also indicate that the addition of PMMA has a positive effect on the chain orientation.

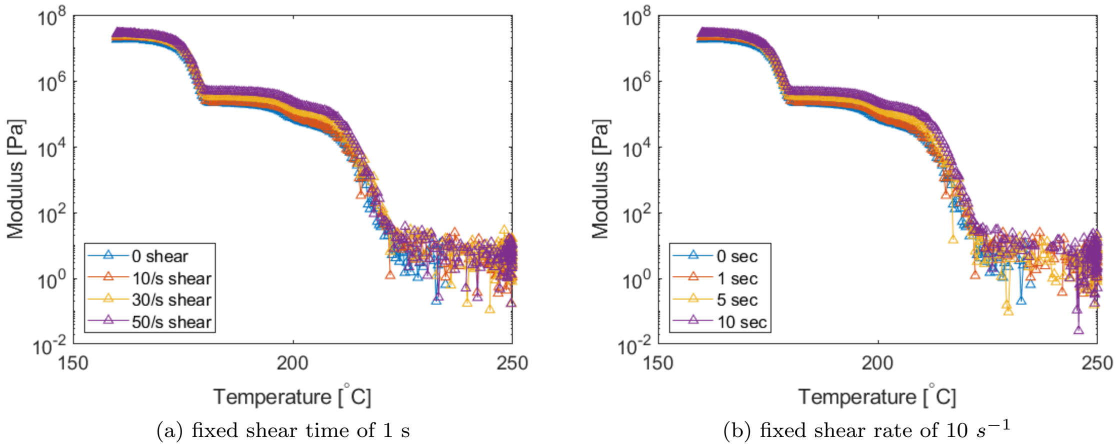


(a) G' of fully crystallised sample versus shear rate

(b) G' of fully crystallised sample versus shear time

Figure 4.23: G' at the end of crystallisation versus shear rate and shear time of a 1:1 PLLA/PDLA mixture containing different wt% of PMMA after isothermal crystallisation at 160°C. Different shear rates and shear times where applied at the start of crystallisation.

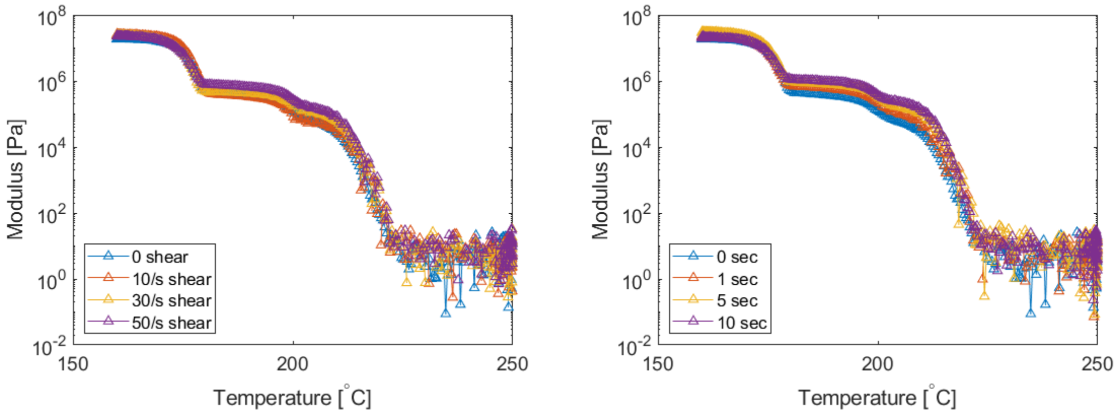
To get more insight in the crystallinity of the sample after crystallisation an oscillatory time sweep was performed during the melting of the samples after crystallisation, as discussed in the previous chapter. The results of these experiments can be found in Figures 4.24, 4.25, and 4.26. In general, a rapid increase or decrease in G' indicates the nucleation and growth of crystals or the melting of crystals respectively. This is caused by the fact that a semi-crystalline polymer can be considered as a suspension of particles in an amorphous polymer matrix [9, 14]. In the results of Figures 4.24, 4.25, and 4.26 the drop between the first and second plateau is at a temperature of around 180°C, this is the melting of the HC crystals which lowers G'. When comparing this drop for the different PMMA contents it is clearly visible that with increasing amount of PMMA the drop becomes significantly smaller. This leads to the conclusion that with increasing PMMA amount the HC crystallinity decreases. The next drop can be seen for the temperature range of 215-230°C, this is the melting of the SC crystals. Here it can be seen that this drop becomes larger with increasing PMMA content, indicating an increase in SC crystallinity for increasing PMMA content. Since the HC crystals melt first the plateau visible between 180-200°C is an indication for the SC crystallinity in the sample after crystallisation. A higher G' in this plateau indicates a higher SC content. Looking at this plateau in the graphs shows that with increasing shear rate and shear time the SC content increases. This is in accordance with the literature as Song et al. [28, 29] also observed an increase in SC content for increasing shear rates in PLLA/PDLA mixtures without PMMA, and Bai et al. [9] also found that both an increase in shear rate and shear time resulted in a higher SC crystallinity in PLLA/PDLA mixtures with different PLLA/PDLA ratios.



(a) fixed shear time of 1 s

(b) fixed shear rate of 10 s^{-1}

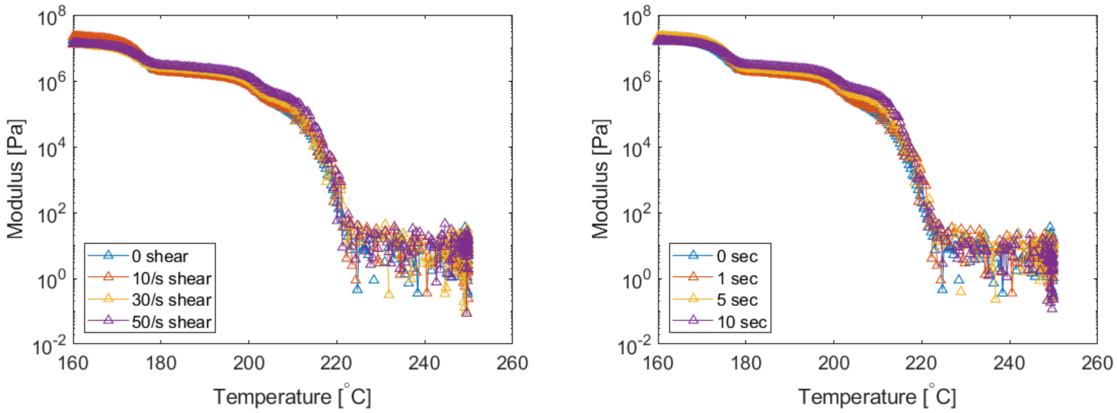
Figure 4.24: G' during melting of a 1:1 PLLA/PDLA mixture after isothermal crystallisation at 160°C. Different shear rates and times where applied at the start of crystallisation.



(a) fixed shear time of 1s

(b) fixed shear rate of $10s^{-1}$

Figure 4.25: G' during melting of a 1:1 PLLA/PDLA mixture containing 10wt% of PMMA after isothermal crystallisation at 160°C. Different shear rates and times where applied at the start of crystallisation.



(a) fixed shear time of 1s

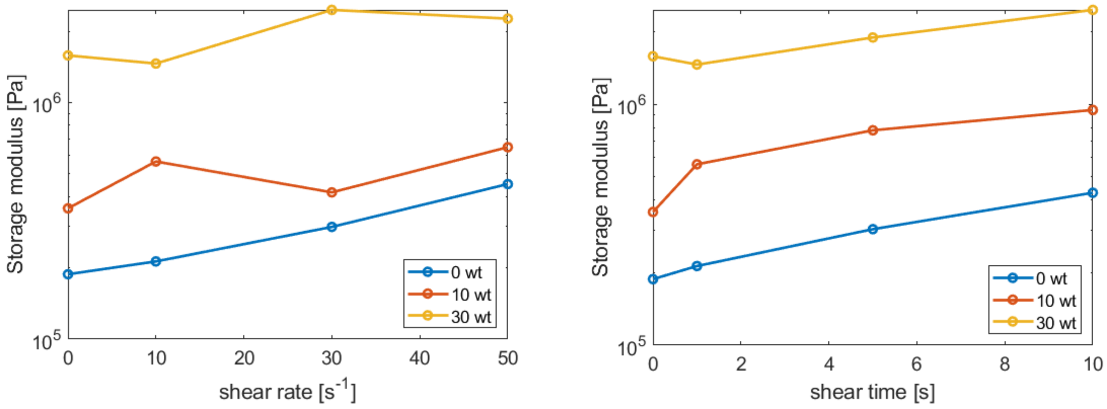
(b) fixed shear rate of $10s^{-1}$

Figure 4.26: G' during melting of a 1:1 PLLA/PDLA mixture containing 30 wt% of PMMA after isothermal crystallisation at 160°C. Different shear rates and times where applied at the start of crystallisation.

In order to determine the effect of the PMMA content on the SC crystallinity in a quantitative manner, the value of G' at a temperature of 190°C is plotted against the shear rate and shear time for all the different PMMA contents in Figure 4.27. These graphs show that both increasing the PMMA content and increasing the shear rate or shear time leads to a higher G'. This higher G' could indicate both a higher SC crystallinity or the chains are less oriented leading to more cross links and thus a higher G' [23]. It is most likely that for increasing shear rate and time the increase in G' is due to a higher SC crystallinity, since with increasing shear the chains become more oriented instead of less. However since G' is not directly proportional to the SC crystallinity, the relative modulus is calculated as:

$$G'_{rel} = \frac{G'_{190}}{G'_{160}} \tag{4.3}$$

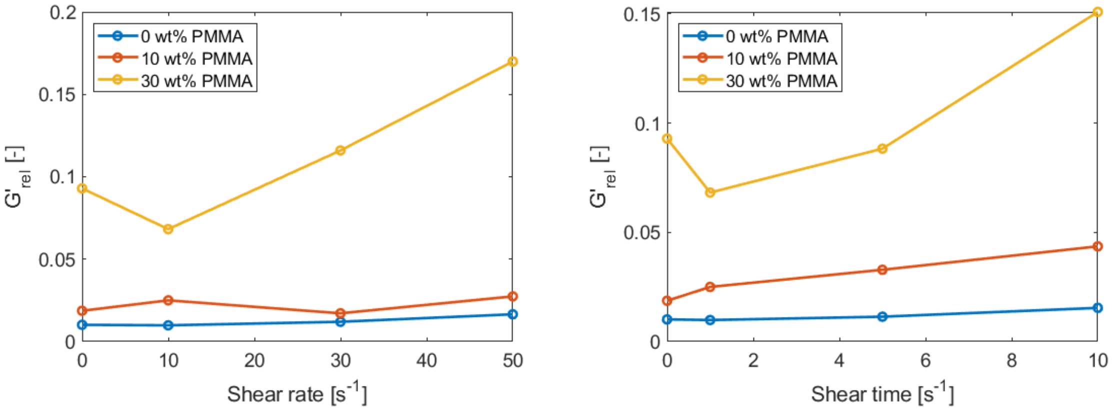
where G'_{rel} is the relative storage modulus, G'_{160} is G' at a temperature of 160°C, and G'_{190} is the G' at a temperature of 190°C. This relative G' gives a better indication of the SC crystallinity of the samples after crystallisation. Figure 4.28 shows the relative G' plotted against the shear rate and shear time for all the different PMMA contents. Figure 4.28 shows that the addition of PMMA increases the SC crystallinity significantly, where the higher the amount of PMMA the higher the SC content after crystallisation. In the case where a shear rate of 50 s^{-1} is applied for 1 s adding 30wt% PMMA increases the SC crystallinity by 10 times. Furthermore Figure 4.28 also shows that the SC crystallinity increases with increasing applied shear. This is due to the shear induced crystallisation as explained in Chapter 2, and is in accordance with the observations found by Bai et al. [9] and Song et al. [28, 29] for PLLA/PDLA mixtures without PMMA. It also seems that the effects of PMMA and shear enhance each other, since with increasing shear the effect of the PMMA on the SC crystallinity increases. These observations lead to the conclusion that applying shear and adding PMMA might lower the overall crystallinity but definitely enhances the SC crystallinity.



(a) G' of SC only versus shear rate

(b) G' of SC only versus shear time

Figure 4.27: G' during melting at a temperature 190°C versus shear rate and shear time of a 1:1 PLLA/PDLA mixture containing different wt% of PMMA after isothermal crystallisation at 160°C. Different shear rates and shear times where applied at the start of crystallisation.



(a) G'_{rel} versus shear rate

(b) G'_{rel} versus. shear time

Figure 4.28: Relative G' versus shear rate and shear time of a 1:1 PLLA/PDLA mixture containing different wt% of PMMA after isothermal crystallisation at 160°C. Different shear rates and shear times where applied at the start of crystallisation.

Conclusions and recommendations

5.1 Conclusions

The goal of this research was to investigate how SC crystallisation in PLLA/PDLA mixtures can be optimized using PMMA and shear. To gain more insight in how the crystallisation process and temperature, PMMA content and applied shear affect the crystallisation of SC-PLA, systematic fundamental research is done on these aspects both separately and combined.

First the influence of both temperature and PMMA content on the quiescent crystallisation of 1:1 PLLA/PDLA mixtures was tested making use of DSC tests. One set of tests, looking into the isothermal melt crystallisation, showed that with increasing crystallisation temperature and increasing amount of PMMA the HC crystallinity decreases and the SC crystallinity increases. This is due to the fact that PMMA suppresses HC crystallisation. For an isothermal crystallisation temperature of 150°C and higher the SC crystallites are likely to start forming a network. Furthermore an optimal PMMA content for the highest overall crystallisation is determined to be in the range of 30 to 40 wt% PMMA. With regards to the crystallisation kinetics the crystallisation time increases with increasing temperature and PMMA content. Furthermore in the isothermal crystallisation temperature range of 120-140°C an asymmetric exothermal crystallisation peak is present, meaning that in this range the material experiences a primary and secondary crystallisation.

Next the influence of both temperature and PMMA content on recrystallisation from HC to SC has been tested using DSC. A second isothermal recrystallisation step was applied in a temperature range between the melting temperatures of HC and SC crystallites after the first isothermal crystallisation step. These tests lead to the conclusion that both pure α-HC crystals and pure α'-HC crystals recrystallise easier for higher recrystallisation temperatures. When a mixture of both α-HC and α'-HC are present a lower recrystallisation temperature leads to the highest SC crystallinity. Furthermore for higher recrystallisation temperatures PMMA obstructs the recrystallisation from α'-HC crystals to SC crystals, while increasing the recrystallisation from α-HC crystals to SC crystals. Lastly with increasing recrystallisation temperature the recrystallisation either starts later or is slower, as is the case for regular isothermal crystallisation.

Lastly rheometry tests to look into the combined effect of flow-induced crystallisation and PMMA were performed. These tests showed that flow-induced crystallisation also occurs for these materials. With either increasing shear rate or increasing shear time the crystallisation starts significantly sooner and happens faster. However with increasing amount of PMMA the crystallisation takes longer, even when flow-induced crystallisation occurs. Furthermore it can also be seen that with a higher strain, or PMMA content the crystallisation starts to separate into two crystallisation phases. This could indicate that after crystallisation of the material the crystals start to form a network [9, 33], or it could mean that the crystallites start to impinge with each other and their growth could then be related to the subsidiary lamellae or to the thickening of lamellae [21]. The shear seems to mostly effect the primary crystallisation. Another interesting conclusion is that with increasing shear rate the influence of PMMA on the crystallisation time becomes less. For a varying shear time the influence of PMMA on the crystallisation time stays constant. Furthermore some conclusions with regards to the crystallinity of the material are that with increasing PMMA amount the HC crystallinity decreases and the SC crystallinity increases. For increasing strain the SC crystallinity also increases. One example is that for a shear rate of 50 s^{-1} applied for 1 s adding 30wt% PMMA increases the SC crystallinity by 10 times. Lastly the effects of PMMA and shear enhance each other with regards to SC crystallinity, since with increasing shear the effect of PMMA on the SC crystallinity increases.

5.2 Recommendations

This report has shown that both adding PMMA and applying shear increase the SC crystallinity of 1:1 PLLA/PDLA mixtures, and that the effects of both even enhance each other with regards to SC crystallinity. However this has only been proven under certain conditions, more research is needed to gain more insights into how PMMA and shear influence each other in other conditions. It would also be beneficial to gain more insight into the effects observed in this research.

First it would be interesting to see if the results found for the combined effects of PMMA and shear on the SC crystallinity are also found for different crystallisation temperatures. This could be done by applying the same temperature and shear protocol as described in this thesis for lower crystallisation temperatures, but instead of trying to follow the crystallisation using an oscillatory time sweep the sample could be analysed with WAXD after crystallisation to gain information on the SC and HC crystallinity.

Next it would also be interesting to see if applying shear would influence the recrystallisation of HC crystals to SC crystals. This could be done by applying shear before the initial crystallisation and use a rheometer for the initial crystallisation and then put the samples in the oven at a higher temperature for the recrystallisation. Afterwards the samples can be analysed using WAXD to again gain information on the SC and HC crystallinity.

Next, in this thesis it has not been investigated whether the effects seen during crystallisation are affecting the crystal nucleation or growth. This could also give more insights into what happens inside the material during processing. A way to investigate this would be with the use of polarised optical microscopy (POM). Applying the same crystallisation protocols as used in this research while looking at the material using POM shows exactly how the crystals nucleate and grow under specific crystallisation conditions. This could give information on the difference between the primary and secondary crystallisation as observed during this research.

Lastly it would be interesting to find out why repeating the same DSC test on the same sample while removing the thermal history in between does not give consistent results. This could be investigated by using POM and rheometry. With POM it can be checked if during the heating step to erase of the thermal history any crystallites still remain which could cause the observed effect. Rheometry can be used to monitor G', G" and the complex viscosity during the entire procedure. If any of these values changes when the tests are repeated after erasing the thermal history this could give an indication for the cause of the observed effect.

Bibliography

[1] A. Jalali, S. Shahbikian et al. “Effect of molecular weight on the shear-induced crystallization of poly(lactic acid)”. *Polymer* 112 (2017), 393–401. DOI: `http://dx.doi.org/10.1016/j.polymer.2017.02.017`.

[2] C. Samuel, J. Cayuela et al. “Stereocomplexation of Polylactide Enhanced by Poly(methyl methacrylate): Improved Processability and Thermomechanical Properties of Stereocomplexable Polylactide-Based Materials”. *ASC Applied materials and interfaces* 5 (22) (2013), 11797–11807. DOI: `https://doi.org/10.1021/am403443m.`.

[3] C. Samuel, J. Raquez et al. “PLLA/PMMA blends: A shear-induced miscibility with tunable morphologies and properties?” *Polymer* 54 (15) (2013), 3931–3939. DOI: `https://doi.org/10.1016/j.polymer.2013.05.021`.

[4] G. Eder, H. Janeschitz-Kriegl et al. “Theory of shear-induced crystallization of polymer melts”. *Colloid Polymer Science* 226 (1988), 1087–1094. DOI: `https://doi.org/10.1007/BF01414398`.

[5] H Tsuji, S. H. Hyon, Y. Ikada. “Stereocomplex Formation between Enantiomeric Poly(lactic-acid)s. 3. Calorimetric Studies on Blend Films Cast from Dilute Solution”. *Macromolecules* 24 (20) (1991), 5651–5656. DOI: `https://doi.org/10.1021/ma00020a026`.

[6] H Tsuji, Y. Ikada. “Stereocomplex formation between enantiomeric poly(lactic acids). 9. Stereocomplexation from the melt”. *Macromolecules* 26 (25) (1993), 6918–6926. DOI: `https://doi.org/10.1021/ma00077a032`.

[7] H. Bai, S. Deng et al. “Recent Advances in Processing of Stereocomplex-Type Polylactide”. *Macromolecular Rapid Communications* 38 (23) (2017), 1700454 (1–12). DOI: `https://doi.org/10.1002/marc.201700454`.

[8] H. Tsuji, S.Noda et al. “Configurational Molecular Glue: One Optically Active Polymer Attracts Two Oppositely Configured Optically Active Polymers”. *Scientific reports* 7 (2017), 45170 (1–12). DOI: `https://doi.org/10.1038/srep45170`.

[9] J. Bai, J. Wang et al. “Stereocomplex Crystallite-Assisted Shear-Induced Crystallization Kinetics at a High Temperature for Asymmetric Biodegradable PLLA/PDLA Blends”. *ASC Sustainable Chemistry and Engineering* 4 (1) (2016), 273–283. DOI: `https://doi.org/10.1021/acssuschemeng.5b01110`.

[10] J. Bofill. *Development Solutions: Big plans to cut microplastics*. July 2020. URL: `https://www.eib.org/en/essays/plastic-pollution#`.

[11] J. Wang, J.Bai et al. “Shear-induced enhancements of crystallization kinetics and morphological transformation for long chain branched polylactides with different branching degrees”. *Scientific reporter* 6 (2016), 26560 (1–13). DOI: `https://doi.org/10.1038/srep26560`.

[12] J. Zhang, K. Tashiro et al. “Disorder-to-Order Phase Transition and Multiple Melting Behavior of Poly(L-lactide) Investigated by Simultaneous Measurements of WAXD and DSC”. *Macromolecules* 41 (4) (2008), 1352–1357. DOI: `https://doi.org/10.1021/ma0706071`.

[13] J.W. Cahn. “Transformation kinetics during continuous cooling”. *Acta Metallurgica* 4 (6) (1956), 572–575. DOI: `https://doi.org/10.1016/0001-6160(56)90158-4`.

[14] K. Boutahar, C. Carrot et al. “Crystallization of Polyolefins from Rheological Measurements - Relation between the Transformed Fraction and the Dynamic Moduli”. *Macromolecules* 31 (6) (1998), 1921–1929. DOI: `https://doi.org/10.1021/ma9710592`.

[15] L. Xie, H. Xu et al. “Structural Hierarchy and Polymorphic Transformation in Shear-Induced Shish-Kebab of Stereocomplex Poly(Lactic Acid)”. *Macromolecular Rapid Communications* 37 (9) (2016), 745–751. DOI: `https://doi.org/10.1002/marc.201500736.`.

[16] M. Avrami. “Kinetics of Phase Change. II Transformation-Time Relations for Random Distribution of Nuclei”. *J. Chem. Phys.* 8 (2) (1940), 212–224. DOI: `https://doi.org/10.1063/1.1750631`.

[17] Q. Dong, Y.Bian et al. “Miscibility and crystallization behaviours of stereocomplex-type poly(L- and D-lactide)/poly(methyl methacrylate) blends”. *Journal of Thermal Analysis and Calorimetry* 118 (2014), 359–367. DOI: `https://doi.org/10.1007/s10973-014-3966-1`.

[18] R. Ahmed. “Poly(lactic acid) stereocomplex formation in the melt :limitations and prospectives”. *Technische Universiteit Eindhoven* (2011). DOI: `https://doi.org/10.6100/IR719381`.

[19] R. auras, L. Lim et al. *Poly(Lactic Acid): Synthesis, Structures, Properties, Processing, and Applications.* John Wiley Sons, 2010.

[20] R. Y. Bao, W. Yang et al. “Polymorphism of a high-molecular-weight racemic poly(L-lactide)/poly(D-lactide) blend: effect of melt blending with poly(methyl methacrylate)”. *RSC Advances* 5 (25) (2015), 19058–19066. DOI: `https://doi.org/10.1039/C5RA00691K`.

[21] R. Y. Bao, W. Yang et al. “Polymorphism of Racemic Poly(L-lactide)/Poly(D-lactide) Blend: Effect of Melt and Cold Crystallization”. *The journal of physical chemistry B* 117 (13) (2013), 3667–3674. DOI: `https://doi.org/10.1021/jp311878f`.

[22] S. Saeidloua, M. A. Huneaulta et al. “Evidence of a dual network/spherulitic crystalline morphology in PLA stereocomplexes”. *Polymer* 53 (25) (2012), 5816–5824. DOI: `https://doi.org/10.1016/j.polymer.2012.10.030`.

[23] S.F. Edwards, H. Tanko et al. “Dynamic mechanical response of polymer networks”. *The journal of Chemical Physics* 113 (13) (2000), 2–18. DOI: `https://doi.org/10.1063/1.1290134`.

[24] S.Vleeshouwers, H.E.H. Meijer. “A rheological study of shear induced crystallization”. *Rheologica Acta* 35 (1996), 391–399. DOI: `https://doi.org/10.1007/BF00368990`.

[25] T.-Y. Cho, G. Strobl. “Temperature dependent variations in the lamellar structure of poly(L-lactide)”. *Polymer* 47 (4) (2006), 1036–1043. DOI: `https://doi.org/10.1016/j.polymer.2005.12.027`.

[26] H Tsuji. “Poly(lactide) Stereocomplexes: Formation, Structure,Properties, Degradation, and Applications”. *Macromolecular bioscience* 5 (7) (2005), 569–597. DOI: `https://doi.org/10.1002/mabi.200500062`.

[27] Y. Igushi, S. Akasaka S. Asai. “Formation of PLA stereocomplex crystals during melt-blending of asymmetric PLLA/PDLA/PMMA blends of varying miscibility”. *Polymer journal* 52 (2020), 225–235. DOI: `https://doi.org/10.1038/s41428-019-0256-6`.

[28] Y. Song, X. Zhang et al. “Crystallization of equimolar poly(L-lactide)/poly(D-lactide) blend below the melting point of a crystals under shear”. *European Polymer Journal* 75 (2015), 93–103. DOI: `https://doi.org/10.1016/j.eurpolymj.2015.12.001`.

[29] Y. Song, X. Zhang et al. “Enhancement of stereocomplex formation in poly(L-lactide)/poly(D-lactide) mixture by shear”. *Polymer* 72 (2015), 185–192. DOI: `http://dx.doi.org/10.1016/j.polymer.2015.07.023`.

[30] Y. Yin, G. Liu et al. “Formation of stereocomplex in enantiomeric poly(lactide)s via recrystallization of homocrystals: An in-situ X-ray scattering study”. *European Polymer Journal* 82 (2016), 46–56. DOI: `https://doi.org/10.1016/j.eurpolymj.2016.05.033`.

[31] *Your tap water may contain plastic, researchers warn (Update).* Apr. 2017. URL: `https://phys.org/news/2017-09-plastic.html`.

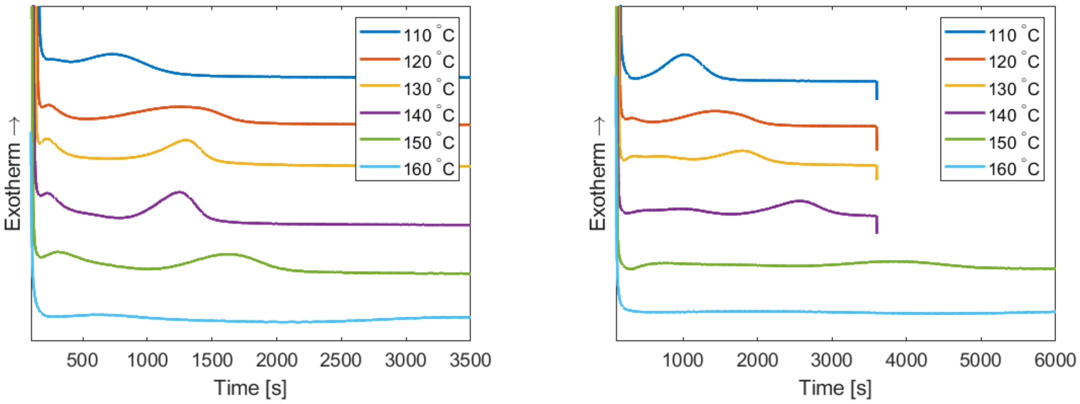
[32] Z. Xiong, G. Liu et al. “Temperature dependence of crystalline transition of highly-oriented poly(L-lactide)/poly(D-lactide) blend: In-situ synchrotron X-ray scattering study”. *Polymer* 54 (2) (2013), 964–971. DOI: `https://doi.org/10.1016/j.polymer.2012.11.076`.

[33] Z. Zhang, Z.Sang et al. "Enhanced Heat Deflection Resistance via Shear Flow-Induced Stereocomplex Crystallization of Polylactide Systems". *ASC Sustainable Chemistry and Engineering* 5 (2) (2017), 1692–1703. DOI: `https://doi.org/10.1021/acssuschemeng.6b02438`.

A.1 Additional results

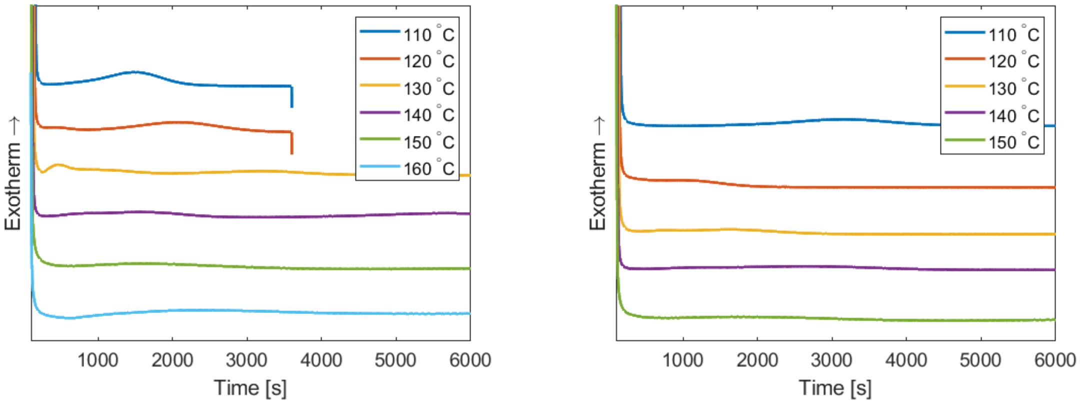
DSC results

Crystallisation curves



(a) crystallisation curves for 10wt

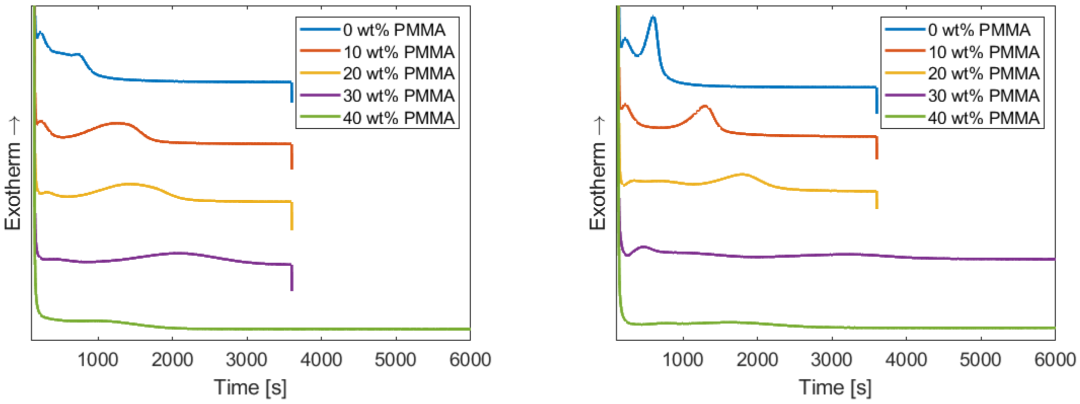
(b) crystallisation curves for 20wt



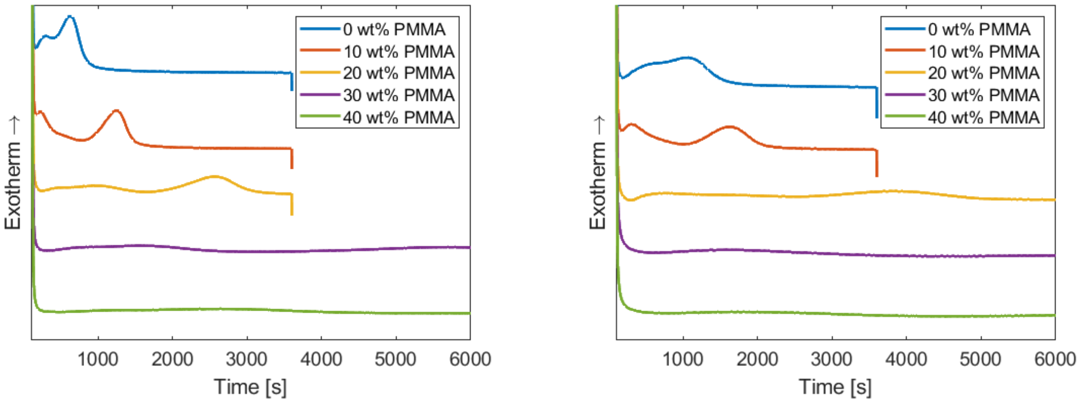
(c) crystallisation curves for 30wt

(d) crystallisation curves for 40wt

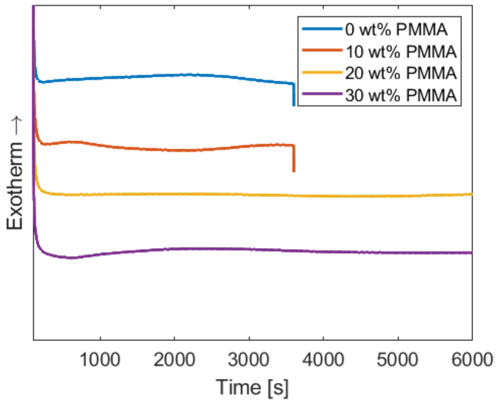
Figure A.1: Crystallisation curves of a 1:1 PLLA/PDLA mixture containing different wt% PMMA, after crystallisation at different temperatures. Shown per wt% PMMA.



(a) crystallisation curves crystallised at 120° (b) crystallisation curves crystallised at 130°



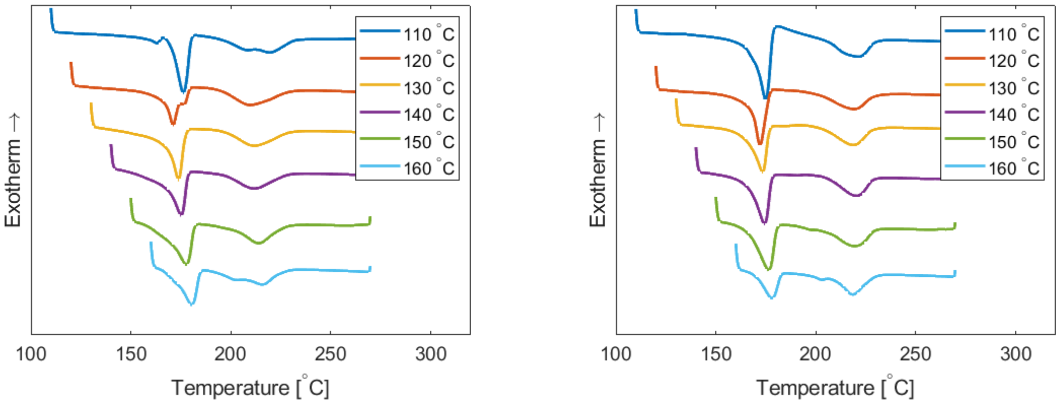
(c) crystallisation curves crystallised at 140° (d) crystallisation curves crystallised at 150°



(e) crystallisation curves crystallised at 160°

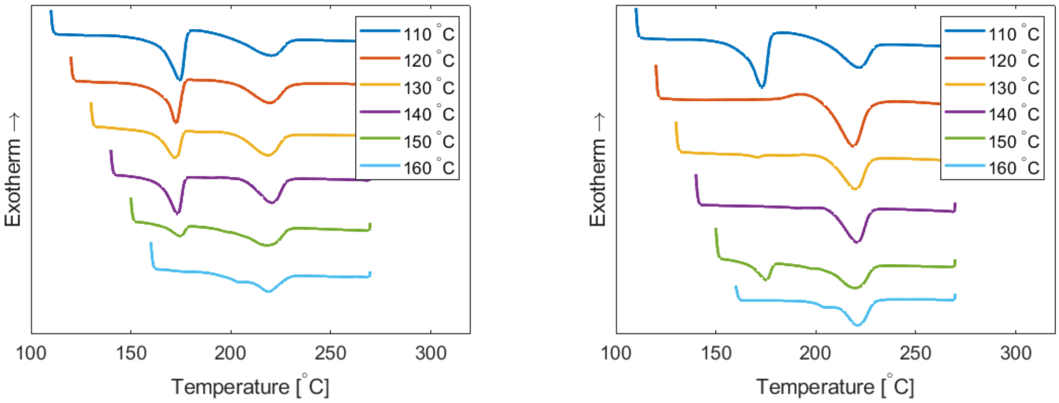
Figure A.2: Crystallisation curves of a 1:1 PLLA/PDLA mixture containing different wt% PMMA, after crystallisation at different temperatures. Shown per crystallisation temperature.

Melting curves



(a) melting curves for 0wt

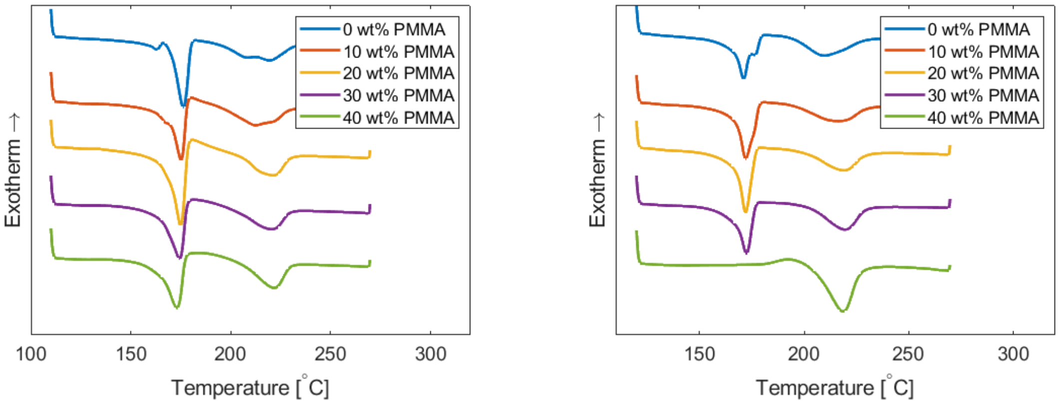
(b) melting curves for 20wt



(c) melting curves for 30wt

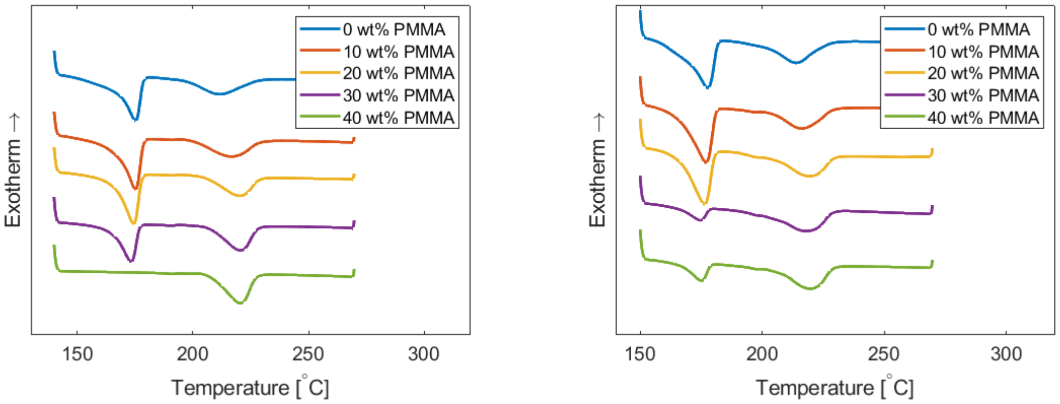
(d) melting curves for 40wt

Figure A.3: Melting curves of a 1:1 PLLA/PDLA mixture containing different wt% PMMA, after crystallisation at different temperatures. Shown per wt% PMMA.



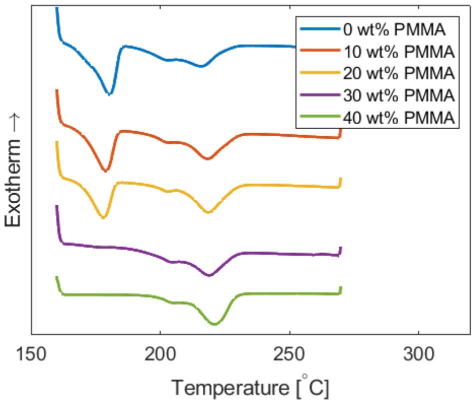
(a) melting curves crystallised at 110°

(b) melting curves crystallised at 120°



(c) melting curves crystallised at 140°

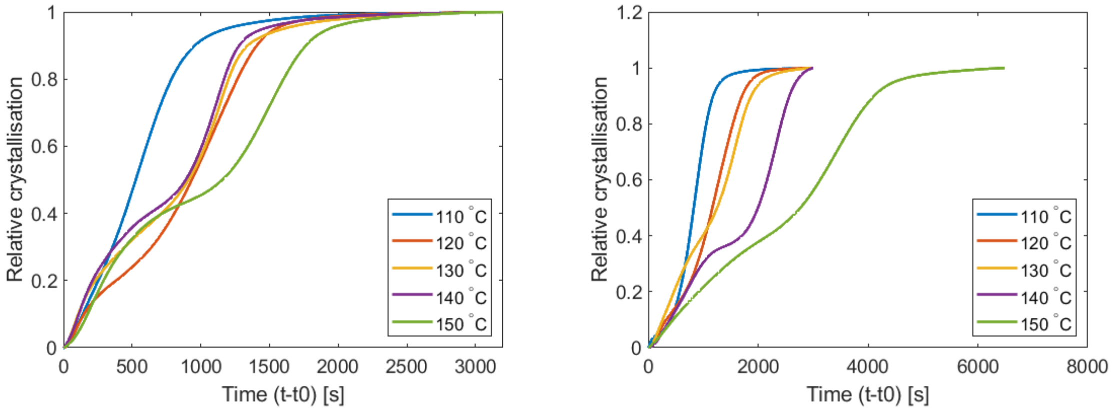
(d) melting curves crystallised at 150°



(e) melting curves crystallised at 160°

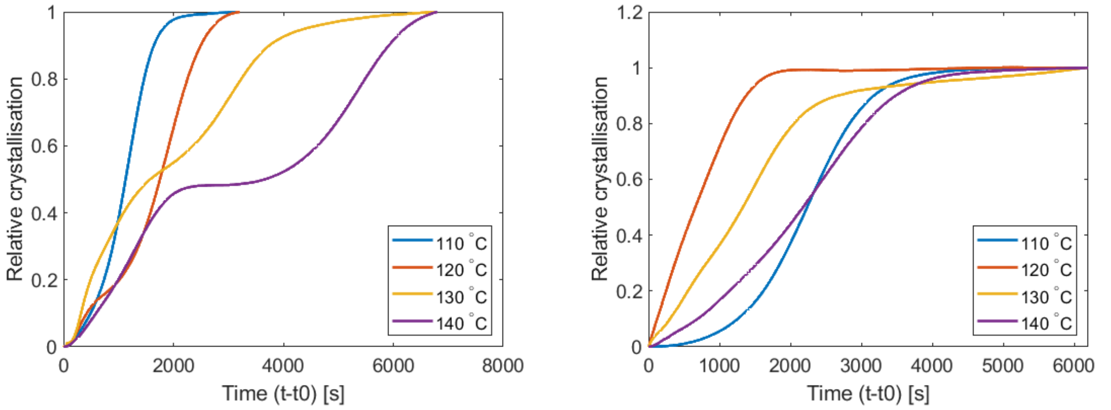
Figure A.4: Melting curves of a 1:1 PLLA/PDLA mixture containing different wt% PMMA, after crystallisation at different temperatures. Shown per crystallisation temperature.

Relative crystallisation



(a) Relative crystallisation for 10wt

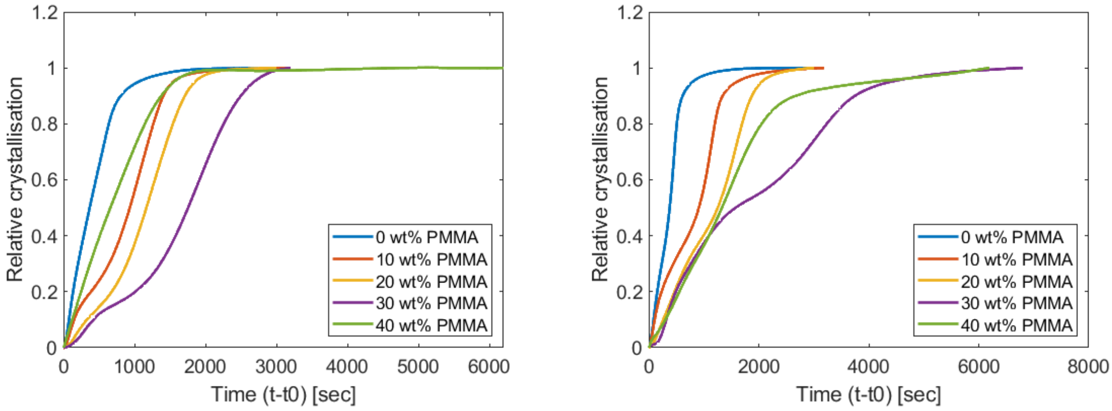
(b) Relative crystallisation for 20wt



(c) Relative crystallisation for 30wt

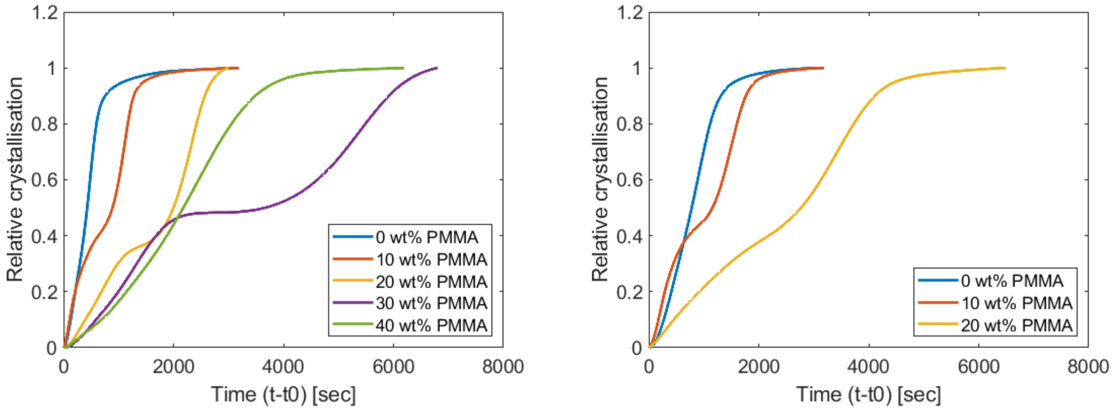
(d) Relative crystallisation for 40wt

Figure A.5: Relative crystallisation of a 1:1 PLLA/PDLA mixture containing different wt% PMMA, after crystallisation at different temperatures. Shown per wt% PMMA.



(a) Relative crystallisation crystallised at 120°

(b) Relative crystallisation crystallised at 130°

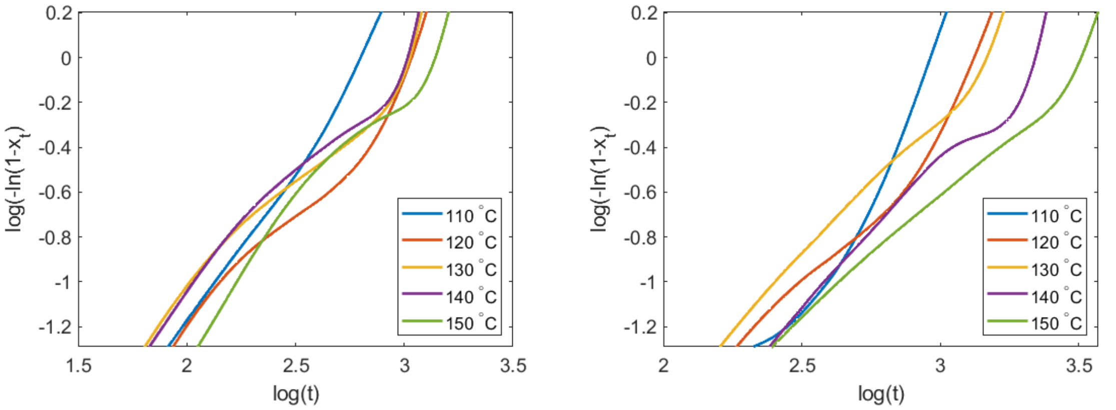


(c) Relative crystallisation crystallised at 140°

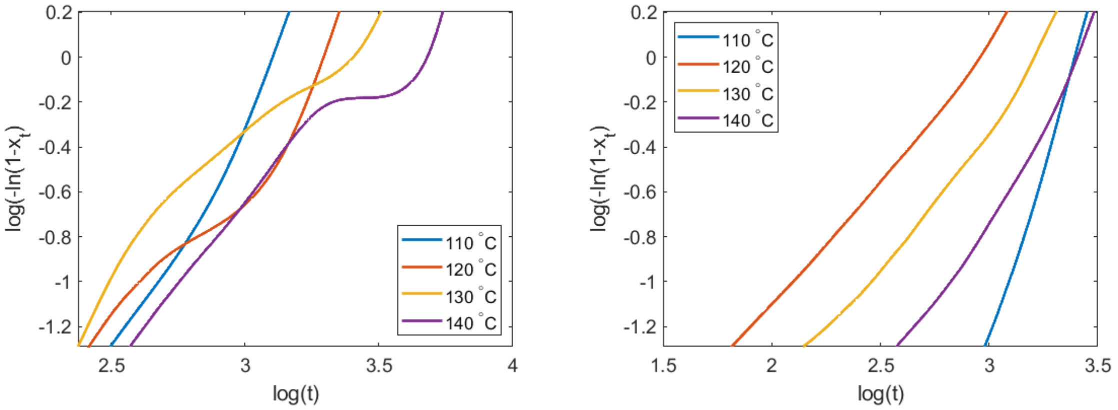
(d) Relative crystallisation crystallised at 150°

Figure A.6: Relative crystallisation of a 1:1 PLLA/PDLA mixture containing different wt% PMMA, after crystallisation at different temperatures. Shown per crystallisation temperature.

Avrami plots

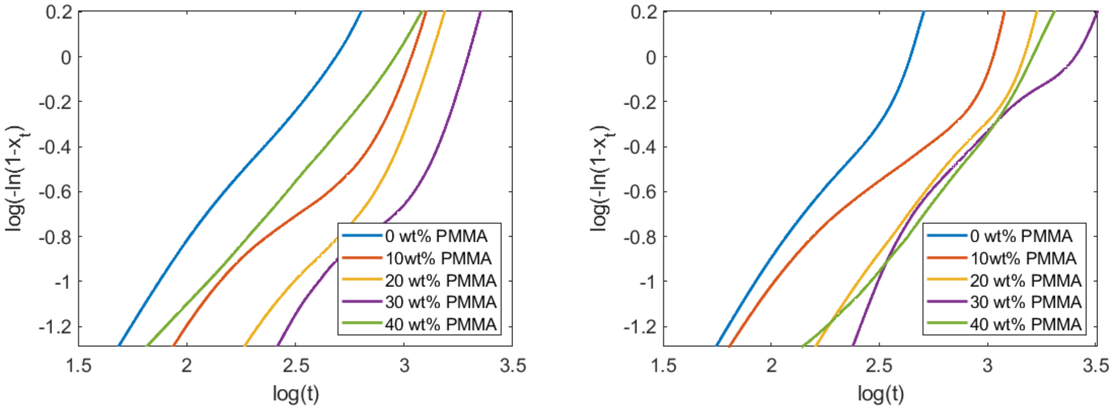


(a) Avrami plots for 10wt (b) Avrami plots for 20wt



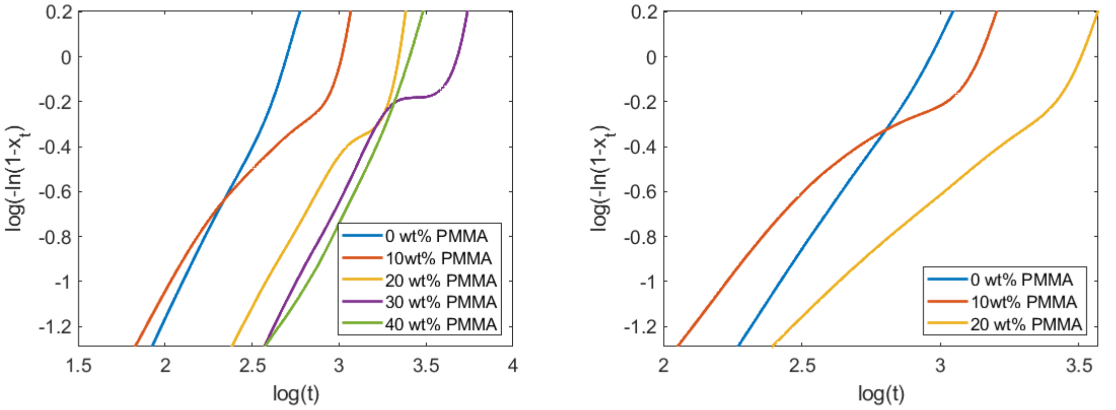
(c) Avrami plots for 30wt (d) Avrami plots for 40wt

Figure A.7: Avrami plots of a 1:1 PLLA/PDLA mixture containing different wt% PMMA, after crystallisation at different temperatures. Shown per wt% PMMA.



(a) Avrami plots for crystallisation at 120°

(b) Avrami plots for crystallisation at 130°

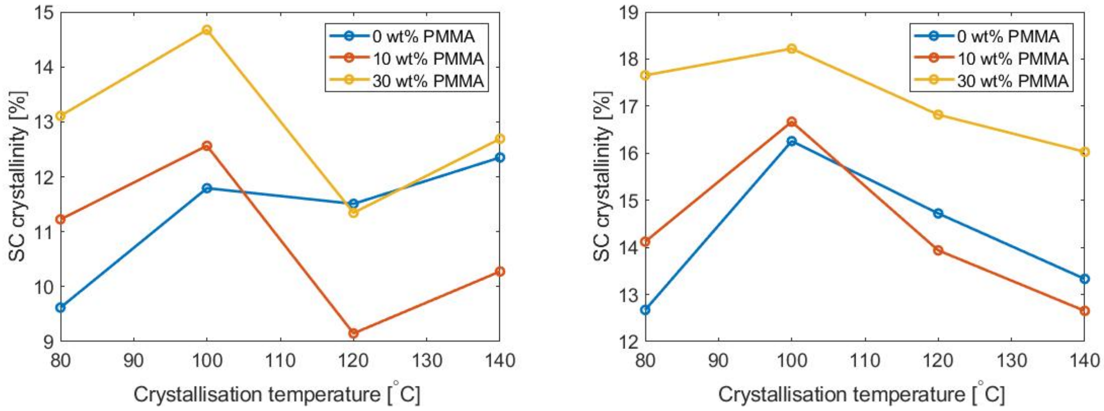


(c) Avrami plots for crystallisation at 140°

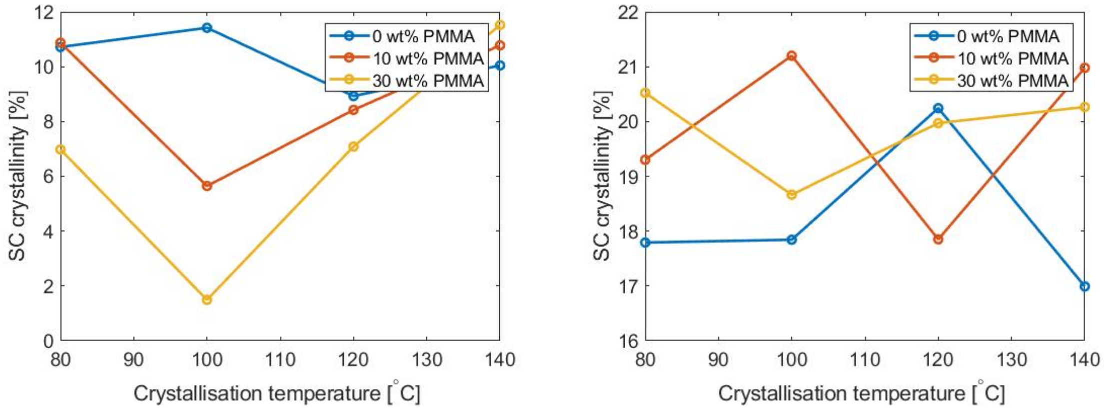
(d) Avrami plots for crystallisation at 150°

Figure A.8: Avrami plots of a 1:1 PLLA/PDLA mixture containing different wt% PMMA, after crystallisation at different temperatures. Shown per crystallisation temperature.

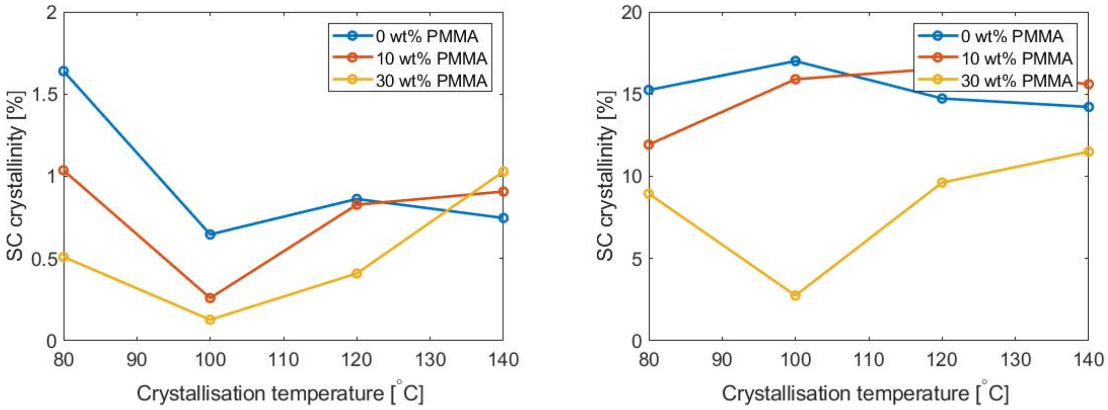
Recrystallisation results



(a) recrystallises at 190°C for 1 min (b) recrystallises at 190°C for 30 min

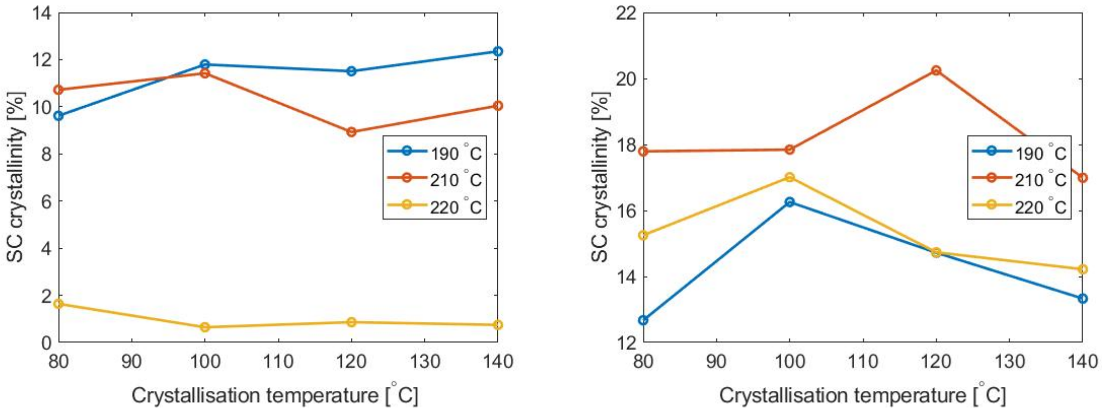


(c) recrystallises at 210°C for 1 min (d) recrystallises at 210°C for 30 min



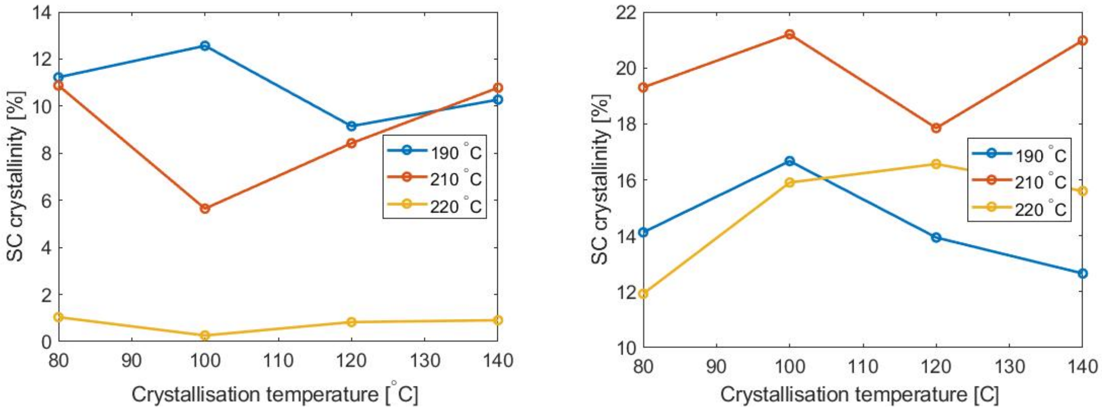
(e) recrystallises at 220°C for 1 min (f) recrystallises at 220°C for 30 min

Figure A.9: Crystallinity of a 1:1 PLLA/PDLA mixture containing different wt% PMMA, after crystallisation and recrystallisation at different temperatures. Shown per recrystallisation temperature.



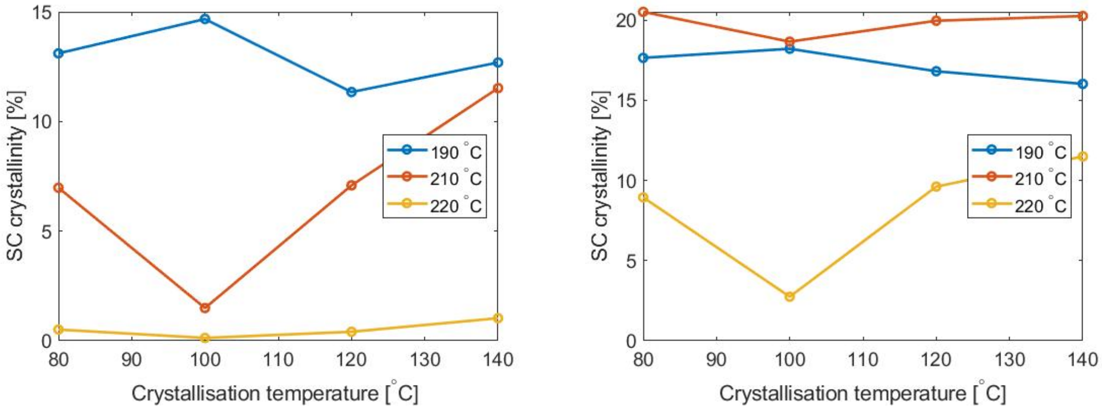
(a) 0wt% PMMA recrystallises for 1 min

(b) 0wt% PMMA recrystallises for 30 min



(c) 10wt% PMMA recrystallises for 1 min

(d) 10wt% PMMA recrystallises for 30 min



(e) 30wt% PMMA recrystallises for 1 min

(f) 30wt% PMMA recrystallises for 30 min

Figure A.10: Crystallinity of a 1:1 PLLA/PDLA mixture containing different wt% PMMA, after crystallisation and recrystallisation at different temperatures. Shown per wt% PMMA.

B.1 Preparation phase report

Department of Mechanical Engineering, Polymer technology research group

Stereocomplexation of poly(L-lactide)/poly(D-lactide) powders: Exploring their application potential for laser sintering.

Preperation phase report

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0854765

Supervisors:
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Dr. Ir. Ruth M. Cardinaels
Hamid Ahmadi, MSc.

Eindhoven, October 19, 2020

Contents

Introduction

1.1 Background and motivation

Polylactic acid (PLA) is biodegradable, compostable, producible from renewable resources, and nontoxic to the human body and the environment [20] . All these qualities make that it has gained a lot of interest over the past few decades. Especially with the environmental issues happening at the moment it would be of great help if PLA could replace more widely used polymers which put a strain on the environment [5].

PLA is currently almost exclusively used for short-time commodity applications. This is because PLA has a poor heat resistance, a low melting point, and poor hydrolysis stability compared to currently used engineering plastics [5]. A good way to improve these properties in PLA is to utilize stereocomplexation (SC) between enantiomeric poly(l-lactide) (PLLA) and poly(d-lactide) (PDLA). Where as the melting temperature of either pure PLLA or PDLA is approximately 170-180°C, for PLLA/PDLA stereocomplex crystals this is approximately 220-230°C [5, 20]. Besides the higher melting temperature PLLA and PDLA chains have a denser packing together and stronger intermolecular hydrogen bonds and bipolar interactions. This leads to enhanced properties, such as hydrolysis resistance, thermal stability, mechanical strength, and heat resistance, in SC-PLA [5].

To maximally exploit the possibilities of SC-PLA, a lot of research is focussed on producing PLA with a high SC content. Below a certain MW for the PLLA and PDLA only SC crystals can form and the homocrystallisation (HC) of PLLA and PDLA is suppressed [5, 19]. However the commercially available PLLA and PDLA has a Mw above this threshold which is also necessary for good mechanical properties and processability. For high Mw PLLA/PDLA blends there have been quite some studies which succeeded in creating SC-PLA with exclusively SC crystals. Unfortunately most of these processes required very specific, tedious and complicated procedures which makes them not suitable for commercial use [5]. The general focus for SC-PLA research at the moment is to use more widely used production processes to create SC-PLA with high SC content or exclusively SC.

The production process the present study is going to focus on is selective laser sintering (SLS). During SLS a thin layer of powder is spread over the build plate after which a laser scans a specific area to heat the particles above their melting temperature end thus make them sinter together. After one layer is finished, the build plate lowers and a new layer of powder is distributed and the process repeats itself until the entire plastic part is ready [18].

1.2 Problem definition

As stated above regular PLA does not have the best mechanical properties. This study will focus on enhancing these properties by utilizing the formation of SC crystals, specifically for the SLS printing process.

Two different methods to will be used to attempt to enhance SC formation during SLS printing. It is demonstrated in literature that both adding polymethylmethacrylate (PMMA) and applying shear can enhance the formation of SC crystals [2, 6, 12, 14, 15, 16]. To gain more insight in how crystallisation process and temperature, PMMA content and applied shear influence the crystallisation of SC-PLA, systematic fundamental research will be done on these aspects both separately and combined.

To gain more insight in the printability of the PLA, selected combinations of materials and processing steps which have shown to be beneficial for the SC formation will be tested during the SLS printing process.

Lastly, if there are any SLS processes which produce properly printed products, these products will be mechanically tested to quantify if and by how much the mechanical properties are enhanced by optimizing the SC content in PLA.

Literature study

2.1 Main characteristics of stereocomplex crystallisation in PLA

Over the past 2 to 3 decades a lot of research has been done on the topic of renewable and biodegradable polymers. Early on in this research PLA came out as one of the most promising options, since it has a performance that is comparable to that of engineering plastics in regards to mechanical strength and stiffness, processing versatility and relatively low pricing [5]. Ever since it was discovered that SC crystallites could provide a solution for the low melting temperature, poor heat resistance and low hydrolysis stability a lot of different studies have been done on the crystallisation behaviour, crystal structure and properties of SC-PLA.

in 2017, Bai et al. [5] reviewed the current state of the art of processing technologies for SC-PLA based on linear HMW PLAs. According to thermodynamics a 1:1 ratio for PLLA/PDLA is necessary to achieve full SC crystallisation, which is confirmed by multiple studies. However SC crystallites also act as a nucleation agent for HC crystallites. Hence, even though a 1:1 ratio of PLLA/PDLA in theory could contain only SC crystallites, HC and SC crystallistes will most likely coexist in SC-PLA due to HC crystallites having a lower kinetic barrier and SC acting as a nucleation agent for HC crystallites. Both molecular weight (Mw) and fabrication route have shown to be the two most important factors in HC and SC formation. Solution blending and a low Mw seems to be favourable for SC formation. There even is a threshold Mw of 6×10^3 and 4×10^4 g/mol for melt blending and solution blending respectively below which only SC are formed. Unfortunately both values are lower than the Mw of most commercially available PLLA and PDLA. So regardless of the production method when using commercially available PLLA and PDLA there will always be both HC and SC formed when processing these materials. A study of Tsuji et al. [19] also showed that within the range of commercially available PLLA and PDLA there will most likely be no significant difference in SC formation for PLLA/PDLA with equal Mw or different Mw. Based on previous studies it is decided to use equal Mw PLLA/PDLA in a 1:1 ratio for the present study.

The review of Bai et al. [5] had its focus on processing technologies for SC-PLA that are suitable for industrial and commercial use. This is also one of the main goals for this current research. Some production methods that are discussed are solution processing, melt processing, and low temperature sintering. All these methods have their own advantages and difficulties and thereby result in interesting research topics for producing SC-PLA products. However to set some boundaries regarding this study, we will only use melt blending to create the different PLLA/PDLA mixtures and focus on the SLS printing process to produce products.

Bai et al. [5] also discuss several strategies to enhance SC crystallisation during processing, looking at the processing temperature, applying shear or elongational flow, or through the use of additives. These are all topics taken into account in the present study. However to keep the study systematic but also practical and applicable, the focus is on two specific routes to enhance SC crystallisation, namely application of shear and addition of PMMA. These specific topics will be discussed in the upcoming sections.

2.2 Effect of the crystallisation method and temperature on stereocomplex crystallisation

A broad study on the effects of the isothermal crystallisation temperature and the difference between melt and cold crystallisation has been executed by Boa et al. [13]. They looked at the influence of the above parameters on the crystallisation half time and the degree of crystallinity for both HC and SC crystallites. In this study the PLLA/PDLA mixture is solution blended in a 1:1 ratio. Making use of DSC measurements they heated a sample to 270 $°C$ for 2 minutes to erase the thermal history. For melt crystallisation the sample was cooled with a rate of $60°C$/min to the isothermal crystallisation temperature. For cold crystallisation the sample was quenched, after erasing the thermal history, and than heated to the isothermal crystalliastion temperature with a rate of $200°C$/min. For both crystallisation processes they kept the sample at the isothermal crystallisation temperature for one hour. The results of this study are summarized in Table 2.1. Some conclusions can be drawn from Table 2.1. First, cold crystallisation is overall significantly faster than melt crystallisation. Second, cold crystallisation also gives a higher SC content than melt crystallisation, and an overall higher crystallinity except for the temperature range 130-150 $°C$. Furthermore at a temperature of 170 $°C$ and above only SC can be formed, which is due to the fact that this is above the melting temperature of HC. At temperatures of 180 $°C$ and above no more exothermal peaks were observed for melt crystallisation during DSC, so the crystallisation could not be measured, if it even occurred.

Due to the faster crystallisation and the higher SC crystallinity cold crystallisation is favoured over melt crystallisation for creating SC rich products. Unfortunately during SLS printing the particles are molten together and afterwards stay in the powder bed for a certain amount of time at a certain temperature which is comparable to the melt crystallisation process used by Boa et al.[13]. Due to the favourable properties of cold crystallisation, a two-step crystallisation process could bring advantages, or in other words, a post treatment of the SLS printed product may be relevant. This is something which will be tested during the present research. Furthermore it is important to also look into how these results are affected by the addition op PMMA. These results are thus good to refer to during the research but the addition of PMMA could have some unpredicted influences on the crystallisation behaviour of the PLLA/PDLA mixtures which could alter the conclusions drawn above.

Table 2.1: Crystallisation of PLLA/PDLA, in a 1:1 ratio, under different conditions [13].

	Melt			Cold		
T $°C$	$t_{1/2}$ min.	X_{HC} %	X_{SC} %	$t_{1/2}$ min.	X_{HC} %	X_{SC} %
90	9.4	41	0	4.8	42	0
100	4.9	37	2.5	1.8	45	3
110	8.6	32	5	1.4	33	13
120	13.6	28	7.5	1	33	16
130	8.7	31.5	10	1.2	23	12.5
140	10.9	34	9	2.2	26	19
150	23	27	17	6	18	22
160	14.4	3	12	0.97	17.5	20
170	31.9	0	13	1.4	0	27
180	-	-	-	2	0	33
190	-	-	-	3.6	0	35
200	-	-	-	12.2	0	37

2.3 Effect of PMMA on stereocomplex crystallisation

Studies have shown a good miscibility between PMMA and SC-PLA [11], and adding PMMA to PLLA/PDLA mixtures has a positive effect on the formation of SC crystallites [2, 12, 16]. Dong et al. [11] showed good miscibility between PMMA and SC-PLA. Here different wt% of PMMA were solution blended with PLLA/PDLA with a 1:1 ratio. The miscibility and crystallisation behaviour were investigated. In this research Dong et al. observed an increase in glass transition temperature and cold crystallisation temperature with increasing PMMA content. Furthermore a decrease of the melting temperature and equilibrium melting point of SC-PLA was seen when PMMA content increased. All these results are indicators for a good miscibility between PMMA and SC-PLA. In the present study good miscibility between PMMA and SC-PLA is thus assumed, without further research into this topic.

Boa et al. [12] looked at the effects of adding PMMA to a 1:1 ratio PLLA/PDLA material on the SC formation during isothermal melt crystallisation. This was done with DSC experiments in which the samples where heated to 270°C for two minutes, to erase the thermal history, then cooled to the crystallisation temperature at a rate of 50°C/min, and kept at that temperature for one hour. After this procedure the samples were quenched and analysed using WAXD to determine the HC and SC crystallinity. The results are shown in Figure 2.1. What is interesting to see is that different combinations of thermal condition and sample composition can yield the same results. Both 25 wt% PMMA crystallised at 160°C and 50 wt% PMMA crystallised at 120°C result in the same amount of HC and SC crystallites. This is beneficial because it gives more options for printing procedures which can potentially create SC rich materials and products. Another noteworthy observation is that the highest SC content and the highest overall crystallinity come from different conditions. The highest SC content comes from either of the two conditions mentioned above, but the highest overall crystallinity comes from the PLA containing 10 wt% PMMA crystallised at 140°C or 120°C. This might indicate that applying a two step crystallisation protocol as mentioned in the previous section can lead to the recrystallisation from HC to SC crystallites to create SC rich materials. An additional advantage of the different procedures which show potential to reach similar results is the fact that comparable results can be achieved with a lower PMMA content. If less additives are needed the advantages of pure PLA are also less compromised. What stands out most in these results, but has not been mentioned so far, is that the SC content increases with increasing temperature and PMMA content except for PLA with 50 wt% PMMA (above 120°C). This indicates that between the range of 25 and 50 wt% there is most likely an optimal wt%, after which the addition of more PMMA hinders the SC crystallisation at higher temperatures.

Samuel et al. [2] gave more insight in the influence of PMMA within the range of 20-50 wt%, again the ratio of PLLA/PDLA was 1:1. After melt blending the PLLA/PDLA/PMMA for 10 min at 230°C, the samples where tested with DSC. The crystallisation temperature and enthalpy of both the HC and SC crystallites, and the melt temperature of the SC crystallites were determined. This was done by first heating the samples to 230°C at a rate of 10°C/min to erase the thermal history, then cooling to -40°C at a rate of 10°C/min, and then heating again to 230°C at a rate of 10°C/min. The results for the melt temperature of SC crystallites were gathered during the second heating scan, all the other results where from the cooling scan. The results are shown in Table 2.2. There are no results for HC above 20 wt% PMMA, because for this cooling pattern there were no HC crystals found. This is because the addition of PMMA restrains HC formation. This effect has also been reported in PMMA/PLLA blends [3]. For the SC crystallites both the crystallisation temperature and the melt temperature go down with increasing PMMA content. For the enthalpy, which is an indicator for the amount of SC, an increase is seen with increasing PMMA content up to 40 wt%. For PLLA/PDLA with 50 wt% PMMA the enthalpy goes down again which is in accordance with the results from Boa at al. [12] presented above. One note to make regarding these results is that the enthalpy shown here is normalized to the amount of

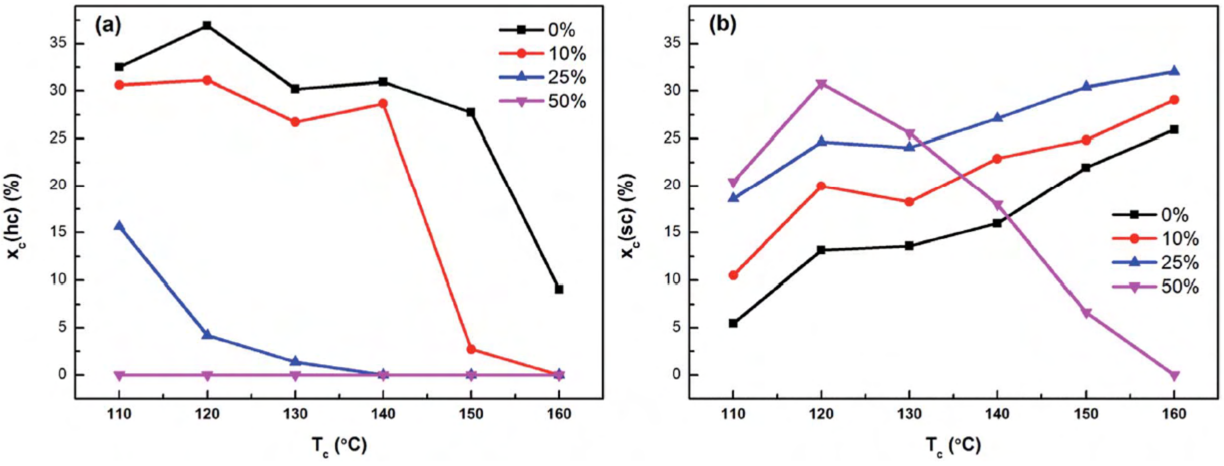


Figure 2.1: HC(a) and SC(b) content of PLA with different wt% PMMA after isothermal melt crystallisation at different temperatures [12].

PLLA/PDLA present in the sample. This means that the absolute amount of SC in the whole sample could be lower even though a higher enthalpy is shown in these results. The absolute values for the enthalpy given in Table 2.2 are not stated in the article [2], but computed using the relative value for the enthalpy and the wt%.

The results of Igushi et al. [16], shown in Table 2.3, give a good visualisation of the difference between the as measured SC content and the SC content normalized to the amount of PLA, for different mixing ratios between PLLA, PDLA and PMMA. The samples used in this research were melt blended at 190°C, next they were compression molded into films again at a temperature of 190°C, afterwards the samples were annealed at 130°C for 1,12 and 24h. The results as shown in Table 2.3 are gathered through DSC tests where the samples wehre heated from 20°C to 255°C with a heating rate of 20°C/min. These results show that with increasing amounts of PMMA the SC formation in the PLA is enhanced. Unfortunately with higher amounts of PMMA the PMMA more or less 'dilutes' the high SC-PLA so the overall material has approximately the same amount of SC as material with a lower PMMA content. The goal is to find an optimum so the overall SC content is as high as possible with the least amount of PMMA added. The utilization of different thermal protocols to enhance the overall SC content, for instance the two step crystallisation mentioned in section 2.2, has not been reported yet in combination with PMMA.

Table 2.2: Effect of PMMA on crystallisation kinetics during cooling for 1:1 PLLA/PDLA [2].

PMMA [wt%]	$T_{c,HC}$ $[°C]$	$\Delta H_{c,HC}$ $[\frac{J}{g_{PLA}}]$	$T_{c,SC}$ $[°C]$	$\Delta H_{c,SC,rel}[\frac{J}{g_{PLA}}]$	$\Delta H_{c,SC,abs}[\frac{J}{g_{PLA}}]$	$T_{m,SC}$ $[°C]$
0	131.9	32	190.3	17	17	220.1
20	103.0	4	183.5	22	17.6	218.4
30			183.3	29	20.3	217.8
40			179.4	34	20.4	216.8
50			165.7	26	13	215.1

Table 2.3: Comparison between measured SC and normalized SC for different ratios PLLA:PDLA:PMMA [16].

(PLLA/PDLA/PMMA) wt%	X_{SC} % As measured	X_{SC} % Normalised
90/10/0	11.4	11.4
70/10/20	12.1	15.1
50/10/40	13.3	22.2
30/10/60	16.0	40.0
80/20/0	22.2	22.2
60/20/20	22.1	27.6
40/20/20	23.5	39.2
20/20/60	23.9	59.8

2.4 Effect of shear on stereocomplex crystallisation

It is a well known phenomenon in polymer science that shear induces crystallisation. So naturally the influence of shear on the SC crystallisation in PLA has been researched already. Bai et al. [6] looked at how shear time, shear rate and PLLA/PDLA ratio affect the SC crystallisation. This was done by solution blending the PLLA/PDLA mixture. During both POM and rheomerty tests the samples were heated too 200°C for 5 mintues to erease thermal history. next the samples where cooled to 160°C with a cooling rate of 30°C/min for the POM tests and 15°C/min for the rheomerty tests. As soon as the samples reached 160°C a step shear was applied at different rates and for different shear times. Afterwards the samples were isothermally crystallized at 160 °C. The shear times were in the range of 0-40 s, the shear rates in the range of 0-20s^{-1}, and the wt% of PDLA ranged from 0 to 10. They found that a longer shear time, higher shear rate, and higher PDLA concentration all resulted in a higher nucleation density. However none of these parameters affected the crystal growth rate. A higher shear rate also shortens the impingement time. A higher wt% PDLA was also responsible for faster crystallisation. For all of the different parameters in these ranges no shish-kebab structures were found during crystallisation.

The effect of shear rate and crystallisation temperature on the crystallisation of both SC and α-HC, was studied by Song et al. [14]. Here 1:1 PLLA/PDLA mixtures were heated to 230°C for 3 min. and then cooled to the crystallisation temperature at a rate of 30°C/min after which a shear pulse was applied for 5s. The shear rates ranged from 0 to 180s^{-1} and the crystallisation temperatures used were 150, 160 and 180°C. In-situ WAXS was used afterwards to determine the crystallisation of the samples, see Figure 2.2 for the results. There are no results for the α-HC crystals at a temperature of 180°C since this is above the melting temperature of HC-crystallites. The results show that for both the overall crystallinity and the SC-crystallinity it holds that the higher the shear rate, the higher the crystallinity, apart from the shear rate of 140s^{-1}. For the overall crystallinity it is also shown that a lower crystallisation temperature results in a higher crystallinity. This is due to the temperature range being in the same range as the melting temperature for HC crystallites. Thus a small increase in temperature can lead to more HC crystallites melting, thereby reducing the overall crystallinity. In the SC graph it is visible that at a crystallisation temperature of 160°C, the shear has more influence on the crystallisation than at a temperature of 180°C. Song et al. [14] also looked at the nucleation density using POM and the half-crystallisation time ($t_{1/2}$) for shear rates in the range of 0-100s^{-1}. The conclusions were that for both SC and HC crystallites the nucleation density increases with increasing shear rate, and $t_{1/2}$ reduces for both a higher shear rate and a lower crystallisation temperature for both HC and SC crystallites.

In another research Song et al. [15] looked at the shear enhanced SC-formation. Here solution blended PLLA/PDLA with a 1:1 ratio were heated to 230°C for 3 minutes to erase the thermal history. Next the sample was cooled at 30°C/min untill the desired shear temperature was reached after which the sample was cooled at 5°C/min to room temperature. The moment the sample reached 2,5°C before the desired shear temperature a shear pulse was applied for 5s. Three different shear rates where tested: 50, 100 and 178 s^{-1}. Both the effect of shear rate and shear temperature on crystallinity have been studied, the results are shown in Figure 2.3 and 2.4 respectively. These results show that crystallisation of SC is greatly enhanced by high shear rates and low shear temperatures, resulting in a higher final SC content after cooling. Figure 2.3 shows that the SC content significantly increases for a shear rate of 178 s^{-1}. However, due to the increased SC content the formation of α-HC is significantly hindered by the restricted mobility of the polymer chains, leading to a comparable overall crystallinity for all shear rates. The same restricted mobility can be seen for low temperature in Figure 2.4. Here the lowest temperature of 150°C has the highest SC content, but also the lowest overall crystallinity due to the limited formation of α-HC.

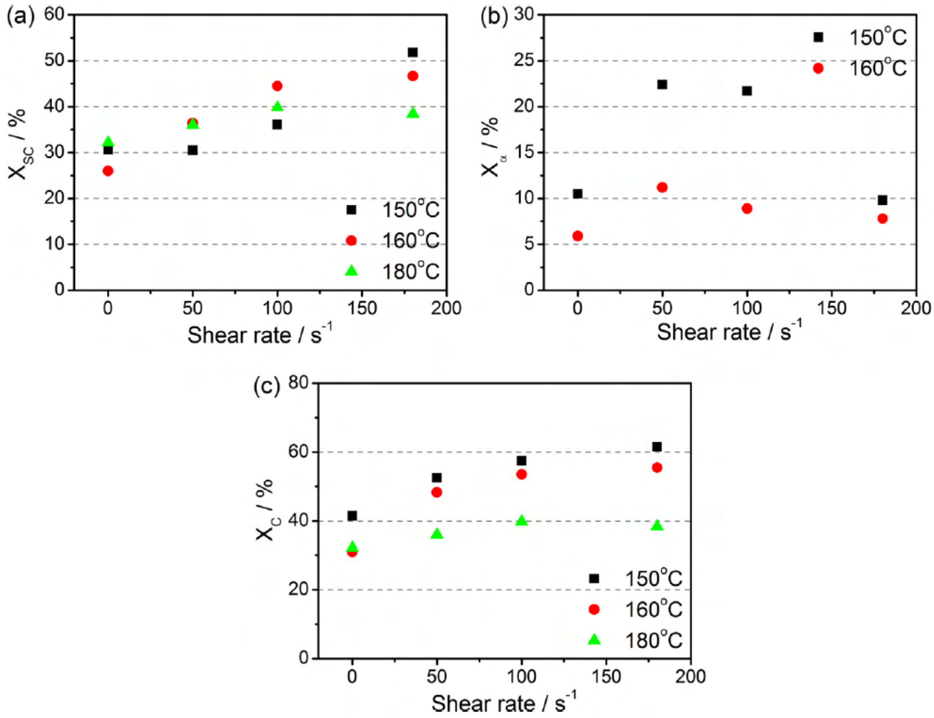


Figure 2.2: The phase contents of SC (a) and α-HC (b) and overall crystallinity (c) of PLLA/PDLA versus shear rate after isothermal crystallisation at different temperatures.[14]

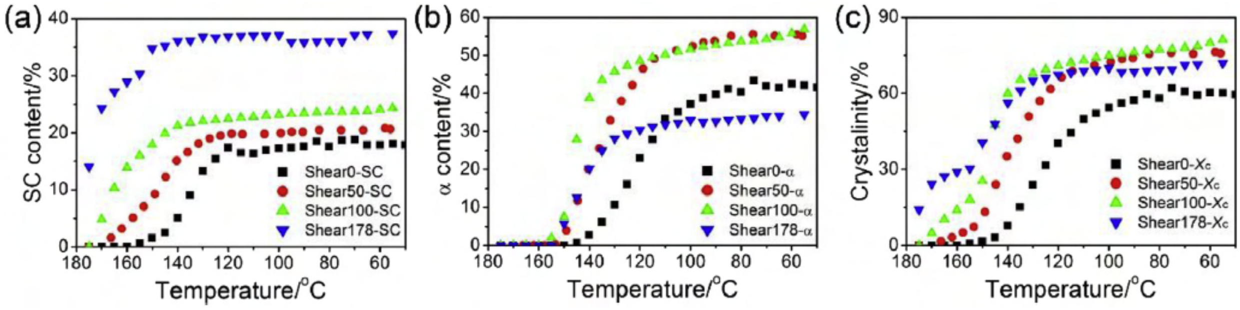


Figure 2.3: The phase contents of SC (a) and α-HC (b) and overall crystallinity (c) of PLLA/PDLA versus temperature during non-isothermal crystallisation after shear at 175°C for different shear rates.[15]

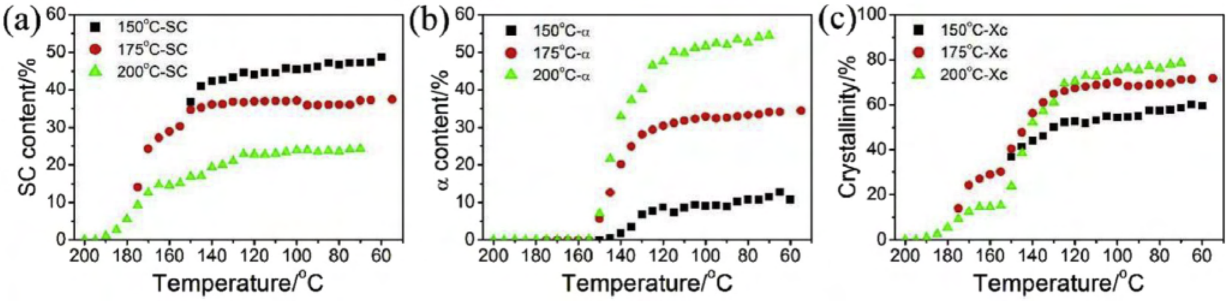


Figure 2.4: The phase contents of SC (a) and α-HC (b) and overall crystallinity (c) of PLLA/PDLA versus temperature during non-isothermal crystallisation after shear with a shear rate of $178s^{-1}$ for different shear temperatures.[15]

Xie et al.[10] looked into the effects of crystallisation temperature on shear induced shish-kebab structures in SC-PLA. The samples used were 1:1 PLLA/PDLA, and were sheared for 1 second with a shear rate of $100s^{-1}$. The shear was applied when the samples reached the crystallisation temperature after being heated to erase the thermal history. The used crystallisation temperatures were 150, 165, and 180°C. For the different temperatures the sizes of the shish, the structural basis of the shish, and the structure of the lamellae were analyzed. The results from this analysis are schematically shown in Figure 2.5. It can be seen that above the melting temperature of HC ($T_{m,HC}$) the lamellae consist out of only SC, whereas below $T_{m,HC}$ the lamellae consist of both HC and SC. Furthermore both the shish itself and the extended chain bundles in the center of the shish have a larger diameter for lower temperatures. There has not been any research done so far on the combined effects of PMMA and shear on the SC crystallisation.

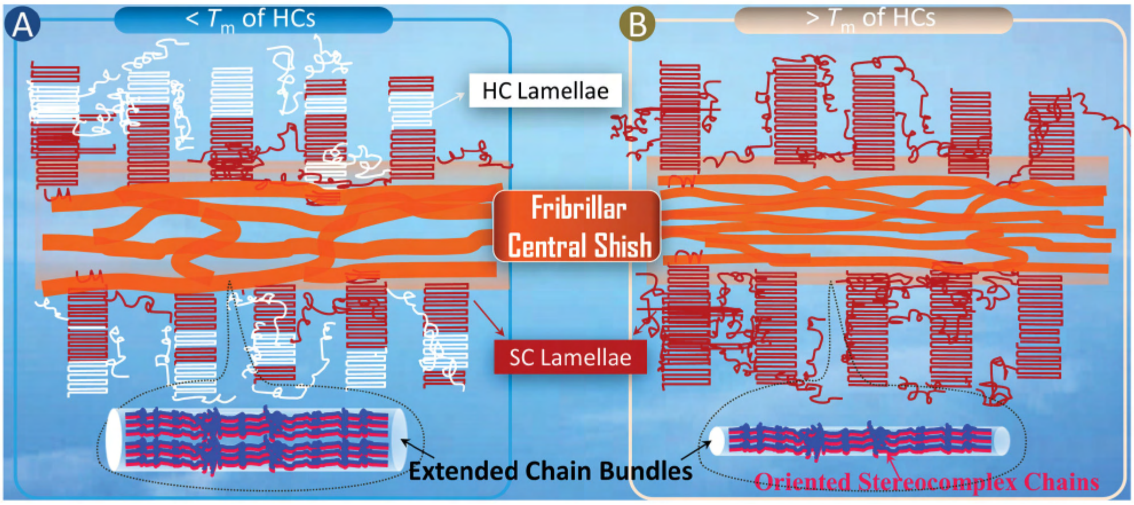


Figure 2.5: Schematic overview of shear induced shish-kebad structure of SC-PLA at different temperatures (shear time: 1s, shear rate:$100s^{-1}$).[10]

2.5 Important parameters and difficulties in selective laser sintering

As previously mentioned in this report it is important to look into processing technologies of SC-PLA which are already used in industry. Additive manufacturing is gaining more and more traction in industry for quite some time now. Van den Eynde et al. [18] published a review on the 3D printing of PLA. For the present research the focus will be on SLS printing.

Van den Eynde et al. [18] gave a set of material properties which are important for SLS printing. These parameters are:

- *Particle size*: The particle size needs to be between 10-80 μm for proper SLS printing. this is due to the fact that the layers have a thickness of approximately 100-150 μm which limits the maximum particle size [9].
- *Powder flow properties*: Good flow properties require low interparticle adhesion and friction. This can be achieved by having particles with a smooth surface and high sphericity. Another option to enhance the flow properties are flow additives, such as small silica particles.
- *Coalescence of molten powder*: To achieve a higher density finished product a good coalescence of the molten powder is necessary. This is largely governed by the zero shear viscosity. The surface tension also plays a role, but there is little possibility to vary this so it can not be used to improve coalescence.
- *Crystallisation and melt temperature*: If too much crystallisation happens during the process shrinkage can occur. To prevent shrinkage it is important to postpone crystallisation. This can be done by having the powderbed temperature above the crystallisation temperature and below the melting temperature. Hence having a larger gap between crystallisation and melting temperature gives a larger processing window.

One of the biggest difficulties in SLS printing of PLA is preventing or minimizing wrapage and stresses. The complex temperature distribution during processing leads to differences in crystallisation and thus non-uniform shrinkage. This non-uniform shrinkage leads to wraped products and stresses in the product. A solution for warpage is to postpone crystallisation by heating and processing the powder just below the melt temperature. However the only step in the process where the material is sheared is when the particles are molten. So to make use of any shear induced crystallisation benefits crystallisation needs to happen as fast as possible after shearing. So postponing crystallisation to avoid non-uniform shrinkage will most likely suppress any shear benefits.

2.6 Conclusion

The sections 2.2, 2.3, and 2.4 show the influence of the crystallisation method, addition of PMMA and application of shear on the SC crystallisation in PLLA/PDLA mixtures. The results showed that these are all methods which can be used to enhance SC-crystallisation. However it is still unclear how these methods influence each other. Hence, the present research will look into combining these methods and look at the influence combining methods has on the SC crystallisation. Furthermore these methods will be implemented in SLS printing, which is also something that has not been researched so far. All of this will be done with the goal to enhance the properties of PLA, by enhancing the SC crystallisation, for a more widely used production process.

Experiments

In this chapter the experimental methods which will be used during the research will be discussed. A short explanation will be given on what measurements will be executed.

3.1 Materials and sample preparation

Equal parts PLLA and PDLA (both with Mw = 115 kg/mol) were melt blended together in a DSM Xplore mini extruder, with various wt% of PMMA (Mw = 19 kg/mol) at a temperature of 240°C and 100 rpm. The addition of the materials took approximately 1.5 min each, after which everything was mixed together for another 8 minutes. Afterwards the materials are compression molded into flat disks, which are used for both rheology and DSC tests. This was done in a Fontijne Holland TP400 table press, first heating the plates and material for 4 minutes without any pressure at a temperature of 230°C. Next with 5 small increments of applying and releasing pressure, the pressure is build up to 50 kN which is then put on the material for 1 minute. The disks made for rheology tests have a diameter of 25 mm and a thickness of 1 mm, the disks for DSC have a diameter of 25 mm and a thickness of 0.5 mm. Before testing the samples are dried at 70°C for a minimum of 2 hours, and afterwards stored in a vacuum oven at 35°C to keep the samples dry.

3.2 Differential scanning calorimetry

Differential scanning calorimetry (DSC) tests will be used for a general thermal analysis of the materials. This will give information such as glass transition temperature, crystallisation temperature, melting temperature, and whether or not HC and SC crystallites are present. DSC results for 1:1 PLLA/PDLA mixtures with 30 and 40 wt% PMMA are shown in Figure 3.1 and Figure 3.2. Here two curves are compared for equal and different molecular weights of PLLA and PDLA, obtained from the initial heating curve after mixing and compression molding. The test was preformed on a Mettler Toledo DSC823^e, and the protocol was a heating curve from 25°C to 270°C with a heating rate of 10°C/min. The results confirm the literature in that there is no significant difference in material behaviour between equal and nonequal Mw for PLLA and PDLA. For both Figures 3.1 and 3.2, the glass transition temperature (T_g), shown by the shift in plateau on the left, is comparable for equal and non equal Mw of both PLA components. In both figures the equal and nonequal Mw PLLA/PDLA mixtures show comparable exothermic crystallisation and endothermic melting peaks. The area inside the peaks can be determined by integration and represents the crystallisation or melting enthalphy ΔH. The higher the absolute value for ΔH, the more crystallites are formed or molten. The melting peaks at 160-180°C and 200-235°C are the melting of the HC and the SC crystallites respectively. The normalized value for ΔH in Figures 3.1 and 3.2 are normalized to the sample weight. The only significant difference between mixtures containing equal and non equal Mw PLAs shown in these results is a slightly higher melting enthalpy for SC crystallites for the equal Mw PLLA/PDLA mixtures, which indicates a slightly higher SC content. This difference is most likely due to the fact that the Mw of the PLLA used for the nonequal Mw samples is higher than the Mw of the PLLA and PDLA of the equal Mw samples, and a lower Mw gives a higher SC content. So even though the Mw of all the samples is within a range that should not show a significant effect according to literature [19], the effect is noticeable. Based on both the literature and these results, the present research will only make use of PLLA en PDLA of equal Mw. The DSC tests will be used to look at the influence of different crystallisation processes and PMMA contents on the crystallinity of the material. For these tests the samples will first be heated to 270°C for two minutes to erase the thermal history. Next the crystallisation method will be applied, and a second heating curve will be done which will be analysed.

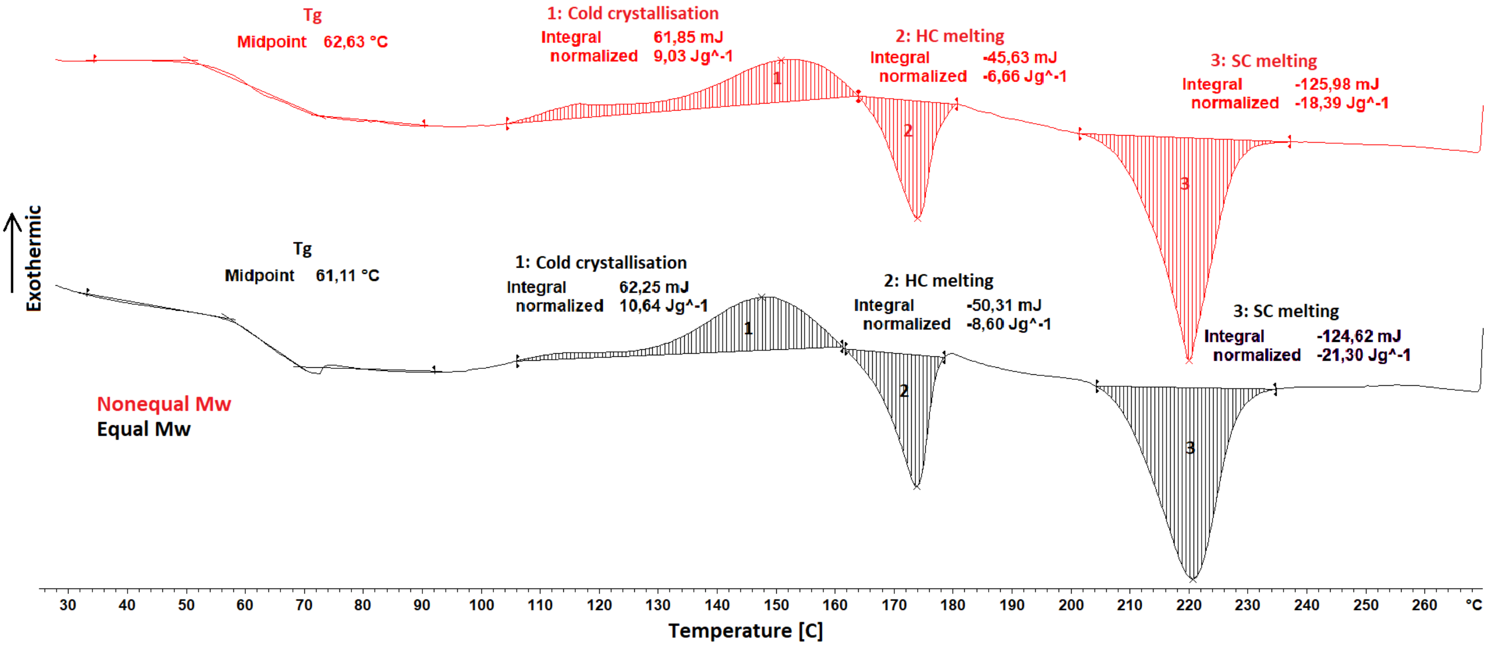


Figure 3.1: Heating curves of DSC tests of Mw 1:1 PLLA/PDLA mixture containing 30 wt% PMMA. Heating rate is 10°C/min. Mw of PDLA for both samples is 115 kg/mol, MW of PLLA for equal Mw sample is 115 kg/mol, for the unequal Mw sample is 210 kg/mol

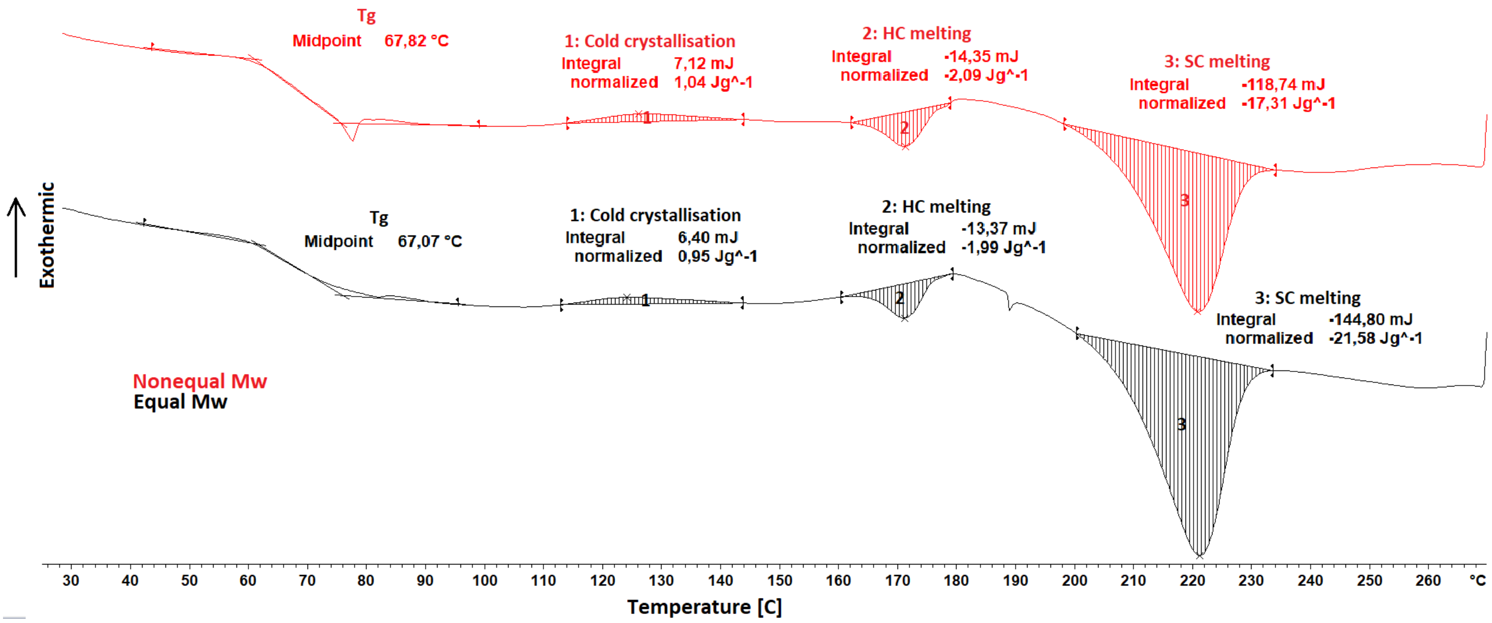
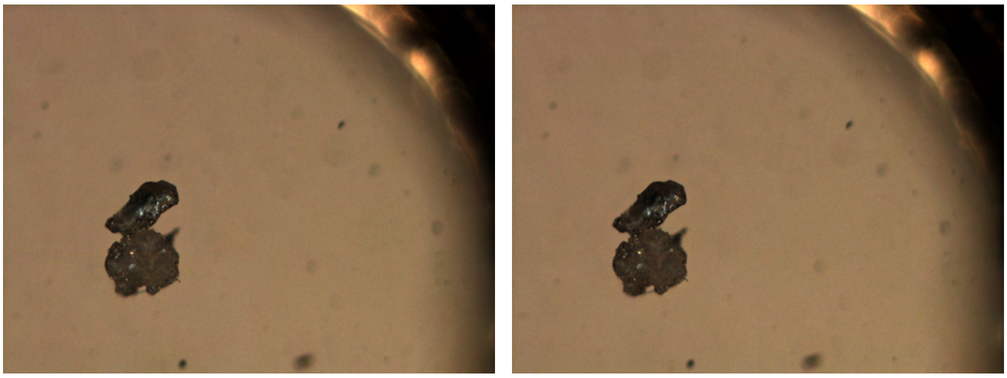


Figure 3.2: Heating curves of DSC tests of Mw 1:1 PLLA/PDLA mixture containing 40 wt% PMMA.Heating rate is 10°C/min. Mw of PDLA for both samples is 115 kg/mol, MW of PLLA for equal Mw sample is 115 kg/mol, for the unequal Mw sample is 210 kg/mol

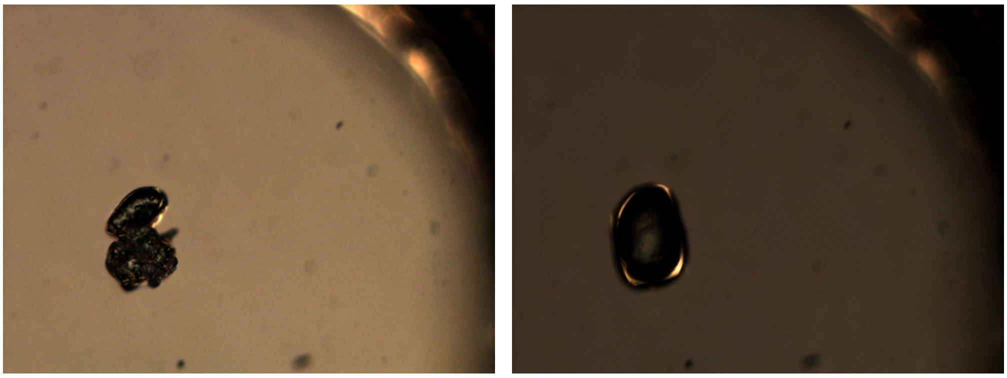
3.3 Polarized optical microscopy

Polarized optical microscopy (POM) can be used to visualize the crystallisation and melting process. One can use this technique to determine nucleation density, crystal growth, impingement time, and general visualization of the crystal structure. Two small preliminary tests have been executed. The first test was done to generate a visualisation of what happens when two particles melt together. This was done using microscopy, on a Olympus BX51 microscope and an objective of 5x. For this test two particles of a 1:1 PLLA/PDLA mixture of equal molecular weight and 40 wt% PMMA are put next to each other on a heating stage and then the temperature is raised at a rate of 5°C/min until the two particles are molten together. A few images at different temperatures are shown in Figure 3.3. It can be seen that at a temperature of 225°C the particles start to melt and at 230°C they are fully fused together. This is a good indication for the required temperature during the SLS process. In the second test the crystal structure during isothermal melt crystallisation at 140°C of 1:1 PLLA/PDLA mixture of equal molecular weight PLA containing 30 wt% PMMA has been made visible, as shown in Figure 3.4, here the same Olympus BX51 microscope is used with an objective of 20x. These results are obtained after first heating the sample to 270°C to erase thermal history, next the sample was cooled to 140°C with a cooling rate of 30°C/min. The first picture is taken as soon as the sample reached the isothermal crystallisation temperature. The crystallites show up in blue. Here it can be seen that during the first 10 minutes of crystallisation both nucleation and crystal growth occur, while after 10 minutes it is mostly crystal growth which drives the crystallisation. Using POM it is unfortunately not possible to distinguish a difference between HC and SC crystallites.



(a) 215°C

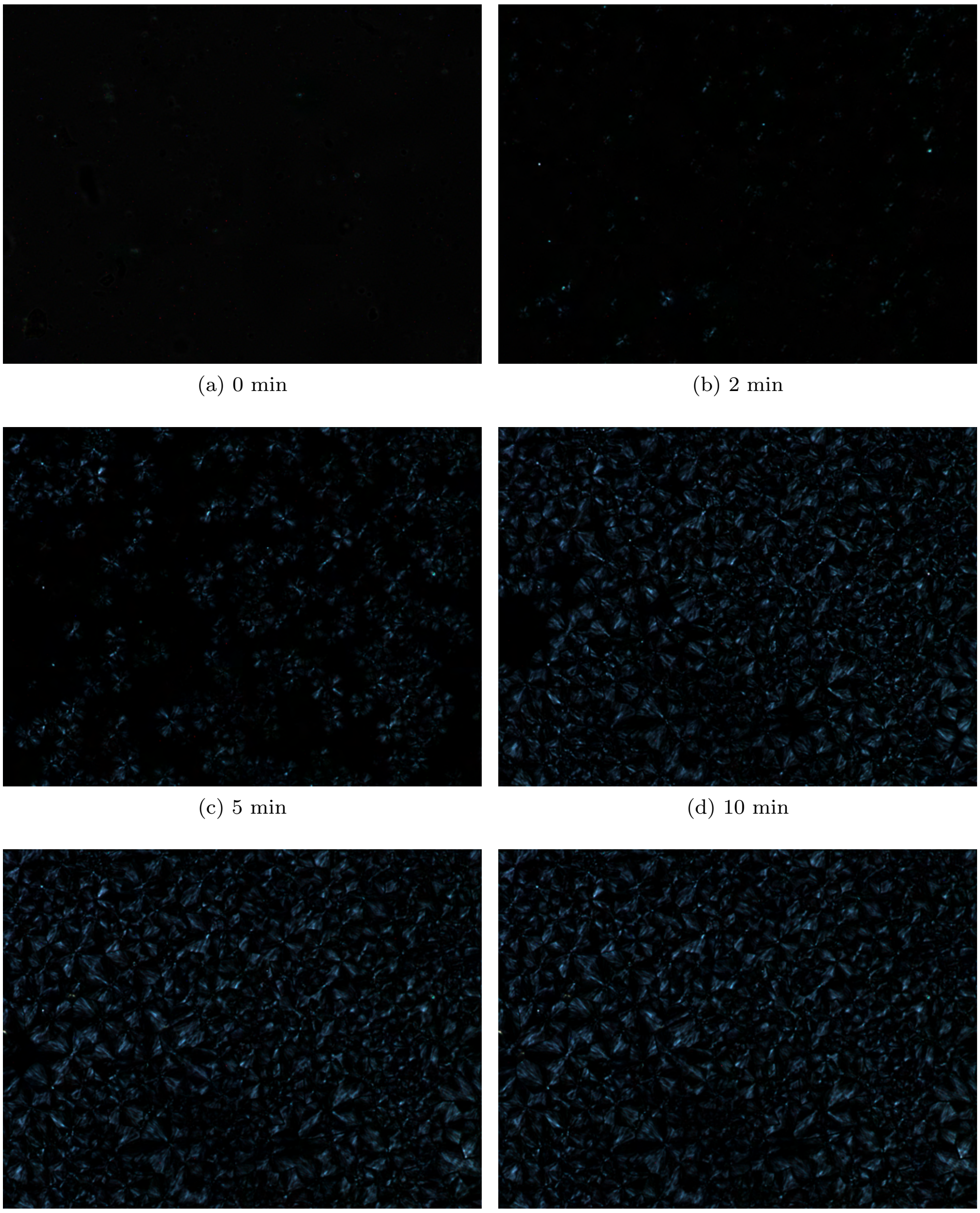
(b) 220°C



(c) 225°C

(d) 230°C

Figure 3.3: Two particles of a 1:1 equal Mw PLLA/PDLA mixture containing 40 wt% PMMA fusing together. Each image is 1.752 mm x 1.314 mm.


(a) 0 min

(b) 2 min

(c) 5 min

(d) 10 min

(e) 15 min

(f) 20 min

Figure 3.4: POM images of isothermal crystallisation at 140°C of a 1:1 equal Mw PLLA/PDLA mixture containing 30 wt% PMMA. Each image is 437.9 μm x 328.4 μm.

3.4 Rheometry

Rotational rheometry will be used to measure the rheological properties, such as the zero shear viscosity, storage modulus (G'), and loss modulus(G"). Furthermore it will be used for measuring the isothermal crystallisation kinetics after application of shear. The measurements of the storage modulus over time can be used to determine the crystallinity over time, and crystallisation half time. Shear induced crystallisation only occurs when polymer chains are orientated due to an applied shear. The chains can only be orientated when the shear rate is fast enough in relation to the relaxation time of the material. if this is not the case the polymer flows upon applying shear instead of being stretched and thus orientated. This relation is expressed by the Weissenberg number:

$$Wi = \frac{elastic \quad forces}{viscous \quad forces} = \dot{\gamma}\tau \tag{3.1}$$

Where $\dot{\gamma}$ is the shear rate and τ the relaxation time. Depending on the definition of the relaxation time the defined Weissenberg number also changes. For shear induced crystallisation two relaxation times and thus Weissenberg numbers are important, namely reptation time (τ_d) and Rouse relaxation time (τ_R). τ_d indicates the time needed for orientated chains to move back to un-oriented chains, τ_R indicates the time needed for stretched chains to become un-stretched again. For any shear induced crystallisation to occur the reptation Weissenberg number (Wi_d) needs to be larger than one. If both Wi_d and the Rouse relaxation Weissenberg number (Wi_R) are above one shish-kebad structures can occur[1, 7]. For the present research any type of shear induced crystallisation is considered so Wi_d and τ_d are used to determine the critical shear rate to observe shear induced crystallisation. The critical shear rate for shear induced crystallisation to occur can be determined using the longest relaxation time. τ_d can be defined as in equation 3.2:

$$\tau_d = \frac{1}{\omega} \tag{3.2}$$

Where ω is the frequency of the intersection point of the tangents of G' and G" in low frequencies. Where the tangent for G' has a slope of 2 and the tangent of G" has a slope of 1. This intersection point can can be determined by a frequency sweep. Combining equation 3.1, 3.2 and the fact that Wi_d needs to be lager than 1, the critical shear rate determined as:

$$\begin{gathered} Wi_d = \dot{\gamma}\tau_d > 1 \\ \tfrac{\dot{\gamma}}{\omega} > 1 \\ \dot{\gamma} > \omega \end{gathered} \tag{3.3}$$

Frequency sweeps have been done for PMMA/PLLA in different ratios and at different temperatures to determine the critical shear rates for these materials and temperatures. For these frequency sweeps the strain was set at 1% and the frequency range was 0.01-100 Hz, the storage modulus, loss modulus and complex viscosity were measured. The storage and loss modulus of 1:9 ratio PMMA/PLLA mixture at 210°C is shown in Figure 3.5. The tangents and their intersection point are also shown in Figures 3.5, this means the critical shear rate for a 1:9 ratio PMMA/PLLA mixture at 210°C is 96 s^{-1}. The storage and loss modulus for a 1:9 ratio PMMA/PLLA mixture at a larger range of temperatures is given in Figure 3.6. Here it can be seen that at low frequencies G' seems to plateau. This is not typical behaviour for a polymer. This could be due to the fact that it is a mixed material and an extra relaxation is measured from the added PMMA. However the same plateau is visible for pure PMMA. The fact that for a pure component of the mixture this plateau is also happening and the signal becomes noisy in the same area as where the plateau seems to occur it is for now assumed that this plateau is due to the measurement becoming unstable and noisy at very low frequencies. But this needs to be checked later. For the determination of the tangents and critical shear rates these frequencies of approximately 0.01 - 0.1 Hz are not taken into account. Using this method an overview of the critical shear rates for all measured materials and temperatures is given in Table 3.1.

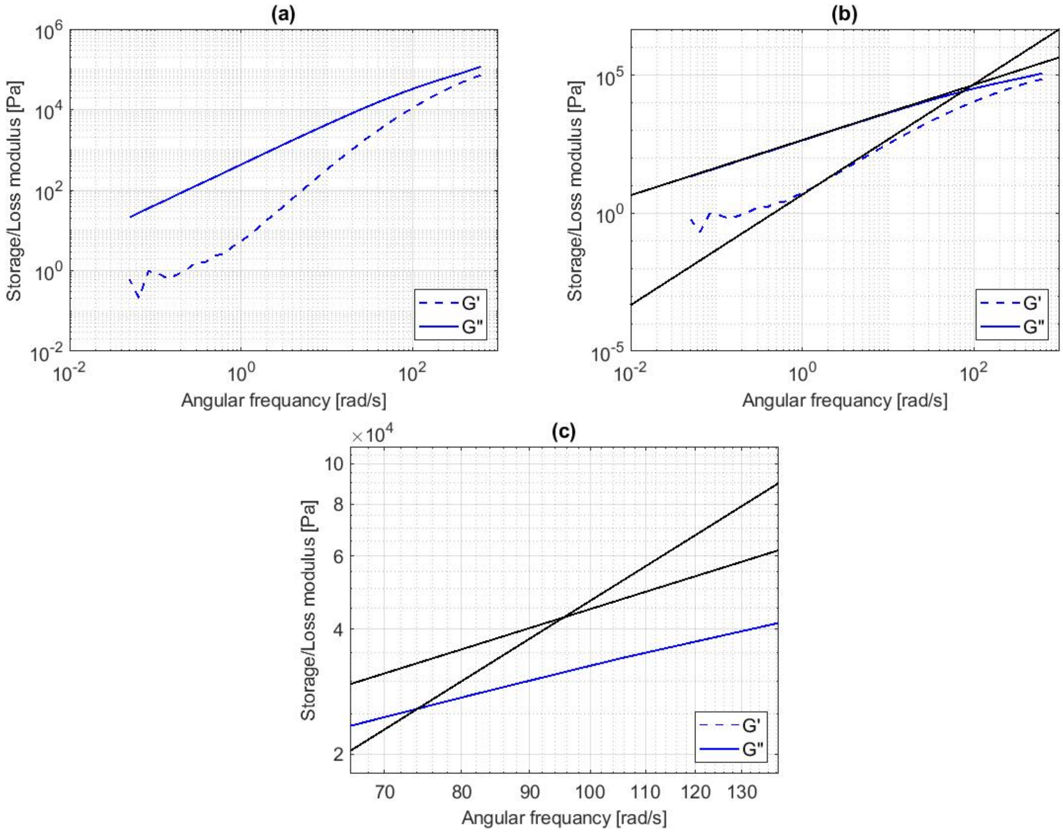


Figure 3.5: The storage and loss modulus of 1:9 ratio PMMA/PLLA mixtures at 210°C. Full frequency spectrum (a). the Tangents of G' and G" in low frequencies with slopes 2 and 1 respectively (b) Zoomed in section of graph (b) around the intersection point of the tangents (c).

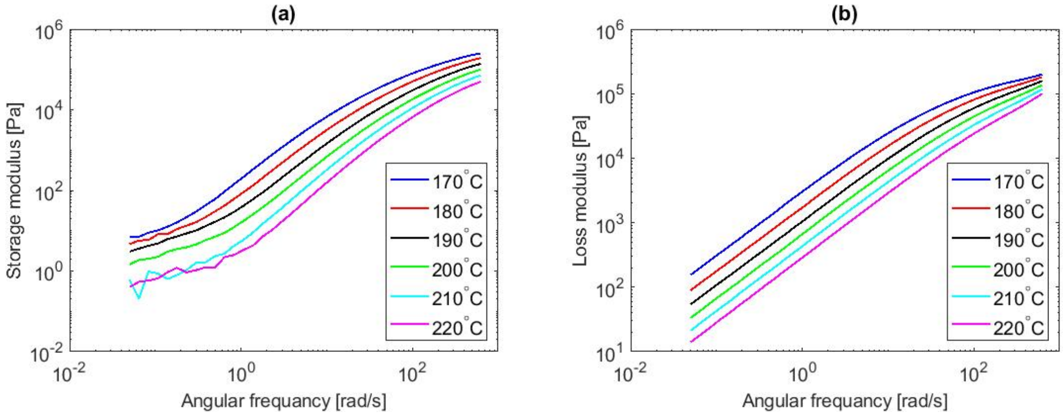


Figure 3.6: The storage modulus (a) and loss modulus (b) of 1:9 ratio PMMA/PLLA mixtures for different temperatures.

Table 3.1: Critical shear rates for different ratios PLLA:PMMA and temperatures.

Temperature [°C] \ wt% PMMA	10	20	30	40
170	13	8.5	4.5	1.6
180	35	16.5	7	4.5
190	50	34	14	6
200	72	50	25	11
210	96	85	39	25
220	160	141	63	43

To keep the shear measurements relevant for the SLS process the limits of shear time and shear rate during the SLS process need to be taken into account. During the SLS printing process the only moment when shear on the material comes into play is when the particles are being molten and start to flow. Since the particles melt together very fast the shear time is set to 1 s. Furthermore there is also no shear force actively applied to the material, leading to lower shear rates during the SLS process. The limits for shear rate are therefore set to 0-100 s^{-1}. The results of Table 3.1 show that within this range of shear rate only a few temperature and PMMA content combinations will most likely show little to no shear induced crystallisation. But it is expected for most materials to experience shear induces crystallisation under these assumptions, and thus most likely also during SLS printing. Hence it is useful to investigate how this shear induced crystallisation, combined with the PMMA and crystallisation procedure, influences the crystallinity of SLS printed products.

3.5 Mechanical testing

The final step of this research is to evaluate some basic mechanical properties of the SLS printed products and to compare them to that of pure PLLA. This way a conclusion can be drawn if the SC crystals have an influence on the properties of the products. Some interesting parameters are the heat deflection temperature, tensile strength, and Young's modulus. The heat deflection temperature can be measured by putting a fixed load on a bar of the material and raising the temperature to the temperature where the bar deflects a certain amount, which is then the heat deflection temperature. The tensile strength, and Young's modulus can be measured with a tensile test. For the SLS printed tensile bars it would be important to take into account the different printing directions.

Research description

4.1 Research overview

In the previous chapters the research done so far and the experimental methods applicable to this research are discussed. In this chapter a more specific overview of what will be done during this research will be given. The research questions and subquestions are given in this chapter.

The main research question this research will try to answer is:
How to optimize and utilize stereocomplex crystallisation in PLLA/PDLA mixtures, using PMMA and shear, to improve SLS printed products of PLA?

This question will be answered by answering multiple subquestions. All subquestions and a description on what will be done to answer them is given below.

What crystallisation procedure leads to the highest SC content? How does PMMA influence the crystallisation kinetics of PLLA/PDLA mixtures?
These questions will be answered together. The literature showed that having a PMMA content of 50 wt% or higher is (in most cases) not beneficial for the SC crystallisation anymore. This led to the decision that this research will look at PMMA contents in the range of 0-40 wt%. For these PMMA contents different crystallisation protocols will be looked at. Both melt and cold crystallisation and two step crystallisation will be taken into account. Based on the literature the range for melt crystallisation in this research will be 110-160°C, for cold crystallisation the range will be 110-200°C. These tests will be done making use of DSC and POM, as discussed in the experiments chapter.

How does shear influence the crystallisation kinetics of PMMA/PLLA/PDLA mixtures?
In the SLS printing process the only moment when shear on the material comes into play is when the particles are being molten and start to flow. This puts a quite severe limitation on the influence one has on the applied shear during SLS printing. To keep the research relevant for the SLS process these limitations are taken into account by using a fixed shear time of 1 s, and a shear rate in the range of 0-100 s^{-1}. Even though a specific shear rate can not be given to the material during the SLS process, it can be somewhat controlled by the fact that the smaller the particle size the higher the shear rate, since the capillary driving force for coalescence is larger[17]. All shear tests will be executed using rotational rheometry as described in the previous chapter.

How can the optimal conditions for SC formation be recreated during SLS printing?
Based on the outcome of the previous subquestions there will hopefully be a few combinations of PMMA content, shear rate, and crystallisation procedure which lead to a high SC-content. Guided by these conditions and the set of important material parameters for SLS printing as given in the last section of Chapter 2, different materials and printing conditions will be tested to see how the quality of the prints is and how much shrinkage and warpage occurs.

How does the SC content influence the mechanical properties of SLS printed products?
The material and procedure combinations that produce good products need to be tested for the influence of the SC content on the mechanical properties. This can be done by printing bars and tensile bars in different directions and test them as mentioned in the experiments chapter.

4.2 Planning

The planning of the research is shown in Table 4.1.

Table 4.1: Research planning

Start	End	Description
1 October	24 December	Quiescent crystallisation: Make materials. DSC and POM tests on influence different PMMA wt% and crystallisation parameters on the crystallisation of PLLA/PDLA mixtures.
4 January	31 January	Shear-induced crystallisation: Rheology tests on influence of shear on crystallisation and zero shear viscosity of PLLA/PDLA mixtures.
1 February	1 April	SLS printing: Test influence of different SLS printing parameters on printability and quality of the printed product. Print test samples.
6 April	18 April	Mechanical properties: Mechnical tests on SLS printed samples.
19 April	30 April	Work on report.
1 May	31 May	Final preparations for report and presentation.

4.3 Interesting topics for further research

As an extra note, during any 3D printing method the interface between layers is often the weakest spot. The research during this project focuses on the SC crystallisation in the bulk material. This could lead to a mismatch between the fundamental research in this project and the results of the printed products due to the interface effect between the layers. For this reason it would be very interesting to look at the first three sub questions in this research but then specifically at an interface. Some interesting research on the interfacial SC crystallisation in PLLA/PDLA has already been done.[4, 8]

Another interesting topic to research would be the effect of the powder crystallinity before sintering on the crystallinity of the final product. In this research it is assumed that during the SLS process the particles are completely molten and thus amorphous when sintered together and only the crystallisation process after fusion of the particles is being optimized to increase SC crystallinity. However the particles are heated in the powder bed before sintering which can also lead to crystallised particles which could have an effect on the crystallinity of the sintered product. The reason these topics are not incorporated in this research is simply due to time limitations.

Bibliography

[1] A. Jalali, S. Shahbikian et al. “Effect of molecular weight on the shear-induced crystallization of poly(lactic acid)”. *Polymer* 112 (2017), 393–401. DOI: `http://dx.doi.org/10.1016/j.polymer.2017.02.017`.

[2] C. Samuel, J. Cayuela et al. “Stereocomplexation of Polylactide Enhanced by Poly(methyl methacrylate): Improved Processability and Thermomechanical Properties of Stereocomplexable Polylactide-Based Materials”. *ASC Applied materials and interfaces* 5 (22) (2013), 11797–11807. DOI: `https://doi.org/10.1021/am403443m.`.

[3] C. Samuel, J. Raquez et al. “PLLA/PMMA blends: A shear-induced miscibility with tunable morphologies and properties?” *Polymer* 54 (15) (2013), 3931–3939. DOI: `https://doi.org/10.1016/j.polymer.2013.05.021`.

[4] D. Bai, H. Liu et al. “Low-temperature sintering of stereocomplex-type polylactide nascent powder: the role of poly(methyl methacrylate) in tailoring the interfacial crystallization between powder particles”. *Polymer* 210 (2020), In press. DOI: `https://doi.org/10.1016/j.polymer.2020.123031`.

[5] H. Bai, S. Deng et al. “Recent Advances in Processing of Stereocomplex-Type Polylactide”. *Macromolecular Rapid Communications* 38 (23) (2017), 1700454 (1–12). DOI: `https://doi.org/10.1002/marc.201700454`.

[6] J. Bai, J. Wang et al. “Stereocomplex Crystallite-Assisted Shear-Induced Crystallization Kinetics at a High Temperature for Asymmetric Biodegradable PLLA/PDLA Blends”. *ASC Sustainable Chemistry and Engineering* 4 (1) (2016), 273–283. DOI: `https://doi.org/10.1021/acssuschemeng.5b01110`.

[7] J. Wang, J.Bai et al. “Shear-induced enhancements of crystallization kinetics and morphological transformation for long chain branched polylactides with different branching degrees”. *Scientific reporter* 6 (2016), 26560 (1–13). DOI: `https://doi.org/10.1038/srep26560`.

[8] J. Xu, Y. Li et al. “Shear-induced stereocomplex cylindrites in polylactic acid racemic blends: Morphology control and interfacial performance”. *Polymer* 140 (2018), 179–187. DOI: `https://doi.org/10.1016/j.polymer.2018.02.048`.

[9] L. Verbelen, S. Dadbakhsh et al. “Characterization of polyamide powders for determination of laser sintering processability”. *European Polymer Journal* 75 (2016), 163–174. DOI: `http://dx.doi.org/10.1016/j.eurpolymj.2015.12.014`.

[10] L. Xie, H. Xu et al. “Structural Hierarchy and Polymorphic Transformation in Shear-Induced Shish-Kebab of Stereocomplex Poly(Lactic Acid)”. *Macromolecular Rapid Communications* 37 (9) (2016), 745–751. DOI: `https://doi.org/10.1002/marc.201500736.`.

[11] Q. Dong, Y.Bian et al. “Miscibility and crystallization behaviours of stereocomplex-type poly(L- and D-lactide)/poly(methyl methacrylate) blends”. *Journal of Thermal Analysis and Calorimetry* 118 (2014), 359–367. DOI: `https://doi.org/10.1007/s10973-014-3966-1`.

[12] R. Y. Bao, W. Yang et al. “Polymorphism of a high-molecular-weight racemic poly(L-lactide)/poly(D-lactide) blend: effect of melt blending with poly(methyl methacrylate)”. *RSC Advances* 5 (25) (2015), 19058–19066. DOI: `https://doi.org/10.1039/C5RA00691K`.

[13] R. Y. Bao, W. Yang et al. “Polymorphism of Racemic Poly(L-lactide)/Poly(D-lactide) Blend: Effect of Melt and Cold Crystallization”. *The journal of physical chemistry B* 117 (13) (2013), 3667–3674. DOI: `https://doi.org/10.1021/jp311878f`.

[14] Y. Song, X. Zhang et al. “Crystallization of equimolar poly(L-lactide)/poly(D-lactide) blend below the melting point of a crystals under shear”. *European Polymer Journal* 75 (2015), 93–103. DOI: `https://doi.org/10.1016/j.eurpolymj.2015.12.001`.

[15] Y. Song, X. Zhang et al. “Enhancement of stereocomplex formation in poly(L-lactide)/poly(D-lactide) mixture by shear”. *Polymer* 72 (2015), 185–192. DOI: `http://dx.doi.org/10.1016/j.polymer.2015.07.023`.

[16] Y. Igushi, S. Akasaka, S. Asai. “Formation of PLA stereocomplex crystals during melt-blending of asymmetric PLLA/PDLA/PMMA blends of varying miscibility”. *Polymer journal* 52 (2020), 225–235. DOI: `https://doi.org/10.1038/s41428-019-0256-6`.

[17] P.Hejmady, L.C.A. van Breemen, et al. “Laser sintering of PA12 particles studied by in-situ optical, thermal and X-ray characterization”. In preparation for publishing

[18] M. Van den Eynde, P. Van Puyvelde. “3D Printing of Poly(lactic acid)”. *Advances in Polymer Science* 282 (2017), 139–158. DOI: `https://doi.org/10.1007/12_2017_28`.

[19] H Tsuji, S. H. Hyon, Y. Ikada. “Stereocomplex Formation between Enantiomeric Poly(lactic-acid)s. 3. Calorimetric Studies on Blend Films Cast from Dilute Solution”. *Macromolecules* 24 (20) (1991), 5651–5656. DOI: `https://doi.org/10.1021/ma00020a026`.

[20] H Tsuji. “Poly(lactide) Stereocomplexes: Formation, Structure,Properties, Degradation, and Applications”. *Macromolecular bioscience* 5 (7) (2005), 569–597. DOI: `https://doi.org/10.1002/mabi.200500062`.