Temperature-controlled reversible pore size change of electrospun fibrous shape-memory polymer actuator based meshes

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Abstract

Fibrous membranes capable of dynamically responding to external stimuli are highly desirable in textiles and biomedical materials, where adaptive behavior is required to accommodate complex environmental changes. For example, the creation of fabrics with temperature-dependent moisture permeability or self-regulating membranes for air filtration is dependent on the development of materials that exhibit a reversible stimuli-responsive pore size change. Here, by imbuing covalently crosslinked poly(ε-caprolactone) (cPCL) fibrous meshes with a reversible bidirectional shape-memory polymer actuation (rbSMPA) we create a material capable of temperature-controlled changes in porosity. Cyclic thermomechanical testing was used to characterize the mechanical properties of the meshes, which were composed of randomly arranged microfibers with diameters of 2.3 ± 0.6 μm giving an average pore size of approx. 10 μm. When subjected to programming strains of εm = 300% and 100% reversible strain changes of εʹrev = 22% ± 1% and 6% ± 1% were measured, with switching temperature ranges of 10 °C–30 °C and 45 °C–60 °C for heating and cooling, respectively. The rbSMPA of cPCL fibrous meshes generated a microscale reversible pore size change of 11% ± 3% (an average of 1.5 ± 0.6 μm), as measured by scanning electron microscopy. The incorporation of a two-way shape-memory actuation capability into fibrous meshes is anticipated to advance the development and application of smart membrane materials, creating commercially viable textiles and devices with enhanced performance and novel functionality.

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(Some figures may appear in colour only in the online journal)
in vivo microenvironments. The introduction of shape-memory functionality to electrospun fibrous materials should enable switchable and environmentally-responsive permittivity, leading to a new generation of smart membranes and biomedical devices.

The one-way shape-memory behavior of electrospun fibrous meshes has been widely reported for a variety of polymers [5–14]. Recent work has demonstrated that the magnitude of the pore size change can be controlled by modifying the microfiber structure. For example, fibrous meshes composed of hollow microfibers displayed higher pore size change ratios when compared to those composed of solid microfibers [13]. However, the shape-memory effect of such electrospun fibrous meshes has been limited to a single, irreversible change in pore size. In other work a reversible change in pore size was achieved, but only through the application of an external stress [15]. Here, we explore whether a reversible and programmable pore size change under stress-free conditions can be achieved for electrospun fibrous meshes, and whether the magnitude of pore size change can be controlled by altering the microfiber structure during processing.

Polymers capable of a reversible bidirectional shape-memory polymer actuation (rbSMPA) can repeatedly alternate between two different programmable shapes under stress-free conditions when triggered by an external stimulus [16–18]. To realize a rbSMPA a polymer network must contain crystalizable actuation domains (ADs), which provide the driving force for shape-change, as well as geometry-determining domains (GDs), which provide the network anisotropy necessary to coordinate the changes in macromolecular orientation during crystallization [16, 17, 19]. Covalent or physical cross-links are also necessary to provide mechanical stability and prevent polymer slippage. ADs and GDs can be provided by a copolymer with two separate melting peaks or by separating the broad melting transition of a homopolymer into two parts. While the variation of macromolecular architecture has been vital in the development of polymeric shape-memory, morphological innovation on the macro- and microscale has also significantly enhanced performance and enabled the introduction of novel functionality. A rbSMPA has been previously demonstrated in bulk materials [20, 21], microparticles [22], and microscopically patterned substrates [23]. The realization of rbSMPA with electrospun microfiber meshes should yield a reversible pore size change under stress-free conditions, which can be triggered dynamically by an external stimulus.

For applications as membranes or biomedical devices, such electrospun fiber meshes should possess a low actuation temperature range for system compatibility, a slow degradation rate to ensure a long lifetime, and should be reasonably inexpensive to produce. In this work, semi-crystalline linear poly(ε-caprolactone) (PCL) was used for the preparation of covalently crosslinked electrospun fibrous meshes. The low melting point (around 60 °C), relatively slow degradation rate, and commercial viability of PCL make it suitable for a wide range of applications. Further, its compatibility with aqueous environments [15] should make it suitable for use as membranes in filtration and biomedicine. To achieve pronounced rbSMPA, ensure good spin-ability, and maintain the fibrous mesh morphology, a three-step preparation procedure was employed as shown in figure 1. In the first step electrospun PCL fiber meshes were prepared (figure 1(a)), while in
the second the as spun fiber meshes underwent photo-initiated crosslinking (figure 1(b)). In this work, a blend of PCL with triallyl isocyanurate (TAIC) and benzophenone (BP) was utilized with UV irradiation to achieve highly crosslinked PCL (cPCL), as has been reported elsewhere [24, 25]. In the final step the meshes underwent deformation at an elevated temperature and cooling while keeping the deformation strain, programming their shape-memory actuation behavior (figure 1(c)). After fabrication the actuation of the meshes was triggered by heating and cooling between 10 °C and 60 °C (figure 1(d)). To determine the necessary programming procedure, the thermal and mechanical properties of the materials were measured by differential scanning calorimetry (DSC) experiments and tensile testing. Further cyclic, thermo-mechanical testing was performed to determine the rbSMPA of cPCL fibrous meshes. Finally, the microscale pore size change of the cPCL fibrous meshes was investigated by scanning electron microscopy (SEM).

**Experimental**

**Materials**

Poly(ε-caprolactone) (PCL) with a number average molecular weight ($M_n$) of 80 000 g mol$^{-1}$ (CAPA® 6800, Solvay, Germany) was used as received. Benzophenone BP (99%) was served as photo initiator while triallyl isocyanurate TAIC (≥99%) was employed as crosslinker for ultraviolet (UV) irradiated networks. Chloroform (≥99.8%) and ethanol (99%) with the volume ratio of 7/3 were used as solvent for the electrospinning solution preparation and chloroform was also applied to determine the degree of gelation ($G$). All these reagents were purchased from Sigma-Aldrich (Steinheim, Germany) and used without any purification.

**Preparation of electrospun fibrous meshes**

PCL fibrous meshes were prepared via electrospinning of 15\% w/v PCL/chloroform-ethanol solutions with 2 w\% UV crosslinker (2 wt\% of TAIC and 2 wt\% of BP). Here, a mixture of chloroform and ethanol (7:3 by volume) was used as solvent to dissolve PCL [26]. A custom built setup was used consisting of a high voltage power supply (PNC 40000-1 ump; Heinzinger, Rosenheim, Germany), a 20 ml polyethylene syringe as solution depot, a stainless steel capillary with an outer diameter of 0.8 mm, which serves as hot electrode, and a rotating mandrel with the radius of 5 cm as collecting electrode. The electrospinning was carried out in an enclosure with a controlled air flow, at a relative humidity of 20\%. The PCL microfibers were deposited at ambient temperature on a polypropylene (PP) film with a thickness of about 40 μm. The distance between the substrate and needle was 30 cm, and an applied voltage of 20 kV was used. For the electrospun PCL random fibrous meshes preparation, the speed of drum was 1 rpm.

After drying the as spun PCL fibrous meshes in the hood, cPCL fibrous meshes were achieved by UV crosslinking via an OmniCure radiometer (S2000, Excelitas Technologies Philippines, Inc., Laguna, Philippines) with a UV wavelength of 350–450 nm.

**Characterization of electrospun fibrous meshes**

**Morphology.** The morphology, size, and size distribution of PCL fibrous meshes with and without UV crosslinking were characterized by SEM. A Phenom G2 pro (L.O.T.—Oriel, Darmstadt, Germany) was used after conductive coating with a thin gold layer (5 nm). For images shown in figure 2(c), SEM imaging was carried out by a ESEM Quanta 250 FEG, on a sample without coating, in low vacuum mode (33 Pa), at 2 kV, and with a large field detector (secondary electrons 2). The obtained SEM images were analyzed using ImageJ (version 1.44; National Institutes of Health) [27]. To determine the average diameter of PCL and cPCL microfibers and their diameter distribution approximately 100 single fibers were measured. A CT-Compact from ProconXray GmbH (Sarstedt, Germany) was used for characterization of surface texture. Recording of gray shadow images was realized with an x-ray output of 40 kV and 0.2 mA at small spot. The distance between x-ray source and sample resulted in a voxel dimension of 3 μm edge length. The integration time was 750 ms at averaging of 7 images. Overall 360 images, recorded with an angle distance of 0.45 grd, were used for reconstruction of 3D image. The post treatment of 3D-images was carried out with MAVI software (Fraunhofer Society, Germany). The reconstructed...
3D-images were filtered with a binomial filter stage 19 and binarized by ‘Otsu’ algorithm.

Crosslinking characterization

The photoinitiated crosslinking of the meshes was confirmed by Fourier-transform infrared (FTIR) performed on a Nicolet Magna IR 550 spectrometer (Thermo Scientific, Dreieich, Germany). Spectra were collected by averaging 10 scans at a resolution of $2 \text{ cm}^{-1}$ in transmission mode using an 8400S FTIR spectrophotometer. The electrospun cPCL fibrous meshes were analyzed by overnight swelling experiments in chloroform at ambient temperature, followed by drying for 12 h in a fume hood after removing from chloroform. The gelation degree $G$ was calculated from the initial weight $m_i$ of the sample and the dry weight $m_d$ after swelling using equation (1) [28]

$$G = \frac{m_d}{m_i} \cdot 100\%.$$  (1)

Thermal properties. DSC experiments were carried out on a Netzsch DSC Phoenix (204, Netzsch, Selb, Germany), which was used to investigate the thermal properties of the prepared electrospun fibrous meshes. All experiments were conducted in the same temperature range from $-100\degree \text{C}$ to $200\degree \text{C}$ with a constant heating and cooling rate of 10 $\text{K min}^{-1}$ and a waiting period of 2 min at the maximum and minimum temperature. Melting temperature ($T_m$) was determined from first DSC heating run while crystallization temperature ($T_c$) was obtained from the cooling run. The weight percent crystallinity ($\chi_c$) of cPCL fibrous meshes was calculated from the enthalpy of fusion data of the first heating run by equation (2):

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^0} \cdot 100\%,$$  (2)

where $\Delta H_f$ is the apparent enthalpy of fusion per gram of electrospun PCL fibrous meshes, and $\Delta H_f^0$ is the enthalpy of fusion per gram of PCL in its completely crystalline state ($\Delta H_f ^{\text{PCL}} = 139 \text{ J g}^{-1}$ [29]).

Wide-angle x-ray scattering (WAXS). WAXS measurements with non-programmed and programmed cPCL samples were performed at ambient temperature using a D8 Discover diffractometer with a two-dimensional Hi-Star-detector (105 $\mu \text{m}$ pixel size; Bruker AXS, Karlsruhe, Germany) using x-rays with 0.154 nm wavelength. A three-pinhole collimator with an opening of 0.8 mm was used. The distance between sample and detector was 150 mm, whereas the samples with a thickness of about 1 mm were illuminated for 2 min in transmission geometry. In situ WAXS measurements of a programmed cPCL sample at 10 $\degree \text{C}$ and 60 $\degree \text{C}$ (three repetitive cycles) were conducted using a custom-build heating-cooling device operated with a heating gun and a cooled nitrogen gas stream. The respective temperature was equilibrated for 5 min before the measurement.

Mechanical testing. Test specimens with a thickness of approximately 50–100 $\mu \text{m}$, a width of 10 mm, and a length of 40 mm were utilized for evaluation of the cPCL fibrous meshes mechanical properties. cPCL test specimens were investigated at ambient temperature with a Zwick Z005 (Zwick GmbH, Ulm, Germany) and at 90 $\degree \text{C}$ with a Zwick Z1.0 tensile tester (Zwick, Ulm, Germany) equipped with a temperature controlled thermo chamber (Eurotherm Regler, Limburg, Germany). The stretching rate was kept constant at 10 $\text{mm min}^{-1}$ for all tensile tests. Three to five samples were investigated for each fibrous mesh. The Young’s modulus ($E$) of the fibrous meshes was determined from the stress–strain curve at the strain region of 1%–5%.

Macroscale rbSMPA characterization. Cyclic, thermomechanical tensile tests with three repeating cycles were performed on a Zwick Z1.0 tensile tester (Zwick, Ulm, Germany) equipped with a temperature controlled thermo chamber (Eurotherm Regler, Limburg, Germany). Geometrically similar test specimens were used for the tensile testing and rbSMPA testing. Similar to the tensile testing, the rbSMPA investigation was carried out for cPCL random fibrous meshes. For programming, the samples were heated to 90 $\degree \text{C}$, stretched to programming strains $\varepsilon_{prog}$ (chosen between 100% and 300%) and cooled to 0 $\degree \text{C}$ at a rate of 5 $\text{K min}^{-1}$. An equilibration time of 10 min was used, before the force was released with 0.9 $\text{N min}^{-1}$. Temperature cycles were carried out in a stress-free mode: the specimens were heated up to separation temperature ($T_{sep}$, 60 $\degree \text{C}$) and cooled down to low temperature ($T_{low}$, 10 $\degree \text{C}$). The temperature cycle was repeated three times for each measurement. Heating and cooling rates of 3 $\text{C min}^{-1}$ were used if not separately specified in the rest of the paper.

Curling actuator. For creation of a curled cPCL fiber mesh actuator a stripe with a length of 70 mm and a width of 5 mm was cut from a cPCL fiber mesh. Programming was realized by heating the actuator stripe to 90 $\degree \text{C}$ and winding it around a rod with a diameter of 1 cm in such a way that 6 curls were obtained, which were fixed by cooling to 10 $\degree \text{C}$. For evaluation of the actuation performance of the curled programmed specimen repetitive heating to 60 $\degree \text{C}$ and cooling to 10 $\degree \text{C}$ was conducted in a custom-made, transparent thermo chamber heated by a hot air generated with a heat gun and cooled by cold nitrogen gas, while a digital camera was utilized for recording.

Reversible change in pore size. SEM investigations at different temperatures were conducted on a Phenom G2 pro (L.O.T.—Oriel, Darmstadt, Germany) to record the change in pore size for programmed cPCL fibrous membranes without conductive coating. The test specimens were programmed as described in the previous paragraph with $\varepsilon_{prog} = 300\%$. For determination of the change in average pore size about 30 pores were analyzed using ImageJ (version 1.44; National
Institutes of Health) [25] at each temperature, 60 °C and 10 °C, respectively.

**Reversible actuation of single fibers.** Single cPCL fiber actuator properties were examined by depositing single fibers across the clamps of a closed micro-benchvise device (Additional insert for AFM holder with a clamping range of 2 mm, Leica Mikrosysteme GmbH, Vienna, Austria). After crosslinking the micro-benchvise was heated to 90 °C, the clamps were opened to \( \varepsilon_{\text{prog}} \approx 300\% \) and subsequently cooled to \(-10^\circ\text{C}\) (ice water). Stress was released by closing the clamps half way. Actuation properties were then examined on a light microscope (VHX100, Keyence Corp., Osaka) by cyclic heating to 60 °C and cooling to 10 °C.

**Determination of error.** Errors were determined by taking multiple measurements of the same sample with identical conditions and then calculating the standard deviation. The listed data values (e.g. for Young’s modulus) represent the average of the measurements.

**Results and discussion**

**Morphology**

For the electrospinning of poly(ε-caprolactone) blend fibers, a polymer solution in a solvent mix of chloroform/ethanol (7/3, v/v) with a concentration of 15% w/v was used. To facilitate the crosslinking reaction within the fibers a UV crosslinker (2 wt% of TAIC and 2 wt% of BP) was added before spinning, which enabled crosslinking by irradiation with UV light. The fibers were collected on a rolling collector (1 rpm) and investigated by SEM before and after crosslinking to determine their diameter and surface topology. The diameter of the pristine fibers was measured as 2.3 ± 0.6 μm, with a narrow distribution not significantly influenced by UV crosslinking (2.2 ± 0.7 μm). For determination of the crosslinking efficiency, swelling experiments using chloroform were performed with the UV irradiated cPCL fiber meshes. Here, a high gel content of 80%–90% was observed, which is similar to that reported for (TAIC) UV crosslinked cPCL films in our previous work [25]. The crosslinking of the fibers was also confirmed by FTIR measurements, where the disappearance of the C=–C bond associated with TAIC at 1658 cm\(^{-1}\) was observed. (supplementary figure 2 is available online at stacks.iop.org/SmartMat/28/055037/mmedia). Both the electrospinning process and the post-spinning treatment (UV crosslinking) of the fibers has a significant influence on the crystallinity of the fibers.

The crossing of randomly distributed polymer fibers, which have a smooth surface, led to the formation of open porous fiber meshes (figures 2(a), (b)). After heating to 90 °C (selected programming temperature), where the cPCL mesh is in the completely rubbery elastic state, partial fusion of single fibers as well as local curling of fibers becomes apparent (figure 2(c)), which can be attributed to temperature related relaxation phenomena. Finally, in figure 2(d) the morphology of a programmed cPCL fiber mesh is displayed, where strong alignment of the fibers in the direction of deformation can be observed.

To characterize the 3D structure of the meshes micro-x-ray computer tomography (μ-CT) was used to explore changes to the cPCL samples: after heating to 90 °C and cooling to 25 °C, and before and after programming to an elongation of 300%. The 3D reconstructions of the three samples are shown in figures 3(a)–(c). The μ-CT results revealed similar values in porosity (63%) and mean void size (31 ± 6 μm) for the programmed sample, when compared to the non-programmed mesh (68%; 36 ± 6 μm) and programmed sample after heating and cooling (63%; 36 ± 6 μm) (figures 3(d)–(I)). Further, the pore size distribution of the three samples was similar with a maximum around 40 μm (48 μm). While the macroscopic stretching of the fibrous mesh to 300% results only in a slight reduction of its pore characteristics, a significant change in the order parameter was observed, with an increase in the level of anisotropy after programming (figures 3(g)–(i)).

DSC (figure 4(a)) was used to characterize the thermal properties of the fibers. The measurements showed a melting transition in the range of 35 °C–63 °C and a crystallization in the range of 40 °C–12 °C for all samples, attributable to PCL. The position of the peak maximum of the PCL melting transition (\( T_m \)) for the uncrosslinked (PCL), crosslinked (cPCL) and cPCL programmed samples determined from 1st run DSC results was found at the same temperature of 58 °C ± 1 °C. In contrast the position of the PCL crystallization peak (\( T_c \)) also slightly varied from \( T_c = 26^\circ\text{C} \pm 1^\circ\text{C} \) for PCL meshes, \( T_c = 27^\circ\text{C} \pm 1^\circ\text{C} \) for cPCL meshes and \( T_c = 30^\circ\text{C} \pm 1^\circ\text{C} \) for cPCL samples programmed with a strain of 300%. The weight percent crystallinity (\( \chi_c \)) of the different fibers determined from the 1st DSC heating run was found to be identical with \( \chi_c = 42\% \pm 1\% \). The obtained values were similar to that reported for cPCL films (\( \chi_c = 45\%–48\% \)) with different gel contents in the range from 40% to 95% [25]. In contrast WAXS analysis revealed a degree of crystallinity (DOC) of 33% for both cPCL meshes and programmed cPCL meshes (figure 4(c)).

**Mechanical properties**

The fibers were investigated further to identify changes to the fiber’s mechanical properties under tensile testing. While untreated PCL meshes exhibit high elongation at break values (\( \varepsilon_{bl} \)) of 950% ± 20%, the effect of the crosslinking on the chain mobility and crystallinity significantly reduces this value, cPCL (610% ± 70%) at 25 °C. Tensile tests conducted with cPCL samples at 90 °C showed a similar \( \varepsilon_{bl} \) of 620% ± 50% (figure 4(b)). However it is important to note that Young’s modulus and failure strength is difficult to compare for the different meshes as the initial stress applied to the system results in the orientation/alignment of the randomly distributed fibers in the mesh (<20% strain), followed by the subsequent application of stress directly to the fibers (>50% strain).
Actuation behavior

For quantifying the actuation performance of cPCL fiber meshes specimens programmed with a strain of 100% or 300% were explored in repetitive heating cooling cycles between 60 °C and 10 °C. Here, heating the crystalline domains to beyond their melting point triggers the recoil of the macromolecules, leading to volume change and contraction, while during cooling the orientated crystallization of the PCL domains leads to an elongation of the sample. Usually the temperature dependent behavior strongly correlates with the actuation temperature range chosen for the investigation. The DSC thermogram can be divided into two separate ranges: (1) the actuation temperature range in which most of the crystals melt and are able to generate actuation, and (2) the temperature range in which the skeleton forming crystalline domains remain, enabling the fixation of the oriented domains. The reversible effect was macroscopically observed for a twisted and programmed free-standing membrane, which was heated and cooled in a small chamber. Figure 5 depicts changes of this specimen upon increasing and decreasing the temperature, as extracted from supplementary video S1 that demonstrates the reversible curling and straightening of a cPCL fiber mesh stripe.

To accurately quantify this reversible movement, cyclic thermomechanical testing was applied in a thermo chamber. The results are shown in figure 6(a). The reversible strain (ε′rev) of cPCL fibrous meshes could be calculated by

Figure 3. (a)–(c) Reconstructions of the 3D structure of unprogrammed (a), heated to 90 °C and cooled to 25 °C (b), and programmed to 300% strain (c) cPCL samples obtained by x-ray computer tomography. Each grid bar represents 20 × 20 μm. (d)–(f) Pore size measurements obtained by x-ray computer tomography of cPCL samples, which were unprogrammed (blue) (d), heated to 90 °C and cooled to 25 °C (teal) (e), and programmed to 300% strain (red) (f). Measurements of the order parameter of unprogrammed (blue) (g), heated to 90 °C and cooled to 25 °C (teal) (h) and programmed samples (red), (i).
equations used in previous work [17]. For a programming strain of 100% a reversible microscopic effect for cPCL of 6% ± 1% was measured, while it increased to 22% ± 1% for a programming strain of 300%. The observed actuation performance of the meshes was superior to that of cPCL film actuators (ε_{rev} = 15%) programmed with the same strain [25]. The higher actuation performance of the cPCL microfiber when compared to the film, can be attributed to a higher degree of molecular orientation generated by the electrospinning process. *In situ* WAXS experiments with programmed cPCL meshes revealed the reversible change in DOC during repetitive heating from 10 °C (DOC = 35% ± 1%) to 60 °C.
To investigate whether macroscale programming can result in a reversible pore size change on the microscale, SEM characterization was used to record the average pore size at 60 °C and 10 °C in the absence of external stress. In figures 7(a) and (b) representative SEM images taken at 60 °C and 10 °C by conducting in situ measurements are displayed. Here, an apparent change of individually measured pore size of 11% ± 3% during actuation, from an average value of 10.5 ± 0.5 μm at 60 °C to 11.8 ± 0.6 μm at 10 °C was obtained for the cPCL fiber meshes.

By electrospinning onto a substrate with a pronounced channel, the isolation of a single fiber was possible. Here, single cPCL fibers were imaged using optical microscopy while the surrounding environment was cycled between 10 °C and 60 °C. By tracking the length change of the fibers during the temperature transition, the heating-induced contraction and cooling-induced elongation could be rudimentarily visualized, as shown in figures 7(c), (d).

**Conclusion**

In this paper we create poly(ε-caprolactone) (PCL) fibrous meshes capable of a reversible shape-memory polymer actuation (rbSMPA). Using a three-step fabrication process consisting of electrospinning, photo-initiated crosslinking and programming, cPCL fibrous meshes composed of randomly arranged microfibers were created. Cyclic thermomechanical
testing and SEM were used to characterize the mechanical properties of the meshes and their microscale structural change respectively. Here, programming strains of ε_m = 300% and 100% yielded reversible actuations of ε_rev = 22% ± 1% and 6% ± 1%, while measurement of the temperature-dependent pore size showed a 11% ± 3% variation between 10 °C and 60 °C. Finally, the rbSMPA of a single suspended fiber was visualized by optical microscopy. In this paper, we demonstrate that a reversible temperature-controlled pore size change is possible through the implementation of rbSMPA into crosslinked electrospun fibrous meshes. The main limitation of this technique is that the generation of reversible microscale structural changes requires large changes in macroscale dimensions. Future research will aim to address this dependency. Nevertheless, we expect such materials to offer manifold benefits in the manufacture of fabrics, where the enhanced breathability of fiber meshes has already been reported [30]. Finally, this work represents a significant development in the production of smart membrane materials for textiles and filtration, where reversible stimuli-responsive pore size change is highly desirable.

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