# Shear controlled orientation in injection moulding of starch based blends intended for medical applications

## H. Altpeter, M. J. Bevis, M. E. Gomes, A. M. Cunha and R. L. Reis

Biodegradable polymeric implants are considered to be good alternatives to metallic implants in several temporary applications. Aliphatic polyesters have been extensively investigated and have been employed in several biomedical applications. More recently, biodegradable starch based polymeric blends have also been considered as alternative materials. In this study, the effect of shear controlled orientation injection moulding (SCORIM) on the mechanical properties and degradation behaviour of starch–polylactide and starch–poly-(ethylene-co-vinyl alcohol) blends has been investigated and compared with those produced by conventional injection moulding. The changes in these properties has also been studied when using an hydroxyapatite filler to reinforce the polymeric matrixes. The SCORIM processing enhanced the unidirectional mechanical properties substantially. The incorporation of hydroxyapatite into the polymer matrix had a stiffening effect but also reduced the strength and toughness. Generally, the mechanical properties deteriorated substantially in vitro. Reinforcement by hydroxyapatite was found to be less effective than expected in a wet environment.                                PRC/1890

## INTRODUCTION

Biodegradable polymers are increasingly used in biomedical applications. These polymers are utilised for drug delivery systems, sutures, scaffolds for tissue engineering and other temporary applications. Aliphatic polyesters such as polylactide (PLA) and polyglycolide (PGA) as well as poly(ε-caprolactone) (PCL) have been widely investigated and have been used as materials for absorbable implants.[1-3] However, in the case of PLA the slow degradation of the crystalline phase can cause several complications. For example, an inflammatory response carries a risk of inducing cancerous tissue.[4,5] Starch based blends are also claimed to have potential for several biomedical applications.[6,7]

Owing to the bioabsorbable nature of these polymers, removal surgery is not necessary, in contrast to metallic implants. Moreover, the lower modulus of polymeric devices reduces the stress shielding effect arising from mismatching stiffnesses of implant and bone and thus limits possible atrophies and osteoporotic complications.[8] However, the use of polymer based implants is still limited in load bearing applications because generally the mechanical performance of polymers compares unfavourably with that of metals.

Melt processing of degradable polymers is generally difficult compared with that of commodity plastics. The molecular weight and consequently the mechanical properties of mouldings are strongly dependent on the processing conditions, such as moisture content of the polymer and the melt temperature.[9,10] The fabrication of long fibre reinforced polymers by compression moulding is effective but also limited to simple shapes. By contrast, injection moulding is a suitable processing method for forming complex shapes. To enhance the mechanical properties of injection moulded devices, a non-conventional moulding technology was developed: shear controlled orientation in injection moulding (SCORIM).[11] A schematic diagram of the process is shown in Fig 1. In contrast to conventional injection moulding (CIM), two oscillating pistons shear the melt during the holding time. The application of shear until solidification causes enhanced orientation and lamination of mouldings and thereby improves the mechanical properties of the resulting mouldings in the orientation direction. This enhancement of properties has been extensively demonstrated in commodity plastics such as polyalkenes.[12-15]

The objective of this study was to investigate the effect of SCORIM on biodegradable polymers, in this case unreinforced starch based blends and blends filled with hydroxyapatite, a bioactive filler. Their mechanical
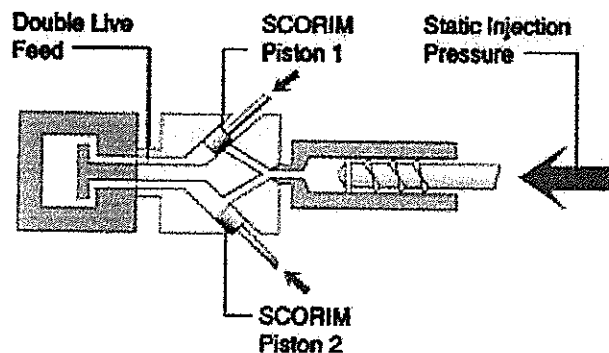


1 Schematic diagram of SCORIM process

properties and degradation behaviour were analysed. Previous investigations have already shown enhanced strength and stiffness with SCORIM processed corn starch–(ethylene-*co*-vinyl alcohol) (EVOH) blends (SEVA-C).[6,7]

## MATERIALS AND METHODS

### Materials

Two different blends of corn starch and PLA were used in the current investigation. These materials were specially produced and supplied by Novamont Spa, Novara, Italy. The grade named SPLA50 contained 50%* starch and 50% PLA; SPLA30 consisted of 30% starch and 70% PLA. The melting point of the SPLA blends ranged between 140 and 150°C and the glass transition temperature was 56°C.

Based on prior investigations of starch based compounds, additionally a (50:50 wt-%) corn starch–EVOH blend (60:40 mol/mol) was used for reference purposes. This SEVA-C, melting point 140°C, was also supplied by Novamont, Novara, Italy.

Hydroxyapatite (HA), provided by Plasma Biotal Ltd, UK, was used as reinforcement of the polymeric matrixes. The non-sintered Captal 'R' powder has a mean particle size of 5 μm and a maximum agglomerate size of ~10 μm.

### Compounding and injection moulding

A Betol (UK) 30 mm co-rotating twin screw extruder was used for compounding the SEVA-C grade with 20% HA. Both the matrix and filler material were fed into the hopper using K-Tron (Switzerland) metering devices. The extruded strand was pelletised inline. The maximum processing temperature was set in the die and metering zone to 160°C. The SPLA30 was compounded with 35% HA in a Brabender (UK) Z-Blade mixer at 120°C. This equipment was selected because of the softening point at 58°C and the low crystallinity of SPLA, unlike the SEVA-C grade.

The processing of tensile test bars was carried out on a MCP Sprite 7/50 (MCP Equipment, UK) mini injection moulding machine. The machine features a pneumatic powered screw plasticiser and a separate injection plunger with 750 bar (1 bar = $10^5$ Pa) maximum injection pressure. The maximum shot size (Euromap size: 5–5·25) is 7 cm³. Since moisture accelerates molecular degradation during processing,

*All percentages given are wt-% unless otherwise indicated.
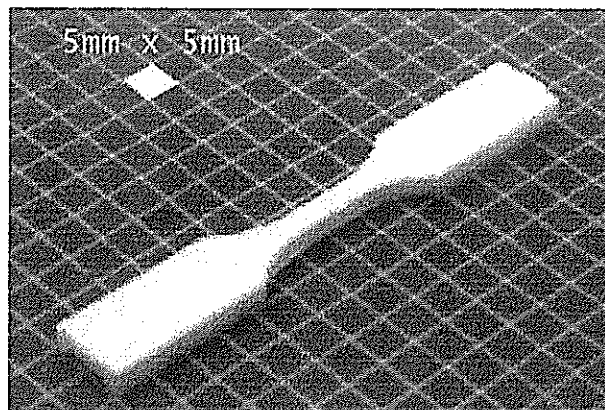


**2 Tensile test specimen**

the material was kept in a sealed bag and immediately processed after opening. Small amounts of material were filled into the hopper to reduce the residence time and subsequently minimise the moisture uptake.

The mould tool contained the SCORIM device, a hot runner system with two injection ports. While processing, one gate was blocked by a SCORIM piston during the injection phase to avoid weld lines within the specimen. In the conventional injection moulding (CIM), this gate remained blocked during the holding time. The process parameters were kept constant apart from the difference in holding pressure, which was related to the processing method. While a constant pressure was applied from a single injection port for CIM, the moving SCORIM pistons caused an oscillating holding pressure generated from either gate. The piston pressures were gradually reduced with holding time to avoid applying extensive shear to the remaining melt within the cavity. The resulting tensile test bars (Fig. 2) had a length of 70 mm and a thickness of 3 mm. The width of the grips was 10 mm, and the 10 mm long midsection was 3 mm wide.

The process temperatures for SEVA-C were chosen according to prior investigations. The melt temperature was set to 180°C and mould temperature to 60°C. For the HA filled SEVA-C, the melt temperature was increased to 190°C to reduce the viscosity.

Prior to SCORIM processing of SPLA, a process optimisation was carried out on SPLA50 and SPLA30. Rectangular flexural test bars (90 × 4 × 4 mm) were moulded by varying three parameters: holding pressure; melt; and mould temperature. Each parameter was varied between two levels: a high (+); and a low (−)

### Table 1 Parameters for process optimisation of SPLA50/SPLA30 (CIM)

| Melt temp., °C | Mould temp., °C | Holding pressure, bar* | Holding time, s | Cooling time, s | Injection pressure, bar | Injection time, s |
|---|---|---|---|---|---|---|
| 175 | 45 | 500 | 13 | 24 | 600 | 0·7/0·5 |
| 175 | 45 | 250 | 13 | 24 | 600 | 0·7/0·5 |
| 175 | 45 | 500 | 11 | 19 | 700 | 1·3/1·0 |
| 160 | 45 | 250 | 11 | 19 | 700 | 1·3/1·0 |
| 175 | 30 | 500 | 10 | 14 | 650 | 0·9/0·9 |
| 175 | 30 | 250 | 10 | 14 | 650 | 0·9/0·9 |
| 160 | 30 | 500 | 8 | 10 | 650 | 1·1/1·3 |
| 160 | 30 | 250 | 8 | 10 | 650 | 1·1/1·3 |

*1 bar = $10^5$ Pa.

level. Eight different batches were produced representing a $2^3$–full factorial design. The parameters used for the process optimisation are summarised in Table 1.

Using the optimised process parameters, tensile test bars of both SPLA grades were processed by CIM and SCORIM at 160°C melt and 25°C mould temperature. This melt temperature represented the lowest possible setting required to plasticise the material. The SPLA30 filled 35% HA was moulded at a melt temperature of 170°C to reduce the viscosity. Despite the elevated temperature, the injection time for the filled material was 11 s, owing to a lack of sufficient injection pressure on the moulding machine used. Therefore, only conventional mouldings were obtained since the remaining holding time was insufficient for SCORIM processing. The process parameters used for CIM and SCORIM processing of filled and unfilled SEVA-C and both SPLA grades are given in Table 2.

## Degradation study

The degradation behaviour was assessed after several pre-fixed ageing periods (1, 2, 3, 7, 14, and 30 days) in an isotonic saline solution (0·154 M NaCl) at 37°C. A minimum of five samples of each type per degradation period was tested. At the end of each degradation period, the samples were removed from the solution, rinsed with distilled water and weighed, to determine the water uptake; finally the samples were dried to constant weight (6 days at 60°C) to determine the dry weight loss.

In the case of the SPLA30 based samples, one batch of the tensile specimens was dried as described above for the remaining materials, and another batch was subjected to mechanical tests without a drying process to evaluate the changes in mechanical properties during degradation.

## Tensile testing

All specimens were tested on an Instron 4206 universal mechanical testing machine equipped with a 5 kN load cell and a clip on extensometer. The extensometer gauge length was 12·5 mm and grip distance 40 mm. The testing was carried out at room temperature at 1 mm min$^{-1}$ crosshead speed. Eight samples per batch were tested to calculate the mean and standard deviation. Five specimens were used per batch in the case of the immersed specimen.

## Thermal analysis

Differential scanning calorimetry (DSC) was performed on both the raw materials and the injection moulded samples to detect changes in crystallinity and transition temperatures. The characterisation was performed on a Perkin Elmer thermal analyser (7 series) at a heating rate of 10 K min$^{-1}$.

## Analysis of molecular orientation

Shrinkage testing of SPLA was performed to observe the differences in molecular orientation between SCORIM and conventionally processed specimens. Therefore, a thin section (3 × 3 × 0·5 mm) was cut from the middle of the specimen parallel to the melt flow direction. The section was placed onto a hot stage plate (Linkam TMS 92) in combination with a

**Table 2  Processing parameters for injection moulding of tensile test bars**

| Material | Processing method | Melt temp., °C | Mould temp., °C | Injection time, s | Holding time, s | Cooling time, s | Injection pressure, bar | Holding pressure, bar | Duration of SCORIM piston movements, s | Number of movements per Scorim piston |
|---|---|---|---|---|---|---|---|---|---|---|
| SEVA-C | CIM/SCORIM | 180 | 60 | 1·8 | 14 | 8 | 700 | 500/580–480 | .../10 | .../4 |
| SEVA-C+20% HA | CIM/SCORIM | 190 | 60 | 2·6 | 12 | 8 | 750 | 550/660–540 | .../10 | .../4 |
| SPLA30 | CIM/SCORIM | 160 | 25 | 1·2 | 14 | 18 | 650 | 450/560–440 | .../12 | .../4 |
| SPLA30+35% HA | CIM | 170 | 25 | 1·1 | 4 | 7 | 750 | 550 | | ... |
| SPLA50 | CIM/SCORIM | 160 | 25 | 1·3 | 13 | 12 | 650 | 450/640–440 | .../10 | .../4 |

microscope (Olympus SZ-PT) equipped with imaging facilities. The sample was heated from room to deformation temperature at a heating rate of $20\,\mathrm{K\,min^{-1}}$.

This test could not be performed with SEVA-C. A characteristic of this grade is the increase in melting temperature with decrease in moisture content. As a consequence, the material degraded thermally before relaxation occurred. Therefore, a Leitz micro-indenter was used to evaluate the Vickers hardness of unfilled SEVA-C. A cross-section was cut from the middle of the CIM and SCORIM processed test bars orthogonal to the flow direction. The sections were then ground and polished. The samples were indented diagonally from one corner to the opposite one.

## Scanning electron microscopy of fracture surface

The fracture surfaces of tensile tested SEVA-C and SPLA specimens were coated with Au/Pd alloy and analysed using a Jeol scanning electron microscope.

## RESULTS AND DISCUSSION

### Process optimisation of SPLA

The flexural properties (Table 3) of SPLA were differently influenced by the process parameters. In general, SPLA30 showed less dependence on the varied parameters compared with the other grade. The strength values of SPLA50 ranged from 42 to 56 MPa and strain at yield varied between 1·5 and 2·1%. The modulus of 2·9 GPa was marginally effected. Lower processing temperatures influenced these values positively. It was found that modulus (3·4 GPa) and strain at yield (2·05%) of SPLA30 were not substantially affected by the variation of processing conditions. The strength values, ranging from 67 to 70 MPa, followed the same trend with process conditions as in the case of SPLA50, but at a reduced level.

The dependence of properties upon process parameters was statistically analysed by using the energy to break data (Fig. 3). The energy to break values were chosen for evaluation because they reflect changes in stiffness as well as strength. The energy to break
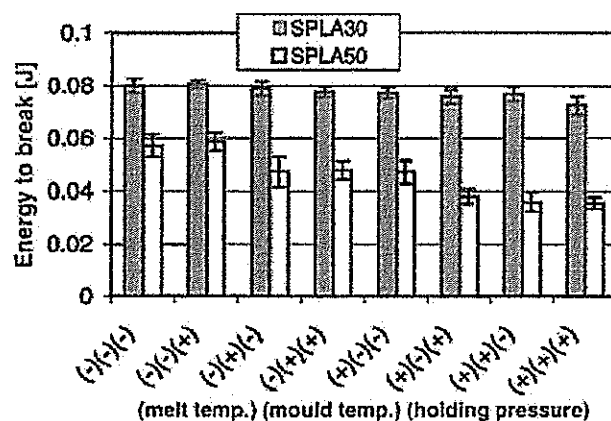
3  Energy to break of flexural tested SPLA
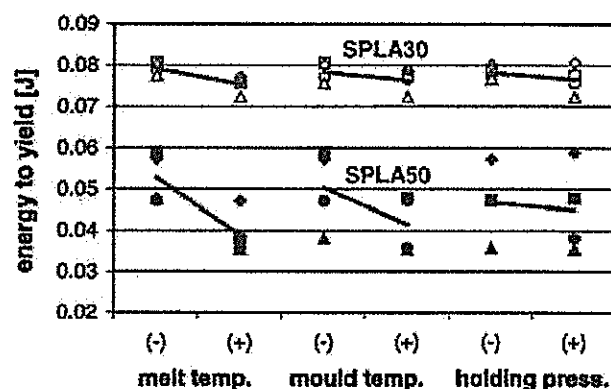
4  Effect of process parameters

of SPLA50 substantially decreased when the material was processed at elevated temperatures. In the case of SPLA30, this decrease was more marginal. The effects of the main factors, melt temperature, mould temperature and holding pressure, were analysed. The average values were calculated from all low level and high level responses of a single parameter and compared with each other (Fig. 4). The variation of melt temperature gave the most significant response. The mould temperature also proved to influence the melt

Table 3  **Flexural properties of conventially moulded SPLA by variation of process parameters (average value ± standard deviation)**

| Material | Design – levels: (melt temp.) (mould temp.) (holding press.) | Flexural strength, MPa | Strain at yield, % | Flexural modulus, MPa |
|---|---|---|---|---|
| SPLA30 | (−)(−)(−) | 69·85 ± 0·82 | 2·08 ± 0·03 | 3478 ± 31 |
|  | (−)(−)(+) | 69·62 ± 0·61 | 2·11 ± 0·02 | 3411 ± 21 |
|  | (−)(+)(−) | 68·83 ± 0·94 | 2·08 ± 0·03 | 3434 ± 36 |
|  | (−)(+)(+) | 69·13 ± 0·69 | 2·04 ± 0·03 | 3498 ± 29 |
|  | (+)(−)(−) | 68·10 ± 0·74 | 2·04 ± 0·03 | 3438 ± 64 |
|  | (+)(−)(+) | 67·60 ± 0·83 | 2·04 ± 0·04 | 3432 ± 43 |
|  | (+)(+)(−) | 68·09 ± 0·88 | 2·04 ± 0·05 | 3409 ± 27 |
|  | (+)(+)(+) | 66·96 ± 1·86 | 1·98 ± 0·05 | 3444 ± 117 |
| SPLA50 | (−)(−)(−) | 55·28 ± 2·10 | 1·90 ± 0·08 | 2965 ± 29 |
|  | (−)(−)(+) | 56·35 ± 1·72 | 1·91 ± 0·07 | 2995 ± 24 |
|  | (−)(+)(−) | 50·10 ± 3·31 | 1·73 ± 0·11 | 2974 ± 24 |
|  | (−)(+)(+) | 50·34 ± 1·98 | 1·74 ± 0·06 | 2935 ± 36 |
|  | (+)(−)(−) | 49·55 ± 2·27 | 1·74 ± 0·08 | 2895 ± 30 |
|  | (+)(−)(+) | 43·27 ± 1·60 | 1·61 ± 0·07 | 2737 ± 52 |
|  | (+)(+)(−) | 42·07 ± 1·91 | 1·55 ± 0·01 | 2744 ± 111 |
|  | (+)(+)(+) | 43·61 ± 1·25 | 1·49 ± 0·07 | 2951 ± 123 |

5 Stress–strain curves of SPLA
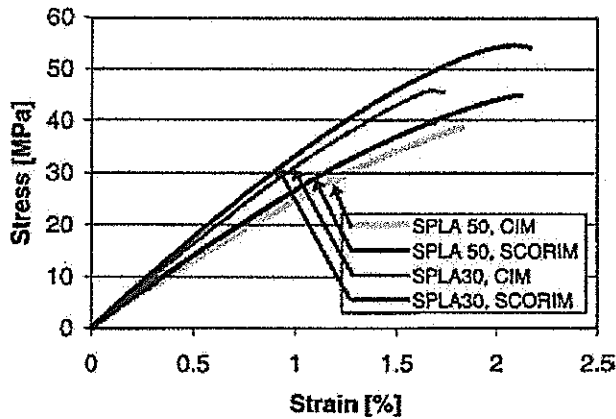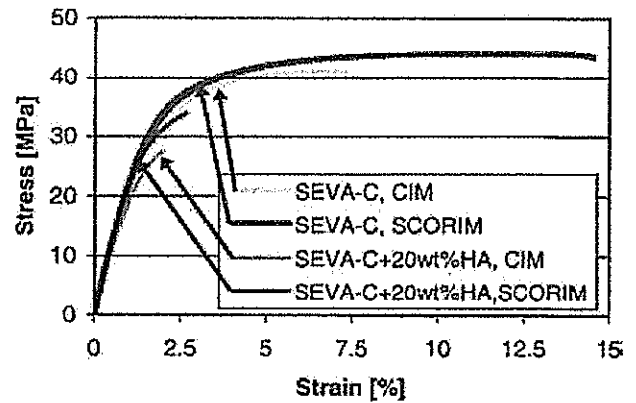


6 Stress–strain curves of SEVA-C

temperature substantially. The effect of the holding pressure was limited. Lower holding pressures and consequently reduced shear stress during the holding phase enhanced the properties, but to a relatively minor extent.

## CIM and SCORIM processing of SEVA-C and SPLA

Generally, SCORIM processing improved the tensile properties of the investigated starch blends (Table 4). Both grades of SPLA were similarly effected by the processing method (Fig. 5). The tensile strength increased to 45 MPa for SPLA50 and 54 MPa for SPLA30. In addition, the strain at peak value shifted from 1·7 to 2·2% in both grades. However, the modulus was not significantly affected by the processing method. Because of the enhanced strength and strain values, the toughness (defined as the energy to break divided by the tested sample volume) was substantially higher when mouldings were processed using SCORIM.

The SEVA-C was differently influenced by SCORIM compared with the relatively brittle SPLA grades (Fig. 6). The modulus of 2·5 GPa remained unaffected and the strength increased marginally by 5% to 44 MPa. However, SCORIM processing substantially enhanced the strain at peak and hence the toughness. The strain at peak doubled from 6 to 12% and the toughness increased from 2·5 to 6 MJ m$^{-3}$. The HA had a stiffening effect on the material, but the general strength of the composite decreased to 31–34 MPa. The SCORIM processing improved the tensile properties, but to a minor extent compared with unfilled SEVA-C.

In summary, the relatively ductile SEVA-C grade showed a substantial improvement in strain at peak of 90% when processed by SCORIM, while the more
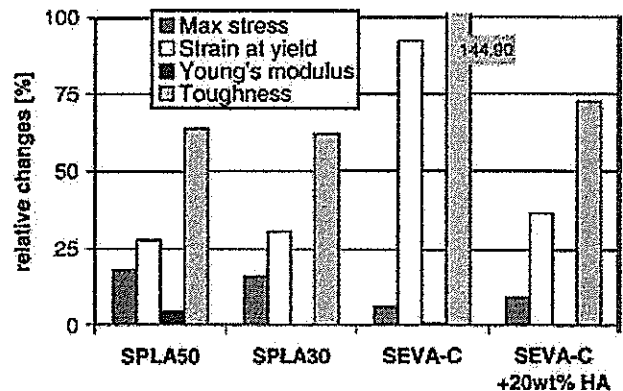


7 Improvement in properties achieved with SCORIM processing over CIM processing

brittle SPLA grades showed an increase in strength of 15% and in strain at peak of 30%. With all grades, applying the SCORIM process led to a major enhancement of toughness, 60% in the case of SPLA and 140% in the case of unfilled SEVA-C (Fig. 7). The improvement in properties was a result of SCORIM induced unidirectional molecular orientation within the mouldings as revealed by micro-indentation in the case of SEVA-C (Fig. 8) and the relaxation behaviour in SPLA (Fig. 9).

The differently processed SEVA-C samples exhibited a significant difference in hardness across the sections tested. The middle area and the corner areas exhibited similar hardness values while the SCORIM sample displayed an increased hardness at ~1 mm from the centre. This reflects the increase in molecular orientation and hence mechanical properties. However, the

Table 4 Tensile properties of CIM and SCORIM processed SPLA and SEVA-C (average value ± standard deviation)

| Material | Method | Max. stress, MPa | Strain at max. stress, % | Young's modulus, GPa | Toughness, MPa |
|---|---|---|---|---|---|
| SPLA50 | CIM | 37·8 ± 3·6 | 1·72 ± 0·16 | 2·77 ± 0·13 | 0·36 ± 0·07 |
| | SCORIM | 44·7 ± 3·8 | 2·20 ± 0·28 | 2·90 ± 0·14 | 0·59 ± 0·12 |
| SPLA30 | CIM | 45·9 ± 0·3 | 1·70 ± 0·08 | 3·40 ± 0·15 | 0·45 ± 0·06 |
| | SCORIM | 53·4 ± 2·9 | 2·22 ± 0·22 | 3·29 ± 0·20 | 0·73 ± 0·17 |
| SEVA-C | CIM | 41·3 ± 0·5 | 6·25 ± 0·84 | 2·45 ± 0·16 | 2·45 ± 0·72 |
| | SCORIM | 43·8 ± 1·5 | 12·03 ± 0·73 | 2·47 ± 0·12 | 6·00 ± 0·99 |
| SEVA-C+ | CIM | 31·1 ± 2·1 | 1·94 ± 0·34 | 2·96 ± 0·28 | 0·29 ± 0·16 |
| 20 wt-% HA | SCORIM | 33·9 ± 2·1 | 2·65 ± 0·27 | 2·88 ± 0·22 | 0·50 ± 0·10 |
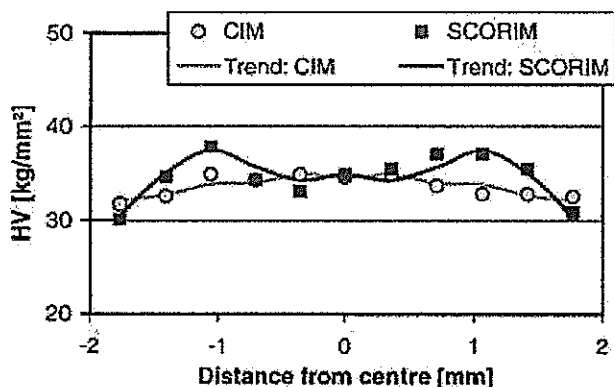
**8 Micro-indentation of CIM and SCORIM processed SEVA-C**

size of the central ringlike region with greater hardness proved to be insufficient to affect the Young's modulus positively.

In the case of SPLA, molecular relaxation was observed on the skin area of the conventional moulding. This was due to the shear induced frozen orientation 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 subsequently had no memory effect within this area. By contrast, the constant shear during the holding time induced by the SCORIM process resulted in frozen orientations within a ringlike region. There is a substantial relaxation of molecules in this area. However, shrinkage was not observed in the centre of the section, which is explained as follows. The shear during the holding phase could be applied only until the gates froze off. After this time, the unfrozen polymer melt within the cavity was able to relax and therefore the SCORIM sample exhibited a non-orientated core region. A modification at the gates by increasing their diameter or temperature

would increase the time to freeze off the polymer. Therefore, a modification would be likely to improve the overall molecular orientation owing to the longer periods that shear could be applied during holding time. In addition, an increase in piston pressure and hence greater shear heating within the gates would increase the freezing off time, but since the SPLA was shown to be very sensitive to the processing conditions, the overall properties are very likely to deteriorate as a result of molecular degradation.

The change in ductility when applying the SCORIM process is reflected by different fracture surfaces (Fig. 10). The fracture surfaces of tensile tested conventional SPLA30 mouldings were planar, which is consistent with brittle behaviour. The more ductile SCORIM sample exhibited a distinct skin–core morphology resulting from the different levels of orientation within the cross-section, as shown previously by the molecular relaxation and micro-indentation tests.

## In vitro degradation of SEVA-C and SPLA

Both blends exhibited hydrophilic behaviour as shown by analysis of the water uptake during immersion (Fig. 11). A rapid increase in moisture content occurred after three days *in vitro*. The water content remained fairly constant after that period. The level of saturation was 25% for SEVA-C and 30% in SPLA50. The SPLA30 was the starch blend with the lowest hydrophilicity. The level of moisture exhibited an increasing trend during immersion and was 20% after 30 days. Generally, SCORIM processing appeared to slow down the water uptake, but not significantly. The composite material was saturated with 12% moisture after 7 days *in vitro*. The HA affected neither the absorption rate nor the saturation level of the more hydrophilic SEVA-C. The moisture content for the matrix material calculates at 27% when it is assumed that the mineral filler does not absorb any water. The SPLA30, which has the lowest absorption
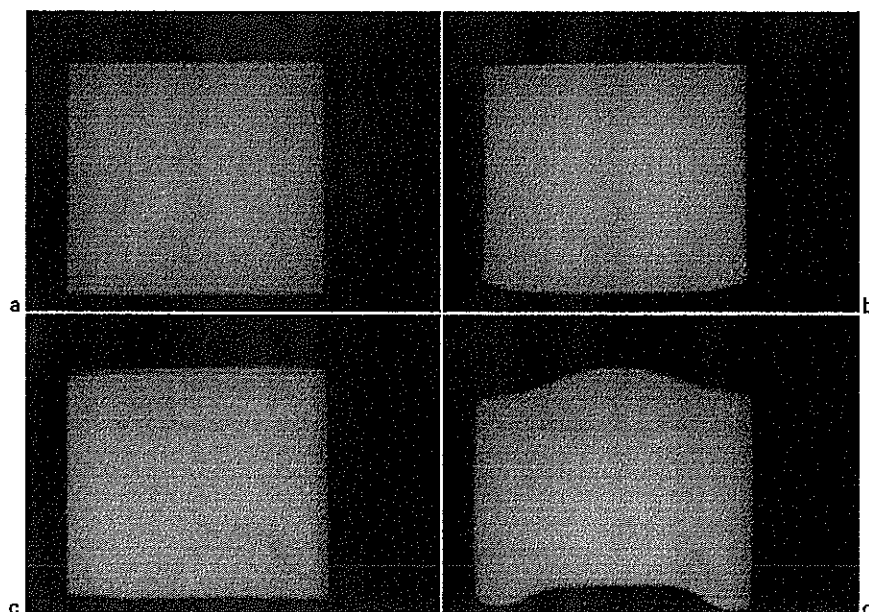


*a* CIM, room temp.; *b* CIM, 120°C; *c* SCORIM, room temp.; *d* SCORIM, 120°C

**9 Relaxation behaviour of CIM and SCORIM processed SPLA30**

a

b
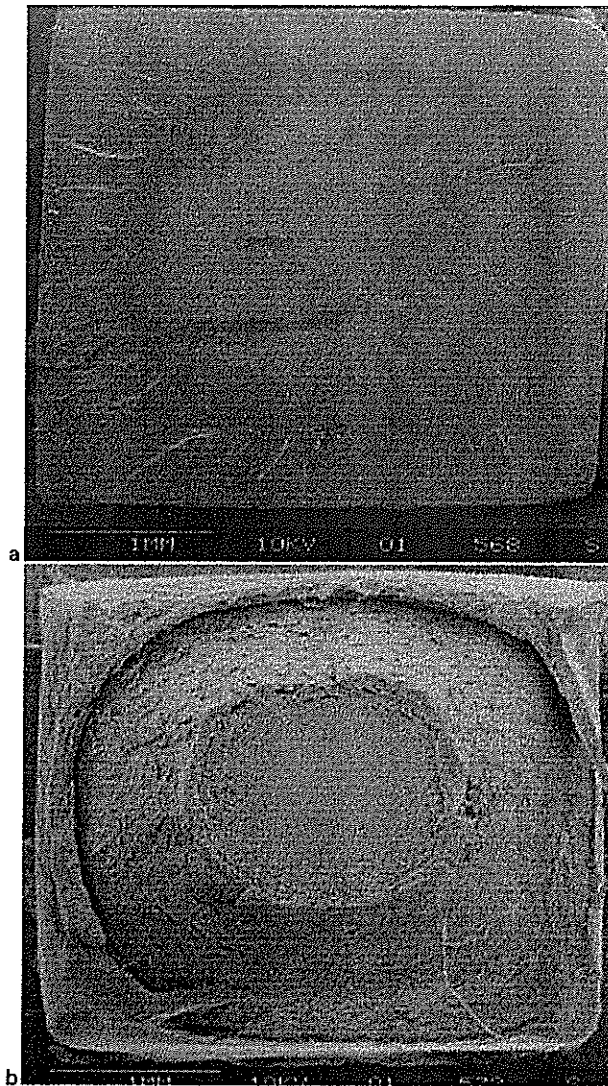
**10 Fracture surface of tensile stressed SPLA30: a CIM; b SCORIM**

rate and best mechanical properties, was selected for further investigation, regarding changes in mechanical properties due to *in vitro* degradation.

The mechanical properties deteriorated rapidly during immersion. It is known that starch based materials become softer and more ductile at higher moisture contents. The stiffness of SPLA30 (Fig. 12) exhibited the characteristic relation to the water content. The modulus decreased rapidly within the first 7 days. After this period, when the moisture content increased little, the modulus hardly changed. The modulus after 30 days *in vitro* was 1·5 GPa, 45% of its initial value. The stiffness of the SCORIM processed samples was marginally higher during immersion compared with the conventional mouldings. Owing to the faster absorption rate, the decrease in stiffness of HA filled SPLA30 was more rapid than in the unfilled material. The modulus levelled off after 3 days *in vitro*. The steady state modulus was, similarly to the unfilled material, 1·5 GPa, 35% of its initial stiffness. The tensile strength of SPLA (Fig. 13) was 30 MPa after 3 days *in vitro*, 40% less than the initial strength. The strength decreased further but remained fairly constant after 14 days of immersion with 40–45%
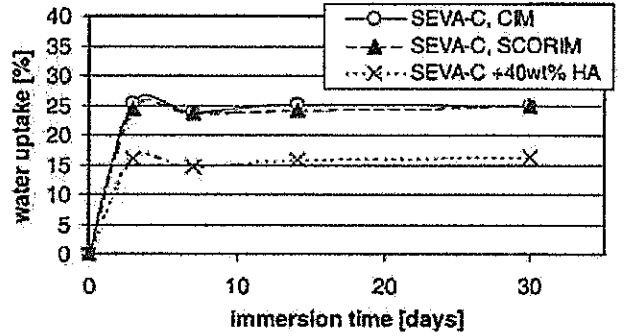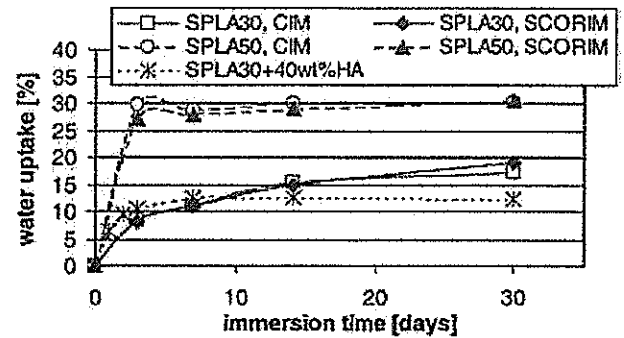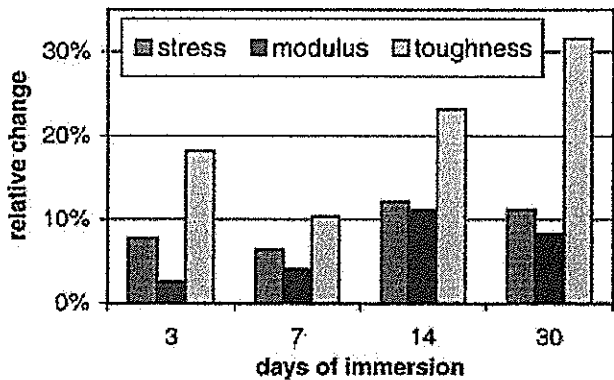


**11 Water uptake v. immersion time in saline solution of SPLA and SEVA-C samples obtained by conventional and SCORIM processing and by CIM using HA reinforcement**
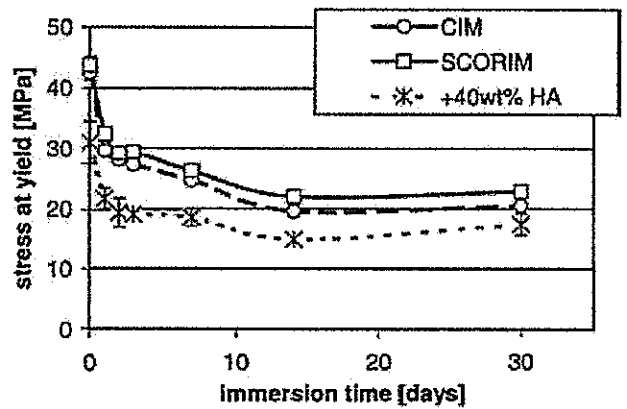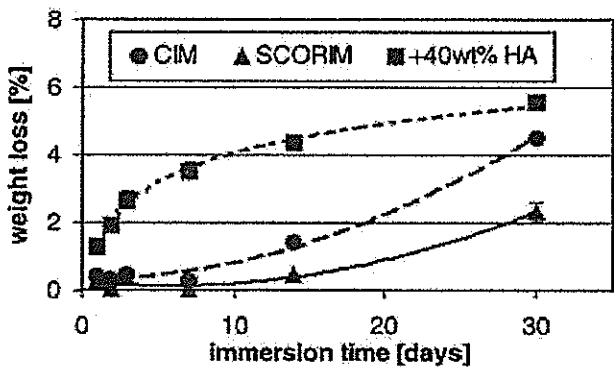


**12 Tensile strength of SPLA30 based samples obtained by conventional and SCORIM processing and by CIM using HA reinforcement after several degradation periods in saline solution**
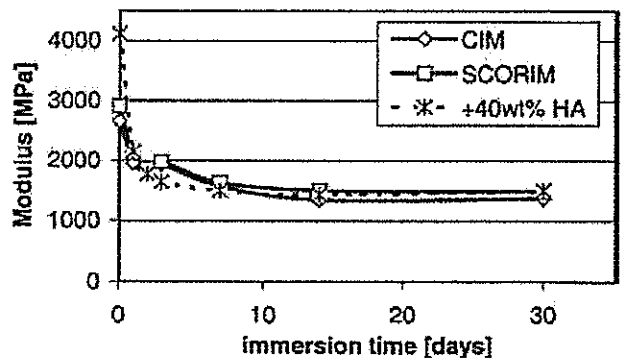


**13 Modulus of SPLA30 based samples obtained by conventional and SCORIM processing and by CIM using HA reinforcement after several degradation periods in saline solution**

**14**  Comparison of improvement in tensile properties after immersion for varying periods in saline solution in SPLA30 obtained by SCORIM processing over CIM processing



**15**  Weight loss *v.* degradation period for SPLA30 samples obtained by conventional and SCORIM processing and by CIM using HA reinforcement

of its initial strength remaining. The SCORIM mouldings exhibited an identical trend, but with strength values at a higher level. In HA filled SPLA30, the strength decreased at a faster rate. The values varied marginally between 3 and 30 days *in vitro* and remained

at 45% of the initial value. Generally, SCORIM processed materials exhibited higher strength, stiffness and in particular toughness values during immersion than conventionally moulded SPLA30 (Fig. 14). The relative difference appeared to increase with immersion time. The toughness of SCORIM samples was 31% higher after 30 days *in vitro*.

The reason for the increasing gap between SCORIM and CIM samples can be found in the weight loss of SPLA during immersion (Fig. 15). The weights of the mouldings started to decrease between 7 and 14 days *in vitro*, but at a slower rate in the case of SCORIM processed samples. The conventional mouldings exhibited a 4% change of weight after 30 days immersion, double the value of SCORIM samples. Immersion had the strongest effect on the HA–SPLA composite. A weight loss was detected within the first 3 days *in vitro*. The overall decrease was 5–6% after 30 days. The rapid mass loss is explained by the different swelling characteristics of starch, PLA and the mineral filler when water is absorbed. During expansion the hydrophilic starch granules swelled, unlike the hydrophobic PLA, which caused microcracks within the material. The incorporation of HA intensified the mismatch of volume expansion and therefore the composite structure became more sensitive towards fluids, resulting in weight loss and further decrease in mechanical properties.

The DSC analysis shows the changes in the microstructure of SPLA30 resulting from immersion and the use of different processing methods (Fig. 16). The recrystallisation peak shifted from 100 to 105°C when SPLA was processed using SCORIM. Neither the glass transition temperature at 56°C nor the stress relaxation peak was influenced. In addition, the processing method did not appear to have an effect on the two melting peaks at 145 and 157°C. These two characteristic melting peaks merged after 30 days *in vitro*. A sharp peak occurred at 158°C, indicating that a chemical reaction took place, which was probably caused by the phosphate buffered saline solution.
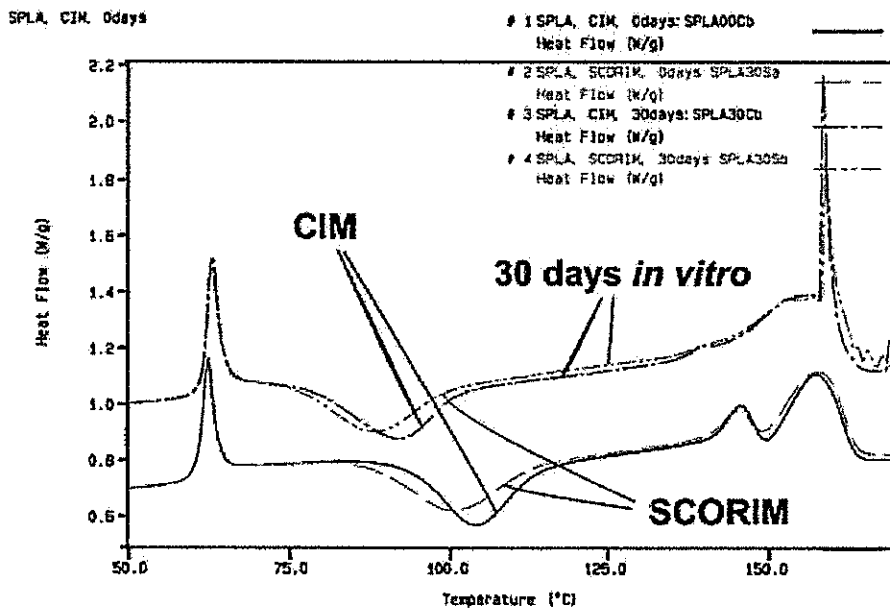


**16**  DSC of SPLA30

Since such a reaction is likely to affect the mechanical properties, the marginal increase in tensile strength of SPLA30 between 14 and 30 days *in vitro* can be explained. The recrystallisation of the immersed specimens took place at lower temperatures, the peaks are at 88 and 92°C, indicating higher mobility of polymer chains due to molecular degradation.

## CONCLUSIONS

The SCORIM processing created an anisotropic microstructure within the mouldings and the mechanical properties were improved unidirectionally. In particular the toughness was increased by 60% for both SPLA grades. The toughness of SCORIM processed SEVA-C was more than doubled compared to conventionally processed samples. However, the influence of SCORIM processing on the mechanical properties of biodegradable starch based blends proved to be less than that observed in commodity polymers such as polyalkenes. One reason for this is thought to be the sensitivity of the biodegradable polymers to the process parameters, in particular melt and mould temperatures. The very narrow processing window does give sufficient opportunity to change parameters, to enhance the level of anisotropy without compromising the properties by molecular degradation.

The stiffness and strength of SPLA30 decreased substantially *in vitro*. However, SCORIM processed samples maintained their superior properties throughout the degradation period. The incorporation of HA in SEVA-C and SPLA30 led to an increase in stiffness but also loss in strength. The relatively fast degradation of SPLA in respect to weight loss makes it an interesting candidate for medical applications.

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