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RESEARCH ARTICLE OPEN ACCESS

Solution electrospinning of particle-polymer composite fibres

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Abstract – Electrospinning is a fast, simple way to produce nano/microfibers, resulting in porous mats with a high surface to volume ratio. Another material with high surface to volume ratio is aerogel. A drawback of aerogels is its inherent mechanical weakness. To counteract this, aerogels can be embedded into scaffolds. The formation of a particle/polymer composite results in improved mechanical stability, without compromising the porosity. In the presented study, aerogel and poly(ethylene oxide) are mixed into a solution, and spun to thin fibres. Thereby a porous membrane, on the micro- and nano-scale, is produced. The maximum polymer-silica weight-ratio yielding stable fibres has also been determined. The morphology of the fibres at different weight ratios has been investigated by optical microscopy and scanning electron microscope (SEM). Low aerogel concentrations yield few particles located in polymer fibres, whereas higher amounts resulted in fibres dominated by the aerogel particle diameters. The diameters of these fibres were in the range between 13 um to 41 um. The flowrate dependence of the fibre diameter was evaluated for polymer solutions with high particle contents. The self-supporting abilities of these fibres are discussed. It is concluded that selfsupporting polymer/aerogel composites can be made by electrospinning.

Key words: Electrospinning, Composite fibres, Poly(ethylene oxide), Aerogel particles

1. Introduction

Electrospinning is an old technique gaining new interest with the increase in nano sized materials. Therefore it becomes an attractive method to produce nanometre sized fibres in a fast and reproducible way [1]. The fibres can be produced from polymer solutions or melts, by placing a polymer droplet into a high electrostatic field. Once the Coulomb attraction overcomes the surface tension, a thin fibre is formed at the tip of the droplet [2]. There after the fibre will be stretched thinner during the migration process towards the collector plate [3]. Fibre diameters have been reported down to a lower limit of 10 nm [4]. The thin fibres are collected as a chaotic fibre mat. This mat, which is porous, can reach surface areas up to 1,000 m^2/g, and has been used as porous membranes in the filter industry [5]. In recent years, electrospun polymer fibres have been used for scaffolding for e.g. biological tissue [6] or for particles [7]. Nano particles have been added for biomedical [8] or energy storage [9] applications, but also micro particles, which were linked together by polymer fibres [10].

Silica aerogel is a type of porous nanomaterial, characterised by its high porosity and extremely low density [11]. The typical formation of aerogels is through solution polymerisation of silica precursors with subsequent solvent exchange followed by supercritical drying [12]. Silica aerogel particles are very brittle, with a typical Young's modulus in the range of 1–10 MPa [13]. For applications where they are subject to load, the introduction of a polymer, and hence the creation of a composite material, will lead to an increase in Young's modulus. Several porous silica composites have been produced. Clay and epoxy in a silica aerogel matrix have been produced, where the gel exhibit elastomeric behaviour [11]. Furthermore, aerogel/polymer microfiber mats can be made by mixing aerogel precursors and microfibers in a mould [14].

The incorporation of small particles, fibres or plates into a composite material can improve its properties. Examples hereof are aluminium metal composites [15], ceramics [16] or epoxy polymer composites [17]. A composite between aerogel and polymer can be used to combine the properties of the flexible polymers and the highly porous but brittle aerogels. Immobilisation of aerogel particles in a fibre matrix combines the properties of both materials forming a composite material with improved mechanical properties of the aerogel. Composites with particles in electrospun fibres have been made [10, 18]. This has been achieved by polymer-particle solution electrospinning [18] as well as core-shell spinning where the particles have been added to the core of the polymer fibre [19].

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In the present study, a novel approach to incorporate silica aerogel particles into polymer fibre scaffolds is presented. Furthermore the upper limit for the silica content in solution with respect to fibre formation, and the fibre morphology at different polymer/silica ratios, has been investigated in detail.

2. Materials and methods

2.1. Materials

Porous silica particles were supplied by Svenska Aerogel. The particles are hydrophilic and have an average diameter of 14 um. Poly(ethylene oxide) (PEO), with a molecular weight of 900.000 was bought from Sigma Aldrich. Furthermore 99.9% ethanol supplied from VWR Chemicals was used as a solvent. All chemicals were used without further purification.

2.2. Experimental procedure

Polymer solutions were prepared as follows: polymer and silica particles were added into a beaker and gently mixed. First the desired amount of ethanol, followed by deionised water was added under stirring. Typically solutions contained 1.5 g polymer, 30 mL ethanol and 30 mL demineralised water. A varying amount of silica aerogel particles was added, to form 1:1 (w/w) up to 1:9 (w/w) ratio solutions with respect to the polymer. After addition of water, the solutions were placed in a 40 kHz ultrasonic bath for an hour to ensure homogeneous polymer/particle distribution. The solution was stirred overnight.

Electrospinning was performed on an electrospinning setup from Y-Flow. The electrospinning setup has a needle mounted on a moving X-Y stage. The polymer solution is fed from a syringe pump, controlling the flowrate, and high voltage is attached to the spinning needle. The inner diameter of the needle in the spinneret was 0.8 mm. The relative humidity of the electrospinning encasing was kept at 20% via the environmental control system of the setup. For the electrospinning, the needle collector distance was kept at a constant 15 cm. The applied voltage to the needle was 9 kV, and the flowrate was 1.0 mL/h. Microscope glass slides and silicon wafer substrates (1.5 × 1.5 cm) were placed on the collector plate, for sample collection.

Furthermore, for the solution with the highest aerogel particle concentration, resulting in stable fibre formation, the flowrate was varied between 0.25 mL/h and 2.00 mL/h. These samples were further characterised with scanning electron microscopy (SEM).

2.3. Characterisation

The viscosity of the spinning solutions was measured using a Brookfield DV-E rotary viscometer. A 16 mL sample was added to a cavity with a rotating cylinder. The angular velocity was set to 0.3 rpm to determine the viscosity.

After electrospinning, the produced samples were characterised with optical microscopy. Representative overview images were acquired and the morphology of the fibre network was analysed.

SEM was performed on fibres with the highest particle content. A layer of 10 nm gold was deposited on the sample surface by plasma vapour deposition. This was done to ensure conductivity of the sample surface, and prevent charging of the structure during the imaging process. Images were acquired with a Zeiss EVO 60 SEM. The average diameter of each sample was found through analysis with ImageJ. Ten measurements were performed on each fibre batch produced from the flowrate experiments.

Table 1. Solution numbers, weight rations and spinability for different polymer/silica particle ratios.

Solution number	Ratio w/w	Spinability
1	1:1	✓
2	1:2	✓
3	1:4	✓
4	1:6	✓
5	1:8	✓
6	1:9	–

Table 2. Flowrate, average diameter and standard deviation of fibres spun from Solution 5.

Flowrate (mL/h)	Average diameter (um)	Standard deviation (um)
0.25	13.4	4.3
0.50	18.1	4.6
1.00	21.9	7.1
1.50	36.4	6.6
2.00	41.1	15.2

3. Results and discussion

3.1. Spinning solutions and electrospinning

Six solutions were created according to the above described procedure. Their weight ratios between polymer and silica aerogel particles were 1:1, 1:2, 1:4, 1:6, 1:8 and 1:9. They are referred to here as Solution 1–6, and an overview of the numbers, ratios and their respective spinability is summarized in Table 1.

The viscosity of Solution 1 and 6 was measured to 1.38 kCPS and 1.55 kCPS, respectively. The electrospinning of the six solutions was done according to the protocol in Section 2. The flowrate was 1 mL/h for the initial spinning of all six solutions, which all were able to form a Taylor cone with the same electrical field applied. It implies that the amount of silica aerogel particles is of minor importance with respect to Taylor cone formation. However, for Solution 6, no stable fibres have been acquired. It is observed that the minor difference in viscosity did not have any significant effect on the Taylor cone formation and the fibre formation.

Solution 5 proved to be the solution with the highest silica aerogel content, but still yielding stable fibres. With this solution an additional set of experiments was performed in order to investigate the relation between morphology and flowrate. During these experiments the flowrate was varied between

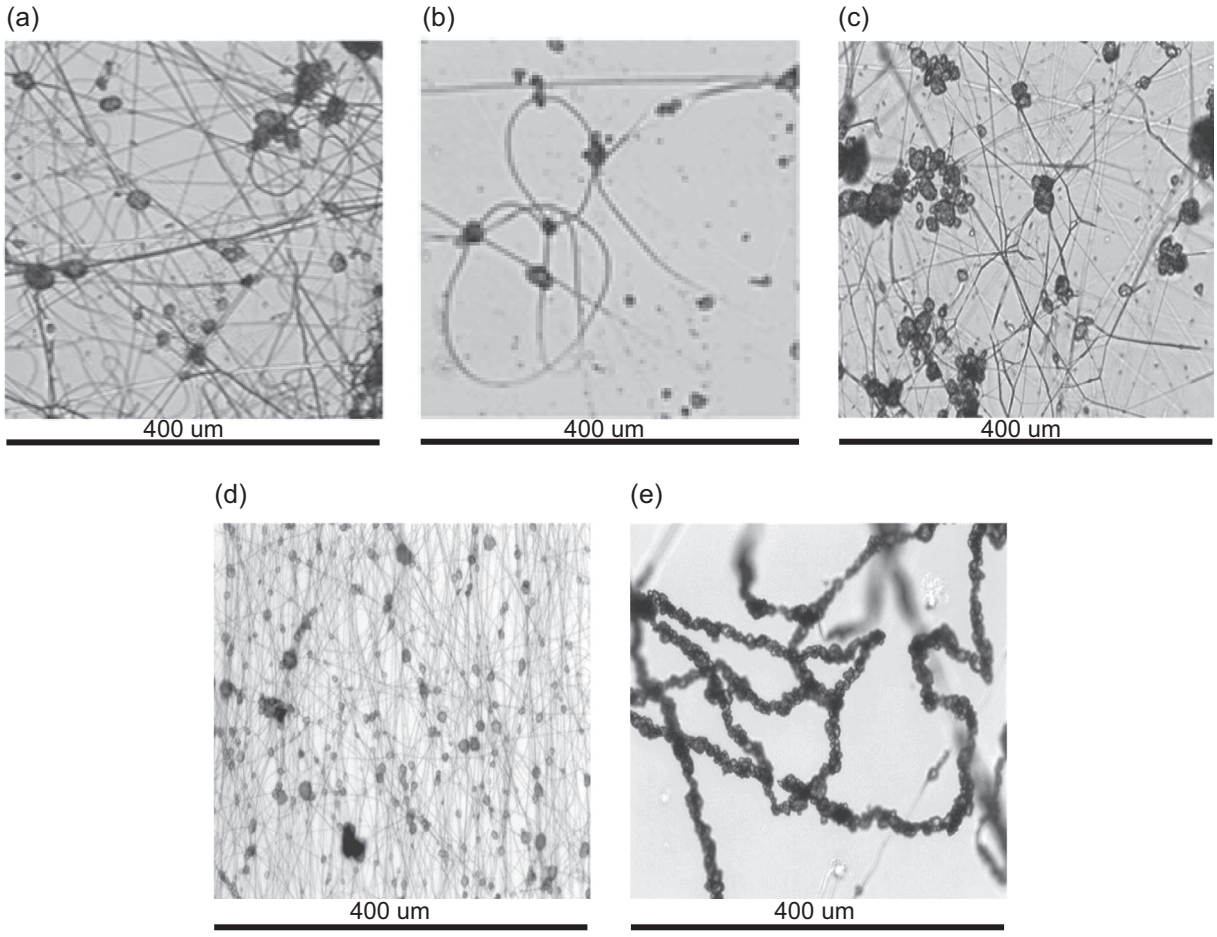

Figure 1. Optical microscopy of fibres spun from polymer/silica aerogel particle solutions with weight rations (a) 1:1, (b) 1:2, (c) 1:4, (d) 1:6 and (e) 1:8. It is seen that the amount of particles increases until the silica aerogel particles packs closely in the fibre.

0.25 mL/h and 2 mL/h. The average diameter of the fibres can be seen in Table 2.

3.2. Optical microscopy

All samples were investigated by optical microscopy. In Figure 1, microscopy images of electrospun fibres from Solution 1–5 are presented (Figures 1a–1e). The fibres with Solution number 1–4 (Figures 1a–1d) all have a pearl-chain shape, where a particle was located in the fibre, with some distance of thin polymer fibre in between the separated particles. The length of polymer fibre between the particles tends to drop with increased particle concentration in the spinning solution. It is also observed that particle aggregates are located inside the fibre matrix, where several aerogel particles stick together.

It is seen that the fibre morphology changes drastically from Solution 4 to 5. By electrospinning the solution, fibres containing closely packed particles are formed. The particles are enveloped in polymer, and stick together. These fibres are the dominant species. This is a change from Solution 1 to 4, where particles are located in the fibre with thin polymer fibre spacing in between. This change can be attributed to a very low amount of polymer available to form fibres. Instead, the silica aerogel particles touch each other, and pack the particles closely in the fibre.

Even though particles are more dominant by weight in all solutions, except Solution 1, the polymer fibre is still the dominant species in the microscopy images. This is due to the relatively low amount of polymer used to create a thin fibre, with diameters in the nanometre range. The particles, on the other hand, are spherical and generally have a much larger diameter than the fibres. For Solution 5, the amount of particles becomes too high that fibres between the particles can be formed. Instead, the polymer glues the silica aerogel particles together.

3.3. Scanning electron microscopy

The fibres spun from Solution 5 were analysed with SEM to obtain more detailed information on the fibre morphology. Solution 5 fibres were spun at flow rates ranging from 0.25 mL/min to 2 mL/min. With increased flowrates, the fibre diameter seemed to increase. This corresponds with the general electrospinning theory of polymer solutions [4]. These fibres are presented in Figure 2. It is seen that thin polymer fibres are still present, but fibres with closely packed particles are the dominant species. The fibres with closely packed particles

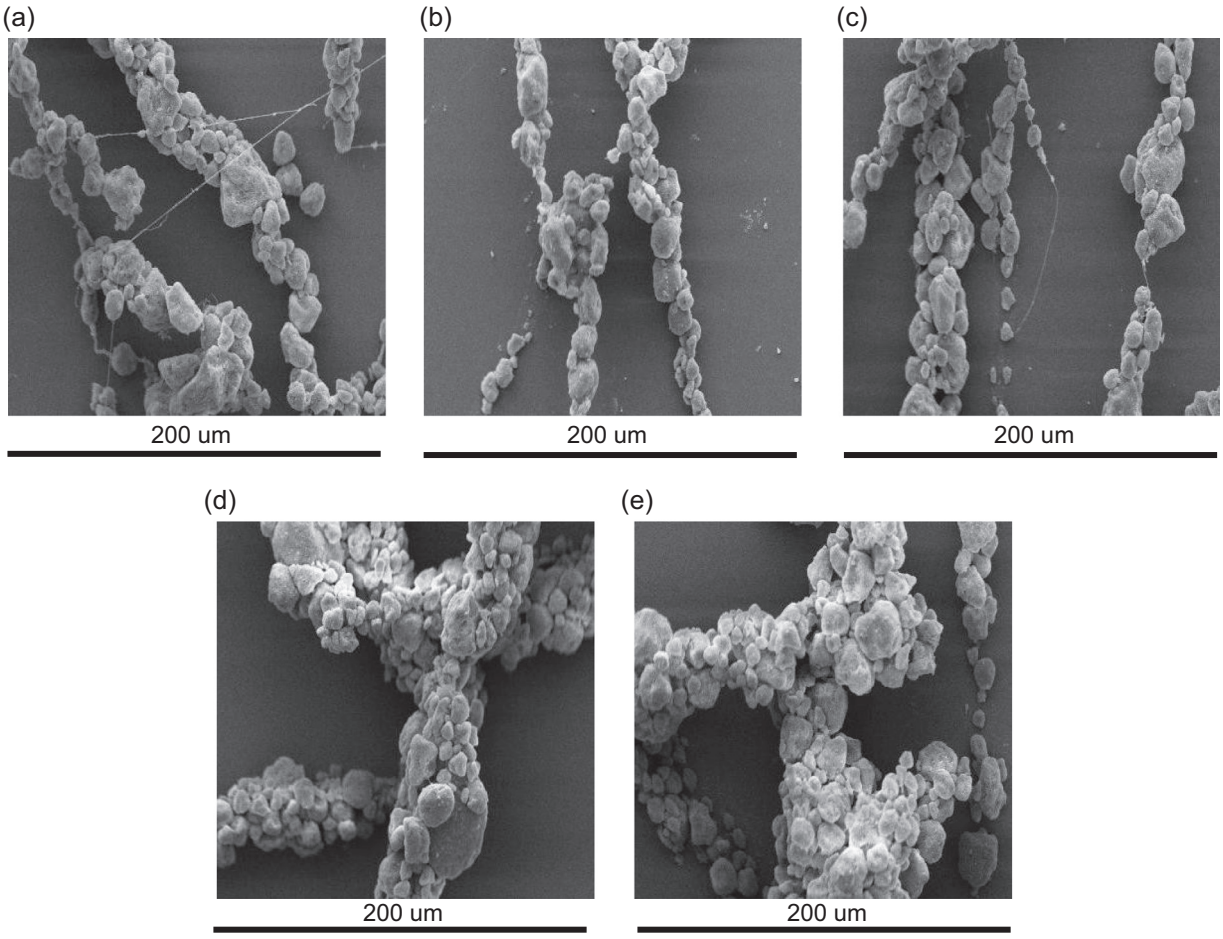

Figure 2. SEM images of fibres spun from Solution 5 with polymer/particle weight ratio 1:8. They are spun at different flowrates: (a) 0.25 mL/h, (b) 0.50 mL/h, (c) 1.00 mL/h, (d) 1.50 mL/h and (e) 2 mL/h. It is seen that higher flowrates in general promoted thicker fibres. All images are 200 um × 200 um.

produced with the same flowrate had a diameter variation of 4–15 um. This can be caused by the turbulent whipping motion where the non-deformable silica aerogel particles have to be held together by the polymer, and hence only the contact surfaces are able to bend.

An in depth analysis of the fibre morphology is presented in Figure 3. The silica aerogel particles are enveloped in polymer and linked together by polymer fibres. The polymer fibres between the particles have diameters between 500 and 800 nm, while polymer fibres not connecting particles had diameters between 200 and 300 nm. This difference can be explained by the increased stretching of the fibres located between particles.

3.4. Fibre characteristics and the influence of silica content

Solution 1–5 produced stable polymer/particle composite fibres. When spun for a longer time period, fibre mats were formed. When spun in a single line over a prolonged period of time, Solution 5 formed a 3D structure, which was strong enough to sustain its own weight. Since Solution 5 contained the highest amount of silica aerogel particles and all the prior analysis of the fibres showed a densely packed particle structure in those fibres, it can be concluded that self-supporting composite fibres containing silica aerogel particles can be created, through embedding them into a fibre matrix. Hence, the method has proven to embed silica aerogel particles into a solid polymer fibre matrix, able to support itself. The self-supporting particle/polymer fibres are presented in Figure 4. The self-supporting fibres have been electro-spun with a line needle movement of 10 mm/s, and a flowrate of 2 mL/h.

Electrospinning of Solution 6 did not produce stable fibres. Instead, a polymer/particle powder was obtained. The particle concentration was too high for the polymer to hold the silica aerogel particles together, and was therefore not forming stable fibres. Hence, this high concentration of silica aerogel particles could not be held together efficiently by the polymer, which in turn did not provide the desired scaffolding for the particles.

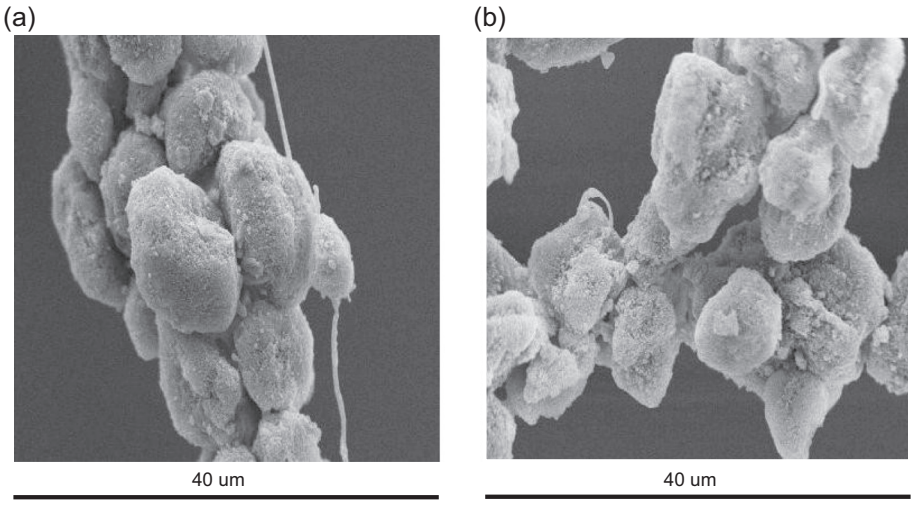

Figure 3. Close-up images of fibres spun from Solution 5. It is seen that the polymer fibres are located among the silica aerogel particles. The images are 40 × 40 um.

Figure 4. Solution 5 electrospun with a 1D needle movement. The structure is seen to be self-supporting.

4. Conclusion

Polymer/silica aerogel particle composite fibres have been produced with polymer/particle weight ratios from 1:1 to 1:8. Increasing particle ratios resulted in increased amounts of particles in a polymer fibre matrix, for Solution 1–4, with silica aerogel/polymer ratios from 1:1 to 1:6. For the solution with a silica aerogel/polymer ratio 1:8, the morphology of the fibres changed from thin polymer fibres supporting particles, to closely packed particles in fibres held together by polymer. For this solution, the flow rate has varied between 0.25 mL/h and 2 mL/h to investigate the influence of flowrate on the fibre morphology. These experiments showed that the fibre diameter increased with flowrate.

Furthermore electrospinning of an aerogel solution with a polymer/particle weight ratio of 1:9 w/w, was also attempted, but did not produce stable fibres. The maximum achievable aerogel/polymer ratio resulting in stable fibres has been found to be 1:8.

5. Implications and influences

This article delivers insight into the topic of production of particle composites by electrospinning. This can be useful for scaffolding of silica aerogel particles of sizes larger than the normal fibre diameter. With increased particle content, it is possible to obtain a structure, where the particles are closely packed in the fibres. Furthermore, if the particle/polymer ratio exceeds an upper limit, no stable fibres can be formed.

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