Non-conventional injection molding of poly(lactide) and poly(ε-caprolactone) intended for orthopedic applications

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Biodegradable polymers such as poly(lactide) (PLA) and poly(ε-caprolactone) (PCL) are increasingly used in biomedical applications as temporary implants. However, melt processing of these materials in particular of PLA is difficult due to the temperature sensitivity. Within this study, PLA and PCL were injection molded conventionally and by using the process shear controled orientation in injection molding (SCORIM) in order to investigate the effect of processing parameters on the physical properties of the moldings. Therefore, flexural testing, differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), molecular weight (MW) and orientation measurements were performed.

PLA showed high sensitivity to melt temperature. In the case of amorphous poly(DL-lactide), the molecular weight and subsequently the ductility is substantially reduced by processing at higher melt temperatures. In the case of crystallizable poly(L-lactide), higher melt temperatures and shear induced by the SCORIM process resulted in enhanced crystallinity, which compromised the mechanical properties. Generally, SCORIM processing improved the mechanical properties, in particular the ductility, by orientating the molecular structure. PCL was shown to be less sensitive to shear and temperature than PLA. Stress at yield and stiffness are more improved by SCORIM processing. However, the processing temperature in combination with the grade used proved to be influential for the mechanical properties of resulting moldings.

1. Introduction

Aliphatic polyesters such as poly(lactide) (PLA) are well known biocompatible and bioresorbable polymers already used in biomedical applications [1]. Absorbable implants have advantages over metal when only a temporary application is required since no removal operation is needed and long-term complications are substantially reduced [2]. Typical applications of PLA and their copolymers are bone plates and screws for bone fixation. PLA degrades by chain scission in the body to monomeric units of lactic acid, which is a natural intermediate in carbohydrate metabolism. Therefore, this material is suitable for drug carriers and implants for orthopedic surgery as well as blood vessels, which finally can be replaced by the body's tissue [3]. Drawn poly(L-lactide) was found to exhibit a piezoelectric effect that can promote the fracture healing significantly [4]. However, the slow degradation of the crystalline phase of PLA can cause complications. An inflammatory response carries a risk of inducing cancerous tissue. [5, 6].

Poly(ε-caprolactone) (PCL) is believed to be a suitable implant material due to its high biocompatibility with osteoblasts and is primarily aimed as bone substitute material for maxiofacial reconstructive surgery [7, 8]. In combination with a reinforcing filler, PCL is also proposed for load bearing implants such as intramedullary pins [8, 9].

Melt processing of PLA is generally difficult compared to commodity plastics. Temperature and moisture have a substantial influence on molecular weight reduction and therefore on the resulting mechanical properties [10, 11]. Compression molding is an effective method for the fabrication of long-fiber-reinforced materials, however the design of moldings is limited to simple shapes. In contrast to compression, injection molding is a suitable processing method for forming complex shapes.

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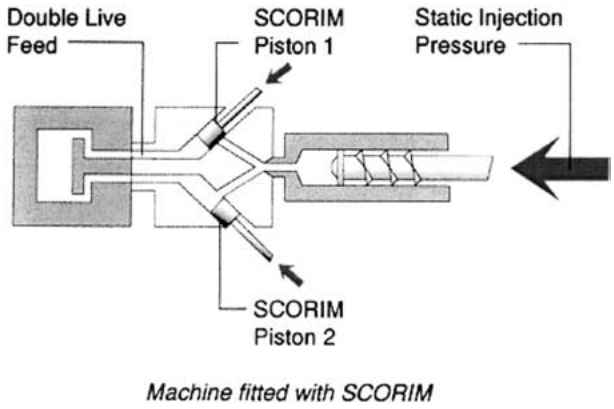


Figure 1 Principle of SCORIM technique.

The aim of this study is to investigate the effect of shear controlled orientation in injection molding (SCORIM) on the properties of PCL and PLA. In contrast to conventional injection molding (CIM), the melt is sheared during holding time by two oscillating pistons [12]. A schematic of the process is shown in Fig. 1. The applied shear until solidification causes enhanced orientation and lamination of moldings resulting in substantially improved mechanical properties as shown with non-degradable polymers [13, 14]. The application of SCORIM also showed improvement in properties of bioabsorbable starch-based blends [15, 16].

2. Materials and Methods

2.1. Materials

Two different medical grades of PLA were supplied by PURAC biochem bv, The Netherlands. The first grade was a semi-crystalline poly(L-lactide) (PLLA). The polymer has melting range between 180–192 °C and a glass transition temperature (T_g) of 63 °C. The second grade was an amorphous, non-crystallizable poly(DL-lactide) (P[DL]LA) with a T_g of 52 °C.

Two grades of PCL, supplied by Solvay Interox, UK, were used in this study. Both grades have a melting point at 58–60 °C but differ in their MW and subsequently their viscosity. The MW of PCL Capa650 is 50 000 and of Capa680 80 000. The melt flow indices (MFI) are 28 and 7.3 g/10 min, respectively (2.16 kg at 190 °C).

2.2. Injection molding of flexural test specimen

For processing of flexural test bars a MCP Sprite 7/50 mini injection molding machine (MCP Equipment, UK) was used (Euromap size: 5–5.25). The maximum shot volume is 7 cm^3. The hopper was sealed and purged with nitrogen during processing to keep PLA free from moisture. The mold tool was equipped with a hot runner system containing the SCORIM device. For conventional molding and for SCORIM processing, the melt was injected from one gate until the filling of the cavity was completed in order to avoid weld lines. The processing parameters were kept constant between CIM and SCORIM apart from the process method related difference in holding pressure. While a constant pressure was applied from both gates in the case of conventional moldings, the moving SCORIM pistons caused an oscillating holding pressure from either gate. The pressure of the pistons was reduced with holding time in order to lower shear stress within the melt. The resulting moldings were test bars with 90 mm length and a cross-section of 4 mm × 4 mm.

PLLA was processed with different melt temperatures ranging from 205 to 215 °C and three different mold temperatures, 25 °C, 50 °C and 75 °C. The melt temperature of the amorphous P(DL)LA was varied between 135 and 165 °C at a cavity temperature of 25 °C. PCL Capa650 was molded using melt temperatures between 100 and 140 °C while the more viscous grade Capa680 was processed at 140–160 °C. The mold temperature was kept constant at 25 °C in both cases. The low profiles represent the lowest possible melt/mold temperature in order to fill the cavity. The processing conditions used are summarized in Table I.

2.3. Characterization methods

2.3.1. Flexural testing

The specimens were tested on an Instron 4206 universal mechanical testing machine using a 5 kN load cell and 3-point bending equipment with 60 mm span. The tests were carried out at room temperature with a crosshead speed of 2 mm/min. In the case of PCL, flexural testing was performed at 10 mm/min test speed using a 100 N load cell. Due to the ductile behavior of PCL, the mechanical testing was stopped after passing the yield point. At least six specimens were tested to obtain the average and standard deviation (SD).

2.3.2. Statistical Analysis

Analysis of variance (ANOVA) was performed on the mechanical test data. The energy values were chosen for statistical analysis since they reflect changes in stiffness as well as strength. The F-value, which is the individual variance divided by the variance of the mean, was calculated for these data in order to evaluate the significance of the process parameters varied. The variance (V) were obtained by dividing the sum of squares (SS) by the degree of freedom (v). Further details to the statistical analysis may be found elsewhere [18].

The change of melt temperature and processing method for molding P(DL)LA and PCL represents a full factorial designed experiment. In the case of PLLA, the results for low and high melt temperatures (205 and 215 °C), low and middle mold temperatures (25 and 50 °C) and the two processing methods were selected to create a full factorial design with three factors and two levels each.

2.3.3. Differential scanning calometry (DSC) and wide angle X-ray diffraction (WA-XRD)

DSC and XRD were performed in order to investigate the effect of SCORIM processing on the microstructure of the molded materials. DSC was carried out on a Perkin-Elmer thermal analyzer (7-series) at a heating rate of

TABLE I Processing parameters

Grade processed at melt temperature	Processing method	Mold temperature (°C)	Injection time (s)	Holding time (s)	Cooling time (s)	Injection pressure (bar)	Holding pressure (bar)	Duration of piston movements (s)	Number of movements per piston
PCL 650 at 140 °C	CIM	25	1.3	16	18	700	400	—	—
	SCORIM	25	1.3	16	18	700	600–380	13	6
PCL 650 at 120 °C	CIM	25	1.9	16	18	750	400	—	—
	SCORIM	25	1.9	16	18	750	740–540	13	6
PCL 650 at 100 °C	CIM	25	3	16	18	800	450	—	—
	SCORIM	25	3	16	18	800	740–600	13	5
PCL 680 at 160 °C	CIM	25	2	20	16	750	400	—	—
	SCORIM	25	2	20	16	750	640–400	16	7
PCL 68 at 150 °C	CIM	25	2.6	16	18	750	500	—	—
	SCORIM	25	2.6	16	18	750	740–570	13	5
PCL 680 at 140 °C	CIM	25	6	14	18	800	600	—	—
	SCORIM	25	6	14	18	800	740–570	13	5
P(DL)LA at 165 °C	CIM	25	0.8	18	4	650	350	—	—
	SCORIM	25	1	18	4	650	640–420	16	7
P(DL)LA at 155 °C	CIM	25	1	16	6	650	400	—	—
	SCORIM	25	1	16	6	650	640–520	13	5
P(DL)LA at 145 °C	CIM	25	2.0	16	6	750	450	—	—
	SCORIM	25	2.0	16	6	750	700–570	13	5
P(DL)LA at 135 °C	CIM	25	4	16	6	800	600	—	—
	SCORIM	25	4	16	6	800	840–700	13	5
PLLA at 215 °C	CIM	25	1.5	16	10	750	550	—	—
	SCORIM	25	1.5	16	10	750	1060–810	13	6
PLLA at 210 °C	CIM	25	2.5	12	10	800	600	—	—
	SCORIM	25	2.5	12	10	800	1060–880	10	4
PLLA at 205 °C	CIM	25	3.5	12	10	800	600	—	—
	SCORIM	25	3.5	12	10	800	1060-880	10	4
PLLA at 205 °C	CIM	50	2	25	12	750	400	—	—
	SCORIM	50	2	25	12	750	1000-700	16	7
PLLA at 205 °C	CIM	75	1	35	23	600	350	—	—
	SCORIM	75	1	35	23	600	810–540	23	20
PLLA at 215 °C	CIM	50	1	20	24	650	350	—	—
	SCORIM	50	1	20	24	650	570–400	18	11

10 °C/min. A thin section of about 0.5 mm was cut orthogonal to the melt flow direction from the middle of the specimen.

A Phillips 1080 X-ray diffractometer was used for analyzing PLLA. For scanning the surface, a 0.6 mm cross-section was sectioned from the middle of the specimen parallel to the melt flow direction. For taking the Debey patterns a 0.5 mm cross-section was cut perpendicular to the flow direction.

2.3.4. Shrinkage test

A shrinkage test of PLA was performed in order to access differences in molecular orientation between SCORIM and CIM. Therefore, a thin section (4 mm × 3 mm × 0.5 mm) was cut from the middle of the specimen parallel to melt flow direction. The specimen was placed onto a LEICA hot-stage microscope equipped with imaging facilities and heated from room to deformation temperature.

2.3.5. Molecular weight measurements

MWs were determined by gel permeation chromatography (GPC) with chloroform as the eluent. Measurements were performed at room temperature using a Waters model 150 pump, a Waters differential refractometer, a Viscotek H502 viscometer and 10^5–10^4–10^3–500 Å. Waters Ultra-Styragel columns placed in series. Narrow polystyrene standards were used for calibration.

3. Results and discussion

3.1. PLLA

The flexural strength (Fig. 2) increases with elevated melt and mold temperatures. SCORIM values remain marginally higher but at high thermal stress, 50 °C and 215 °C mold and melt temperature, the SCORIM values remain high unlike the strength of conventionally molded

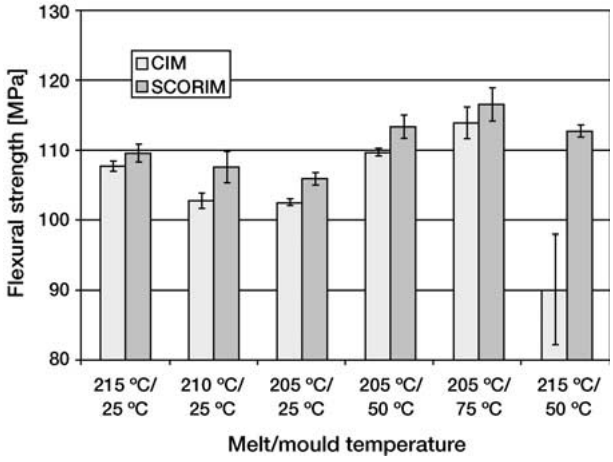


Figure 2 Flexural strength of PLLA.

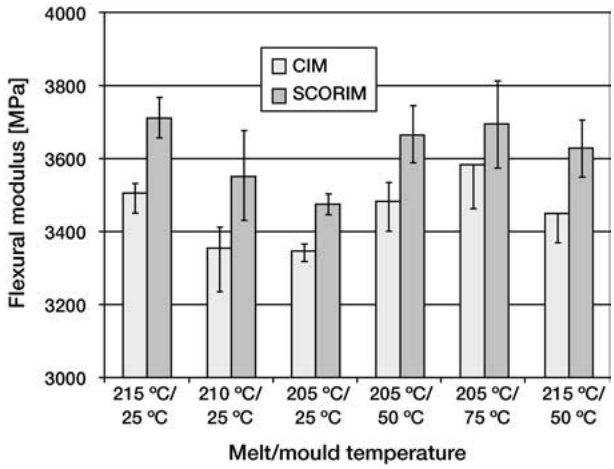
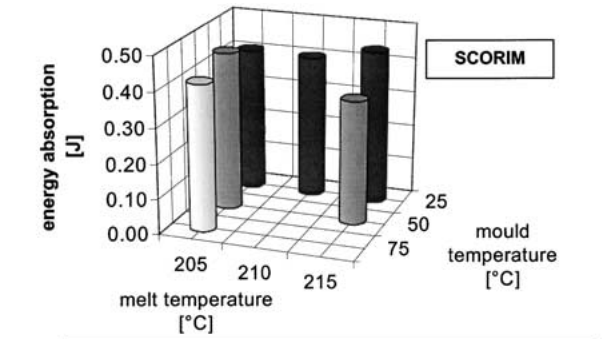
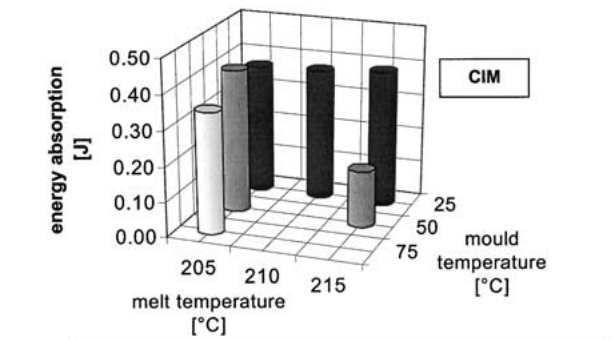


Figure 3 Flexural modulus of PLLA.

samples. However, the flexural modulus (Fig. 3) decreases with increase of the melt and mold temperature. The modulus of SCORIM samples remains about 5% higher independent of the processing temperatures. In contrast to the yield properties, temperature and SCORIM processing are shown to have a significant influence on the ductile behavior of PLLA. The energy absorption was measured at 8 mm displacement (Fig. 4). The absorption increases with elevated melt temperatures. Processing at a low melt temperature and an elevated mold temperature below T_g (50 °C) increases the ductility while at a high melt temperature this elevation causes a substantially reduced ductility. The polymer also becomes more brittle at a mold temperature



	205	210	215
25	0.41	0.41	0.44
50	0.45		0.35
75	0.42		



	205	210	215
25	0.37	0.38	0.39
50	0.41		0.16
75	0.35		

Figure 4 Energy absorption of PLLA to 8 mm deflection.

TABLE II Experimental design of PLLA

Energy absorption to 8 mm deflection (J)	Melt temperature				
	Low: 205 °C		High: 215 °C		
	AV	SD	AV	SD	
Mold temperature					Processing method
Low: 25 °C	0.3706	0.0038	0.3893	0.0166	CIM
Low: 25 °C	0.4102	0.0055	0.4390	0.0081	SCORIM
Middle: 50 °C	0.4092	0.0172	0.1610	0.0326	CIM
Middle: 50 °C	0.4511	0.0125	0.3519	0.0818	SCORIM

AV, average; SD, standard derivation.

TABLE III ANOVA for energy absorption of PLLA

Source	SS	v	V	F
A: Melt temp.	0.0675	1	0.0675	64.4
B: Mold temp.	0.0417	1	0.0417	39.8
C: CIM/SCORIM	0.0778	1	0.0778	74.3
A × B	0.1170	1	0.1170	111.6
A × C	0.0190	1	0.0190	18.1
B × C	0.0154	1	0.0154	14.7
A × B × C	0.0145	1	0.0145	13.8
Error	0.0430	41	0.0010	$F_{0.01;1;41}$
Total	0.3958	47		$=7.30$

SS, sum of squares.

above T_g (75 °C). However, SCORIM processing reduces this decrease in ductility significantly.

The statistical analysis (Tables II and III) shows that all three main effects and two-factor interactions are significant at a confidence level of 99%. The most influential main effect is the processing method followed by the processing temperature. The highest F-value is calculated for the interaction of melt and mold temperature. The significant interactions of melt or mold temperature and the processing method reflects that SCORIM is more effective at higher temperature profile due to the slower solidification of the polymer melt within the cavity.

The increase in properties with higher melt temperatures and elevated mold temperature below T_g is caused by an increase in crystallinity due to the higher mobility of the polymer chains. But also SCORIM promotes the

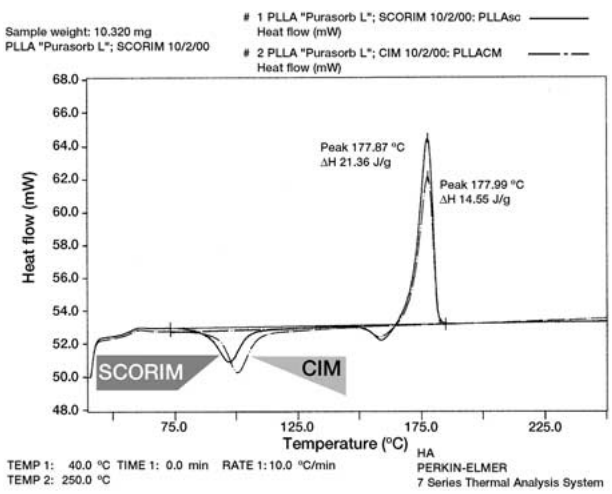


Figure 5 DSC of PLLA (processed at 205 and 75 °C melt and mold temperature).

crystallinity as shown by DSC and XRD scans. In the case of DSC analysis (Fig. 5) the higher degree crystallinity is reflected by the increase in the required specific heat in order to melt the crystalline phase. PLLA recrystallizes between 75 and 125 °C and to a more limited extent beginning at 150 °C as shown by the two exothermic peaks. The endothermic peak is at 178 °C. The exothermic reaction was subtracted from the endothermic for calculation of the specific energy (ΔH). SCORIM processed samples required a 46% higher specific heat than the conventional molding to melt the crystalline structure. In the case of XRD scan of PLLA (Fig. 6), the higher degree of crystallinity of SCORIM samples is reflected by significantly more pronounced peaks at 2θ-angles of 16.6°, 18.9° and 22.3°. The degree of crystallinity is 21% for the SCORIM and 4% for the conventional sample. The crystalline structure of SCORIM processed moldings are orientated, as

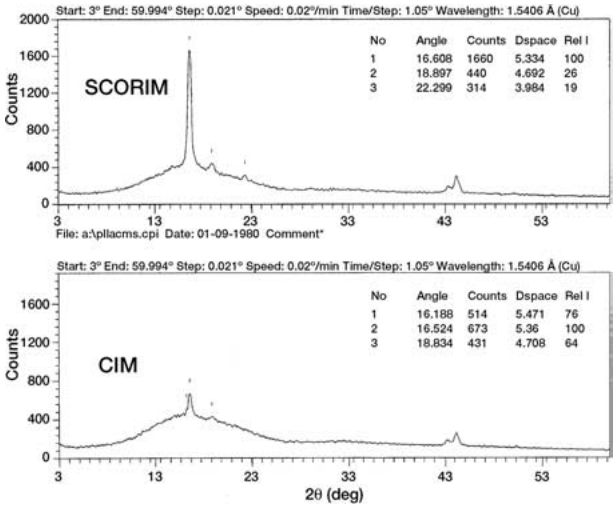


Figure 6 WA-XRD scan of PLLA (processed at 205 and 75 °C melt and mold temperature).

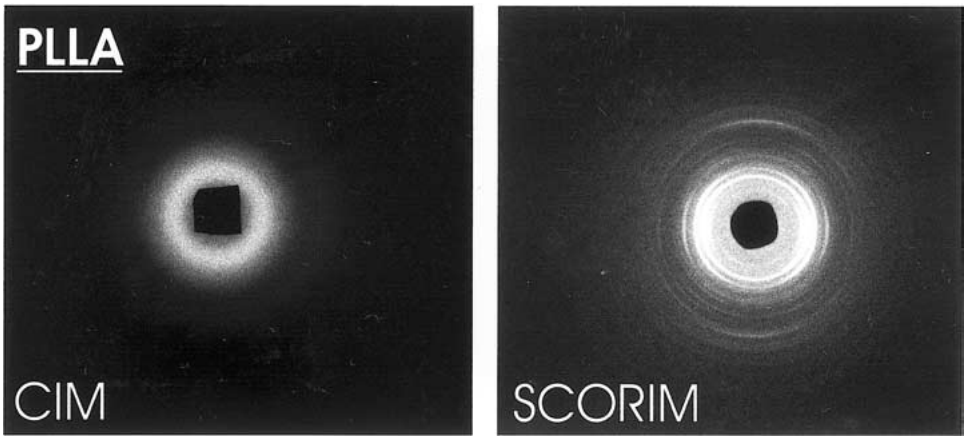


Figure 7 Debey-pattern of PLLA (processed at 205 and 75 °C melt and mold temperature).

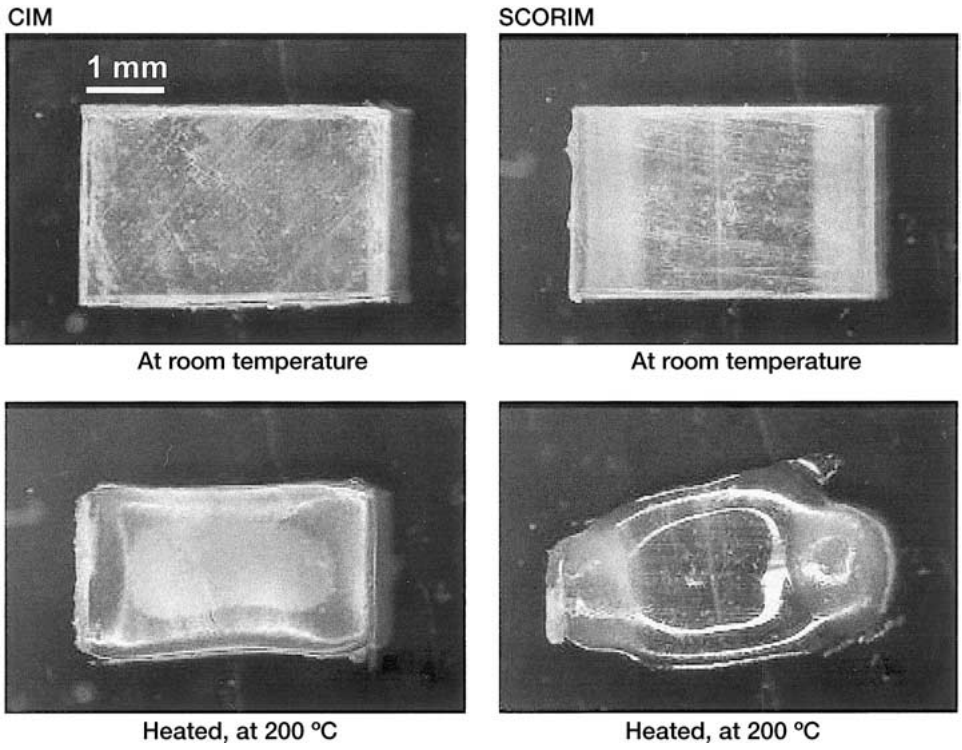


Figure 8 Shrinkage behavior of PLLA (processed at 205 and 75 °C melt and mold temperature).

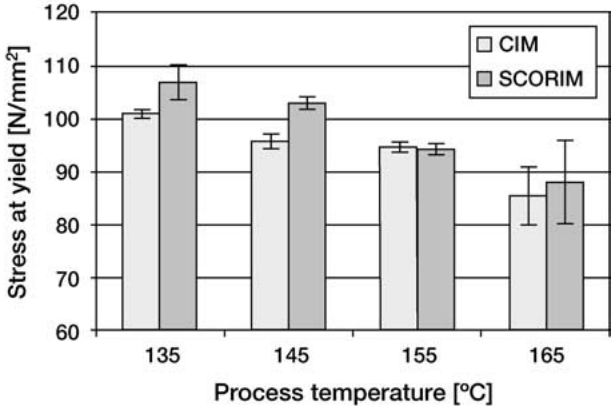


Figure 9 Ultimate tensile strength of P(DL)LA.

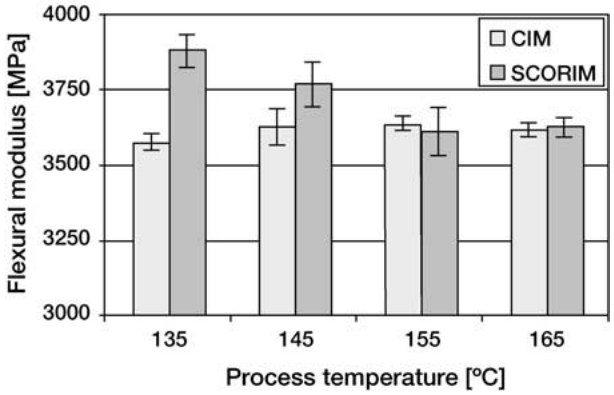


Figure 10 Flexural modulus of P(DL)LA.

represented by the unequally distributed intensity of the rings on the Debey patterns (Fig. 7).

Generally, SCORIM processing increases the molecular orientation. The shrinkage behavior (Fig. 8) of PLLA is different for the SCORIM sample compared to the conventional molding. The molecular relaxation is substantially higher. The oriented crystalline region is clearly visible in the SCORIM sample at room temperature.

3.2. P(DL)LA

In contrast to the PLLA grade, the flexural properties of P(DL)LA increase with lower melt temperatures. Stress at yield decreases with elevated melt temperatures (Fig. 9). At lower temperatures, SCORIM processing marginally strengthens the polymer by 5–8%, while at higher processing temperatures an enhancement could not be observed. The flexural modulus remains constant at about 3600 N/mm^2 independent of the melt temperature in case of conventionally molded samples (Fig. 10). However, SCORIM processing enhances the modulus by nearly 10% at 135 °C melt temperature while at higher temperatures a stiffening effect is not evident compared to CIM. The toughness values, the energy to break divided by the tested specimen volume, clearly show the effect of process temperature and processing method on the ductility of P(DL)LA (Fig. 11). With elevated melt temperature the toughness decreases substantially, by a factor of 5 for processing at 135 °C compared to 165 °C. SCORIM processing enhances the ductility by 25–75%.

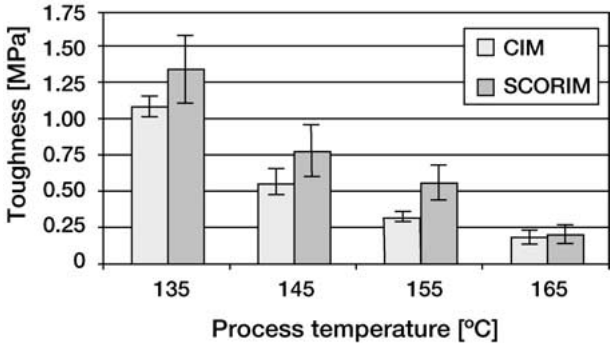


Figure 11 Toughness of P(DL)LA.

However, at a high processing temperature no improvement in toughness could be observed by the unconventional processing method.

The statistical analysis (Table IV) shows the major importance of the processing temperature on the flexural properties (F=173). Also SCORIM processing influences the ductility significantly (F=39) at a confidence level of 99%. However, the interaction of processing method and melt temperature cannot be regarded as significant compared to the response due to variation of both single factors.

The MW measurement shows the reduction in chain length after melt processing (Table V). Higher melt temperatures cause a substantial decrease in the MW. Despite processing at the lowest possible melt temperature (135 °C) in order to fill the cavity, the MW is reduced 5 times compared to the raw material showing the heat sensitivity of this polymer grade. Due to the shear applied during SCORIM processing, the MW is 5–10% lower compared to conventional molded P(DL)LA. However, the toughness of SCORIM processed polymer remain higher despite the lower MW (Fig. 12).

Since P(DL)LA is an amorphous polymer, DSC and XRD were not carried out in this case. The increase in

TABLE IV ANOVA for toughness of P(DL)LA

Source	SS	v	V	F
A: Melt temp.	7.584	3	2.528	172.79
B: CIM/SCORIM	0.573	1	0.573	39.18
A × B	0.013	3	0.004	0.29
Error	0.746	51	0.015	$F_{0.01;1;51}$
Total	8.916	58		$= 7.17$

SS, sum of squares.

TABLE V Molecular weight measurement of P(DL)LA

Processing method	Processing temperature (°C)	M_w (g/mol)	M_n (g/mol)
Unprocessed	—	508 600	258.600
SCORIM	135°	97 400	60 400
	145°	82 400	51 200
	155°	72 500	44 800
	165°	58 600	34 900
CIM	135°	106 900	66 500
	145°	89 000	55 100
	155°	76 900	49 100
	165°	61 700	38 500

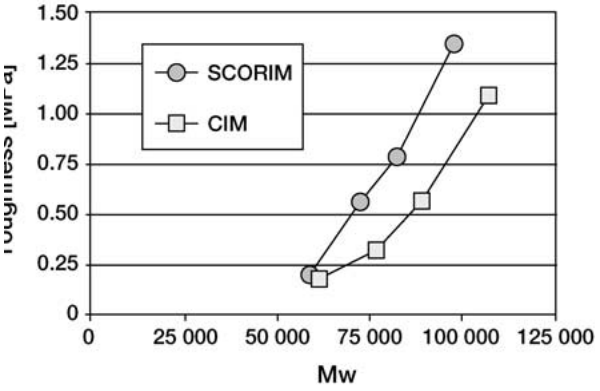


Figure 12 Toughness of P(DL)LA in dependence of molecular weight.

properties is a result of SCORIM induced enhanced molecular orientation in the moldings as shown by the difference in shrinkage behavior of CIM and SCORIM processed P(DL)LA (Fig. 13). Molecular relaxation can be observed on the skin area of the conventional molding. This is due to the shear induced frozen orientation (rephrase) during the injection phase. Since the melt was not immediately solidified within the middle section of the specimen after injection, the molecules were able to relax and show no memory effect within this area. In contrast, the constant shear during holding time by the SCORIM process resulted in frozen orientations within a ring like area. The relaxation of molecules within this area is major. However, the middle section shows no significant shrinkage effect. The shear during the holding phase can only be applied until the gates are frozen off. After this time, the unfrozen polymer melt within the cavity is able to relax and therefore the SCORIM sample has a non-orientated core area. A modification of gates in terms of increasing their diameter or temperature, would increase the time of which the melt at gates is freezing off. Therefore, a modification is very likely to improve the overall molecular orientation due to longer periods that shear can be applied during holding time. Also a higher piston pressure and therewith higher shear heating within the gates increase the freezing-off time, but since the P(DL)LA was shown to be very sensitive toward shear stress, the overall properties are very likely to decrease due to the resulting molecular degradation.

3.3. PCL

The melt temperature shows an opposite effect on the low and high viscous PCL grades, Capa650 and Capa680. While elevated temperatures marginally reduce the flexural modulus and stress at yield in the case of Capa650, these values considerably improve with increased processing temperatures with Capa680 (Figs 14 and 15). SCORIM processing has a major influence on the modulus of both PCL grades. The stiffness improves up to 28% in the case of the high viscous grade (Fig. 16). However, the relative improvement decreases with

TABLE VI Energy absorption to 15 mm deflection (J) during flexural testing of PCL

Processing temperature (°C)	Processing method			
	CIM		SCORIM	
	AV	SD	AV	SD
Capa 650				
Low: 100	0.2062	0.002	0.2378	0.006
Middle: 120	0.2024	0.002	0.2234	0.008
High: 140	0.1998	0.003	0.20791	0.002
Capa 680				
Low: 140	0.1655	0.007	0.2013	0.010
Middle: 150	0.1736	0.003	0.1896	0.006
High: 160	0.1841	0.006	0.1931	0.009

AV, average; SD, standard derivation.

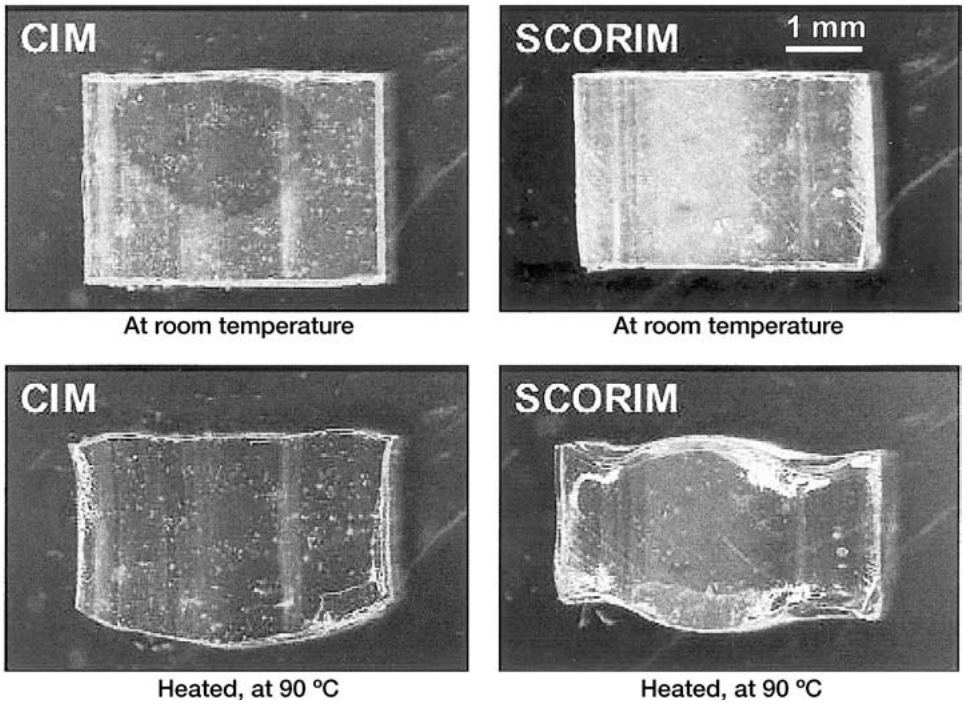


Figure 13 Shrinkage behavior of P(DL)LA.

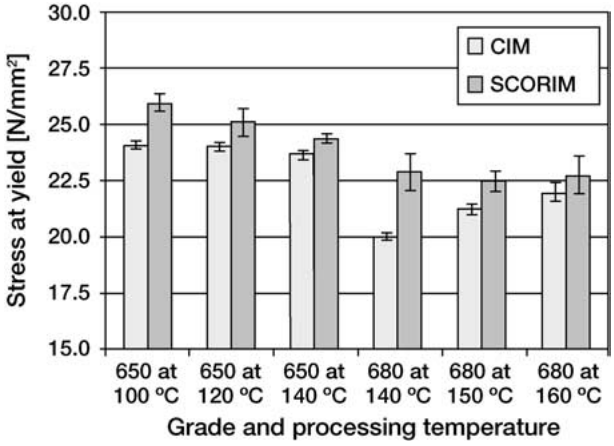


Figure 14 Stress at yield of PCL.

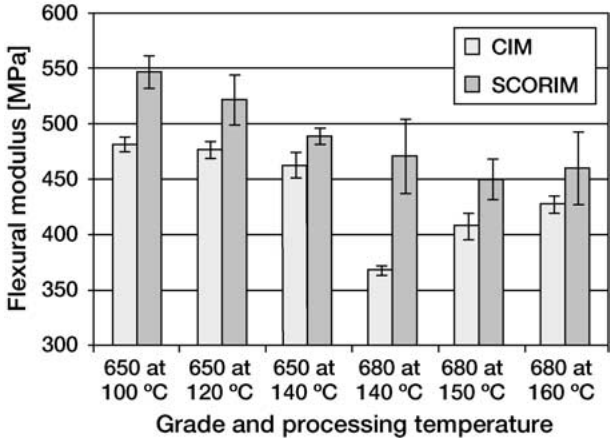


Figure 15 Flexural modulus of PCL.

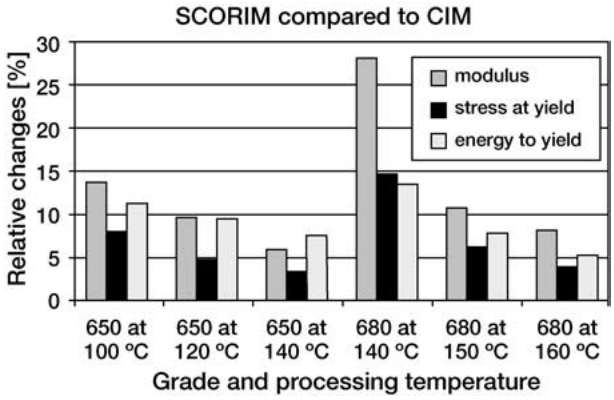


Figure 16 Relative improvement of flexural properties of PCL by SCORIM processing.

elevated melt temperatures. The same trend applies to the stress values, which could be enhanced up to 15% in the case of Capa680 processed at 100 °C. Generally, SCORIM processing was shown to have a major influence on the properties of the high viscosity grade compared to Capa650. The relative maximal improvement of stress and modulus between CIM and SCORIM processed Capa680 is twice that of Capa650.

The absorbed energy to 15 mm deflection was calculated (Table VI) and the statistical analysis performed using these data (Table VII). SCORIM processing proved to be most significant factor influencing both grades. In the case of the low viscosity grade Capa650, the melt temperature has a significant influence on properties, an increase in temperature decreases the properties. The interaction of both factors is also highly significant at a confidence level at 99%. This reflects the

TABLE VII ANOVA for energy absorption of PCL

Capa 650				
Source	SS	v	V	F
A: Melt temp.	0.001975	2	0.000988	53.7
B: CIM/SCORIM	0.003686	1	0.003686	200.3
A × B	0.000830	2	0.000415	22.6
Error	0.000552	30	0.000018	
Total	0.007044	35	$F_{0.01;1;30} = 7.56$	
			$F_{0.01;2;30} = 5.39$	
Capa 680				
Source	SS	v	V	F
A: Melt temp.	0.000317	2	0.000159	3.3
B: CIM/SCORIM	0.003697	1	0.003697	78.0
A × B	0.001159	2	0.000580	12.2
Error	0.001423	30	0.000047	
Total	0.006596	35	$F_{0.01;1;30} = 7.56$	
			$F_{0.01;2;30} = 5.39$	

SS, sum of squares.

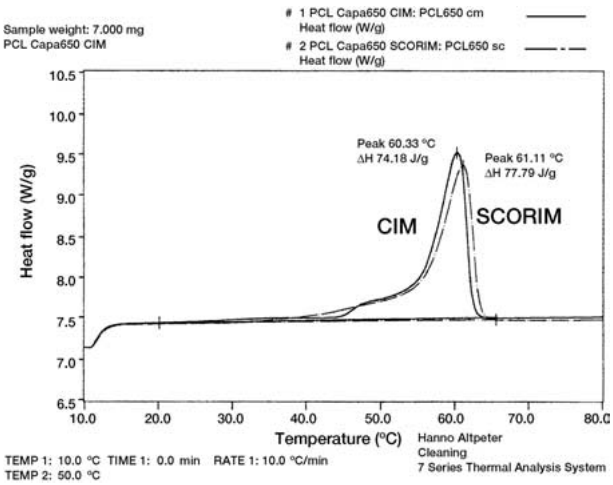


Figure 17 DSC analysis of PCL (CIM & SCORIM).

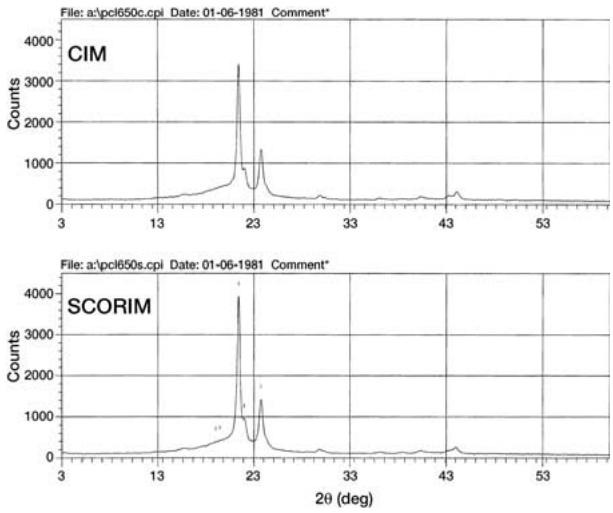


Figure 18 WA-XRD scan of PCL.

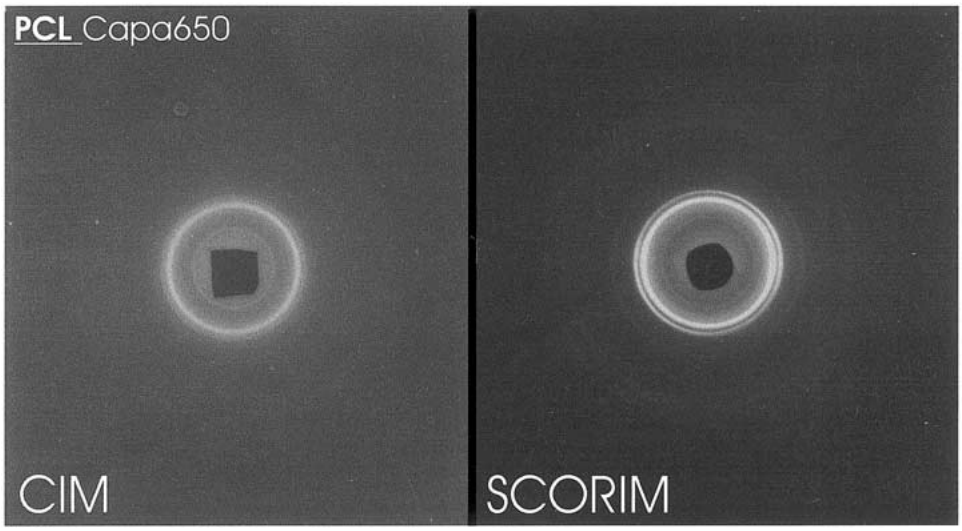


Figure 19 Debey pattern of PCL.

observation that the melt temperature hardly shows any effect on the energy values in the case of conventional molding while elevated temperatures influence the properties negatively in the case of SCORIM processing. For the high viscosity grade Capa 680, the melt temperature was calculated as statistically not significant due to the high SDs and different trends using both processing methods. Similar to Capa650, this contrast is reflected by the highly significant interaction of melt temperature and processing method. However, the SCORIM values remain fairly constant independent of the factor varied while the conventional moldings absorb more energy when processed at higher temperatures.

The enhancement of mechanical properties due to SCORIM processing is not a result of a significant increase in crystallinity as shown by XRD and DSC of Capa650 (processed at 100 °C). The general specific heat calculated from the DSC run (Fig. 17) differs marginally between the CIM and SCORIM samples. The XRD scan (Fig. 18) confirms the minor increase in crystallinity of the SCORIM sample. The degree of crystallinity of the conventional molding is 45% and of SCORIM specimen 46%. The Debey-pattern (Fig. 19) shows some orientation of the crystalline structure in case of the SCORIM sample. The intensity of X-rays is uniformly distributed with the conventional molding in contrast to the SCORIM sample. Therefore, improvement in flexural properties can be considered to be a result of shear induced enhancement of molecular orientation and not of shear induced crystallinity as in case of PLLA.

4. Conclusion

PLA proved to be difficult to process due to its high temperature and shear sensitivity. The temperature sensitivity is clearly shown with the amorphous P(DL)LA where the MW and subsequently the ductility is substantially reduced by processing at higher melt temperatures. SCORIM processing improves the mechanical properties by orientating the molecular structure. In the case of PLLA the enhancement is partly due to shear induced crystallinity. This preliminary study shows the shear induced by SCORIM results in an enhanced molecular orientation but also a reduction in MW, which compromises the mechanical properties. However, maintaining or improving the mechanical properties with reduced MW might be a desirable feature since generally shorter chains accelerate degradation speed in physiological environments.

PCL was shown to be less sensitive to shear and temperature than PLA. Stress at yield and stiffness are more improved by SCORIM processing. However, the processing temperature in combination with the grade used proved to be influential for the mechanical properties of resulting moldings.

For safe fracture fixation the strength of the implant material should exceed the strength of cortical bone which makes reinforcement necessary [2]. SCORIM has been shown in the past also to enhance the orientation of reinforcing fibers [17]. Therefore, SCORIM processing with biodegradable fiber reinforced sytems are likely to enhance the mechanical properties to a larger extent than shown with the unfilled PLA and PCL.

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References

1. M. VERT, G. SCHWARCH and J. COUDANE, *J.M.S.-Pure Appl. Chem.* **A32** (1995) 4.
2. P. TÖRMÄLÄ, T. POHJONEN and P. ROKKANEN, *Proceedings of Instn. Mech. Engrs.* **212** (1998) H, p. 101.
3. A. G. ANDREPOPOULOS and T. THEOPHANIDES, *J. Elastomers and Plastics* **26** (1994) 308.
4. Y. IKADA, Y. SHIKINAMI, Y. HARA, M. TAGAWA and E. FUKADA, *J. Biomed. Mater. Res.* **30** (1996) 553.
5. J. E. BERGSMA, R. R. M. BOS, F. R. ROZEMA and C. A. P. JOZIASSE, *J. Craniomaxillof. Surg.* **26** (1998) 17.
6. T. NAKAMURA, Y. SHIMIZU, Y. TAKIMOTO, T. TSUDA,

Y.-H. LI, T. KIYOTANI, M. TERAMACHI, S.-H. HYON, Y. IKADA and K. NISHIYA, *J. Biomed. Mater. Res.* **42** (1998) 475.
7. N. GURAV and S. DOWNES, *J. Mater. Sci.: Mater. in Med.* **3** (1994) 784.
8. T. J. CORDEN, S. DOWNES, I. A. JONES, K. E. MCDOUGAL, C. D. RUDD and S. E. FISHER, *Biomaterials* **21** (2000) 713.
9. K. J. LOWRY, K. R. HAMSON, L. BEAR, Y. B. PENG, R. CALALUCE, M. L. EVANS, J. O. ANGLEN and W. C. ALLEN, *J. Biomed. Mater. Res.* **36** (1997) 536.
10. R. G. SINCLAIR, *J.M.S.-Pure Appl. Chem.* **A33** (1996) 585.
11. R. VON OEPEN and W. MICHAELI, *Clin. Mater.* **10** (1992) 21.
12. P. S. ALLAN and M. J. BEVIS, *British Pat:* 2170-140-B.
13. G. KALAY, R. A. SOUSA, R. L. REIS, A. M. CUNHA and M. J. BEVIS, *J. Appl. Polym. Sci.* **73** (1999) 2473.
14. G. KALAY, P. S. ALLAN and M. J. BEVIS, *Kunststoffe plast europe* **87** (1997) 768.
15. R. A. SOUSA, G. KALAY, R. L. REIS, A. M. CUNHA and M. J. BEVIS, *J. Appl. Polym. Sci.* **77** (2000) 1300.
16. R. L. REIS, A. M. CUNHA, P. S. ALLAN and M. J. BEVIS, *Adv. Polym. Technol.* **16** (1997) 263.
17. P. S. ALLAN and M. J. BEVIS, *Plast. Rubb. Process. Appl.* **7** (1987) 3.
18. P. J. ROSS, in ''Tagushi Techniques for Quality Engineering'' (McGraw-Hill, New York, 1988).

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