| 1 | Characterization and Preparation of 3D Tubular Scaffolds for |
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| 2 | Fabricating Artificial Vascular by Combining Electrospinning |
| 3 | and Rapid Prototyping |
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46 Electronic Supplementary Information (ESI) For

47 Experimental: Materials and methods

48 1. Materials

Purified chitosan powder (average MW, 370 kDa; deacetylation degree, 85%) was prepared 49 as described previously.^{1, 2} Polycaprolactone (average MW 45 kDa) and trifluoroacetic acid 50 (RegentPlus[®], 99%) were purchased from Sigma-Aldrich (St. Louis, MO). Dichloromethane 51 (Extra Pure, $99.0\%^+$) and N,N-dimethylformamide (grade = 99.5%) were purchased from 52 Junsei (Junsei Chemical Co., Ltd., Japan). Sodium hydroxide (NaOH) was purchased from 53 YPC (Yakuri Pure Chemicals Co., Ltd., Japan). Methanol (MeOH) was purchased from 54 DaeJung (Chemical & Metals Co., Ltd., Korea). Deionized-distilled water (DDW) was 55 produced with an ultrapure water system (Puris-Ro800; Bio Lab Tech., Korea). All other 56 reagents and solvents were of analytical grade and used without further purification. 57

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59 2. Fabrication of tubular nanofibers via ELSP

The fabrication of ENs was performed as our described previously.^{1,2} Additionally, ratio of 60 CTS/PCL volume was fixed as previous report.³ Detailed conditions are shown in Fig. S1. 61 Prior to ELSP, CTS and the CTS/PCL blend (8:2) were dissolved in a mixed TFA/MC (7:3) 62 solvent to produce a 5 wt.% solution. PCL was dissolved in a mixed MC/DMF (9:1) solvent 63 to produce a 20 wt.% solution. The collector was a rotating mandrel with a diameter of 5 mm. 64 The resultant materials were dried overnight under vacuum to remove any residual solvent. 65 After drying, the CTS and CTS/PCL materials were neutralized as described previously^{1, 2} to 66 reduce water solubility and to maintain neutral conditions. 67

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69 3. Manufacture of novel tubular vessels by rapid prototyping

3D-printed PCL strands were fabricated as described previously.^{4,5} Briefly, PCL pellets were melted at 100°C in a heated dispenser. 3D printed strands were extruded in a custom 3D printing system designed in our laboratory. The nozzle size and distance between strands were 300 and 1200 μ m, respectively. After the PCL was melted, a continuous air pressure of 300 kPa was applied to the dispenser, and strands of molten PCL were applied layer by layer onto the EN films. The 5-mm drum holding the EN film was rotated between layers to produce a patterned 0°/45° degree porous structure.

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78 4. Analytical equipment

79 The molecular structure of EN was characterized using an FT-IR spectrophotometer with a resolution of 4 cm⁻¹ between 4000 and 500 cm⁻¹ (Spectrum[™] One System, Perkin-Elmer). 80 Water contact angles were measured using the drop method and a video camera (Phoenix 150, 81 SEO, Korea). To estimate the amount of water uptake, dried samples were initially weighed 82 and subsequently immersed in a 10-mL vial containing distilled water. After 1 h of 83 immersion, the samples were taken out of the water, residual surface water was removed with 84 a paper wipe, and the samples were weighed again. Water uptake (%) was calculated as 85 follows: 86

Water uptake (%) =
$$[(W_{after} - W_{before}) / W_{before}] \times 100.$$

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The compressive modulus of each sample was determined using a Microload[®] system (R&B, Inc., Daejeon, Korea) at a head speed of 0.5 mm/min. The morphology of the EN layer was observed with a scanning electron microscope (SEM, Hitachi S-4700, Japan) at an acceleration voltage of 15 kV. All of the samples were sputter-coated with platinum for 10 minutes prior to SEM analysis.

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| | Weight percent | Voltage | Distance | Needle | Flow rate | Fiber diameter |
|----------------|----------------|---------|----------|---------|-----------|----------------|
| | (%) | (kv) | (cm) | (gauge) | (ml/h) | (nm) |
| (a) CTS EN | 5 | 20 | 15 | 22 | 1 | 441 ± 13 |
| (b) CTS/PCL EN | 5 | 20 | 15 | 22 | 1 | 511 ± 25 |
| (c) PCL EN | 20 | 18 | 15 | 20 | 1 | 998 ± 14 |

Figure S1. The ELSP-fabricated EN characteristics and fiber diameters.

| | 10 sec (%) | 20 sec (%) | 30 sec (%) | 40 sec (%) |
|---------------------------|------------|-------------|-------------|-------------|
| (a) PCL-coated CTS EN | 127 ± 5.8 | 135.4 ± 9.6 | 140.2 ± 8.6 | 140.2 ± 3.6 |
| (b) PCL-coated CTS/PCL EN | 94.5 ± 3.8 | 108.4 ± 9 | 122.2 ± 8 | 122.2 ± 4.2 |
| (c) PCL-coated PCL EN | 30.1 ± 6.7 | 30.2 ± 8.4 | 31.3 ± 5.5 | 31.3 ± 2.1 |

Figure S2. Percent water uptake of the tubular vascular scaffolds.

| | Ultimate tensile strength (MPa) |
|---------------------------|---------------------------------|
| (a) CTS EN | 1.014 ± 0.19 |
| (b) CTS/PCL EN | 3.984 ± 0.14 |
| (c) PCL-coated CTS EN | 4.679 ± 0.22 |
| (d) PCL-coated CTS/PCL EN | 8.266 ± 0.21 |

Figure S3. Ultimate tensile strengths of the tubular vascular scaffolds.