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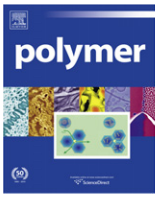

Enzymatic synthesis of silicone fluorinated aliphatic polyesteramides

Aniruddha S. Palsule [a], Yadagiri Poojari [b,*]

[a] Department of Chemical and Materials Engineering, NSF I/UCRC Membrane Applied Science and Technology Center, University of Cincinnati, Cincinnati, OH 45221-0012, USA
[b] Department of Chemistry, The Ohio State University, Columbus, OH 43210, USA

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ABSTRACT

The enzymatic synthesis of silicone fluorinated aliphatic polyesteramides (SFAPEAs) is reported. These materials were synthesized by incorporating both the fluorinated aliphatic segments and the dimethylsiloxane segments into the same linear chain backbone. Immobilized lipase B from *Candida antarctica* (Novozym-435) was used to catalyze the reactions to prepare fluorosilicones containing both amide and ester linkages. Simultaneous reactions of an amidation between α,ω-aminopropyl terminated poly(dimethylsiloxane) (APDMS) and diethyl adipate (DEA) and a transesterification between diethyl adipate and four different fluorinated alkanediols (FADs), respectively were conducted. The condensation reactions were carried out in the bulk, in the temperature range 70–90 °C and under reduced pressure (50 mmHg vacuum gauge). The molar masses of the synthesized fluorosilicones were determined by GPC analysis. The effect of the chain length of the FADs on the molar mass build up of the respective polymers was investigated. The highest molar mass fluorosilicones were obtained with the 3,3,4,4,5,5,6,6-octafluoro 1,8-octanediol (OFOD) monomer, which has an additional methylene ($-CH_2-$) spacer between the fluorocarbon chain ($-CF_2-)_n$ and the hydroxyl end groups ($-OH$) when compared to the other three FAD monomers namely – 2,2,3,3-tetrafluoro 1,4-butanediol (TFBD), 2,2,3,3,4,4-hexafluoro 1,5-pentanediol (HFPD) and 2,2,3,3,4,4,5,5-octafluoro 1,6-hexanediol (OFHD). The formation of amide and ester linkages during the polymerization was confirmed by FTIR and ^1H NMR spectroscopy. A series of copolymers were synthesized by varying the feed ratios of FAD to APDMS. Fluorinated polyesters (FPEs) and silicone polyamides (SPAs) were also enzymatically synthesized under similar reaction conditions. The DSC analysis revealed that the fluorosilicones were semi-crystalline, principally due to the presence of the FPE segments. The FPEs were found to be white solids at room temperature. However, the SFAPEA's were found to be viscous materials due to the presence of highly flexible silicone segments in the backbone chain. The crystallinity was seen to disappear completely for the SFAPEA's with greater than 15 mol% of silicone content. The TGA analysis revealed that thermal degradation/depolymerization characteristics of the fluorosilicones improved with increased silicone content. We envisage that these new fluorosilicones have potential for a variety of low surface energy applications.

1. Introduction

Polysiloxane based materials possess unique properties that make them amenable for use in a variety of applications such as personal care products and biomedical materials. Poly(dimethylsiloxane) (PDMS) $-[(CH_3)_2SiO]_y-$ is the workhorse of the silicones industry. The large Si–O–Si bond angle and low rotational energy of the siloxane backbone are principally responsible for the high chain flexibility. These characteristics result in a low glass transition temperature and excellent low temperature thermal characteristics [1–4]. Silicones also have high thermal stability, good UV resistance and are biocompatible [5]. The presence of non-reactive, non-polar methyl side groups lowers the surface tension and surface energy and they are responsible for the reduction in the solubility parameter. Linear PDMS is thermodynamically incompatible with most other high molar mass polymers. Functional groups may be introduced at the chain ends or as side groups in order to make PDMS reactive. This allows silicones to be incorporated into a variety of block copolymers [5,6].

Fluoropolymers are typically oleophobic and hydrophobic, whereas PDMS is oleophilic and hydrophobic. Fluorine can be incorporated into silicone-based materials in order to lower the surface energies and to introduce oleophobic properties. Similarly, silicones can be incorporated into fluoropolymers in order to improve the

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[*] Corresponding author.
E-mail address: ypoojari@gmail.com (Y. Poojari).

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processability, low temperature properties, adhesion and solubility of fluorocarbons. Fluorosilicones typically either have a fluorocarbon as the side group on a siloxane chain or have fluorocarbons alternating with the siloxane segments in the main chain [7,8]. This later class of materials forms the basis of this research. The fluorosilicones are synthesized by conventional chemistry techniques based on the condensation of silanes and chlorosilanes. The reaction conditions are often harsh and the catalysts employed are either platinum based materials or strong mineral acids or bases. Furthermore, for biomedical and pharmaceutical applications, the use of multiple steps for residual catalyst removal may be required [9,10].

The use of enzymes to catalyze various polymerization reactions, including polysiloxane based materials, is currently a fruitful area of research because the products may be formed under environmentally benign or "green" conditions [11–13]. Enzymes also provide high conversion, stereo-selectivity, regio-selectivity, catalyst recycling and can circumvent the use of toxic metallic compounds [14–16]. These characteristics assume significance in the context of silicone-based materials due to their applications as biomedical implants, drug release formulations and as personal care products.

Recently, we have reported the synthesis of linear silicone aliphatic polyesters by the condensation polymerization of 1,3-bis(3-carboxypropyl)tetramethyldisiloxane with alkanediols (1,4-butanediol, 1,6-hexanediol and 1,8-octanediol) in the bulk (without the use of solvent) in the temperature range 50–90 °C under reduced pressure (50–300 mmHg gauge) using Novozym-435 as a catalyst [17]. An increase in the molar mass of the polyesters depended on the reaction temperature, enzyme activity, enzyme concentration, and to a lower extent on the applied vacuum. We have also synthesized silicone aromatic polyesters and silicone aromatic polyamides in toluene using Novozym-435 under mild reaction conditions [18,19].

In another study, we have reported the enzymatic synthesis of silicone aliphatic polylactones – in particular linear poly(ε-caprolactone)–poly(dimethylsiloxane)–poly(ε-caprolactone) triblock copolymers [20]. The copolymerization was performed by the ring-opening polymerization of ε-caprolactone with α,ω-(dihydroxy alkyl) terminated poly(dimethylsiloxane) using Novozym-435 as the catalyst in toluene at 70 °C. The triblock copolymers were found to be semi-crystalline by DSC and XRD analysis. The degree of crystallinity increased with an increase of the feed [ε-caprolactone]/[PDMS] ratio. The crystal structure of the copolymers was determined by WAXD, and found to be similar to that of the PCL homopolymer. The thermal stability of these copolymers improved over the parent PCL homopolymer with increased mole fraction of PDMS.

Furthermore, we have synthesized silicone aliphatic polyethers – specifically poly(dimethylsiloxane)–poly(ethylene glycol) amphiphilic copolymers in the bulk at 80 °C and under reduced pressure (500 mmHg gauge) [21]. Novozym-435 was used to catalyze the condensation polymerization of 1,3-*bis*(3-carboxypropyl)tetramethyldisiloxane with poly(ethylene glycol) (PEG having a number-average molar mass, $M_n = 400, 1000$ and $3400\ \text{g mol}^{-1}$, respectively). Novozym-435 was also used to copolymerize α,ω-(dihydroxy alkyl) terminated poly(dimethylsiloxane) (HAT-PDMS, $M_n = 2500\ \text{g mol}^{-1}$) with α,ω-(diacid) terminated poly(ethylene glycol) (PEG, $M_n = 600\ \text{g mol}^{-1}$). The thermal stability of the synthesized amphiphilic copolymers was found to increase with increased dimethylsiloxane content in the copolymers.

Polyamides are typically prepared by reacting α,ω-dicarboxylic acids with α,ω-diamines at elevated polymerization temperatures. It is often necessary to employ coupling agents and additional protection–deprotection steps in order to prevent the degradation of useful functionalities under such harsh reaction conditions [22]. However, enzymes have been successfully used for amidation reactions under mild reaction conditions. In particular, lipase was used to catalyze the aminolysis of carboxylic esters to give amides [23]. Recently Gross and coworkers described the formation of organosilicon polyesteramides by the condensation reaction of diamine terminated PDMS, 1,8-octanediol and diethyl or dimethyl adipate. The reactions were catalyzed by Novozym-435 and were carried out at 70 °C in the bulk state [24,25].

The use of lipase enzymes for the polymerization of fluorinated monomers is relatively unexplored. The ring-opening polymerization of fluorinated lactones and fluorinated hydrocarboxylic acids has been carried out using lipases to give polymers of molar masses ranging from 3000 to 11000 g/mol and an optically active product was reported for some of the lactones [26]. Novozym-435 enzyme was also employed to catalyze the formation of fluorinated esters by reacting a series of fluorinated diols with divinyl adipate in bulk, in solvents and in supercritical carbon dioxide [27,28]. It was observed that the enzyme was more selective towards the shorter chain diol monomers and those with an extra methylene spacer group between the fluorinated methylene segments and the reactive hydroxyl end groups.

This research work describes an enzymatic synthesis of fluorosilicones (SFAPEAs) having both siloxane segments and fluorinated aliphatic segments in the main chain. There have been no prior studies of this nature to the best of our knowledge and direct esterification reactions are precluded by the poor reactivity between silicone and fluorinated precursors. The fluorosilicone synthesis was catalyzed by Novozym-435 between α,ω-aminopropyl terminated poly(dimethylsiloxane) (APDMS) and diethyl adipate (DEA) with four different fluorinated alkane diols (FADs), respectively to form amide and ester linkages simultaneously. The DEA was employed to inhibit the phase separation of the FADs and to facilitate the transesterification reactions with the APDMS. Physical properties of the resulting fluorosilicones were characterized by using Gel Permeation Chromatography (GPC), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Finally, we also present details of the enzyme activity in these reactions.

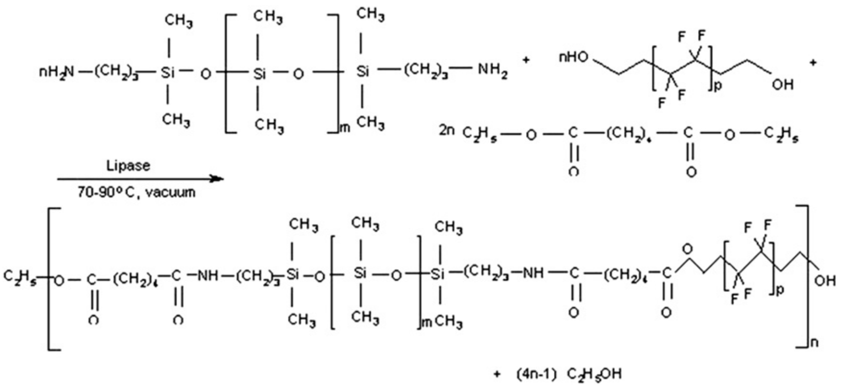
2. Experimental

2.1. Materials

The α,ω-aminopropyl terminated poly(dimethylsiloxane) ($M_n = 1000$ g/mol, $M_w = 1700$ g/mol, PDI = 1.7) was purchased from Gelest, Inc. Diethyl adipate and lipase B from *Candida antartica* (immobilized onto macroporous acrylic beads: Novozym-435) were purchased from Sigma–Aldrich. The fluorinated diol 3,3,4,4,5,5,6,6-octafluoro 1,8-octanediol (OFOD) was purchased from Apollo Scientific, UK and from Oakwood Chemicals, SC. The other fluorinated diols: 2,2,3,3-tetrafluoro 1,4-butanediol (TFBD), 2,2,3,3,4,4-hexafluoro 1,5-pentanediol (HFPD), and 2,2,3,3,4,4,5,5-octafluoro 1,6-hexanediol (OFHD) were obtained from Synquest Laboratories. HPLC grade tetrahydrofuran was obtained from Tedia. All the raw materials purchased were of the highest available purity and were not purified further.

2.2. Synthetic methods

The reaction stoichiometry (DEA:FAD:APDMS) was fixed at a 2:1:1 mol ratio for the synthesis of the fluorosilicones (SFAPEAs) using four different FAD monomers. The reaction mixture containing 0.1 mol of FAD, 0.2 mol (0.404 g) of DEA, and 0.1 mol of APDMS (0.850 g) was placed in a round bottom flask (25 ml). The reactants were heated together at 70 °C until they formed a single phase mixture. Then the Novozym-435 (10% by weight of monomers and vacuum dried for 1 day at 20 mmHg gauge) was added to the



Scheme 1. The lipase catalyzed synthesis of silicone fluorinated aliphatic polyesteramides (SFAPEAs) by transesterification and amidation of α,ω-aminopropyl terminated poly (dimethylsiloxane) (APDMS) and 3,3,4,4,5,5,6,6-octafluoro 1,8-octanediol (OFOD) with diethyl adipate (DEA), respectively.

mixture. The reaction mixture was stirred for 20 h, and then vacuum was applied (30 mmHg vacuum gauge). The reaction was stopped after 30 h, when the reaction mixture became too viscous for magnetic stirring. The respective products were then dissolved in 5 ml of THF. The enzyme was removed by filtration using a glass-fritted filter (medium porosity). The polymer samples and the recovered enzyme were then placed in a vacuum chamber (300 mmHg vacuum gauge) in order to remove the residual solvent. The solvent free samples were characterized as described in the following section.

Two types of copolymer reactions were also carried out under similar reaction conditions. In the first reaction, the HFPD or the OFOD was reacted with the DEA to form fluorinated polyesters (no silicone). In the second reaction, the APDMS was reacted with DEA to form silicone polyamides (no fluorinated component). These samples were labeled FPE (fluorinated polyester) and SPA (silicone polyamide), respectively.

2.3. Characterization methods

The molar masses were determined by Gel Permeation Chromatography (GPC) using a Shimadzu LC-20AT pump, an RID10A refractive index detector, and a Phenogel 5µ Linear 300 × 7.8 mm column (Phenomenex). THF was used as the eluent at a flow rate of 1.0 ml/min. Sample concentrations of 2–5 mg/ml and injection volumes of 20–30 µl were used. Six narrow polydispersity polystyrene standards with molar masses ranging between 500 and 480,000 g mol^{-1} (the standards were obtained from Millipore, Waters Chromatography Division, MA 01757) were used to calibrate the system. System calibration data and relative molar mass calculations were acquired and processed using Shimadzu Class-VP software.

Fourier Transform Infrared (FTIR) spectroscopy was carried out using a Bio-Rad Digilab Division FTS 40 IR-Spectrometer. The THF was completely evaporated from the samples before analysis. Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR) was performed using a Bruker NMR spectrometer (AMX400 model) at 400 MHz with deuterated chloroform (with TMS as internal standard) as the solvent.

Thermogravimetric Analysis (TGA) was performed under a nitrogen atmosphere by means of a TA Instruments TGA2050 thermogravimetric analyzer. The measurements were carried out with a heating rate of 10 °C/min and temperature ranging from 25 °C to 600 °C. Differential scanning calorimetry (DSC) was performed using a TA Instruments 2010 DSC. The DSC scans were run over the temperature range from −130 °C to 110 °C at a rate of 10 °C/min. Quench cooling was applied between heating runs.

After completion of the polymerization reactions the polymer product was dissolved in THF and filtered under vacuum in order to separate the enzyme from the polymer. The recovered enzyme was then dried and stored at room temperature for further analysis.

The activity of the recovered enzyme was determined by the esterification of 20 mg of 1-octanol and lauric acid (1:1 mol ratio) catalyzed by 10 mg of the recovered lipase in 1 ml of isooctane at 36 °C for 1 h. Gas Chromatography (GC) was used to analyze the amount of octyl laurate product formed. 1 µl of reaction sample was injected into the GC (Shimadzu GC-2010) column 0.5 µm × 0.25 mm × 15 m SHRX5 capillary column, split injection at 200 °C, flow rate 30.4 ml min^{-1}, FID detector 350 °C, ramp of 75–300 °C over 18 min. The residual enzyme activity was calculated from the relative peak areas of the product octyl laurate formed by the pure and the recovered lipases. The data were acquired and processed using Shimadzu Class-VP software.

3. Results and discussion

Novozym-435 was used to synthesize fluorosilicones (SFAPEAs) containing both amide and ester linkages formed by a simultaneous transesterification reaction between APDMS and DEA with four different FAD monomers. The overall reaction scheme is shown in the reaction Scheme 1.

The direct reaction between the APDMS and the FADs led to phase separation due to the poor reactivity and compatibility of the silicones with fluorocarbons. Therefore DEA was employed to both inhibit the phase separation of the FADs and also to facilitate the transesterification reactions with the APDMS. All the reactions were carried out at temperatures in the range of 70 °C–90 °C, depending on the melting point of the individual FADs (see Table 1). In this temperature range the reactants formed a monophasic mixture and the reactions were carried out in the bulk state. Furthermore, the lipase has been found to function effectively for polycondensation reactions in the temperature range of 70 °C–90 °C [16,17,25].

Table 1
The fluorinated alkane diols (FADs) used for the synthesis of the fluorosilicones (SFAPEAs) with their chemical structure, molar mass and melting point.

Fluorinated alkane diols	Structure	Molar mass (g/mol)	Melting point (°C)
TFBD	$HOCH_2(CF_2)_2CH_2OH$	162	83–85
HFPD	$HOCH_2(CF_2)_3CH_2OH$	212	78–81
OFHD	$HOCH_2(CF_2)_4CH_2OH$	262	68–71
OFOD	$HO(CH_2)_2(CF_2)_4(CH_2)_2OH$	294	72–74

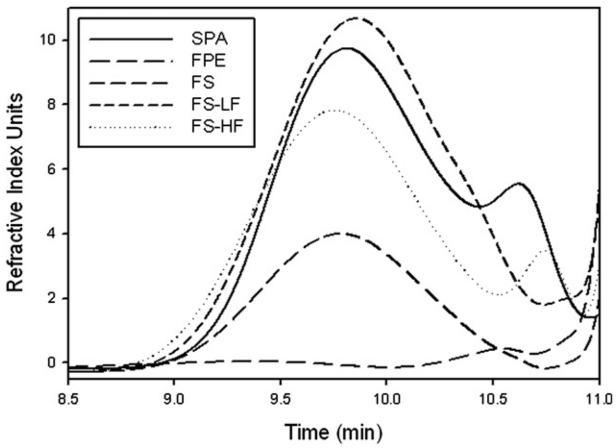


Fig. 1. GPC traces of the fluorinated polyester (FPE), the silicone polyamide (SPA) and the flurosilicone (FS) or (SFAPEAs) samples.

3.1. GPC analysis

For all of the four FAD monomers studied herein, an increase in the viscosity of the reaction mixture and a decrease in the stirrer speed provided a visual indication of the progress of the trans-esterification and amidation reactions. The reactions were stopped by filtering the enzyme from the reaction mixture after the respective reaction mixture became too viscous for magnetic stirring. The molar masses of the fluorosilicones were determined by GPC analysis (See Fig. 1). The number-average molar mass, M_n and the weight average molar mass, M_w and the polydispersity index PDI (M_w/M_n) for fluorosilicones (FS-1 to FS-4), FPE and SPA, respectively are presented in Table 2. For the control reactions carried out in the absence of Novozym-435, a marginal increase in the molar masses (M_n = 1170 g/mol, M_w = 1345 g/mol) was seen and the reaction mixtures did not become viscous. These results confirm that the condensation reactions were indeed catalyzed by the lipase alone.

The presence of the two methylene groups ($-CH_2CH_2-$) in the OFOD resulted in polymers having higher molar masses when compared to the other three fluorinated alkane diols (TFBD, HFPD and OFHD), which had only one methylene group ($-CH_2-$) between the fluorinated alkane segments and the terminal −OH groups. This is in agreement with the finding of Messiano et al., who postulated that the reactive −OH groups need to be shielded from the fluorinated methylene segments in the main chain for optimum enzyme activity [28].

The effect of FAD content on the fluorosilicone molar mass build up was investigated by varying the feed ratios of OFOD and APDMS with fixed DEA content at 50 mol%. Five different feed ratios of the APDMS:OFOD were used namely – 50 mol% OFOD (FPE, 0 mol% silicone), 35 mol% OFOD (FS-HF, 15 mol% silicone), 25 mol% OFOD (FS, 25 mol% silicone), 15 mol% OFOD (FS-LF, 35 mol% silicone) and 0 mol % OFOD (SPA, 50 mol% silicone). The molar masses for each of the products are shown in Table 3 and the related GPC traces are shown in Fig. 1. The appearance of a single peak in the GPC traces with a broad molar mass distribution confirmed the formation of fluorosilicones. As the amount of silicone in fluorosilicones increased, a small peak appeared later in the chromatogram corresponding to the unreacted APDMS. Addition of the APDMS rendered the reaction mixture highly viscous and no further increase in the molar mass was observed. The intensity of the polymer peak in the GPC chromatogram for FPE is much lower than those observed for the rest of the copolymers in Fig. 1.

Table 2
Molar masses (M_n, M_w), polydispersity indices (M_w/M_n) of the fluorosilicones (FS-1 to FS-4) and the homopolymers (FPE and SPA).

Polymer	FAD monomer	M_n (g/mol)	M_w (g/mol)	PDI
FS-1	TFBD	1900	3950	2.07
FS-2	HFPD	2030	6350	3.13
FS-3	OFHD	2400	7360	3.07
FS-4	OFOD	3100	8840	2.84
[a]FPE	HFPD	9900	23670	2.39
SPA	–	4560	9570	3.07

[a] FPE – fluorinated polyester synthesized using HFPD.

Table 3
Molar masses (M_n, M_w), polydispersity indices (M_w/M_n) of fluorosilicones (SFAPEAs) with varying feed ratios (%) of OFOD: APDMS with fixed DEA content at 50 mol%.

Sample Name	Feed Ratios of OFOD: APDMS with DEA fixed at 50%	M_n (g/mol)	M_w (g/mol)	PDI
FPE	50:0	16040	27860	1.73
FS-HF	35:15	5010	10990	2.19
FS	25:25	3100	8840	2.84
FS-LF	15:35	5360	12970	2.42
SPA	0:50	4560	9570	2.09

3.2. FTIR analysis

FTIR spectroscopy was used to confirm the presence of amide and ester linkages in the enzmatically synthesized fluorosilicones (SFAPEAs). The spectra of FPE, SPA and FS are shown in Fig. 2. The amide linkage is manifested in the form of two bands occurring at 1650 cm^{-1} ($C{=}O$ stretching) and 1550 cm^{-1} (bending of N–H and C–N) [28]. Both of these bands were found in the FTIR spectra of the SPA and the FS. The $C{=}O$ stretching of the esters was confirmed by the presence of the band at 1735 cm^{-1} in the FPE and the FS. A broad and overlapped infrared band corresponding to (Si–O–Si) in the region of 1130–1000 cm^{-1} can also be seen in the Fig. 2.

3.3. ^1H NMR analysis

The ^1H NMR spectra of FPE, SPA and FS are shown in Fig. 3, and these provide some insight into the structure of these polymers. For the FPE, the peak assignments are consistent with the reported values in the literature, when the shifts arising due to fluorinated

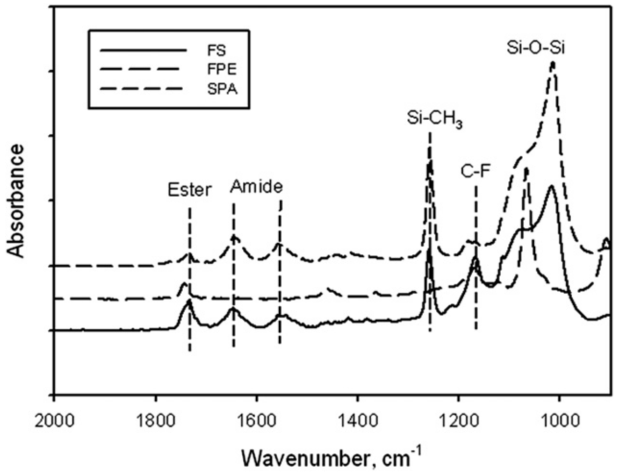


Fig. 2. FTIR spectra of the fluorinated polyester (FPE), the silicone polyamide (SPA) and the flurosilicone (SF) or (SFAPEA) samples.

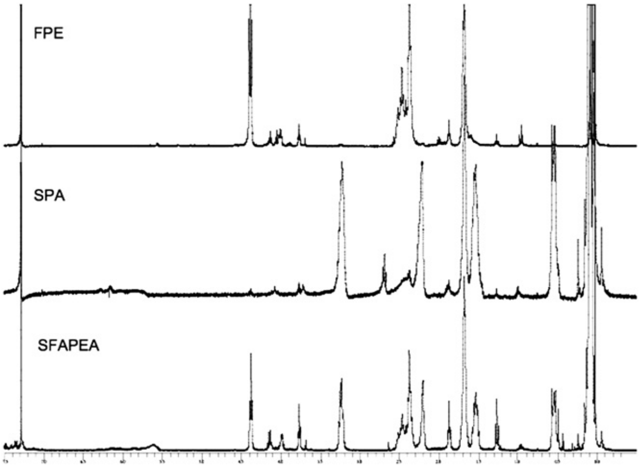


Fig. 3. The ^{1}H NMR spectra for the fluorinated polyester (FPE), the silicone polyamide (SPA) and the fluorosilicone (SFAPEA) samples.

groups were considered [25]. Due to the high electronegativity of the fluorine atom, the chemical shifts of the corresponding groups moved downfield. Comparisons were made with the reference spectra for the FAD monomer to ascertain the magnitudes of these shifts. The low intensity signal at 4.05–4.10 ppm corresponds to the $CH_3C\mathbf{H}_2{-}O{-}CO$ (ester) end group. Also, the signal for the methylene proton of the other end group ($C\mathbf{H}_2OH$) is shifted downfield due to its proximity with the fluorine groups and is seen at around 3.75–3.8 ppm. The strong signal at about 4.35–4.4 ppm corresponds to the methylene protons in the FAD attached to the oxygen in the ester ($C\mathbf{H}_2O{-}CO$). These have again been shifted downfield from the 4.05 ppm due to the strong electronegative influence of the neighboring fluorine and oxygen atoms. The methylene protons in the adipate group, however, remain unaffected by the effect of fluorine and the strong signals at 2.4 ppm and at 1.7 ppm are due to the $C\mathbf{H}_2CO{-}O$ and $C\mathbf{H}_2C\mathbf{H}_2CO{-}O$ groups respectively. Finally, the signal at 2.5 ppm corresponds to the methylene protons in the diol attached to the methylene end group and in the vicinity of the fluorine atom.

The peak assignments for the SPA are consistent with those reported by Gross and coworkers [25]. The protons from the amide group $CH_2N\mathbf{H}{-}CO$ appear as a diffuse band between 5.7 and 6.4 ppm. The ^{1}H NMR spectrum for the fluorosilicone sample is a superimposition of the two spectra described above for the FPEs and the SPAs. The appearance of signals corresponding to the methylene esters and amide linkages is consistent with the formation of a fluorosilicone with both of these linkages in the main chain.

The ratio of amide to ester links in the fluorosilicone was determined by the integration of the spectral intensities of signals corresponding to the methylene protons in the amide and ester linkages. The signals of interest were $C\mathbf{H}_2{-}NH{-}CO$ at 3.13 ppm for amide bond, the low intensity $CH_3C\mathbf{H}_2O{-}CO$ ester end group signal and an additional $C\mathbf{H}_2O{-}CO$ ester signal at 4.38–4.4. The amide and ester linkages in the fluorosilicone were found to be in a 1:1 ratio, which correlates well with the monomer feed ratio (25 mol% APDMS and 25 mol% OFOD). These results confirm the successful synthesis of fluorosilicones of the structure shown in the above reaction Scheme 1.

3.4. Bulk properties

The physical state of the fluorosilicones depended on the relative content of the SPA and the FPE segments. The FPEs were found to be partially crystalline white solids at room temperature. As the silicone content was increased, the fluorosilicone became more waxy and sticky. The SPAs were seen to be highly viscous fluids at room temperature.

3.4.1. DSC analysis

The DSC analysis of the fluorosilicones was performed in order to study the glass transition and also the crystallization phenomena. Fig. 4 shows the DSC scans for the FPEs and fluorosilicones. The FPEs and the fluorosilicones with higher OFOD content were found to be semi-crystalline. The fluorosilicones with higher silicone content were found to be amorphous liquids. The FPEs were observed to be partially crystalline and showed a sharp melting exothermic peak (pointing upwards) between 65 °C and 70 °C. The two-step melting process indicates the presence of a range of crystal sizes. This distribution in crystal sizes could occur due to the heterogeneity of molar masses. The total enthalpy of melting, ΔH_m was obtained from the area under the broad melting peak and was determined to be 110.5 J/g.

The fluorosilicones were found to be more amorphous when compared to the FPEs due to the presence of the highly flexible silicone segments. The location of the melting peak shifted to slightly lower temperature (50 °C) for the fluorosilicone sample with 35 mol% of OFOD content. We can also see a cold crystallization exotherm occurring at about −20 °C, where the kinetics of crystallization were sufficiently accelerated to allow some fraction of the molecules that did not initially solidify, to do so. The enthalpy of melting (ΔH_m) was calculated to be 40.4 J/g and the enthalpy of the cold crystallization (ΔH_c) was 10.5 J/g. These results indicate that partial crystallinity was developed in this particular sample during the melt quenching process.

The transitions of the amorphous fluorosilicones with higher silicone contents were also studied. The T_g for the SPAs occurred around −120 °C, which is consistent with the reported value for linear high molar mass PDMS ($T_g = -123$ °C) [29]. The location of the T_g shifted to higher values in the fluorosilicones with increased amount of the OFOD component. For the samples with 35 mol% APDMS, the glass transition started at about −120 °C but extended a little longer than that of the SPAs. For the fluorosilicone sample containing OFOD (25 mol%) and APDMS (25 mol%), the T_g was shifted to higher temperatures in the range of −80 °C to −75 °C. There was no detectable crystallinity in this sample as can be seen from the absence of any melting or cold crystallization phenomena in the DSC thermogram.

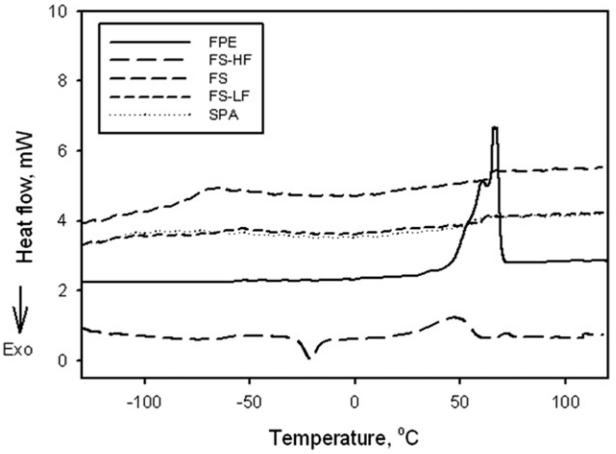


Fig. 4. DSC scans of the fluorinated polyester (FPE), the silicone polyamide (SPA) and the fluorosilicone (FS) or (SFAPEA) samples.

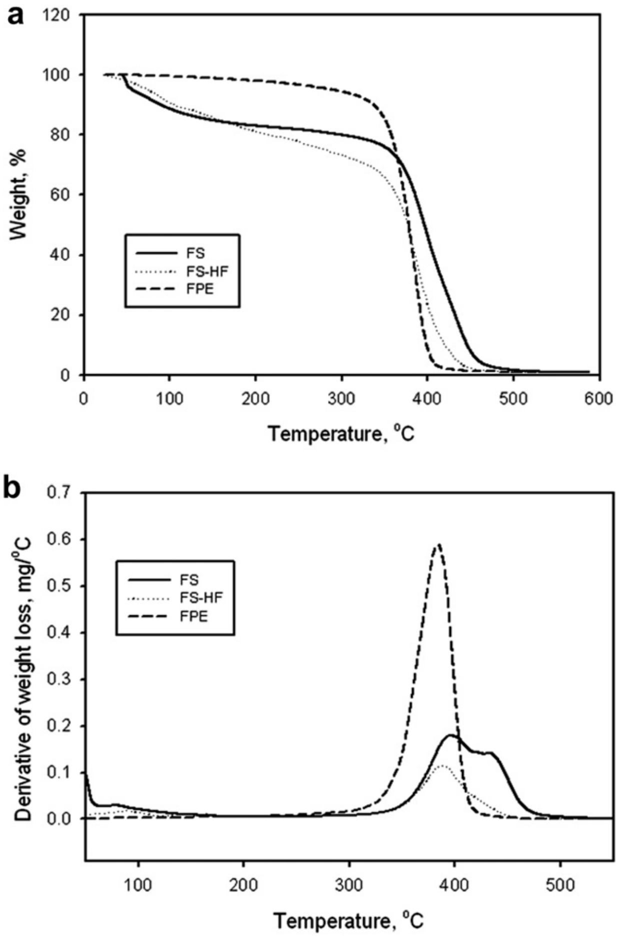


Fig. 5. (a). TGA traces of the fluorinated polyester (FPE) and the fluorosilicone (FS) or (SFAPEA) samples. (b). Derivative of weight loss of the fluorinated polyester (FPE) and the fluorosilicone (FS) or (SFAPEA) samples.

3.4.2. TGA analysis

The TGA analysis were shown for three samples namely – FPE, FS with 35 mol% of OFOD content and FS with 25 mol% of OFOD content in order to study the thermal degradation behavior with increasing APDMS content. The TGA plots of the weight loss and the derivative of the weight loss versus temperature for the three samples are shown in Fig. 5(a) and (b), respectively.

The TGA analysis was carried out under a dry nitrogen atmosphere in order to minimize the formation of oxidation products of PDMS, which would leave a residue at the end of the experiment. For the FPEs, the degradation or depolymerization commenced at about 330 °C with the main degradation step was at about 375 °C. The degradation was complete in a single step at a temperature slightly higher than 400 °C. The degradation profile of the FPEs was similar to the reported profile for non-FPEs with the degradation commencing at about 335 °C and concluding above 400 °C [25]. However, the main degradation step observed for non-FPEs was around 400 °C as compared to 350 °C that we have found for the FPEs herein. The presence of the fluorinated methylene segments in the polyesters did not improve the thermal degradation behavior. However, the presence of silicone in the fluorosilicones pushed the degradation to higher temperatures. This is consistent with the observations made by Kobayashi and Owen, who suggested that PDMS by itself has better thermal stability than its fluorinated copolymers [30]. It can be seen that the degradation for the fluorosilicone sample with equal content of OFOD and APDMS was a two-step process commenced at about 350 °C and extended all the way up to 500 °C as shown in Fig. 5(b). The main weight loss step occurred at about 390 °C followed by a secondary step at about 430 °C.

The thermal stability of linear poly(dimethylsiloxane) (PDMS) has been widely studied [31]. A two-step TGA curve in linear PDMS containing a fraction of low molar mass chains was attributed to molecular mass heterogeneity, since it is known that the thermal stability of PDMS is molecular weight dependent [32,33]. The two-step degradation process could be attributed to the bimodal distribution and the compositional difference of the sample. Due to the higher starting molecular weight of APDMS compared to FAD, the segments of SPA in the final copolymer will be of a higher molecular weight than the segments of the FPE. Low molar mass fractions would be the first to degrade followed by the high molar mass fractions. The overall width of the curve describing the whole degradation process for fluorosilicones with similar compositions was found to be greater than that was observed for non-fluorinated polymers. The degradation was found to be complete at 500 °C. These results indicate that with the optimum fluorinated aliphatic segments and silicone segments in the flurosilicones would lead to polymers with higher thermal stability.

3.5. Enzyme activity analysis

The immobilized enzyme retained approximately 82% and 79% of its initial activity for the reactions performed using TFBD and OFHD, respectively when the reactions were stopped after 28 h. For the reactions using HFPD, no significant drop in the enzyme activity was observed when the reactions were terminated after 28 h. However, when the HFPD reactions were carried out for 70 h, the enzyme activity dropped to about 40%. For the polymer reactions using OFOD, Novozym-435 retained about 57% of its original activity for the FS-LF and 67% of its activity for the FS-HF.

A number of factors are responsible for the drop in activity of the immobilized lipase. Exposure to FADs for a long period of time and the subsequent washing with the polar THF could be responsible for the drop in the enzyme activity. We have also observed the disintegration of the macroporous acrylic resin support material used for the enzyme immobilization in Novozym-435, possibly due to its poor mechanical properties. The instability of the resin severely undermines the use of the enzyme in organic media and necessitates the use of a more stable and robust support material. We are currently exploring various enzyme support materials to solve the problems associated with the enzyme stability in organic media.

4. Conclusions

We have successfully synthesized silicone fluorinated aliphatic polyesteramides (SAFPEAs) using an immobilized lipase B from *Candida antarctica* (Novozym-435). The polymerization reactions were performed in the bulk under reduced pressure in the temperature range of 70–90 °C. DEA was used in order to eliminate the problem of incompatibility of the FADs with the APDMS. FTIR and ^{1}H NMR analysis revealed the formation of amide linkages between DEA and APDMS while ester linkages between DEA and the respective FADs. The highest molar masses were obtained using OFOD, which had an additional methylene ($-CH_2-$) spacer between the fluorocarbon chain ($(-CF_2-)_n$) and the hydroxyl end groups ($-OH$). The physical state of the fluorosilicones depended upon the relative contents of the FPEs and the SPAs in the final product. The FPEs were partially crystalline white solids at room temperature and became progressively viscous and waxy as the silicone content increased in the fluorosilicones. TGA analysis revealed a marginal improvement in the degradation characteristics of fluorosilicones.

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