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Characterisation of Porous Silicon/Poly(*L*-lactide) Composites Prepared using Surface Initiated Ring Opening Polymerisation

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ABSTRACT

Inorganic/organic hybrid or composite materials have in the past shown novel and interesting properties, which are not observed for the individual components. In this context, the preparation of inorganic/polymeric composites from biodegradable and biocompatible constituents is a new concept, which may be of interest particularly for tissue engineering and drug delivery applications. We describe here the synthesis of nanostructured porous silicon (pSi) and poly(*L*-lactide) (PLLA) composites. The composites were produced using tin(II) 2-ethylhexanoate catalysed surface initiated ring opening polymerisation of *L*-lactide onto silanised porous silicon films and microparticles. The subsequent chemical, physiochemical and morphological characterisation was performed using Diffuse Reflectance Infrared Spectroscopy (DRIFTS), X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Contact Angle measurements. DRIFT spectra of the composites showed the presence of bands corresponding to ester carbonyl stretching vibrations as well as hydrocarbon stretching vibrations. XPS analysis confirmed that a layer of PLLA had been grafted onto pSi judging by the low Si content (ca. 3%) and O/C ratio close to that found for PLLA homopolymers. Comparison of the sessile drop contact angle produced by silanised pSi and PLLA grafted onto pSi showed an increase of ca. 40°. This is comparable to the increase in contact angle seen between blank silicon and spin-coated PLLA of ca. 44°. The AFM surface roughness after surface initiated polymerisation increased significantly and AFM images showed the formation of PLLA nanobrushes.

KEYWORDS: Surface initiated ring opening polymerisation, Poly-lactides, Porous silicon

1. INTRODUCTION

The conversion of bulk silicon into its high surface area, biocompatible porous counterpart, porous silicon (pSi), is commonly achieved by anodisation in hydrofluoric acid (HF). By altering wafer resistivity, HF concentrations and current densities, different porous structures are created. Pore sizes ranging from as small as 2 nm and greater than 100nm can be achieved[1].

The exposure of pSi to biological fluids facilitates its breakdown into silicic acid (Si(OH)₄) which is non-toxic and comprises nearly 95% of naturally occurring silicon in the environment[1]. This makes porous silicon a suitable scaffold for a wide range of biomedical applications such as drug delivery systems and tissue engineering scaffolds. The ability of the pSi to degrade in the body and to be easily functionalised with many different chemical entities including polymer layers could lead to a variety of applications in areas such as tissue culture, drug delivery, biosensors and biomaterials[1, 2]. This functionalisation can be performed on either the hydride-terminated surface or the hydroxyl-terminated surface through the creation of Si-C and Si-O-Si bonds. Functionalised pSi has already been used for vapor sensor chips[3, 4] and for the evaluation of interfaces between biological and semiconductor surfaces[5].

Poly-lactides are biodegradable polyesters which have become a focal point for many research groups because they display a wide range of mechanical properties and undergo degradation to biocompatible monomer subunits[6]. The mechanical properties and the degradation kinetics of poly-lactides can be tuned by adjusting the composition of the polymer with the addition of other copolymers[6]. Poly-lactide slowly degrades inside the body releasing lactic acid[7-

10] which is a naturally occurring substance that can be tolerated by the body as it is produced naturally as an intermediate in glycolysis (glucose metabolism)[11]. The varying mechanical properties also enable poly-lactides to be used as sutures, stents and scaffolds or even for biomaterials in contact with hard tissue such as bone plates, screws and pins for orthopaedic devices[7].

Lactones, lactides, glycolides and dioxanones are a group of cyclic monomers that can undergo ring opening polymerisation (ROP) to form aliphatic polyesters. Many groups have worked on the production of biomaterials for drug delivery, tissue engineering or other uses employing various combinations of these monomers[12-19]. The ROP of lactones and lactides can be carried out in bulk or solution, polymerisations in solution are usually carried out in anhydrous organic solvents such as toluene or tetrahydrofuran (THF) to minimise the presence of impurities such as alcohol and water[6]. ROP has been carried out over a wide range of conditions by various groups, for example reaction temperatures varying from 0°C to 110°C have been reported[13, 17, 18, 20-22]. Previous work has shown that lower polymerisation temperatures cause less side reactions to occur, due to minimal intermolecular and intramolecular transesterification of the polymer chains[6]. It is important to note that Sn(Oct)₂ will decompose at around 100°C to produce octanoic acid. The formation of the acid can cause alcohol esterification which in turn causes the formation of water, this water can then react with Sn(Oct)₂ to form various tin hydroxides and stannoxanes. This leads to uncontrolled initiation and can encourage side reaction to occur[6, 23].

A wide range of catalysts have also been developed and utilised for the ROP of poly-lactides. These include chiral aluminium isopropoxides[20], stannous(II) trifluoromethane sulfonate[24], Red-Al (sodium bis(2-methoxyethoxy)aluminium hydride)[22] and Zn(II) alkoxides[21]. However tin (II) 2-ethylhexanoate (Sn(Oct)₂) is the most common and widely used catalyst in research and industry, as it is highly versatile and easy to handle[6]. Furthermore it has been approved for food and biomaterials applications by the FDA regulatory agency in the USA.

The ROP mechanism is complex and not fully understood; consequently many groups have proposed different mechanisms. Penczek's group has suggested a polymerisation mechanism involving the formation of a tin alkoxide complex prior to the polymerisation[6]. The generated tin alkoxide then initiates the polymerisation of *L*-lactide via a coordination insertion mechanism. The surface initiated polymerisation proceeds via this mechanism with the alcohol on the surface acting as the co-initiating alcohol.

Yoon et al.[17] previously demonstrated that the surface initiated ring opening polymerisation is possible on silica (SiO₂) surfaces functionalised with the hydroxyl groups presenting N-(triethoxysilylpropyl)-O-polyethylene oxide urethane. Choi and Langer[18] have also shown that the surface initiated polymerisation of *L*-lactide can be performed at 40 °C on gold functionalised with hydroxyl groups and at 80 °C on silica functionalised with aminosilanes.

It is envisaged that the inherent biocompatibility and biodegradability of both porous silicon and poly(*L*-lactide) will facilitate the production of a biologically safe composite for various drug delivery and tissue engineering applications. The ability of both porous silicon and poly(*L*-lactide) to completely degrade in the body also means that a porous silicon and poly(*L*-lactide) composite should not require any further surgical intervention after insertion to the desired drug-delivery site[7, 25]. For this reason we intend to investigate the creation and properties of these composites for the express purpose of applying their properties to the creation of a new drug delivery device.

2. METHODS

2.1. Sample surface preparation

2.1.1. pSi film preparation

P⁺-type Si wafers supplied by Silicon Quest International (3", boron doped, <1-0-0>, 381±25µm single sided polished wafers with resistivity 3-6Ωcm⁻¹) were etched in 1:1 HF:Ethanol at a current density of 36.67mAcm⁻² using a 1.8cm² etching cell. The pSi films were then washed with copious amounts of methanol, ethanol, acetone and finally DCM before being dried in a stream of nitrogen.

Ozone oxidation was performed using a Fischer OZON, Ozon-Generator 500. The ozone oxidation of surfaces was carried out simultaneously on numerous wafers using a desiccator with an elongated centrepiece to deliver the ozone into the centre of the desiccator. All oxidations were run for 20 minutes at ozone rate of 3.25 grams h^{-1} .

Two different silanes were used as linkers between the oxidised pSi surface and the polymer. N-(hydroxyethyl)-3-aminopropyl trimethoxysilane (**S4**) and N-(triethoxysilylpropyl)-O-polyethylene oxide urethane (**PEG**) (Fig. 1) were purchased from Gelest Inc., USA and used as received.

Surface treatments with silanes were carried out at room temperature for 2 minutes by submersion in anhydrous toluene with silane concentrations of 50 mM. After silanisation the surfaces were rinsed with acetone and dichloromethane (DCM) before being dried under a stream of N_2 . It is envisaged that the use of silanes will increase the amount of polymer that can be grafted to the surface due to a reduction in steric hindrance[26] during the surface initiated polymerisation reaction.

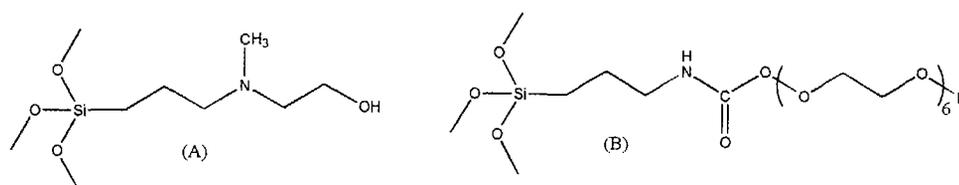


Figure 1: (A) N-(hydroxyethyl)-3-aminopropyl trimethoxysilane (**S4**) and (B) N-(triethoxysilylpropyl)-O-polyethylene oxide urethane (**PEG**)

2.1.2. pSi microparticle preparation

Microparticles were fabricated from boron doped p^{++} -type Si wafers (3", boron doped, <1-0-0>, 500 ± 25 μm single sided polished wafers with resistivity $< 0.001 \Omega cm^{-1}$) supplied by Virginia Semiconductors. The wafer was anodised in a specially designed 18 cm^2 etching cell with 3:1 HF:ethanol and a current density of 222 $mA cm^{-2}$ for 2 minutes and then electropolished for 30 seconds at 500 $mA cm^{-2}$. DCM was then added, which resulted in the "free-standing" porous layer to be fractured into microparticles. The pSi microparticle suspension was transferred to a glass reaction vessel that contained a fine glass frit that allowed the solvent to be removed by aspiration.

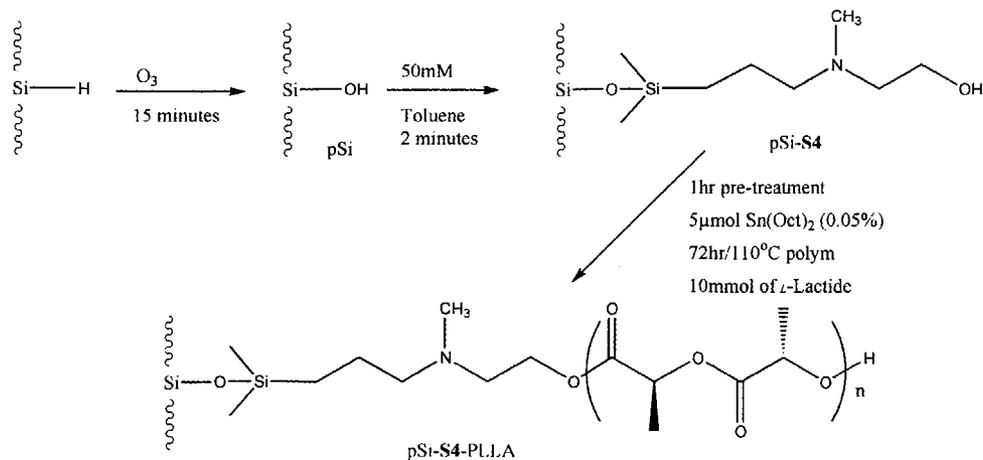
2.2. Sample Polymerisation

2.2.1. Bulk Polymerisation

The bulk polymerisation of *L*-lactide was performed with liquid monomer by heating 10 mmol of *L*-lactide to 110 $^{\circ}C$ and adding 5 μmol of $Sn(Oct)_2$. The mixture was then stirred until polymerisation was complete, typically 2 hours. Bulk polymerised samples used for comparison to PLLA functionalised pSi films were recast for DSC and TGA by dissolution in anhydrous toluene before spin-coating onto a clean Si substrate. Bulk polymerised PLLA used for comparison with pSi microparticles was crushed into a powdered form with a mortar and pestle for DSC and TGA.

2.2.2. Surface polymerisation

Initial polymerisation conditions were adapted from Choi et al.[18] and Yoon et al.[13]. Oxidised and silanised pSi surfaces (films and microparticles) were soaked in 10 ml of toluene containing 10 μmol $Sn(Oct)_2$ catalyst for 1 hour at 50 $^{\circ}C$, before adding 10 mmol of recrystallised *L*-lactide and polymerising for 24 hrs at 80 $^{\circ}C$ (Scheme 1). Upon completion of the polymerisation the pSi film was removed and washed with acetone and DCM before being washed by Soxhlet extraction in toluene for 30 minutes. All polymerisations and pretreatments were carried out under a nitrogen atmosphere. The polymerisation conditions were then optimised by varying the parameters such as the polymerisation temperature and time as well as the lactide and catalyst concentration. Once optimized the polymerisation was also performed on pSi microparticles. Polymerised pSi microparticles were washed with copious amounts of toluene in a glass reaction vessel that contained a fine glass frit that allowed the solvent to be removed by aspiration.



Scheme 1: Conversion from freshly etched pSi to pSi-S4-PLLA functionalised pSi (**Note:** Surfaces functionalisations have been denoted as pSi-S4-PLLA, where pSi indicates that presence of pSi films or microparticles, S4 represents the functionalisation of the pSi prior to polymerisation and PLLA means that polymerisation has been performed from the surface. pSi-PLLA is used as the general term when referring to the composites).

2.3. Characterisation of PLLA on porous silicon

2.3.1. X-ray photoelectron spectroscopy (XPS)

XPS analysis of surface modified samples was performed on an AXIS Hsi spectrometer (Kratos Analytical Ltd, GB), equipped with a monochromatic Al K α source. The pressure during analysis was approximately 5×10^{-8} mbar. The elemental composition of samples was obtained from survey spectra, collected at a pass energy of 320 eV. Binding energies were referenced to the aliphatic carbon peak at 285.0 eV.

2.3.2. Infrared Spectroscopy

All IR spectra were obtained using a Nicolet Avatar 370MCT from Thermo Electron Corporation equipped with a Smart Diffuse Reflectance Accessory or Transmission Accessory. DRIFT spectra of the pSi films were recorded and analysed using OMNIC version 7.0 software, in the range of 650 – 4000 cm^{-1} at a resolution of 1 cm^{-1} or 4 cm^{-1} , all spectra were blanked using an unetched silicon wafer. IR of the polymerised pSi microparticles was also carried out using the transmission accessory with the samples compressed into KBr discs and a blank KBr disc as a reference. Spectra of pSi microparticles were obtained in the range of 400 – 4000 cm^{-1} at a resolution of 4 cm^{-1} .

2.3.3. Contact angle measurements

Contact angle were measured by placing a 1 μL drop of water on the sample surface and capturing a digital image using a Panasonic Super Dynamic wv-BP550 Closed Circuit TV camera. The contact angle measurements were analysed by Scion Image for Windows Framegrabber software (Beta veraion 4.0.2). Three replicate measurements were performed for each different surface functionality.

2.3.4. Atomic Force Microscopy (AFM)

Contact mode AFM was performed on a Nanoscope E microscope (Digital Instruments). Commercial Si cantilevers (OTR8-105, Veeco Corporation, USA) were used for all experiments. The images were processed and analysed using the Nanoscope 4.22 software (Veeco Corporation).

2.3.5. Thermogravimetric analysis (TGA)

TGA experiments were conducted under nitrogen at a flow rate of 50 ml/min on a TA Instruments High Resolution Modulated Thermo-gravimetric Analyzer, TGA 2950. All TGA scans were performed from room temperature to 400 °C at a heating rate of 10 °C/min.

2.3.6. Differential scanning calorimetry (DSC)

All DSC was conducted under nitrogen at a flow rate of 50 ml/min on a TA Instruments DSC 2920 Modulated DSC. The scans were performed from room temperature to 200 °C at a heating rate of 10 °C/min. Exothermic responses are positive and relate to a decreased transfer of heat to the sample compared to the reference.

3. RESULTS AND DISCUSSION

3.1. DRIFT of pSi-PLLA films

It was found that pSi with hydroxyl groups extended away from the surface by silane tether **S4** were favorable for the ROP of *L*-lactide. A 1 hr 50 °C pretreatment with 5 μmol Sn(Oct)₂ catalyst before the addition of 10 mmol *L*-lactide and polymerisation for 24 hrs at 110 °C, proved to be optimal for the grafting of PLLA to pSi-S4. At these conditions a strong carbonyl stretch was observed in the DRIFT spectra. pSi-S4-PLLA polymerised at these conditions was then used for all further characterisation.

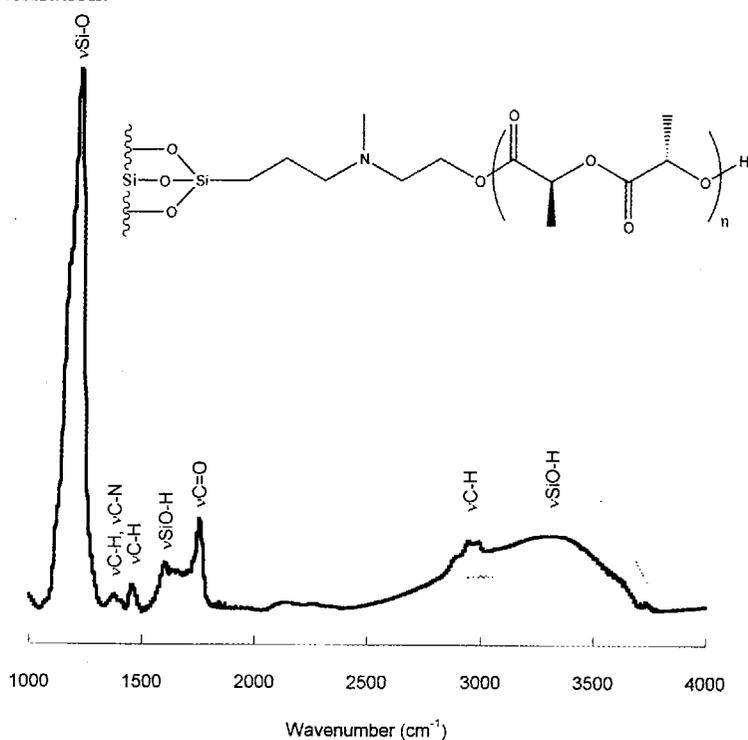


Figure 2: A typical DRIFT spectrum of pSi-S4-PLLA produced at 110 °C for 24 hours

A typical DRIFT spectrum of the pSi-S4-PLLA produced at 110°C for 24 hours is shown in Fig. 2 above. A strong characteristic Si-O-Si peak at 1228 cm⁻¹ is observed due to the pSi surface. The peak at 1652 cm⁻¹ can be attributed to the SiO-H stretch[27]. The peak at 1396 cm⁻¹ may be attributed to the alkane C-H rock in the PLLA. The silane also produces a peak at 1475 cm⁻¹ for CH₂ stretching. The polymer contributes to the 1475 cm⁻¹ for CH₃ and 2900-2996 cm⁻¹ for CH stretching. Notably, a new peak occurs at 1760 cm⁻¹ for the C=O stretch in the PLLA.

3.2. XPS of pSi-PLLA films

XPS results from polymerised samples with similar conditions are shown in table 1 below.

Table 1: Summary of XPS atomic elemental % taken on pSi, pSi-Ox-PLLA and pSi-S4-PLLA

Sample	Polymerisation conditions	O%	C%	Si%	Sn%	O/C
1	Oxidised pSi	56.39	1.80	41.80	0.00	N/A
2	pSi-Ox-PLLA (80°C 24hrs 100 μmol Sn(Oct) ₂)	41.96	24.50	28.96	2.52	1.71
3	pSi-S4-PLLA (80°C 24hrs 100 μmol Sn(Oct) ₂)	41.65	42.53	11.61	1.49	0.98
4	pSi-S4-PLLA (110°C 24hrs 5 μmol Sn(Oct) ₂)	39.63	49.38	8.60	0.50	0.80
5	pSi-S4-PLLA (110°C 72hrs 5 μmol Sn(Oct) ₂)	42.03	48.99	2.98	4.24	0.86

The complete removal of all Sn(Oct)₂ on the polymerised samples was not achieved (table 1) even after 30 minutes of Soxhlet extraction in toluene. The lowest elemental atomic % of tin was 0.5% this was observed on sample 4. Coincidentally, this surface also contained the second thickest PLLA layer, judging by the Si%, however it is important to note that the low Sn% in sample 4 could also be caused by the residual Sn(Oct)₂ catalyst being buried in the polymer layer due to the 10nm information depth of XPS. Sample 5 contained the lowest Si% compared to the other polymerised samples. The lowering of Si% and increase of C% gives an indication that the polymerisation is occurring. Samples 4 and 5 showed an O/C ratio of 0.8 and 0.86 respectively, which is close to that of PLLA (0.66). The O/C ratios for samples 2 and 3 are not as close to this value. The high Sn% content present in sample 5 may indicate that the ½ hour Soxhlet extraction used may not be suitable to remove all the residual Sn(Oct)₂ from the polymer layer, for this reason the washing procedure should be optimised for future work.

3.3. Further characterisation of pSi-PLLA films

3.3.1. Contact angle measurements on pSi-PLLA films

The contact angle results are summarised in table 2.

Table 2: Contact angles measurements on Si, PLLA and treated pSi

Surface	Contact Angle (°)
Untreated silicon	34 ± 2
Spin coated PLLA on Si	78 ± 1
Oxidised pSi	14 ± 2
pSi-S4	29 ± 1
pSi-S4-PLLA (72 hours, 110 °C)	54 ± 2

While untreated silicon has an average contact angle of 34°, a spin-coated PLLA layer produces an average contact angle of 78° (n=3), an increase of ca 44°. The average value is comparable to the literature value of 79±3° for solvent cast films of PLLA[28]. Hence the introduction of the spin coated PLLA layer increases the surface hydrophobicity of the silicon wafer substantially. The silanisation of pSi with S4 (pSi-S4) resulted in an increase of contact angle from 14° to 29°, while the surface initiated polymerisation with S4 leads to a 40° increase in the contact angle from 14° to 54° (Table 2). This indicates that the surface has become more hydrophobic due to the reduction of surface hydroxyl groups and the introduction of the PLLA layer.

The difference between the water contact angle of spin coated PLLA (78°) and pSi-S4-PLLA (54°) can be explained due to the difference in nature between the underlying support structures. Porous substrates are non-ideal surfaces for contact angle because the surface porosity is known to influence the surface energy of the water droplet, by effects such as lack of symmetry and loss of volume due to capillary action drawing in water. Many groups have recently been developing methods that allow the wettability of porous surfaces to be calculated from the contact angle[29].

3.3.2. Atomic Force Microscopy (AFM) of pSi-PLLA films

Contact mode AFM images revealed a significant difference in the roughness of the surface of oxidised pSi (0.236 nm) compared to the pSi-S4-PLLA (1.021 nm) (Fig. 3).

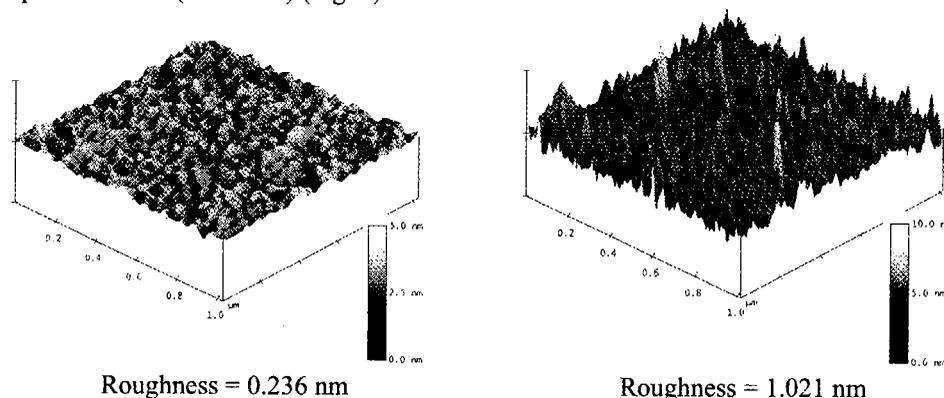


Figure 3: Contact mode AFM image of oxidised pSi (left) and pSi-S4-PLLA (right)

Choi et al.[18] demonstrated the formation of similar surface features on non-porous substrates, they produced nanobrushes of PLLA (roughness = 38 nm) by polymerising at 80 °C for 3 days from a hydroxy terminated surface. It is speculated that the PLLA forms nanobrushes due to the isotactic nature and high crystallinity of the PLLA. The nanobrush structure seen on the pSi-S4-PLLA is only 10 nm high in comparison; this is possibly due the presence of the pSi layer affecting the outward growth of PLLA.

3.4. Transmission IR of pSi-PLLA microparticles

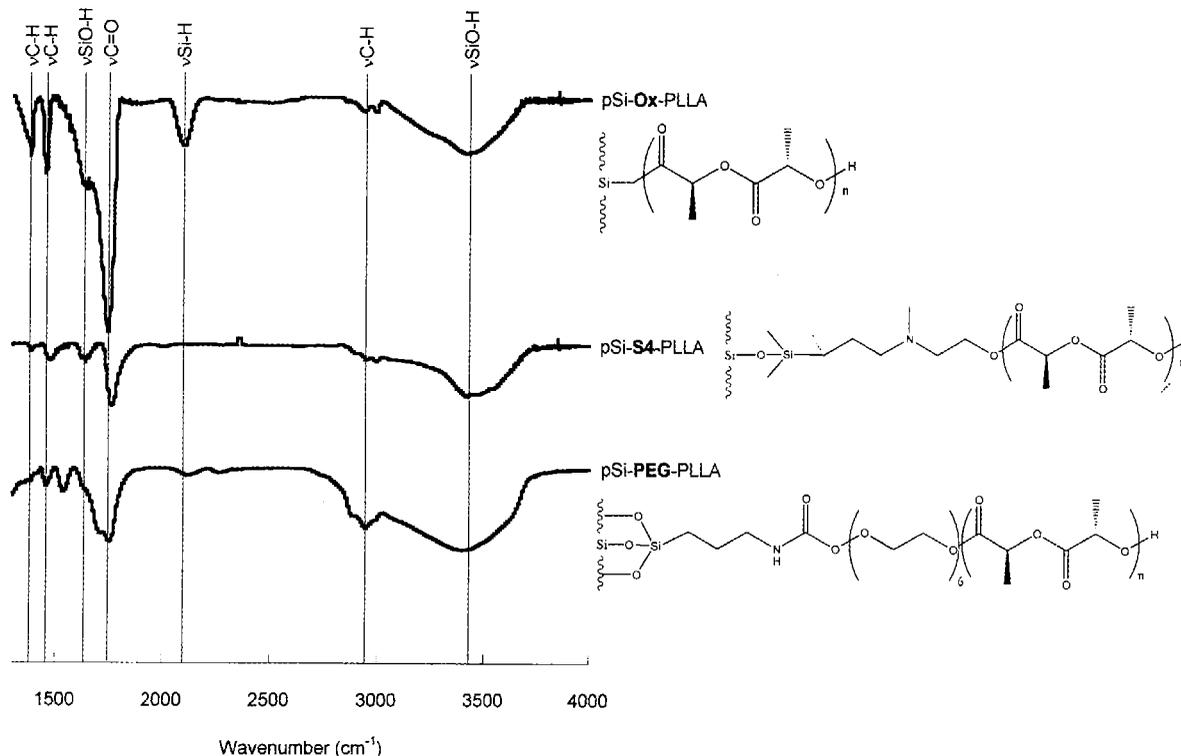


Figure 4: Transmission IR scans of PLLA functionalised pSi microparticles. All spectra were obtained at 4 cm⁻¹. The spectral width has been narrowed for comparison.

The spectra shown above in Fig. 4 illustrate the different functional groups attached to the surface of the pSi microparticles after polymerisation with PLLA. The broad peak at around 2100 cm^{-1} can be attributed to the Si-H stretch[30] and indicates that incomplete oxidation of the surface has occurred. The peak at 1650 cm^{-1} is attributed to the SiO-H bending[27] while the broad OH stretch (interference band) is also seen in all spectra at $3000\text{--}3600\text{ cm}^{-1}$ [27]. It is important to note the presence of the strong C=O stretch at 1750 cm^{-1} from the PLLA layer. The C-H stretches appear at around $2900\text{--}3000\text{ cm}^{-1}$ while the peak at approximately 1460 cm^{-1} can be attributed to C-H bending in both the silane tether and the PLLA. The peaks at 1380 cm^{-1} can be attributed to the C-H rock.

3.5. Preliminary thermal analysis of pSi-PLLA composites

TGA and DSC analysis for both pSi films and microparticles is in an early stage, however the results obtained so far are outlined in the following section.

3.5.1. Thermogravimetric Analysis (TGA) of pSi-S4-PLLA (films)

Various preparations of PLLA produce different glass transition (T_g) and melting temperatures (T_m) in the DSC thermogram and different decomposition temperatures in the TGA scans depending on the molecular weight and composition of the polymer chain. Untreated silicon and pSi-Ox samples were analysed to check for any contributions from the silicon support however, no transitions were observed up to $400\text{ }^\circ\text{C}$. As a reference for the grafted pSi-PLLA a spin-coated sample of bulk polymerised PLLA was used, this spin-coated sample showed a 0.73% weight loss at $269\text{ }^\circ\text{C}$ Fig. 5(A). ($268\text{ }^\circ\text{C}$ and 88.3% weight loss in bulk form). TGA was also run on a solution polymerised (48 hrs, $10\text{ }\mu\text{mol}$, $\text{Sn}(\text{Oct})_2$ and 10 mmol of *L*-lactide without pSi) sample of PLLA that was found to decompose at $282\text{ }^\circ\text{C}$ (94.7% weight loss), in comparison the decomposition temperature of PLLA at infinite molecular weight is $353\text{ }^\circ\text{C}$ [31]. The lower decomposition temperatures indicate that the three standard samples possess low molecular weight PLLA[25].

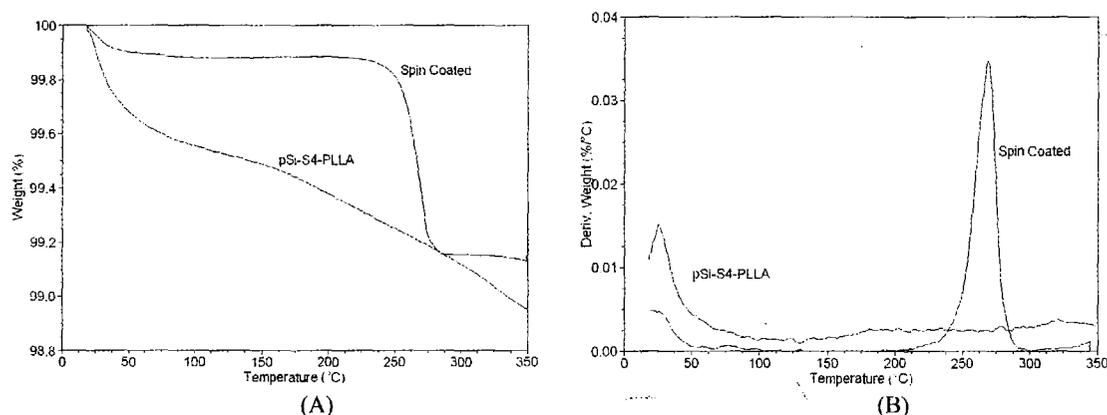


Figure 5: TGA trace (A) and derivatives (B) for the spin-coated bulk polymerised PLLA and one replicate of a pSi-S4-PLLA film.

Significant weight loss transitions were not observed for the pSi-S4-PLLA samples (Fig. 5 (B)), however all replicates did show a consistent mass loss from around $100\text{ }^\circ\text{C}$ onwards (Fig. 5 (A)). Each replicate showed a weight loss, which was averaged to give approximately 0.77% , this corresponds to an average mass loss of $37.65\text{ }\mu\text{g}$. PLLA is a polyester and is therefore subject to hydrolytic degradation[32] which causes a rapid weight loss below $100\text{ }^\circ\text{C}$ due to surface bound water being driven off the sample.

3.5.2. Differential Scanning Calorimetry (DSC) of pSi-S4-PLLA (films)

The expected transitions for PLLA are $T_g = 62\text{ }^\circ\text{C}$, $T_m = 168\text{--}178\text{ }^\circ\text{C}$ [33-35] and a recrystallisation peak is expected to be seen on cooling. The melting transition ($174\text{ }^\circ\text{C}$) for the spin-coated PLLA standard was seen however the transition was small even though there was a visible coating on the wafer. The subsequent attempt to analyse the transitions of the surface bound PLLA resulted in no visible transitions despite the many attempts made to try and obtain good DSC data. It was concluded that the DSC cannot detect the heat flow changes in the polymer due the samples possessing such a

thin PLLA coverage and a large bulk of Si and pSi. In the future it may be possible to overcome this effect by using thinner Si wafers to generate the pSi films.

3.5.3. Thermogravimetric Analysis (TGA) of pSi microparticles

TGA showed that the typical decomposition temperature of the grafted PLLA depends on the underlying surface functionality Table 1 & Fig. 6(A) & (B). All pSi-PLLA samples, except the pSi-Ox, showed a total mass loss of around 20-25%. The pSi-Ox-PLLA decomposes at 282.5 °C, this is comparable to the bulk PLLA (Table 1), however as the length of the silane linker increases so does the decomposition temperatures which indicates more thermal stability and possibly an increase in molecular weight of the grafted PLLA.

It is important to note that decompositions in the TGA scans will not be due to just pure PLLA as the silane linkers will also decompose, for this reason the TGA derivative may show multiple decomposition peaks, Table 1 & Fig 6(B). Unfortunately TGA has not yet been performed on un-polymerised pSi-S4 or pSi-PEG microparticles to determine how the silanes linkers decomposed, this will facilitate accurate assignment of the decomposition peaks in the pSi-S4-PLLA and pSi-PEG-PLLA samples. It is known from literature that amino-silanes degrade from around 210 °C onwards[36, 37].

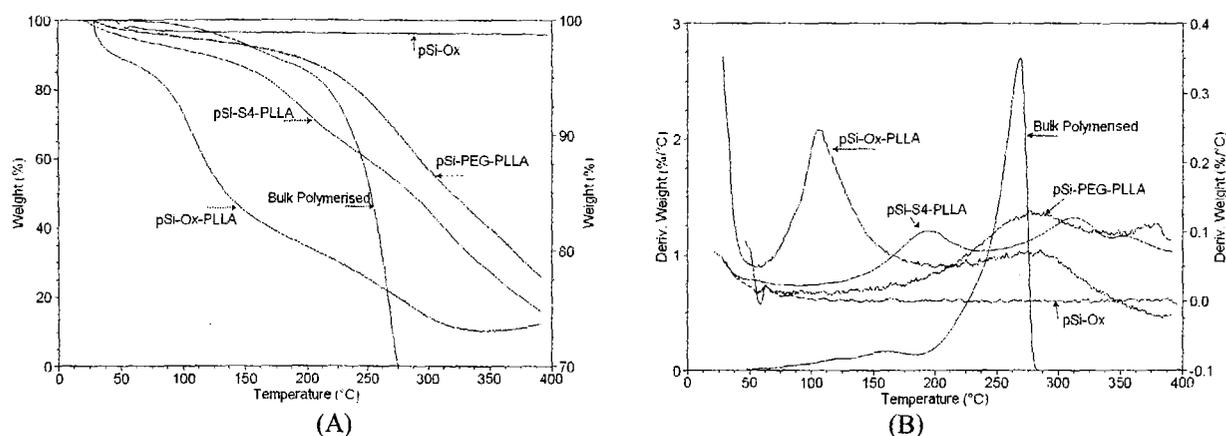


Figure 6: TGA scans (A) and their derivatives (B) of spin-coated bulk polymerised PLLA, pSi-Ox-PLLA, pSi-S4-PLLA, pSi-PEG-PLLA microparticles. pSi-Ox-PLLA, pSi-S4-PLLA and pSi-PEG-PLLA are represented on the right y-axis while the bulk polymerised PLLA is represented on the left y-axis.

Table 1: Decomposition peaks for PLLA functional pSi microparticles

Sample	% Mass Loss	Decomposition Temperatures (°C)		
		1	2	3
Bulk	88.32	268.4	-	-
pSi-Ox-PLLA	26.36	104.9	282.5	-
pSi-S4-PLLA	25.13	195.2	311.8	352.6
pSi-PEG-PLLA	22.05	278.5	377.9	-

3.5.4. Differential Scanning Calorimetry (DSC) of pSi Microparticles

The DSC of pSi microparticles was more successful than DSC of the pSi films most likely due to the increased surface area available for the PLLA to graft onto during the polymerisation. DSC was attempted on all three microparticle functionalisations and a fresh bulk polymerised PLLA standard. The new bulk polymerised PLLA standard showed a melting transition (T_m) at 121.4 °C, however, no glass transition (T_g) or recrystallisation was visible in the DSC thermogram. It is possible that the glass transition were not visible in the DSC thermogram due to broadening effects caused by segmental confinement and restricted polymer chain conformation[38].

The pSi-S4-PLLA and pSi-PEG-PLLA microparticles, showed no transitions, while the pSi-Ox-PLLA microparticles showed a transition at 144.6 °C. Although the peak at 144.6 °C appears as a melting, however, as in the bulk polymerised PLLA standard no recrystallisation appears during the cooling cycle. It is possible that these peaks are melting peaks as there is no recrystallisation in either the bulk polymerised PLLA or the pSi-Ox-PLLA samples. This peak may also be the result of polymerisation of the residual monomer however; further confirmation of this transition is needed and may be obtained from using advanced techniques such as modulated differential scanning calorimetry (MDSC). The absence of a silane on the pSi-Ox sample combined with the pSi-S4-PLLA and pSi-PEG-PLLA samples showing no sharp transitions, indicates that the silanes are not contributing to any transition below 200 °C.

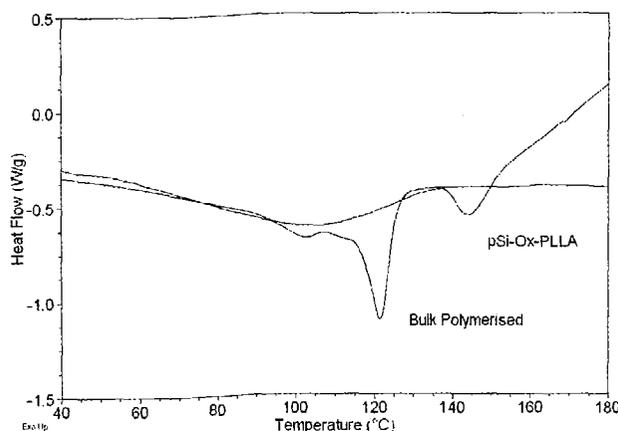


Figure 7: DSC thermogram of powdered bulk polymerised PLLA and pSi-Ox-PLLA

Performing DSC experiments on pSi microparticles is difficult because only 1-2 mg of the pSi microparticles can fit into the DSC pans, while a mass of 10 mg is recommended to allow glass transitions to be seen. The scans should be performed more thoroughly to obtain conclusive data, these runs should be done with a controlled (10 °C/min) heat-cool cycle to ensure the thermal history imparted to the polymer during production is erased before another controlled (10 °C/min) heat-cool cycle to analyse the polymer. A heating rate of 10 °C/min should ensure that the thermogram obtained is sensitive enough to obtain adequate transitions.

4. CONCLUSION

pSi-PLLA composites were successfully produced and characterised using both microparticles and films as the underlying substrate. IR and XPS showed the successful functionalisation of the pSi, by revealing C=O stretches and low atomic % of Si and Sn. The O/C ratio also confirmed the presence of a PLLA layer. Contact angle measurements confirmed the presence of a PLLA layer while AFM revealed the presence of PLLA nanobrushes. Preliminary TGA and DSC showed that functionalisation had occurred however further analysis is required to obtain conclusive data and present an adequate thermal analysis of the pSi-PLLA composites. We believe that the pSi-PLLA composites are suitable for a variety of biomedical applications such as drug delivery, tissue engineering and biomaterials. The application of the newly developed system for drug delivery is still in a preliminary stage.

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REFERENCES

1. Canham, L., Aston, R., *Will a chip everyday keep the doctor away?* Physics World, 2001: p. 27-31.
2. Anderson, S., Elliott, H., Walli, D., Canham, L., Powell, J., *Dissolution of different forms of porous silicon wafers under simulated physiological conditions.* phys. stat. sol., 2003. **197**(2): p. 331-335.
3. Gao, T., Gao, J., Sailor, M., *Tuning the Response and Stability of Thin Film Mesoporous Silicon Vapor Sensors by Surface Modification.* Langmuir, 2002. **18**: p. 9953-9957.
4. Bakker, J., Arwin, H., Wang, G., Järrendahl, K., *Improvement of porous silicon based gas sensors by polymer modification.* Phys. Stat. Sol., 2003. **197**(2): p. 378-381.
5. Wojtyk, J., Morin, K., Boukherroub, R., Wayner, D., *Modification of Porous Silicon Surfaces with Activated Ester Monolayer.* Langmuir, 2002. **18**: p. 6081-6087.
6. Albertsson, A., Varma, I., *Recent Developments in Ring Opening Polymerisation of Lactones for Biomedical Applications.* Biomacromolecules, 2003. **4**: p. 1466-1486.
7. Andreopoulos, A., Hatz, E., Doxastakis, M., *Controlled Release of Salicylic Acid from Poly(D,L-Lactide).* Journal of Materials Science: Materials in Medicine, 2001. **12**: p. 233-239.
8. Zhang, Y., Chu, C., *Biodegradable dextran-poly(lactide) hydrogel networks: Their swelling, morphology and the controlled release of indomethacin.* Biomed Mater Res, 2002. **59**: p. 318-328.
9. Radwan, M., Aboul-enein, H., *In Vitro release and stereoselective disposition of Flurbiprofen loaded to poly(D,L-Lactide-co-glycolide) nanoparticles in rats.* Chirality, 2004. **16**: p. 119-125.
10. Mandal, T., Bostanian, L., Graves, R., Chapman, S., *Poly(d,l-lactide-co-glycolide) encapsulated poly(vinyl alcohol) hydrogel as a drug delivery system.* Pharmaceutical Research, 2002. **19**(11): p. 1713-1719.
11. Lehninger, A., Nelson, D., Cox, M., *Principles of Biochemistry.* 1993, New York: Worth Publishers.
12. Panyam, J., Labhasetwar, V., *Sustained Cytoplasmic Delivery of Drugs with Intracellular Receptors Using Biodegradable Nanoparticles.* Molecular Pharmaceutics, 2004. **1**(1): p. 77-84.
13. Yoon, K., Koh, Y., Choi, I., Chi, Y., Lee, K., Lee, J., Kim, D., Joo, S., Yun, W., *Surface Initiated, Ring-Opening Polymerisation of p-dioxanone from gold and silicon oxide surfaces.* J. Mater. Chem, 2003. **13**: p. 2910-2914.
14. Lee, W., Lee, J., Ha, C., *Growth of Monolayered Poly(l-Lactide) Lamellar Crystals on a Substrate.* Macromolecular Research, 2003. **11**(6): p. 511-513.
15. Tasaka, F., Ohya, Y., Ouchi, T., *Synthesis of Novel Comb-Type Polylactide and Its Biodegradability.* Macromolecules, 2001. **34**: p. 5494-5500.
16. Kowalski, A., Duda, A., Penczek, S., *Kinetics and Mechanism of Cyclic Esters Polymerization Initiated with Tin(II) Octoate. 3. † Polymerization of L,L-Dilactide.* Macromolecules, 2000. **33**: p. 7359-7370.
17. Yoon, K., Koh, Y., Choi, I., *Formation of Silica/Poly(p-dioxanone) Microspheres by Surface-Initiated Polymerization.* Macromol. Rapid Commun., 2003. **24**: p. 207-210.
18. Choi, I., Langer, R., *Surface-Initiated Polymerization of L-Lactide: Coating of Solid Substrates with a Biodegradable Polymer.* Macromolecules, 2001. **34**: p. 5361-5363.
19. Langer, R., *Biomaterials in Drug Delivery and Tissue Engineering: One Laboratory's Experience.* Acc. Chem. Res, 2000. **33**: p. 94-101.
20. Zhong, Z., Dijkstra, P., Feijen, J., *Controlled and Stereoselective Polymerization of Lactide: Kinetics, Selectivity, and Microstructures.* J. Am. Chem. Soc., 2003. **125**: p. 11291-11298.
21. Williams, C., Breyfogle, L., Choi, S., Nam, W., Young, V., Hillmyer, M., Tolman, W., *A Highly Active Zinc Catalyst for the Controlled Polymerisation of Lactide.* J. Am. Chem. Soc., 2003. **125**: p. 11350-11359.
22. Li, H., Wang, C., Bai, F., Yue, J., Woo, H., *Living Ring-Opening Polymerisation of L-Lactide Catalysed by Red-Al.* Organometallics, 2004. **23**: p. 1411-1415.
23. Kricheldorf, H., Kreiser-Saunders, I., Stricker, A., *Poly(lactones) 48. SnOct2-Initiated Polymerisations of Lactide: A Mechanistic Study.* Macromolecules, 2000. **33**: p. 702-709.
24. Moller, M., Nederberg, F., Lim, L., Kange, R., Hawker, C., Hedrick, J., Gu, Y., Shah, R., Abbott, N., *Stannous(II) Trifluoromethane Sulphonate: A Versatile Catalyst for the Controlled Ring-Opening Polymerisation of Lactides: Formation of Stereoregular Surfaces from Polylactide Brushes.* Journal of Polymer Science: Part A: Polymer Chemistry, 2001. **39**: p. 3529-3538.
25. Ferreira, B., Zavaglia, C., Duek, E., *Films of Poly(L-Lactic Acid)/Poly(Hydroxybutyrate-co-Hydroxyvalerate) Blends: In Vitro Degradation.* Mat. Res., 2001. **4**(1): p. 34-42.

26. Gabig, M., Wegrzyn, G., *An introduction to DNA chips: principles, technology, applications and analysis*. Acta Biochimica Polonica, 2001. **48**(3): p. 615-622.
27. Xu, D., Sun, L., Li, H., Zhang, L., Guo, G., Zhao, X., Gui, L., *Hydrolysis and silanisation of the hydrosilicon surface of freshly prepared porous silicon by an amine catalytic reaction*. New J. Chem., 2003. **27**: p. 300-306.
28. Yang, F., Xu, C., Kotaki, M., Wang, S., Ramakrishna, S., *Characterisation of neutral stem cells on electrospun poly(L-Lactic acid) nanofibrous scaffold*. J. Biomater. Sci Polymer Edn., 2004. **15**(12): p. 1483-1497.
29. Rodriguez-Valverde, M., Cabrerizo-Vilchez, M., Rosales-Lopez, P., Paez-Duenas, A., Hidalgo-Alvarez, R., *Contact angle measurements on two (wood and stone) non-ideal surfaces*. Colloids and Surfaces A: Physiochemical and Engineering Aspects, 2002. **206**: p. 485-495.
30. Janshoff, A., Dancil, K., Steinem, C., Greiner, D., Lin, V., Gurtner, C., Motesharei, K., Sailor, M., Ghadiri, M., *Macroporous p-Type Silicon Fabry-Perot Layers. Fabrication, Characterisation and Applications in Biosensing*. J. Am. Chem. Soc., 1998. **120**: p. 12108-12116.
31. Cam, D., Marucci, M., *Influence of residual monomers and metals on poly(L-Lactide) thermal stability*. Polymer, 1997. **38**(8): p. 1879-1884.
32. Gonzalez, M., Ruseckaite, R., Cundrado, T., *Structural Changes of Polylactic-Acid (PLA) Microspheres under Hydrolytic Degradation*. Journal of Applied Polymer Science, 1999. **71**: p. 1223-1230.
33. Sasaki, T., Yamauchi, N., Irie, S., Sakurai, K., *Differential scanning calorimetry study on thermal behaviours of freeze dried poly(L-Lactide) from dilute solutions*. Journal of Applied Polymer Science: Part B: Polymer Physics, 2005. **43**: p. 115-124.
34. Nakafuku, C., Takehisa, S., *Glass transition and mechanical properties of PLLA and PDLA-PGA copolymer blends*. Journal of Applied Polymer Science, 2004. **93**: p. 2164-2173.
35. Abe, H., Takahashi, N., Kim, K., Mochizuki, M., Doi, Y., *Thermal degradation processes of end-capped poly(L-Lactide)s in the presence and absence of residual zinc catalyst*. Biomacromolecules, 2004. **5**: p. 1606-1614.
36. Bois, L., Bonhimmel, A., Ribes, A., Pais, B., Raffin, G., Tessier, F., *Functionalised silica for heavy metal ions adsorption*. Colloids and Surfaces A: Physiochemical and Engineering Aspects, 2003. **221**: p. 221-230.
37. Wahab, M., Guo, W., Cho, W., Ha, C., *Synthesis and Characterisation of Novel Amorphous Hybrid Silica Materials*. Journal of Sol-Gel Science and Technology, 2003. **27**: p. 333-341.
38. Caykara, T., Guven, O., *Effect of Preparation methods on thermal Properties of Poly(acrylic acid)/Silica Composites*. J. Appl. Polym. Sci., 1998. **70**: p. 891-895.