DEVELOPING AN IN-SITU POLYMERISATION PROCESS FOR BIOCOMPOSITE MANUFACTURE

Menghao Chen[1], Derek Irvine[2], Andrew Parsons[1], Christopher Rudd[1], Ifty Ahmed[1]

[1]Divison of Materials, Mechanics and Structures, University of Nottingham,
University Park, Nottingham, UK, NG7 2RD
Email: eaxmc@nottingham.ac.uk, web page: www.nottingham.ac.uk

[2]Division of Energy and Sustainability, University of Nottingham
University Park, Nottingham, UK, NG7 2RD

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ABSTRACT

Investigations have been performed towards developing fully bioresorbable polymer composites intended to improve and replace metal implants in hard tissue repair. Bioresorbable phosphate based glass fibres (PGF) are produced by our group and used as the reinforcement in poly(ε-caprolactone) (PCL) composite production. Conventional manufacturing methods, such as laminate stacking (LS), often give poor interfacial bonding due to difficulty in fibre impregnation caused by the high viscosity of the polymer melt, which results in low mechanical properties and early stage failure of the composites. In order to overcome these issues, low viscosity ε-caprolactone monomer is in-situ polymerized (ISP) within a mould cavity to produce a net shape moulding. PGF mats are placed inside the mould cavity and are impregnated by ε-caprolactone monomer to produce bioresorbable PCL/PGF composites. Specific moulds were designed and made with the aim to ensure that they are well sealed, easy to de-mould and are both chemically and thermally stable for the polymerisation. A kinetic study of the ε-caprolactone polymerisation mechanism was performed in order to determine the optimal reaction parameters. Composites with 35% fibre volume fractions (V_f) were manufactured by both LS and ISP processes and SEM images indicated uniform fibre distribution, significantly better fibre impregnation and stronger interfacial bonding in ISP composites as compared to LS composites. Further work will be undertaken to investigate and compare the degradation behaviour of the LS and ISP composites.

1. INTRODUCTION

There is significant scope for improving and developing currently used load bearing metal devices for hard tissue repair. Metal alloys have been used to produce biomedical implants, such as bone fixation devices, since early 1900s mainly due to their excellent mechanical properties, durability and corrosion resistance [1]. However, several complications associated with traditional metal alloys, such as stainless steel, titanium and cobalt chromium alloys, are clearly identified. Stress shielding is the main issue resulting from the huge stiffness mismatch between metal implants (E=100-200 GPa) and the surrounding bone tissue (E=5-20 GPa) [2, 3]. Bone is a dynamic material that remodels itself according to its loading history. Since the rigid metal devices cover most of the load from the healing bone, the healing bone is not subjected to normal load-induced remodelling, which may lead to bone wakening and resorption [4]. Most European countries require the metal implants to be removed after the bone has healed, which also increases the re-fracture rate due to the weakened nature of the healed bone [5]. The relatively higher density of the metal devices could also cause elevated local stresses around the implant sites. Metals themselves interfere with certain modern imaging techniques as well, such as Magnetic Resonance Imaging (MRI).

Fully bioresorbable polymer composites provide an attractive opportunity to improve and replace the traditional metal implants and are an active research field due to their potential in load-bearing applications. Aliphatic polyesters, such as poly(ε-caprolactone) (PCL) and poly(lactic acid) (PLA),

play a leading role to serve as the matrix material since they have been approved by national regulatory bodies (FDA, etc.) due to their favourable biocompatibility [6, 7]. Biocompatible polymers by themselves are easily processed and well-tolerated by human bodies. However, they tend to have insufficient mechanical properties for load-bearing applications [8]. Therefore, introducing reinforcement materials into the polymers are necessary. Reinforcement can be incorporated into the polymer in the form of particulates and fibres. For bioresorbable composites, common reinforcement materials include bio-ceramics (Hydroxyapatite (HA)), polymeric fibres (PCL fibre), bioactive glass (45S5 bioglass) and phosphate based glass fibre (PGF) [2, 9, 10]. PGFs are biocompatible and able to dissolve completely in aqueous conditions. Their dissolution rate can be easily adjusted by altering the glass composition [8]. This fibre also exhibits high mechanical properties with ~500-1000 MPa and ~70 GPa for tensile strength and modulus respectively, which are directly comparable to commercially available E-glass fibre [11, 12]. PLA/ unidirectional PGF composites plates with fibre volume fractions (V_f) of 35% and 50% have been produced, which gave flexural strengths of ~116 MPa, 170 MPa and flexural modulus values of ~16G Pa and ~15G Pa, respectively [13, 14]. PGFs provide an excellent opportunity to facilitate a fully bioresorable polymer composites with a high initial stiffness to allow fracture fixation and initial bone union, followed by graduate reduction in stiffness to correspond with healing bone's increasing load-bearing capability.

The development and manufacture of fully bioresorbable, load-bearing polymer composites with appropriate biocompatibility and mechanical properties has become an exciting research area in recent decades. The conventional manufacturing technique adapted for bioresorbable polymer composites is laminate stacking (LS) and hot press moulding [15-17]. However, a number of studies have seen a rapid loss of mechanical properties when placing the composites manufactured by LS into a physiological environment [8, 14, 18, 19]. It is believed that rapid hydrolysis of the polymer/fibre interface occurs, which reduces adhesion and prevents efficient stress transfer between matrix and reinforcement. Due to the high viscosity of the polymer melt, it is difficult to achieve a good impregnation and wet-out of the fibre surfaces using the LS technique. Poor interfacial bonding between the fibre and the matrix could result in low mechanical properties and early stage failure of the composites. Since the fibre mats and polymer films are stacked together, the composites produced tend to form polymer rich zones and fail via delamination. The compact layers of fibre also make it more difficult to be fully wet-out by the matrix. In addition, the secondary processing of the biocompatible polymers can cause significant thermal degradation and lower the molecular weight, which in turn lowers the mechanical properties of the matrix and hence the final composites.

In this paper, in-situ polymerisation (ISP), a variant of liquid moulding based on the monomer transfer moulding (MTM) technique, is developed and investigated to manufacture fully bioresorbable PCL/PGF composites. Similar approaches, such as Resin Transfer Moulding (RTM) and Structural Resin Injection Moulding (SRIM) in the thermoset composites manufacturing are well developed. However, the counterpart in the thermoplastic composites manufacturing is rarely reported. Instead of using resin, a reaction mixture (monomer and catalyst) is transferred into the moulds and forms the matrix directly around the reinforcement units. For this ISP technique, ε-caprolactone along with the catalyst and initiator are injected into a mould cavity with PGF mats placed inside, and then polymerisation happens under heat to form PCL/PGF composites in a single step. This system allows the use of low viscosity monomer (1.07 mPa.s) rather than the polymer melt (12,650 Pa.s) [20]. Since the viscosity of the monomer is much lower compare to its polymer melt, good fibre impregnation and significantly better interfacial bonding can be promoted by ISP, which should lead to higher mechanical properties and a better degradation profile for the biodegradable implants. This technique allows direct control of molecular weight of the polymer polymerised by altering the amount of initiator in the system. Composite implants with complicated shapes can also be produced by ISP as closed moulds with complex cavity shapes can be manufactured.

In this paper, a kinetic study of ε-caprolactone polymerisation was performed and reported in order to determine the optimal reaction parameters, using conditions that mimic the static in-mould reaction environment. Monomer conversion rate, molecular weight and polydispersity (PDI) were monitored by Nuclear Magnetic Resonance (NMR) and Gel Permeation Chromatography (GPC). Fully bioresorbable PCL/PGF composites with 35% V_f are manufactured via both LS and ISP in order to

compare the reinforcing efficiency of both manufacturing techniques. SEM images were taken to investigate the fibre distribution and polymer/fibre interface bonding.

2. MATERIALS AND METHODS

2.1. Materials

The monomer ε-caprolactone, catalyst $Sn(Oct)_2$ and initiator benzyl alcohol are all purchased from Sigma Aldrich and are all used as received. PCL granules used in LS are also purchased from Sigma Aldrich, with a weight average molecular weight (M_w) of ~65,000 g/mol and number average molecular weight (M_n) of ~42,500 g/mol. The granules were dried at 50 °C in the vacuum oven for 48 hours before processing. Bioresorbable phosphate based glass and glass fibre are all manufactured in house. PGFs themselves are continuous strands of parallel filaments without any twist and are spray coated with PCL in order to maintain the fibre alignment. The coated UD fibre mates were oven dried at 50 °C for 48 hours prior to use.

2.2. Polymerisation chemistry

PCL can be synthesised from both condensation polymerisation (CP) and ring opening polymerisation (ROP). Because of the difficulty in getting rid of the water during CP, ROP is usually used in order to yield high molecular weight polymers. ROP of ε-caprolactone is chosen here and the reaction follows the coordination insertion mechanism (CIM) using $Sn(Oct)_2$ as the pre-catalyst and benzyl alcohol as the initiator. The reaction mechanism is illustrated in Figure 2.1. $Sn(Oct)_2$ first reacts with benzyl alcohol to form the active catalyst species for ROP. The monomer then coordinates with the catalyst, which induces strain in the monomer ring. The monomer is finally inserted into the Sn-O bond by acyl-oxygen bond scission in such a way that the growing chain remains attached to the catalyst through an alkoxide bond.

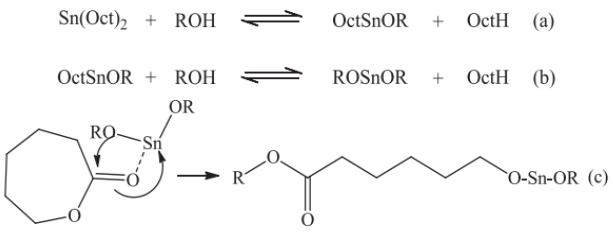

Figure 2.1: Initiation and propagation reactions for CIM polymerisation of ε-caprolactone

2.3. Kinetic study of ε-caprolactone polymerisation

The molecular weight and polydispersity of the PCL synthesised by ISP are dependent on several manufacturing parameters, which are reaction temperature, reaction time under heating, extent of impurities and catalyst and initiator concentrations. It is believed that higher molecular weight and lower polydispersity (≥1) of the polymer can increase its mechanical properties. Meanwhile, more consistent and homogenous performance can also be achieved when the polymer serves as the matrix material of the composites. In order to determine the most suitable polymerisation environment, a kinetic study to simulate the reaction conditions inside the mould and to monitor the polymerisation behaviour is performed. In this study, 5ml glass vials are used to replace the mould as it is difficult to sample from the sealed mould during the polymerisation.

ε-caprolactone was treated with a predetermined amount of $Sn(Oct)_2$ and benzyl alcohol under a dry blanket of nitrogen in a 100 ml two neck boiling flask. Detailed molar ratios and reaction conditions are stated in Table 2.1. All the glassware and needles were dried in a 50 °C oven for 24 hours before use. The reaction mixture was mixed using a magnetic stirrer on a hot plate for 20 minutes. After the mixing was completed, 2 ml of the mixture was then injected into each vial by a syringe. The glass vials were then transferred into an oven at the predetermined temperature. At each

time point (every 30 minutes in this case), one glass vial was then taken out of the oven, and a sample was collected for the chemical analysis.

2.4. ISP mould design

In order to perform ISP of PCL/PGF composites, moulds were designed and made out of PTFE and aluminium (Figure 2.2). PTFE was chosen as the material because it is chemically inert, thermally stable and easy for sample de-moulding. Each mould consists of a female half and a male half PTFE block, and two aluminium blocks, which act as the outer shells to protect the PTFE moulds. The aluminium blocks also helped to flatten the PTFE moulds as PTFE is prone to distortion under stress and heating. The mould halves were assembled using long screws and nuts. Two injection ports were located on the male half, one for liquid injection and one for degasing. The sample cavity was positioned on the female half and surrounded by an O-ring cord groove to provide a tight seal. O-rings were also incorporated around the injection ports.

Reaction parameters	Molar Ratio of [ε-caprolactone : Benzyl alcohol : $Sn(Oct)_2$]; Reaction Temperature (°C)		
Alter $Sn(Oct)_2$ amount only	[1000:1:1]; 130	[1000:1:0.5]; 130	[1000:1:0.1]; 130
Alter Benzyl alcohol amount only	[1000:1.25:0.5]; 130	[1000:1:0.5]; 130	[1000:0.625:0.5]; 130
Alter reaction temperature only	[1000:1:0.5]; 110	[1000:1:0.5]; 130	[1000:1:0.5]; 150
All reactions are monitored up to 24 hours			

Table 2.1: Reaction parameters for polymerisation kinetic study

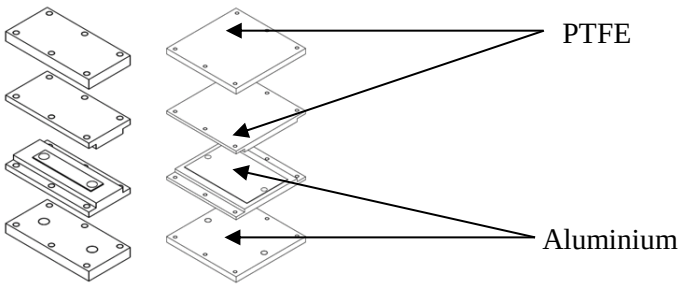

Figure 2.2: PTFE moulds for ISP

2.5. Phosphate based glass and glass fibre production

Bioresorbable phosphate based glass was produced in house in order to make phosphate glass fibre. The precursors used to prepare the glass were sodium hydrogen phosphate (NaH_2PO_4), calcium hydrogen phosphate ($CaHPO_4$), magnesium hydrogen phosphate tri-hydrate ($MgHPO_4 \cdot 3H_2O$), iron(III) phosphate di-hydrate ($FePO_4 \cdot 2H_2O$) and phosphorous pentoxide (P_2O_5). Only one glass formulation was used in this project, which is indicated in Table 2.2. The precursors were mixed and then transferred into a 100 ml Pt/5% Au crucible (Birmingham Metal Company, UK). The crucible was then placed in a preheated oven (350 °C) for 30 minutes to drive off any water in the mixture. The salt mixtures were then melted and reacted in a furnace at 1150 °C for 1.5 hours. Molten glass was poured onto a steel plate to cool down.

The laboratory fibre drawing rig employed a melt-spun method, which is widely used in industry to produce glass fibre. The fibre rig consists of a furnace (Lenton Furnaces) with a Pt/10% Rh crucible (Johnson Matthey, UK) consisting of a bushing with an approximate 1 mm hole and a tip 15 mm long. Glass was placed into the crucible and left to melt and homogenise for 30 minutes. The temperature of the furnace was then dropped to achieve a viscosity suitable for fibre drawing. Different fibre

diameters can be obtained by pulling the glass at different speeds. In order to produce the unidirectional fibre mat, the collecting drum was adjusted to move transversely at constant speed, covering the drum evenly with fibre. After the fibre mat had reached a certain thickness, the fibre drawing was stopped and the drum was taken to a fume hood. With the aim to maintain the integrity of the fibre mat, PCL granules were dissolved in chloroform and the solution was sprayed onto the fibre mat to coat them. After the spraying, the drum was left inside the fume hood for 24 hours to let the chloroform volatilize. Finally, the coated fibre mat was removed from the drum.

Glass code	P_2O_5 content (mol%)	CaO content (mol%)	Na_2O content (mol%)	MgO content (mol%)	Fe_2O_3 content (mol%)	Drying temp/time (°C/h)	Melting temp/time (°C/h)
P45Fe5	45	16	10	24	5	350/0.5	1100/1.5

Table 2.2: Glass code and formulation

2.6. Laminate stacking (LS) and hot press moulding composites production

Pure PCL thin laminates were made by hot press moulding of 4~5 g PCL granules. The granules were placed between two pieces of PTFE glass fabrics and two pieces of metal plates. The whole assembly and granules was heated to 120 °C within the heated press for 10 minutes and then pressed at 3 bars for 1 minute. The assembly was then transferred immediately to a cold press at room temperature to cool down under the same pressure.

The PCL/P45Fe5 laminates were prepared by film stacking technique. Figure 2.3 illustrated the assembly of the tools for laminate production. Both pure PCL laminates and phosphate glass fibre mat were cut into shape to fit in the shim. The assembly was then heated to 120 °C within the heated press for 15 minutes, pressed under 30 bars for 10 minutes. The stack was then transferred immediately to a cold press at room temperature to cool down under the same pressure for 15 minutes. The composite was then cut into certain dimensions by using a band saw. Samples with 35% V_f (LS35) were produced for interface studies.

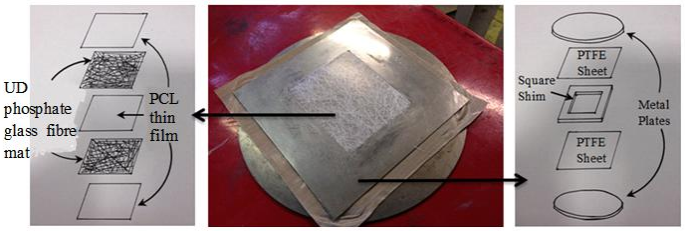

Figure 2.3: Film stacking assembly for hot press moulding

2.7. In-situ polymerisation (ISP) composites production

The mould assembly used for ISP and the mixing and injection apparatus were all dried at 70 °C for 24 hours in a vacuum oven before processing. UD PGF mats were carefully trimmed to fit in the cavity of the mould (70 mm * 15 mm * 2 mm). The trimmed fibre mats were also dried under the same conditions as the moulds. ε-caprolacotone was treated with a predetermined amount of $Sn(Oct)_2$ and benzyl alcohol under a dry blanket of nitrogen in a 100 ml two neck boiling flask. The reaction mixture was mixed by a magnetic stirrer on a hot plate until homogeneous. After the mixing was completed, the mixture was then injected into the moulds by using a syringe. Each injection port was connected with one syringe by PTFE tubing, one with the chemical mixture and one empty. The reaction mixture was injected backwards and forwards from one syringe to the other in order to eliminate air bubbles in the moulds and to ensure a smooth injection process (Figure 2.4). During the injection, the whole mould assembly was placed on a rotating whirl mixer to help removing the trapped air inside the mould. After the injection has completed, two tubing clamps were used to seal the tubing and syringes were then removed. The mould assembly was then transferred into a preheated

oven for a certain time to complete the polymerisation reaction. Finally, moulds were disassembled and samples were taken out of the moulds. Composites with ~35% V_f were produced (ISP35).

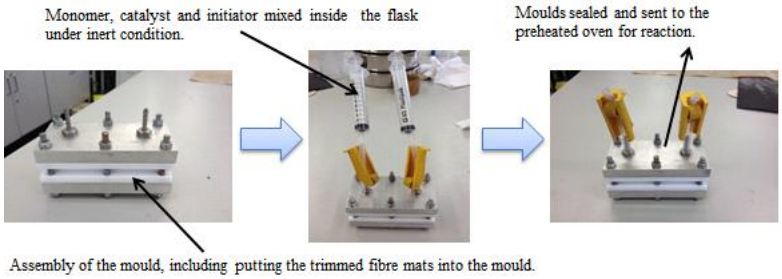

Figure 2.4: ISP composites production procedures

2.8. Scanning Electron Microscopy (SEM)

SEM was performed to analyse the polymer/fibre interface and fibre distribution in fracture surfaces for both LS and ISP samples. Secondary electron mode was used with a voltage of 10 kV. Composite samples were all sputter-coated with platinum to ensure good conductivity. In order to overcome the ductile nature of PCL, samples were immersed in liquid nitrogen for 5 minutes and then immediately fractured into two pieces by a sharp blow from a hammer.

2.9. Nuclear Magnetic Resonance (NMR)

The molecular structure and monomer conversion rate was monitored by NMR technique. ^{1}H spectra were recorded in deuterated chloroform solution by using a Bruker DPX 300 MHz spectrometer. Sample concentration was 5% for the ^{1}H spectra.

2.10. Gel Permeation Chromatography (GPC)

GPC was performed to analyse the molecular weight and molecular weight distribution. The GPC was an Agilent Technologies 1260 Infinity GPC system with mixed D columns at 40 °C and a refractive index detector. Chloroform was used as the mobile phase at a flow rate of 1.0 cm^3/min. Calibration was accomplished against polystyrene standards. The calibration range of the GPC was from elution time of 10 min to 17.35 min, corresponding to molecular weight from 580 g/mol to 377,400 g/mol. Sample concentration was around 5 mg/ml.

3. RESULTS AND DISCUSSIONS

3.1. Effects of $Sn(Oct)_2$ concentration on ε-caprolactone polymerisation

Figure 3.1 showed that monomer conversion after 120 minutes reached ~98% and ~84% when the $Sn(Oct)_2$ concentration was 0.0174 mol/L and 0.00868 mol/L respectively (Reaction temperature and Benzyl alcohol concentration were kept constant). It can also be seen that monomer conversion only reached ~17% after 6 hours with the lowest concentration of 0.00174 mol/L. When the reaction temperature and the initiator concentration were kept at the same level, the catalyst ($Sn(Oct)_2$) concentration revealed the ability to accelerate or decelerate polymerisation of the ε-caprolactone polymerisation.

Figure 3.2 depicts the change of Mw and PDI at each time point with varying catalyst $Sn(Oct)_2$ concentration. It was evident that increasing catalyst concentration increased the rate of reaction significantly, with the polymerisation of the highest catalyst concentration reaching ~30,000 g/mol at 120 minutes and the lowest only reaching ~5,000 g/mol at 210 minutes. It was also noted that polymerisation didn't take place within the first 60 minutes with the lowest concentration. This has been referred to as the polymerisation induction time, in which the pre-catalyst ($Sn(Oct)_2$) and the alcohol (Benzyl alcohol) reacts to form the active catalyst (Figure 2.1). By increasing the catalyst concentration, the induction time is also shortened significantly (<30 mins). However, as the

polymerisation happens faster, the PDI also increased, which indicated that polymer chain lengths were becoming broader. It is known that excessive catalyst in the ring opening polymerisation system can induce extensive inter- and intra-molecular transesterifications due to excessive active chain ends formed by the catalyst, which could considerably lower the molecular weight and increase the polydispersity. Therefore, in order to minimize polymerisation time, the catalyst concentration should be kept as high as possible without jeopardising the molecular weight and polydispersity.

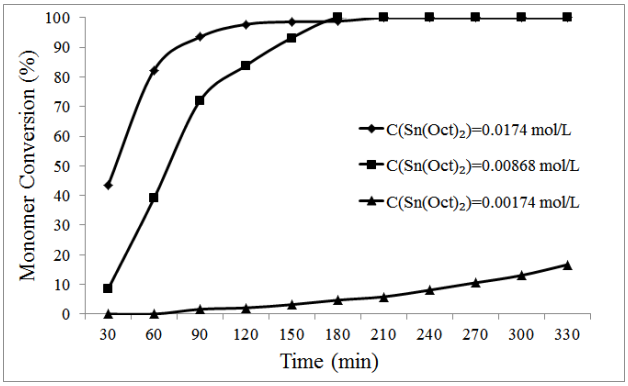

Figure 3.1: Monomer conversion rate at various $Sn(Oct)_2$ concentrations (Benzyl alcohol concentration kept at 0.01159 mol/L and the polymerisation temperature kept at 130°C)

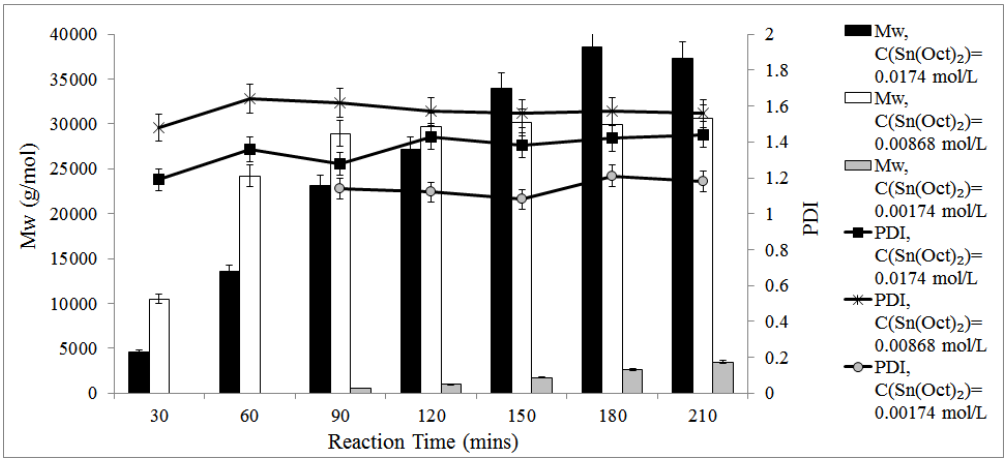

Figure 3.2: Mw and PDI at various $Sn(Oct)_2$ concentrations (Benzyl alcohol concentration kept at 0.01159 mol/L and the polymerisation temperature kept at 130°C)

3.2. Effects of Benzyl alcohol concentration on ε-caprolactone polymerisation

As can be seen in Figure 3.3, the monomer conversion reached ~98% at 180 minutes for both 0.01159 mol/L and 0.0145 mol/L initiator concentration (Reaction temperature and $Sn(Oct)_2$ concentration kept constant), which indicated that the initiator concentration did not have a significant effect on the monomer conversion rate. Kircheldorf stated that initiator alone (i.e. without catalyst) could not initiate the polymerisation process, thus the initiator concentration did not have an effect on the polymerisation rate [21]. However, it was also noticed that when the concentration of benzyl alcohol was reduced to 0.00724 mol/L, the polymerisation only reached ~98% at 240 minutes. This was suggested to be due to the interference from water inside the reaction mixtures acting as a competitive initiator for the ε-caprolactone polymerisation since both water and benzyl alcohol molecules have active hydroxyl groups, which could react and initiate the polymerisation process. As the concentration of benzyl alcohol decreased, the corresponding concentration of water compared to benzyl alcohol increased, thus water could then be more actively involved in the polymerisation process and in turn have a significant effect on the polymerisation rate. As such, removing water in all of the reactants should be stressed going forward.

Regarding Figure 3.4, the Mw was proportional to the initiator concentration in the polymerisation system, which produced molecular weights of ~20,000 g/mol, ~35,000 g/mol and ~45,000 g/mol with increasing benzyl alcohol concentrations. There was no significant difference in the PDI data with different initiator concentrations. Therefore, targeted molecular weight could be achieved by varying the concentration of benzyl alcohol in the ε-caprolactone reaction mechanism.

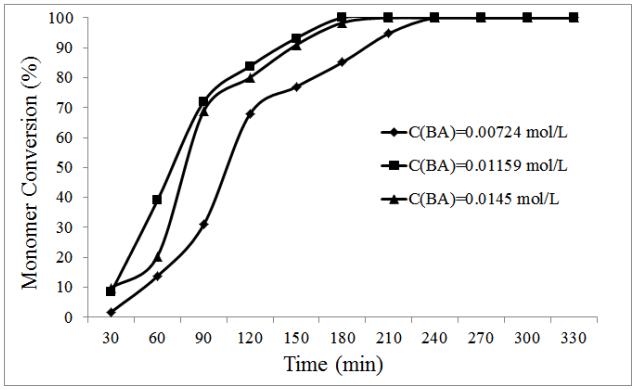

Figure 3.3: Monomer conversion at various benzyl alcohol concentrations ($Sn(Oct)_2$ concentration kept at 0.00868 mol/L and the polymerisation temperature kept at 130 °C)

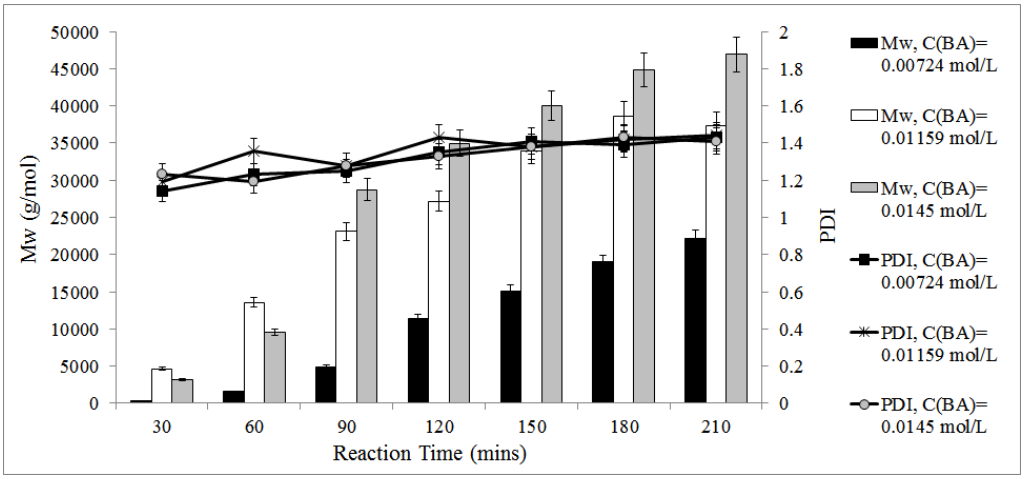

Figure 3.4: Mw and PDI at various Benzyl alcohol (BA) concentrations ($Sn(Oct)_2$ concentration kept at 0.00868 mol/L and the polymerisation temperature kept at 130 °C)

3.3. Effects of reaction temperature on ε-caprolactone polymerisation

Figures 3.5 and 3.6 show the relationship between monomer conversion rate, Mw & PDI and the reaction temperatures. A similar trend with changing $Sn(Oct)_2$ concentrations (Figure 3.1 and 3.2) was observed, in which the reaction rate increased with increasing reaction temperature. Figure 3.5 indicated that the monomer conversion reached ~98% at 90 minutes and at 180 minutes when the reaction temperature was 150 °C and 130 °C respectively. Figure 3.6 revealed that the PDI level and Mw increased with increasing reaction temperature, with the polymerisation at 150 °C reaching ~30,000 g/mol & ~1.6 PDI at 120 minutes, while 110 °C reached ~5,000 g/mol & ~1.2 PDI at 210 minutes. Meanwhile, at 110 °C, the monomer conversion only reached ~22% after 6 hours. According to studies in the literature, side reactions (inter- and intra-transesterification reactions) are sensitive not only to catalyst concentrations (Figure 3.4), but also reaction temperatures. Kricheldorf and his group reported that the molecular weight of PCL produced via their system almost halved by increasing the reaction temperature from 85 °C to 100 °C [21]. The reaction temperature is also a paramount factor for controlling the polymerisation rate. Therefore, polymerisation temperature for PCL should be optimised in order to both increase molecular weight and decrease polymerisation time.

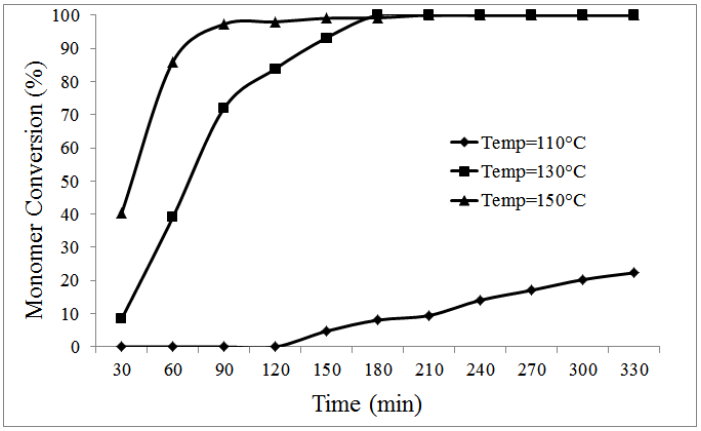

Figure 3.5: Monomer conversion at various reaction temperatures ($Sn(Oct)_2$ concentration kept at 0.00868 mol/L and benzyl alcohol concentration kept at 0.01159 mol/L)

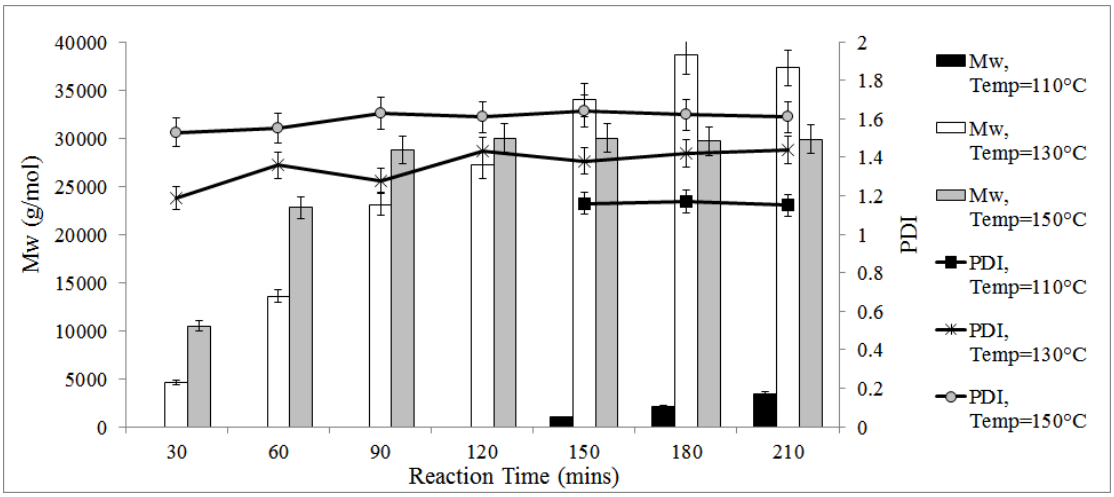

Figure 3.6: Mw and PDI at various reaction temperatures ($Sn(Oct)_2$ concentration kept at 0.00868 mol/L and benzyl alcohol concentration kept at 0.01159 mol/L)

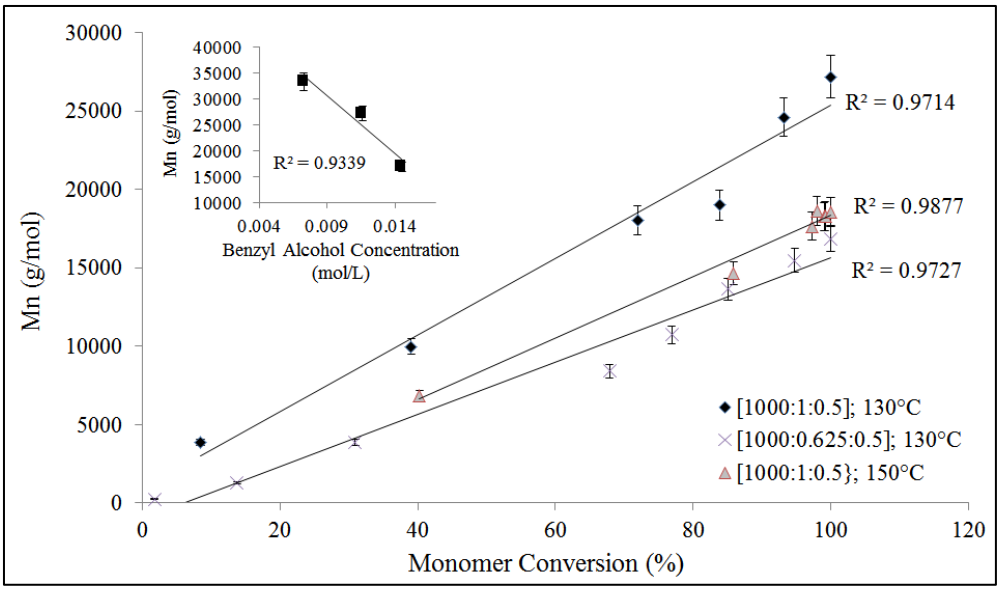

Figure 3.7: Mn against monomer conversion rate with different reaction parameters (Inner figure shows Mn against initiator Benzyl alcohol concentration variation, $Sn(Oct)_2$ concentration and reaction temperature kept at constant)

In Figure 3.7, the relationship between monomer conversion and Mn was plotted at various reaction conditions. Linear relationships were observed for molecular weight growth against monomer conversion (with R^2>0.97). This indicated that the polymerisation itself was stable and could produce good quality PCL with a molecular weight (Mn) of up to ~34,000 g/mol and narrow PDI (ranging between 1.2 and 1.6). The inset figure showed that the Mn of the polymer obtained decreased with increasing amounts of initiator benzyl alcohol in the system. This agreed with Kircheldorf's finding, where Mn was inversely proportional to the initiator concentration [21].

Consequently, it was necessary to optimise the polymerisation rate as well as the molecular weight and polydispersity by choosing the right polymerisation parameters (Reaction temperature, $Sn(Oct)_2$ and benzyl alcohol concentrations). Considering the side reactions and water sensitivity of the polymerisation, the final reaction parameters selected were C($Sn(Oct)_2$)= 0.0174 mol/L, C(Benzyl Alcohol)=0.01159 mol/L and 110°C for reaction Temperature. By using 110°C, the reaction time is prolonged to 24 hours, but in compensation, PCL with high molecular weight and narrow polydispersity can be synthesised.

3.4. Effects of LS and ISP techniques on PCL/PGF composite interface

In Figure 3.8, layers of PGFs and PCL laminates were clearly separated, with heavy polymer rich zones, which lead to very poor fibre dispersity within the composites. Extensive fibre pull-out regions were also observed, which also indicated poor fibre impregnation. Due to the high viscosity of the PCL melt, it was difficult to wet out the fibre surfaces and achieve impregnation into the middle of the fibre layers, which resulted in formation of dry fibre bundles within the fibre layers. Since these dry fibre bundles were not combined together with the polymer matrix (i.e. there was no interfacial bonding), they could only provide limited or no reinforcement for the composites, which significantly lowered the efficiency for fibre reinforcement and the final mechanical properties of the composites. Thus, it was predictable that composites manufactured via LS would be more prone to failure via delamination in comparison to the ISP composites at the early stage of the load-bearing applications, which could limit the potential applicability.

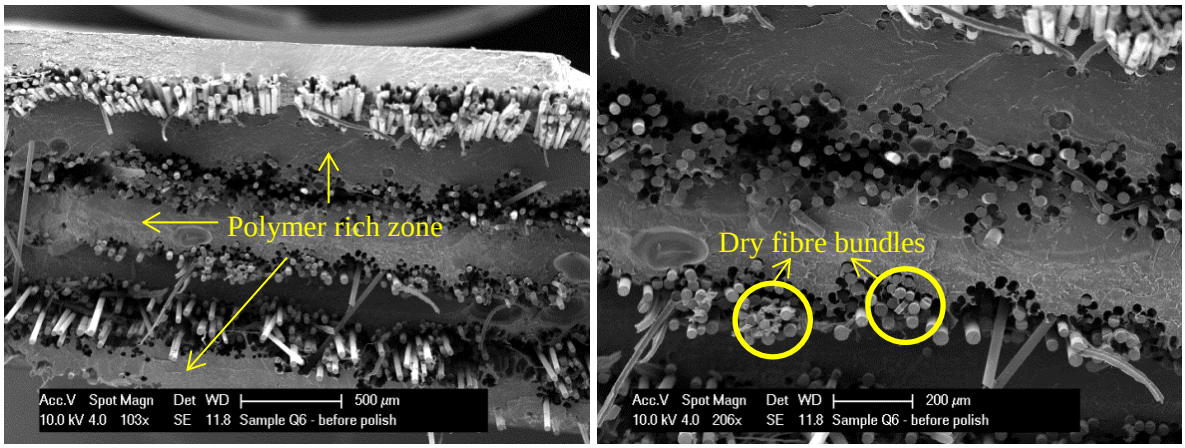

Figure 3.8: SEM images of fractured surfaces of the LS35 UD composites manufactured via LS

By comparison, Figure 3.9 suggested that a more efficient and robust fibre/matrix interfacial bonding had been produced successfully via the ISP technique. Uniform fibre distributions across the entire cross section area of the ISP composites could be seen. No obvious polymer rich zones as well as dry fibre bundles were observed along with clear well impregnated fibres. Fibre pull-out was eliminated and replaced by clean fibre breakages, which would give the composites significantly higher mechanical properties. These improvements were suggested to be due to: 1) the viscosity of the monomer was significantly lower than the polymer melt, which allowed for flow of the liquid monomer within fibre bundles, which in turn improved the fibre wet-out and impregnation when the monomer polymerised. 2) Instead of having the polymer melt and then adhere to the fibre surfaces by reconsolidation, the reactive monomer mixture was directly polymerised around the fibre surfaces,

which allowed for much stronger interfacial bonding. It is well known that the mechanical properties of the fibre reinforced composites are significantly affected by the strength of the fibre/matrix interface. Therefore, as the fibre/matrix interfacial bonding of PGF/PCL composites was significantly improved by the ISP technique, it could also be expected that much higher mechanical properties of the composites should be obtained via ISP technique.

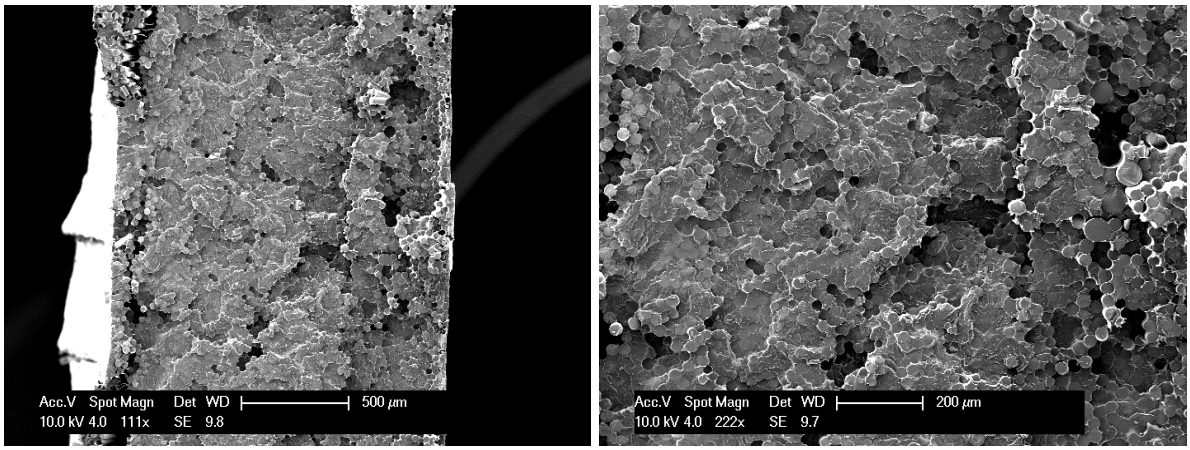

Figure 3.9: SEM images of fractured surfaces of the ISP35 UD composites manufactured via ISP

4. CONCLUSIONS AND FUTURE WORKS

Results from polymerisation kinetic studies have suggested that the ε-caprolactone polymerisation rate was extremely sensitive to the reaction temperature and the amount of the catalyst. Higher reaction temperatures and larger amounts of catalyst were able to accelerate the polymerisation rate of ε-caprolactone. Moreover, the initiator concentration was found to be the key factor in controlling the molecular weight of the polymer produced. Lower initiator concentration could effectively increase the molecular weight. Careful controls over those three factors were necessary in order to effectively yield PCL with high molecular weight and narrow polydispersity. Additionally, the polymerisation system became more sensitive to moisture when the initiator concentration was low since water could also act as a competitive initiator in this mechanism. Therefore, it is of paramount importance to get rid of any excessive moisture before reaction.

It also has been demonstrated that significantly improved fibre impregnation and uniform fibre dispersion due to enhanced interfacial bonding were produced by the ISP technique in comparison to the conventional LS technique. No polymer rich zones and dry fibre bundles were formed during the ISP process. Thus, it could be predicted that significantly higher mechanical properties of the composites could be achieved by the ISP technique. Future works will be conducted on mechanical properties and on degradation profiles of the ISP composites with increasing V_f.

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