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Fabrication of biopolymer-based staple electrospun fibres for nanocomposite applications by particle-assisted low temperature ultrasonication

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ABSTRACT

We demonstrate the fabrication of staple polymer-based fibres by the ultrasound-assisted processing of electrospun meshes. Bioabsorbable Poly-L-Lactic Acid (PLLA) was electrospun from organic solvent mixtures, yielding continuous fibres with diameters in the range of 244 ± 78 nm. Subsequently, the obtained fibres were sonicated at low temperatures in the presence of nanoparticles in order to obtain fibres with small aspect ratios. The influence of the dispersion medium, the sonication process parameters (temperature and time) and the dimensions of the particles used on the respective length distribution of the obtained nanofibres was investigated. Hexane was identified as an optimal dispersion medium for the system studied in this work. When a cooling bath temperature of 0 °C was used, a slight increase in the obtained fibres' average length and distribution was observed as compared to cooling at −80 °C (54 ± 43 μm vs 44 ± 31 μm). Moreover, in the presence of hydroxyapatite and hydrophilic and hydrophobic TiO_2 nanoparticles in the dispersion medium longer fibres were obtained (44 ± 31 μm, 63 ± 47 μm, and 51 ± 52 μm). Finally, the application of the obtained PLLA-fibre–hydroxyapatite (HA) nanoparticle precursors for the fabrication of a fibre-reinforced Brushite-based cement with high compressive strength is shown. This method of obtaining nanoscaled fibre-reinforced materials opens up a wide range of perspectives for the fabrication of composites for tissue engineering applications.

1. Introduction

Dispersed short discontinuous fibres, also known as staple fibres, are widely used as additives in polymeric materials and cement-based matrices to engineer fibre reinforced composites (FRCs) [1–3]. With the increasing interest in micro- and nano-scale composites – especially in the field of bone and tissue engineering – the required raw materials and resulting structures are fabricated in micrometre to nanometre scale to improve mechanical properties or to mimic biological features and elicit specific biological reactions [4–6]. Electrospinning is a very versatile method to produce nano- to micron-sized fibres from a wide range of polymeric and inorganic materials [7–10]. This process typically yields oriented or random non-woven fibre mats [7,11,12]. Electrospinning is used in many applications [13], including tissue engineering [14–17], drug delivery [8], or high performance membranes and textiles [18–21]. The process typically does not yield staple fibres, but it generates meshes and spindles with endless, partially fused fibres [22]. Therefore, subsequent processing steps are required to cut and unbundle into staple fibres of desired length, which can be further dispersed into relevant polymer or inorganic matrices. Different processes for the production of staple fibres with diameters down to 5 μm have been described; however few investigations on the scission of submicron sized fibres have been conducted. Stoiljkovic and co-workers processed electrospun microfibres from polystyrene-co-butadiene containing n-butyl methacrylate and Coumarin as a photocrosslinker. By irradiating the resultant fibre meshes with UV light under a mask the dissolution of non-irradiated areas in THF could be achieved, generating staple fibres of 20 to 150 μm in length dependent on the photomask used [23]. This process is thus suitable only for fibres containing photosensitive groups. Poly-L-Lactic Acid-co-polyethylene oxide staple fibres in the range of 10 μm were obtained by freezing the nanofibre meshes in ethanol using liquid nitrogen, followed by mechanical cutting using a motor driven blade [24]. High shear homogenization was applied for the milling of high molecular weight styrene-co-4-vinylbenzyl 2-brompropionate nanofibre meshes [25]. Greenfeld and collaborators observed the appearance of discrete short fibres up to a length of 1 mm when electrospinning low molecular weight polymethyl-methacrylate (PMMA) (15 kDa) [26]. In a recent work, Sawawi and co-workers

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described the use of ultrasonication as a method for the scission of polystyrene and PMMA fibres down to 10 μm in length [27]. They have also shown the application of this method for the milling of UV/ozone pretreated Poly-L-Lactic Acid (PLLA) fibres.

Sonication was also applied to coat microfibre based cotton bandage fabrics with metal oxide nanoparticles such as Al_2O_3 or MgO [28]. It has been predicted that the addition of nanoparticles enhances the sonication effect by providing nucleation sites for cavitation bubbles, thus increasing the sonication efficacy [29], but to our knowledge the effect of nanoparticles on the outcome of nanofibre cutting by ultrasonication has not yet been investigated.

The goal of the present work was to demonstrate the potential of particle-assisted low-temperature ultrasonication for the fabrication of submicron- to nanometre diameter staple fibres from the use in biomaterials applications, i.e. of biopolymers such as PLLA (a bioabsorbable polymer with a high tensile strength of 70 MPa and a glass transition temperature of 60 °C [30]), without any additional chemical pre- or post-treatments. By performing the procedures well below the glass transition temperature of the materials, the fibres are expected to be brittle enough to be cut under the complex action of the ultrasonic waves, while retaining relevant morphological features such as diameter and surface structure, as well as mechanical characteristics [31,32]. The effect of the dispersion media, ultrasonication temperature and time on the cutting efficiency was evaluated. The nanoparticles were expected to act as cutting moieties and provide additional nucleation sites, thus improving the sonication yield. Moreover, we hypothesized that this approach would allow the simultaneous, homogeneous dispersion of particles and fibres. The morphology of the staple fibres was characterized by optical and scanning electron microscopy. The staple fibres/nanoparticle dispersions were then used to fabricate a calcium phosphate-based cement that can be used as a bone substitute material. The distribution of the fibres in the composite and its mechanical properties were also evaluated.

2. Materials and methods

All solvents were obtained from commercial providers in ACS quality and were used without further purification. Poly-L-Lactic Acid (PLLA, Biomer L9000, Mw: 200 000 kDa), was obtained from Biomer Biopolyesters (Germany). The titanium dioxide (TiO_2) nanopowder, P25, and octylsilane coated, hydrophobic TiO_2-T805, was provided by Evonik/Degussa (Germany), and had a nominal particle diameter of 21 nm, as indicated by the manufacturer. Hydroxyapatite (HA) nanoparticles were purchased from M K Impex Corp (Canada) and the nominal particle diameter was 30 nm as indicated by the manufacturer.

2.1. Electrospinning

A stock solution of 5.6% (w/w) PLLA in chloroform:DMF (8:1 w/w) was prepared (shaken at 200 rpm at room temperature for at least 15 h). After complete dissolution, concentrated formic acid was added at a ratio of 9:1 (w/w) to an aliquot of stock solution and incubated for 20 min; the obtained solution was used immediately for electrospinning.

The electrospinning equipment was an in-house built device, consisting of a syringe pump (KD scientific), a variable high voltage power source (AIP Wild AG Switzerland), and an in-house built rotating collector. The whole system was placed in a Faraday cage. A + 15/− 5 kV potential, with a maximum current of 0.1 mA, was applied between the needle tip (18 G gauge) and collector. The tip–collector distance was set at 18 cm. The rotating speed of collector (20 cm diameter) was constant at 1340 rpm. The whole system was controlled by the LabView™ software. The collected fibres were removed using tweezers and placed on an aluminium foil for storage and post-processing. Prior to processing, the fibre meshes were cut to approximately 0.5 cm × 1 cm sections perpendicular to the fibre length orientation using a surgical blade (KLS Martin Group, Germany).

2.2. Fabrication of staple fibres

The probe sonication was performed with a sonicator (Branson Digital Sonifier Model 450D) equipped with a 1.27 cm tip, a fixed frequency applied of 20 kHz and a maximum output of 400 W. A 30 mL glass flask containing 20 mL of n-hexane was immersed into a bath containing a mixture of dry ice/acetone and cooled to a temperature of −80 °C. The bath temperature was maintained constant during the process by periodically refilling the coolant mixture. Subsequently a weighed sample of aligned PLLA fibre mesh was transferred to the flask together with a corresponding quantity of HA nanoparticles, as to obtain v/v ratios between 2:1 and 1:4 respectively. A similar protocol was applied when using TiO_2 particles, but only a 1:1 v/v ratio was investigated. The sonication tip was immersed in the flask keeping a gap of 5 mm versus the bottom of the flask. The amplitude was set to be 90%. Pulse/pause time was set to be 2/2 sec to allow sufficient cooling of the dispersion during sonication. The sonication experiments in hexane were repeated 3 times.

Three dispersion media were tested for sonication: a) pure water b) ethanol:water 1:4 (v/v) and c) hexane. The experiments involving water-based mixtures were conducted in an ice/water bath at 0 °C. In the case of hexane, the experiments were conducted at −80 ° C in an ethanol/dry ice bath and a comparison experiment was done at 0 °C.

For the materials used in the fibre reinforced cement, multiple batches of 50 to 120 mg PLLA fibres were sonicated together with 400 to 1000 mg of with HA particles at a fixed fibre to a particle ratio of 1:3 (v/v) for 20 min and at a temperature of −80 °C. The resulting fibre/particle dispersion was air dried under a fume hood under ambient conditions for at least 15 h.

2.3. Cement manufacturing

An aqueous solution containing 1.7 M monocalcium phosphate monohydrate (Innophos Inc., USA) and 0.06 M disodium dihydrogen pyrophosphate (Sigma Aldrich, Switzerland) was prepared with ultrapure water. Subsequently, the solution was mixed with the HA/PLLA dry mass at a ratio of 2:1 (w/w). The resulting slurry was mixed for 2 min with a spatula to obtain a cementeous paste, which was transferred into Teflon cylinders of 10 mm in diameter and 12 mm in height. The cement was left to set for 3 days. The resulting PLLA fibre content was calculated to be 5% (v/v) in the final composite cement.

2.4. Nanoparticle characterization

The nanoparticles were characterized in suspensions of isopropanol, as a reference, and hexane, as a dispersion medium used for sonication, to study their agglomeration behaviour. The suspensions were sonicated for 5 min in an ultrasonic bath (Bandelin Sonorex digital) and then analysed using a laser diffractometer particle size analyser (Beckman Coulter LS13320 PIDS), according to the manufacturer's instructions. Sonication was applied throughout the measurement.

2.5. Fibre characterization

The fibres were characterized by scanning electron microscopy (SEM). Meshes were cut into size, while sonicated samples were prepared by collecting aliquots from the bottom of dispersion fluids with a glass pipette and applying a few drops to steel SEM sample holders. The samples were air dried under the fume hood under ambient conditions for at least 15 h. During solvent evaporation, the shortening of the meniscus of the dispersion fluid caused fibre agglomeration. The dried samples were sputter coated with 7 nm gold (Polaron Equipment Ltd. E5100). SEM analysis (SEM, Hitachi S-4800) was performed using a voltage of 2 kV and 10 μA current intensity.

Before the analysis by optical microscopy (using an Keyence VHX 1000 instrument) the fibres were aligned by sliding a coverslip over a