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Effect of annealing on the mechanical properties and the degradation of electrospun polydioxanone filaments

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ABSTRACT

Annealing, or heat treatment, has traditionally been used as a treatment to improve the strength and stiffness of electrospun materials. Understanding the extent to which annealing can improve the mechanical properties and alter the degradation rate of electrospun polydioxanone filaments could influence the range of its potential clinical applications.

In this study, we investigated the effect of annealing electrospun polydioxanone filaments at varying times and temperatures and subsequently subjecting them to *in vitro* degradation in phosphate buffer saline for up to 6 weeks. Fibre alignment, tensile strength and thermal properties were assessed.

It was determined that annealing at 65 °C for 3 h only marginally improved the tensile strength (9 ± 2%) but had a significant effect on reducing strain and rate of degradation, as well as maintaining fibre alignment within the filament. The filament retained significantly more of its force at failure after 4 weeks (82 ± 15%, compared to 61 ± 20% for non annealed filaments) and after 6 weeks of degradation (81 ± 9%, compared to 55 ± 13% for non annealed filaments). Conversely, annealing filaments at 75°C improved the initial tensile strength of the filament (17 ± 6%), but over 6 weeks, both samples annealed at 75 °C and 85 °C otherwise performed similarly or mechanically worse than those not annealed.

These findings suggest that annealing at low temperatures is more useful as a method to tailor degradation rate than to improve mechanical properties. The ability to modulate the degradation profile with annealing may become useful to tailor the properties of electrospun materials without altering the chemistry of the polymer used. This might better match the degradation of the implant and gradual loss of mechanical properties with the new matrix deposition within the structure, enabling multiple regenerative strategies within a single biomaterial system.

1. Introduction

There is a need to improve the outcome of soft tissue repairs and it is indicated that the use of biomaterials will better support and guide tissue regrowth. Biomaterials made by electrospinning, a process by which microscale fibres are drawn out from a polymer solution using electrical charges, has received recent attention in the field of tissue engineering (Reneker and Yarin, 2008). These materials have been shown to have potential in mimicking the major structural components of native extra-cellular matrix, in particular collagen and elastin (Boland et al., 2005). While electrospinning allows for the manipulation of key biophysical parameters (such as fibre diameter and alignment), these materials often lack the necessary mechanical properties for eventual biomedical applications, such as scaffolds, sutures and drug delivery devices (Venugopal and Ramakrishna, 2005). Post-spinning treatments are often needed to enhance the strength and stiffness of the fibres (Tan and Lim, 2006a, 2006b; Srithep et al., 2013; Weir et al., 2004a, 2004b). Annealing, or heat treatment, is one post-spinning treatment known to change the mechanical properties of electrospun materials (Cho et al., 2011; Tan and Lim, 2006a, 2006b; Barber et al., 2013). Its effects on crystal structure, fibre alignment and on mechanical properties are documented in the literature for some polymers (Baji et al., 2010; Bonnet et al., 1999; Takayama et al., 2011; Yeh et al., 1976). Annealing some biodegradable polymers such as poly-L-lactide (PLLA) (Weir et al., 2004a, 2004b; Srithep et al., 2013; Ali et al., 1993; Tan and Lim,

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2006a, 2006b) and polycaprolactone (PCL) (Ali et al., 1993) has led to improvements in their mechanical properties. Recently, polydioxanone (PDO) is emerging as an attractive biodegradable polymer for use as a biomaterial, as it has a good safety profile with mild foreign body reaction and complete degradation between 5 months to one year, depending on manufacturing and processing conditions (Goonoo et al., 2015; Mouthuy et al., 2015; Sabino et al., 2000). It is known that heat treatment changes the microstructural properties and degree of crystallinity of aliphatic polyester polymers (like PDO), which affects the absorption rate of the polymer (Cho et al., 2011). The extent to which annealing can improve the mechanical properties and alter the degradation rate has not been explored for PDO electrospun materials but could influence the range of its potential clinical applications. Hence, the objective of this study was to quantify the effect of annealing on the mechanical and degradation properties of PDO filaments manufactured according to a method recently described (Mouthuy et al., 2015). We hypothesized that annealing will improve the mechanical properties and alter the degradation rate of PDO electrospun materials.

2. Materials and methods

2.1. Electrospun filaments

Polymer solutions were made by dissolving polydioxanone (PDO, Sigma-Aldrich; viscosity 1.5–2.2 dL/g; T_g −10 to −5 °C; T_m 110–115 °C) in HFIP solvent (Apollo Scientific; 1,1,1,3,3,3, -hexafluora-2-propanol) at a 9% weight to volume ratio and stirred for 24 h before electrospinning. HFIP was chosen for its easy dissolution in the polymer and its fast evaporation in electrospinning conditions (Xie et al., 2008).

A custom electrospinning apparatus with a single nozzle and a stainless steel wire collector was used to fabricate continuous electrospun filaments (made up of submicron fibres). The solution feed rate was 1 mL/h, wire feed rate was 0.5mm/s and the filaments spun under an electric field of 6.9 kV. These filaments were then manually stretched until resistance was felt (around 3.5 times their length), to increase the length and align the submicron fibres in the direction of the thread (Mouthuy et al., 2015). These drawn filaments were kept at room temperature of 25 °C in a dessicator until use.

2.2. Annealing

Electrospun filaments were thermally annealed at 65 °C, 75 °C, and 85 °C. It has been proposed that most polymer annealing changes occur in a range below melting temperature (Tm), generally between Tm-60 and Tm (Yeh et al., 1976). While PDO has a melting temperature of about 110 °C (Goonoo et al., 2015), the 65–85 °C temperature range was chosen for this experiment to avoid melting of the polymer chains. The filaments were heat treated for 3, 6, 9, 12 and 24 h. This annealing time range was chosen following optimization work done at 65 °C.

2.3. In vitro degradation

Prior to *in vitro* degradation, filaments were cut and sterilized for 2 h in 70% ethanol. Degradation of the annealed filaments was carried out in phosphate-buffered saline solution (PBS) under pH 7.4 at 37 °C in an incubator. Each set of annealed samples was removed for mechanical testing, scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) characterization at time points of 3 weeks, 4 weeks and 6 weeks. Every week, the samples were washed and replaced with fresh PBS and the pH was monitored with a pH meter. Prior to analysing the degraded filaments, they were washed twice with deionized H_2O and placed in a vacuum for 3 h to dry the filaments.

2.4. Mechanical characterization

Annealed filaments were dried and cut to 2 cm sections. Samples were tested until failure with a 20N load cell using a uniaxial tensile testing machine (Deben Stage Tensile Compression Stage, UK). Both undegraded and degraded filaments were tested and maximum force at failure (N) and clamp-to-clamp breaking strain (%) were recorded. Work done until failure (Nmm) was calculated based on the force-displacement data. Ten specimens were tested for each condition and for each experimental repeat.

2.5. Scanning electron microscopy (SEM)

Scanning electron microscopy (Carl Zeiss Evo LS15 VP-Scanning Electron Microscope) images from each annealing and degradation time point were taken. The samples were washed with phosphate buffered saline (PBS, Sigma-Aldrich, St. Louis, MO, USA), cut and coated with gold using a SC7620 Mini Sputter Coater System (Quorum Technologies Ltd, Laughton, UK), prior to mounting on the SEM machine. Samples were analysed in a high vacuum mode to examine changes in morphology due to degradation, such as fibre fusing or breaking. Fibre diameter was determined using ImageJ software (National Institute of Health, Bethesda, MD, USA).

2.6. Differential scanning calorimetry (DSC)

Polydioxanone is a semi-crystalline polymer with the glass transition temperature of about −10 °C and melting temperature of around 110 °C (Goonoo et al., 2015). A differential scanning calorimeter (TA Q2000-1275 Differential Scanning Calorimeter) was used to examine the thermal properties of PDO samples annealed at different times and temperatures. From each annealing and degradation condition, 3 to 4 mg of sample was cut and mounted in aluminium (TZero Aluminium) pans, along with an empty tin as the reference standard. The pans were heated from 25 °C to 140 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. From DSC thermograms, the melting temperature (Tm), measured heat of fusion (ΔHf) and measured area of the annealing peak (derived from ΔHc), the endothermic peak found about 10–20 °C below the melting temperature (Bonnet et al., 1999), were determined.

2.7. Statistical analysis

Data are expressed as means with standard deviations. The statistical significance was determined by the analysis of variance (two-way ANOVA) and Tukey post-hoc test at the significance level of less than 0.05 ($p < 0.05$) using GraphPad Prism version 7 software (GraphPad Software Inc., La Jolla, CA, USA).

3. Results

3.1. Visual & SEM analysis

The morphology of electrospun PDO filaments and changes following degradation are shown in Fig. 1, for samples annealed for 3 h. Filaments in each set were of similar diameter (1.3 ± 0.5 μm). No differences in fibre arrangement could be seen due to the annealing temperature (Fig. 1a-c). Samples that were annealed at 65 °C maintained a high degree of fibre alignment and there were few visible breaks in the fibres up to 6 weeks (Fig. 1g). Samples annealed at 75 °C maintained a high level of fibre alignment after 4 weeks of degradation (Fig. 1e), but lost much of the linear organization by 6 weeks. These samples took on a more wavy appearance with visible breaks along the length of the filament (Fig. 1h). Samples annealed at 85 °C exhibited these signs of degradation by 4 weeks (Fig. 1f). By 6 weeks, the fibres had fused together, making the samples brittle and difficult to handle

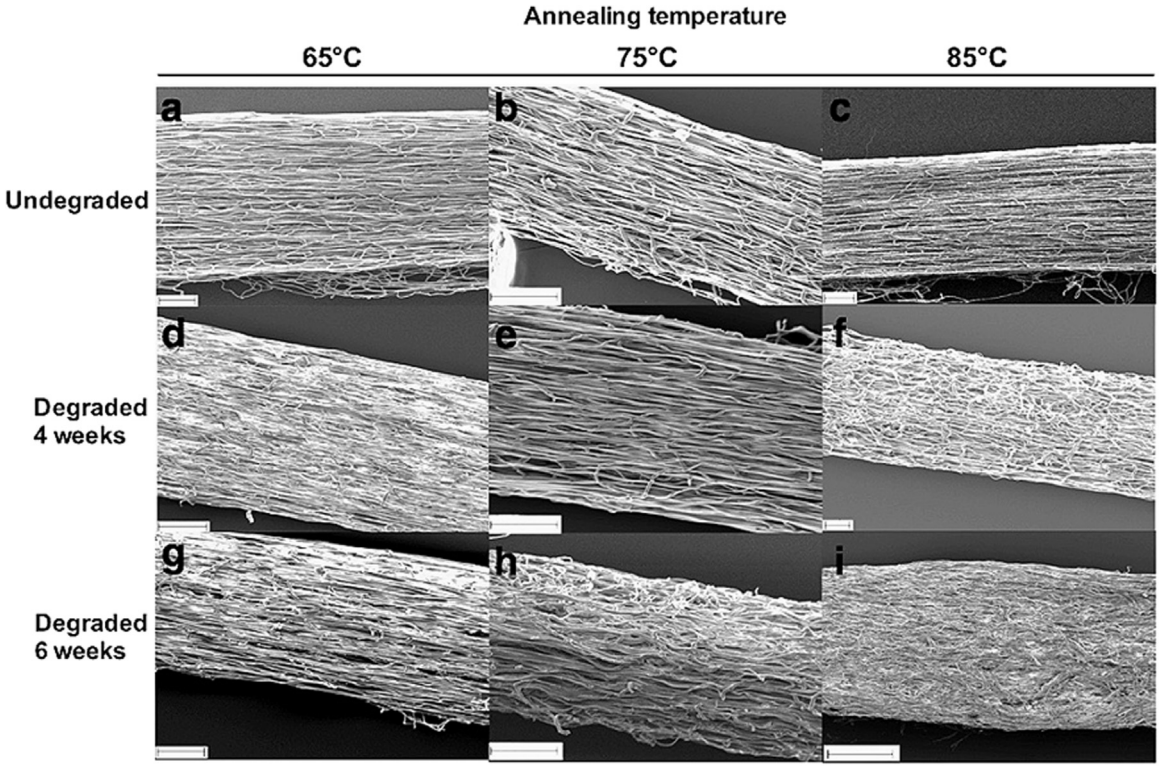

Fig. 1. SEM images of PDO electrospun filaments annealed for 3 h at 65 °C, 75 °C and 85 °C and changes in structure following a 6 week degradation period a-c. Undegraded samples. No visual difference in fibre alignment observed for samples annealed at different temperatures; d-f. Samples degraded for 4 weeks in PBS at pH 7.4. Samples annealed at 65 °C and 75 °C maintain high degree of fibre alignment, compared to samples annealed at 85 °C.; g-i. Samples degraded for 6 weeks in PBS at pH 7.4. High degree of fibre alignment retained for samples annealed at 65 °C, compared with 75 °C or 85 °C. Scale bars represent 100 μm.

(Fig. 1i). An increase in filament size (50 ± 20um) was visible at this time, likely due to the solution expanding in the filament structure.

Samples annealed at 6, 9 and 12 h showed similar patterns of degradation. Samples annealed at 65 °C for 24 h already displayed signs of fibre breaking and fusing by 4 weeks of degradation. Annealing at 75 °C or 85 °C for 24 h did not improve the mechanical properties and rendered the samples more brittle than not annealing. After 6 weeks of degradation, samples that were annealed for 24 h at 85 °C were too brittle to mechanically test.

3.2. Mechanical analysis

3.2.1. Undegraded filaments

Filaments became slightly stronger and more brittle due to annealing for 3 h at 65 °C and 75 °C. Samples annealed at 85 °C for longer than 3 h were mechanically weaker ($p < 0.001$) and more brittle ($p < 0.0001$) than those not annealed. The relative changes in maximal force and strain are shown in Fig. 2. The force at failure increased after annealing filaments at 65 °C and 75 °C for some time points, although the changes were not statistically significant. The maximal force decreased after annealing filaments at 85 °C for more than 6 h ($p < 0.0001$). The strain decreased at all annealing temperatures and this result was significant for samples annealed longer than 6 h ($p < 0.0001$). Annealing for 3 h resulted in an increase in tensile strength of 9 ± 2% and 17 ± 6% and a decrease in strain of 14 ± 3% and 18 ± 7% at annealing temperatures of 65 °C and 75 °C, respectively. Work done until failure, analogous to toughness, decreased for samples annealed for more than 9 h at 75 °C and 85 °C ($p < 0.01$). The Supplementary information contains the exact changes in maximal force and strain and work done until failure after all annealing conditions.

3.2.2. Degraded filaments

Samples annealed at lower temperature and shorter time better maintained mechanical properties. Changes in maximal force and strain of annealed filaments over the 6-week degradation period are shown in Fig. 3. It can be noted that samples annealed at 65 °C for less than 9 h retained a high percentage of their maximal force (74 ± 16%) and strain (56 ± 25%) up to 6 weeks of degradation, compared to samples that were not annealed (> 54% for both force and strain). Samples annealed at 65 °C for less than 6 h retained a higher maximal force at 6 weeks of degradation compared to filaments that were not annealed. In contrast, samples annealed for any time at 75 °C and 85 °C retained less maximal force and strain after 6 weeks of degradation, compared with samples that were not annealed. Samples annealed for 3 h at 75 °C only retained 42 ± 17% of force and 27 ± 14% of strain after 6 weeks of degradation. Samples annealed at 85 °C for longer than 9 h had a lower maximal force compared to samples that were not annealed at all degradation time points.

The mechanical properties of filaments annealed for 3 h and their 6-week degradation profile are shown in Fig. 4. At 65 °C, these annealing parameters resulted in only a 9 ± 2% increase in maximal force compared to samples not annealed, however the filament retained 82 ± 15% of its strength after 4 weeks, and 81 ± 9% in 6 weeks compared to 61 ± 20% and 55 ± 13%, respectively, for non annealed samples ($p < 0.0001$; Fig. 4a). Work to failure showed a more pronounced effect of annealing. Here, only samples annealed at 65 °C showed an improvement at 4 weeks ($p < 0.01$) and at 6 weeks ($p < 0.0001$), compared to samples not annealed, suggesting rapid embrittlement of high temperature annealed fibres with degradation. The percentage of force and strain retained at the 6-week degradation period for all annealing times and temperatures is available in Supplementary information.

3.3. Thermal analysis

The DSC thermographs obtained in this study are presented in

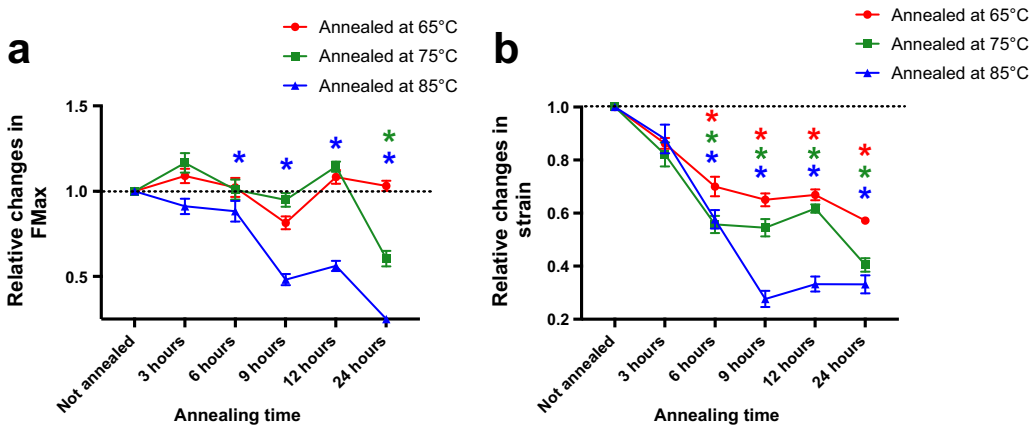

Fig. 2. Changes in mechanical properties of PDO monofilaments after annealing treatments. a. Relative changes in maximal force for annealing times and temperatures. Filaments annealed at 85 °C for more than 6 h were weaker than those not annealed ($p < 0.05$). Annealing for 24 h at 75 °C weakened the filament ($p < 0.001$). b. Relative changes in strain for annealing times and temperatures, compared to not annealed. Annealing at all temperatures for more than 6 h significantly reduced the filament strain ($p < 0.0001$). Error bars represent standard deviations (n=10 for each condition), $p < 0.01$.

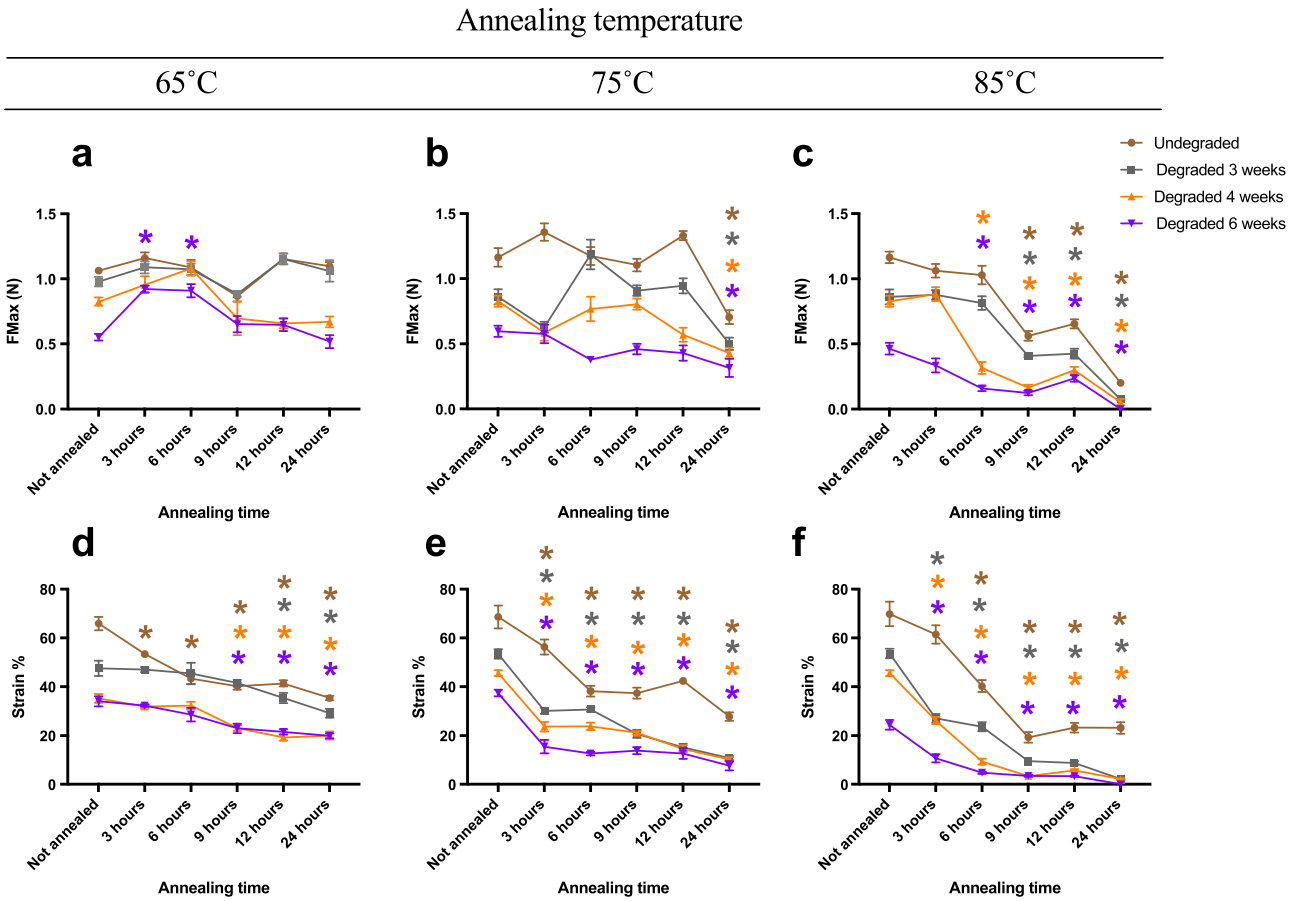

Fig. 3. Effect of a 6-week degradation period on maximal force (FMax) and Strain (%) for filaments at all annealing conditions compared to not annealed. a-c. Changes in maximal force for samples annealed at 65 °C, 75 °C and 85 °C. d-f. Changes in strain (%) for samples annealed at 65 °C, 75 °C and 85 °C. Error bars represent standard deviations (n=10 for each condition), * $p < 0.01$.

Fig. 5. The graphs contain three characteristic regions: (1) an annealing peak (reported from the enthalpy of crystallisation, ΔHc), (2) a melting peak ranging from 90°C to 110°C (reported from the enthalpy of fusion, ΔHf) and (3) a melting point (Tm) with a maximum around 106°C.

From the thermographs of the undegraded samples, both an increase in magnitude and a temperature shift of the annealing peak towards the melting peak were observed with increased annealing time and temperature. This shift was most noticeable for samples annealed at 85%. Annealing peaks appeared at 70–85 °C for samples annealed at 65 °C and 75 °C, but appear at 90–100 °C for samples annealed at 85 °C. Moreover, filaments annealed at 65°C versus 75 °C or 85 °C had a lower heat of fusion (ΔHf, Fig. 6a) and this result was significant at 3, 6 and 24 h. At all annealing times, there was an increase in heat of fusion with increased annealing temperature. The heat of crystallization (ΔHc, Fig. 6c) was significantly lower at 65 °C than at 75 °C or 85 °C for samples annealed for 24 h. Finally, double melting peaks were observed for samples annealed at 65 °C and 75 °C (Figs. 5a and c,

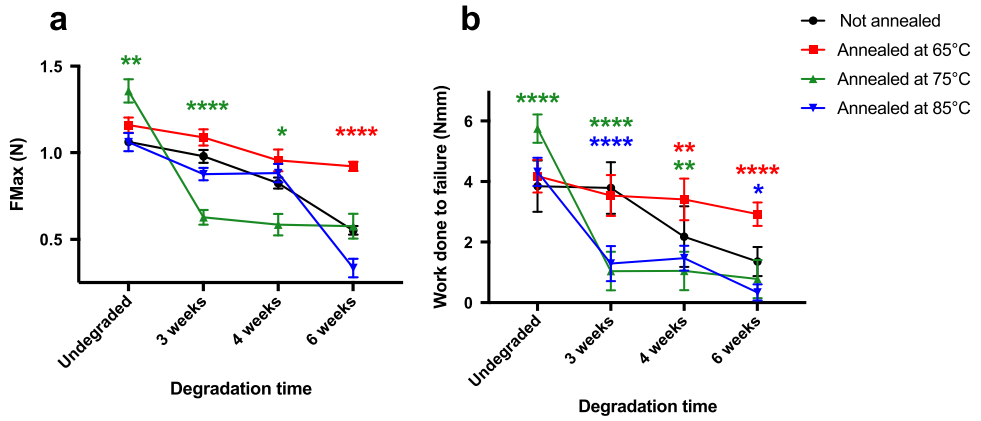

Fig. 4. Changes in mechanical properties for samples annealed for 3 h over a 6-week degradation period, compared to non-annealed samples. a. Maximal force (FMax) shown as a function of degradation time. Samples annealed at 75 °C showed a higher initial FMax ($p < 0.01$), however samples annealed at 65 °C were able to retain a higher percentage of FMax over 6 weeks ($p < 0.0001$). b. Work done to failure shown as a function of degradation time. Samples annealed at 75° and 85 °C had performed worse after degradation than those not annealed ($p < 0.0001$ at 3 weeks). Samples annealed at 65 °C retained a higher work done to failure than samples not annealed at 4 weeks ($p < 0.01$) and 6 weeks ($p < 0.0001$). Error bars represent standard deviations (n=10 for each condition), *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$, ****$p < 0.0001$.

respectively), but only a single melting peak for samples annealed at 85°C (Fig. 5e).

Following degradation, clear annealing peaks were still visible in DSC scans of samples annealed at 65 °C (Fig. 5b), but were barely visible for samples annealed at 75 °C and 85 °C (Figs. 5d and f, respectively). All degraded samples had single melting peaks. For samples annealed at 65 °C for any time period, there was a steady decrease in the heat of fusion (smaller melting peak) compared to samples that were not annealed, as shown in Fig. 6b. No clear pattern in heat of fusion was observed for samples annealed at 75 °C and 85 °C. The changes in melting temperatures derived from the thermographs are available in the Supplementary information.

4. Discussion

The performance deficit between native biological materials and the synthetic structures designed to replace them demands the improvement of base materials, structural organisation, or both. For polymeric materials such as those used in electrospun or printed scaffolds, annealing is an attractive option to improve mechanical properties. Our work investigated the effects of annealing on electrospun polydioxanone (PDO) fibres. In contrast to results from PLLA (Weir et al., 2004a, 2004b; Srithep et al., 2011; Tan and Lim, 2006a, 2006b), we found minimal improvement in the properties of 'pristine' fibres, yet a marked influence on the maintenance of mechanical performance with *in-vitro* degradation.

Semi crystalline polymers such as PDO consist of highly orientated folded chain crystals connected by many highly stretched tie chains in the amorphous regions separating the crystals. Annealing changes the microstructure adopted by the polymer chains and these changes strongly influence the mechanical properties of a fibre (Ping Ooi and Cameron, 2002a, 2002b). Filaments annealed at low temperatures (65 °C) for any time were stronger and less brittle than filaments annealed at high temperatures (75°/85 °C), suggesting there was more of a temperature than a time effect on mechanical properties within the parameter space tested here. The minimal, and in many cases detrimental effect of annealing on mechanical properties of PDO were unexpected. Other studies investigating different polymers showed that annealing substantially increased the tensile strength (Tan and Lim, 2006a, 2006b; Weir et al., 2004a, 2004b; Srithep et al., 2011). Tan and Lim (2006a, 2006b) found that annealing electrospun PLLA at 75 °C for 24 h resulted in a 150% increase in the Young's modulus and a 10% decrease in fibre diameter (melting temperature of as-spun fibres: 182 °C). While annealing can take place at any temperature above the crystallization and below the melting temperature, they annealed at 75 °C, close to the crystallization temperature of electrospun PLLA (72 °C), to avoid melting of short polymer chains. They also chose a long annealing time of 24 h to ensure all rearrangements of polymer chains were complete (Tan and Lim, 2006a, 2006b). The annealing temperatures used in the current study (65–85 °C) were closer to the PDO melting temperature (110 °C), which may explain worsening of the mechanical properties at longer annealing times. Weir et al. (2004a, 2004b) annealed compression-moulded and extruded PLLA fibres at a higher temperature of 120 °C for 4 h, and observed a slight increase in Young's modulus from 620 MPa to 658 MPa, but a decrease in tensile strength, extension at maximum and stress at yield for annealed PLLA. While the study used a different PLLA processing technique and annealing parameters compared to that from Tan and Lim (2006a, 2006b), the dramatic difference in fibre mechanical properties after annealing between the two studies suggest there is an optimal annealing time and temperature combination to maximize the fibre mechanical properties for a specific processing method. This relationship between annealing temperature and time requires further exploration (Srithep et al., 2013).

Our thermal analysis showed changes in annealing peaks (location and size), which are associated with changes occurring in the amorphous phase of the material (Bonnet et al., 1999). Moreover, the increase in heat of fusion (ΔHf) with higher annealing temperature and time is correlated to an increase in measured crystallinity, assuming proportionality to the experimental heat of fusion of 100% crystalline polydioxanone (Ali et al., 1993; Weir et al., 2004a, 2004b). Overall, the measured increase in crystallinity and shifting of annealing peaks points to changes to crystal sizes and morphologies due to rearrangements of the polymer chains in the amorphous regions (Ping Ooi and Cameron, 2002a, 2002b; Tan and Lim, 2006a, 2006b). Since the mobility of polymer chains increases with temperatures, higher annealing temperature and annealing times may lead to bigger crystalline structures, following a rearrangement of the polymer chain in the amorphous regions to decrease the free energy of the system. Bonnet et al. (1999) summarized five proposed models commonly found in the literature to explain how changes to the endothermic annealing peak reflect crystal morphologies, crystal sizes and melting-recrystallization behaviours. Two major challenges in developing these models and interpreting annealing results stems from a lack of standardized method in the literature to explain annealing changes (Hoffman et al. 1969; Yeh et al., 1976), and also that many observed changes after annealing are dependent on factors internal to the material, such as prior thermal history, physical state, chemical structure and composition (Yeh et al., 1976).

Due to the large surface area: volume ratio of electrospun materials,

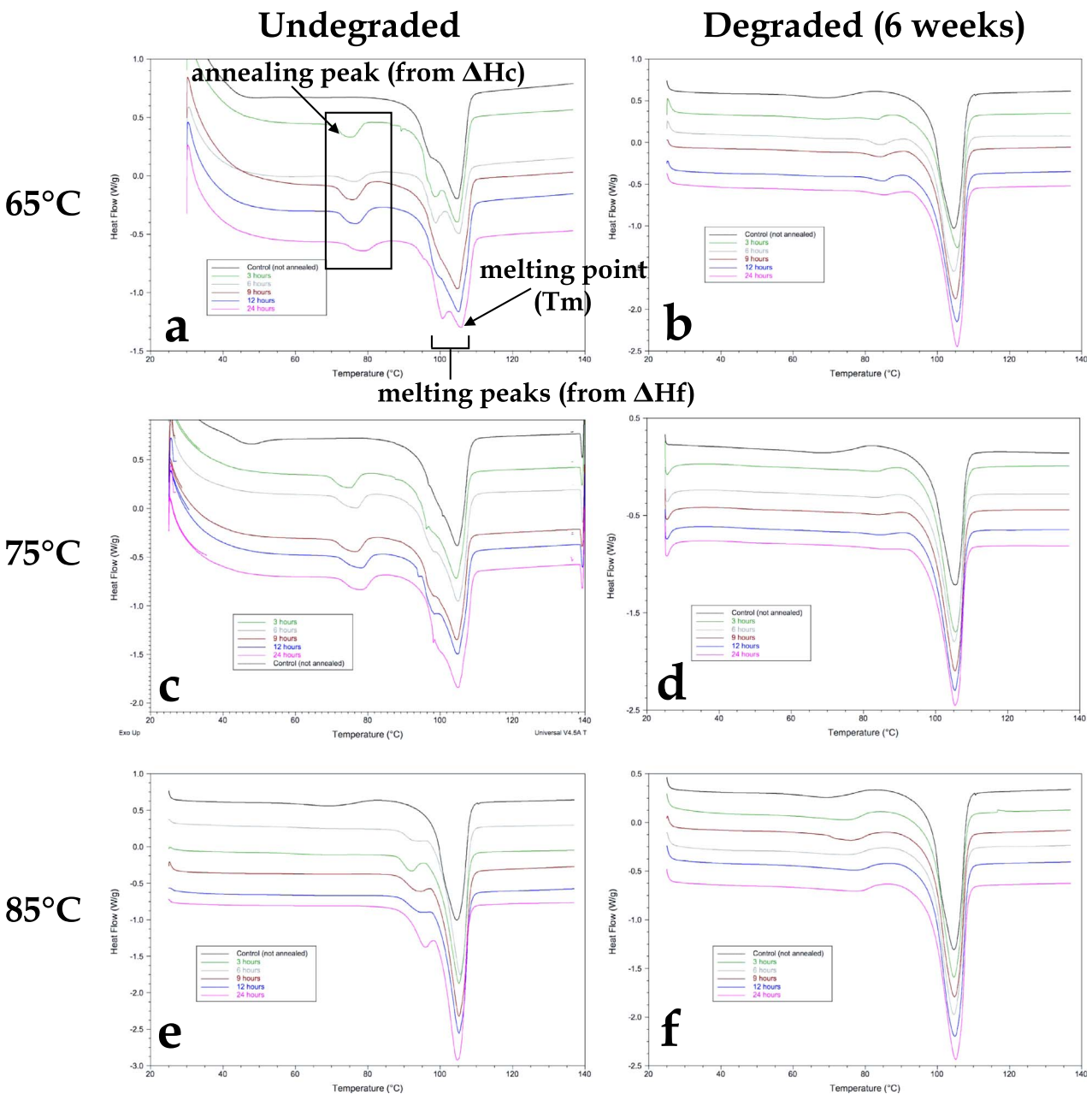

Fig. 5. Differential Scanning Calorimetry (DSC) heating scans of PDO electrospun filaments undegraded and degraded for 6 weeks, annealed at different temperatures. a-b. Samples annealed at 65 °C; c-d. Samples annealed at 75 °C; e-f. Samples annealed at 85 °C. The annealing peak (black box in undegraded samples) appears to be shifting towards the melting peak. A double melting peak can be observed for samples annealed at 65 °C and 75 °C, but disappears during degradation and is not visible for any samples annealed at 85 °C.

degradation is critical. Degradation of PDO is known to occur through hydrolysis, resulting in chain scissioning primarily in the amorphous regions of the material (Ping Ooi and Cameron, 2002a, 2002b; Ali et al., 1993). In the current study, samples annealed at 65 °C retained more tensile strength and strain over 6 weeks, compared to samples that were not annealed. Conversely, samples annealed at 75 °C or 85 °C for any time performed mechanically worse after 6 weeks, compared to samples that were not annealed. The work done to failure is also presented, which is a key material property indicating the amount of mechanical energy a material can absorb before rupturing. Here, samples annealed at 65 °C show a significant improvement compared to non-annealed filaments over 6 weeks of degradation, indicating that under the same conditions, annealing at 65 °C can reduce the risk of filament failure over time. Thermal analysis showed that double melting peaks disappeared after 3 weeks and that there was a gradual increase in the melting peak temperature with degradation time for samples annealed at all times and temperatures. These results suggest structural changes in the material, potentially similar to what Ping Ooi and Cameron, 2002a, 2002b observed studying the degradation of commercial PDSII sutures. They proposed that during degradation, hydrolytic scissioning of chain segments in the amorphous region led to a higher mobility of chain regions and a lack of unity between amorphous and crystalline regions, resulting in a loss of tensile strength (Ping Ooi and Cameron, 2002a, 2002b). In the current study, annealing at high temperatures caused faster degradation and a rapid loss of mechanical properties, however annealing at 65 °C made the amorphous domains less susceptible to degradation. We speculate that annealing closer to the crystallization temperature protected the low molecular weight polymer chains from melting. The ability to modulate the degradation profile with annealing may become useful to further tune the properties of a biomaterial device without altering the chemistry of the polymer used. For instance this might help to better

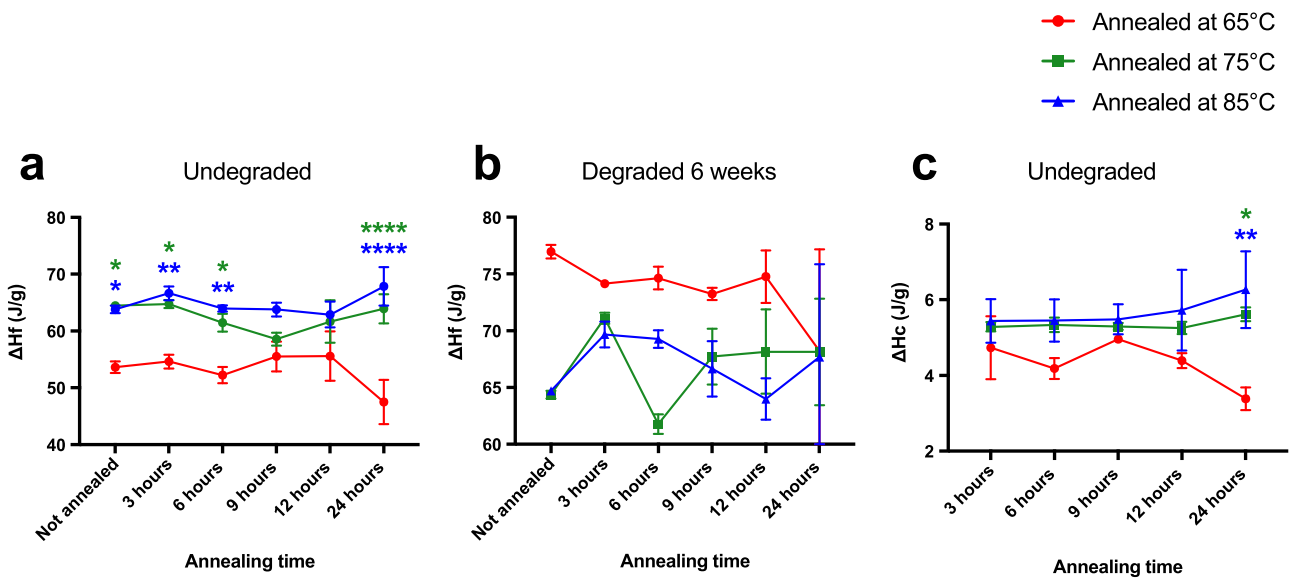

Fig. 6. Thermal changes recorded from the DSC thermographs. a. Changes in heat of fusion (ΔHf) for undegraded samples as a result of annealing. There was a higher ΔHf for samples annealed at 75 °C and 85 °C, compared to 65 °C. b. Changes in heat of fusion for degraded samples as a result of annealing. c. Increase in heat of crystallization (ΔHc) calculated from the annealing peak observed with higher annealing temperature and time. The ΔHc was significantly lower for samples annealed for 24 h at 65 °C, compared to 75 °C ($p < 0.05$) and 85°C ($p < 0.01$). Error bars represent standard deviations (n=3 for each condition), $^{*}p < 0.05$, $^{**}p < 0.01$, $^{****}p < 0.0001$.

match the degradation of the scaffold and gradual loss of mechanical properties with the new matrix deposition within the structure, enabling multiple regenerative strategies with a single biomaterial system.

There are several limitations to be considered. First, the highest performance observed in these samples was at the lowest time and temperature of annealing, suggesting an optimum below these values. Further work investigating lower temperatures and times is needed to optimize processing parameters. However, we have shown that within the space tested here, annealing can improve strength retention and fibre alignment after *in vitro* degradation. This has not been previously reported and has important implications for the potential clinical use of electrospun materials to support and guide tissue regrowth. This study showed that annealing can be used to tailor the degradation rate by extending strength retention and maintaining fibre alignment for at least 6 weeks, which is the critical period after surgery where effective healing is needed (Nixon et al., 2012). Second, this study focused on phenomenological exploration of the annealing time and temperature effects on mechanical performance. Future work aiming at a mechanistic understanding of the observed changes should adopt more detailed analysis of structure, such as wide angle XRD, to determine how changes in proportion and organisation of amorphous and crystalline regions affect the mechanical properties. The main strength of this work includes a large number of repeats (n=10) and the inclusion of a large range of annealing time and temperature points, which has not previously been done for electrospun PDO. The degradation results of this study provide implications for tailoring the properties of the electrospun PDO materials for use in biological environments.

5. Conclusions

This study explored the influence of annealing on the mechanical properties and degradation of PDO electrospun filaments. It was determined that annealing at low temperatures only marginally improved the tensile strength, but had a substantial effect on reducing the strain and rate of degradation of the filament. As a result, for PDO electrospun filaments, annealing appears to be more useful as a method to tailor degradation rate than to improve mechanical properties.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jmbbm.2016.11.023.

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