3D-printed spider-web structures for highly efficient water collection

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ABSTRACT

Fog and moisture in nature are important freshwater resources, and the collection of these fog water is of great significance to arid regions. Inspired by the unique geometric structure of the spindle knot on spider silk, artificial fibers with periodic structures have been fabricated for water collection, which can effectively alleviate the problem of water shortage in arid areas. Traditional manufacturing methods are difficult to replicate the true shape of the spindle knot, and related research has encountered a bottleneck in improving water collection efficiency. 3D printing technology, which is different from traditional subtractive manufacturing, can directly replicate spider silk with periodic knots, making it possible to study water collection by artificial spider webs of various designs. Here, 3D printing technology is used to fabricate artificial spider webs with different geometric structures for efficient transportation and collection of water. In addition, the artificial spider web is treated with hydrophilic surfaces. In the humid environment for 2 h, the spider web with convex-concave multi-size spindle knots and multi-curvature connections has a maximum water collection capacity of 6.2 g, and the mass of water collection is 35% higher than the existing best water collection artificial fibers. This work provides a sustainable and environmentally friendly route for the effective collection of humid air, and has certain reference value for the development of environmentally friendly water collection equipment.

1. Introduction

At present, the impact of the shortage of freshwater resources is becoming more and more significant, and it is very important to effectively solve the problem of shortage of freshwater resources [1]. Fog is a natural freshwater resource, and it is difficult to capture and use, which limits people's research [2,3,4]. There are many creatures in nature that have interesting structures to collect and transport moisture in...
the moist air, such as the back of a desert beetle with a hydrophilic-hydrophobic mixed mode, cactus spines with a multi-directional branching structure also show the ability to collect fog water, and spider webs also has the amazing ability to collect micro-droplets and be able to guide the automatic transmission of the micro-droplets [5,6,7,8,9]. The researchers found that there are periodically arranged spindle structures on the spider silk. The surface of these structures is covered with glycoprotein liquid. In a humid environment, moist air condenses and nucleates on the surface of the spider silk to form small water droplets. Due to the existence of these periodically arranged spindle knots, the curvature of the spider silk is constantly changing. The Laplace pressure difference and the difference in surface energy gradient at the connection of the spindle knots cause uneven force on the spider silk. It moves toward the spindle to achieve the effect of water collection [10,11,12,13,14,15].

Traditionally, there are two main methods for manufacturing spider silk fibers, the dipping method and the electrospinning method. For the first time, Zheng et al. immersed nylon fibers in a poly(methyl methacrylate) (PMMA) solution to successfully fabricate rayon filaments [15,16]. The spindle knot characteristics on the filaments lead to surface energy gradients and Laplace pressure differences, which can achieve the directional aggregation of water droplets around the spindle knot. Hou et al. fabricated biofiber yarns by dip coating method and water drop template method, and studied the influence of the geometry and periodicity of the spindle knot on the hanging ability and collection efficiency of droplets [11,12,14]. Venkatesan et al. used protein-based silk and coating materials to impregnate and fabricate a directional water-collecting fiber with spider silk capture ability, and the water-collecting efficiency is 100 times higher than that of artificial nylon fiber [17]. Tian et al. fabricated a kind of beaded structural fibers (BSFHs) through electrospinning technology, and used this hydrophilic beaded fiber to study the hanging ability of water droplets and the collecting ability of fog water [18,19,20]. Although the above reports have produced artificial fiber yarns, the fabrication method is very cumbersome, and it is only a study on the water collection behavior of a single fiber yarn, and there is still a long way to go for large-scale production of water collection equipment. Research on the direct preparation of polymer bionic spider webs for large-scale water collection has not been reported yet.

In this study, we use 3D printing technology to build a bionic spider web to achieve efficient humid air collection. Using 3D printing technology to print micron-level bionic spider webs, the spindle knots on the spider webs are arranged periodically. The designed spindle knot is a set of two adjacent ones. The Laplacian pressure difference caused by the curvature of the water droplets will accumulate toward the spindle knot. When a certain amount of water droplets are collected, the surface tension of the water droplets is not enough [21,22,23,24]. The formation of a single drop of water sometimes occurs, and it gathers at the groove between the two spindle knots. Compared with one spindle knot, the length of the three-phase contact line of the structure of two adjacent spindle knots will be longer and trapped. There will be more positions, so there will be greater water drop suspension capacity and higher water collection efficiency. Experimental results show that, compared with previous studies, artificial spider webs exhibit a very considerable water collection efficiency. This work provides a certain reference value for solving the shortage of freshwater resources in desert areas. Moreover, compared with other synthetic spider silk fibers, 3D printed bionic spider webs have strong stability and can be used repeatedly in water collection devices.

2. Experimental section

2.1. 3D printed spider webs

The raw material of photosensitive resin is epoxy acrylate resin. Different spider web spindle structures are designed by solidworks2018 software, and convert it into STL format and import it into a 3D printer (EnvisionTec P4 LED Mini) for secondary data processing. Using a 405nm LED light source (intensity of 20 mW/cm²), adjust the XY pixel resolution to 20 microns, and the exposure time to 2 s per layer, and finally cure it with a medium pressure mercury lamp (intensity of 30 mW/cm²).

2.2. Surface wettability modification

The hydrophilic treatment of the 3D printed bionic spider web surface is completed by a plasma cleaning machine (SANHOPTT PT-SSD). The specific steps are as follows: put the 3D printed spider web into the cavity of the plasma cleaner, set the power to 70W, evacuate the cavity and then pass oxygen into the cavity for continuous 200s.

2.3. Water collection testing and measurement

The mist is controlled by a humidifier (MH-400,MELING), mist flow velocity is about 15 cm/s, so that the bionic spider web collects the mist in an environment with a humidity of ~90%. Keep the distance between the humidifier nozzle and the sample at about 5cm. The quality of the collected liquid is recorded by an electronic balance (JJ224BC) in real time, and recorded every 30 min for a total of 4 times.

2.4. COMSOL multiphysics simulation

The COMSOL Multiphysics simulation software was used to simulate the liquid water collection of spider silks with different structures in a humid air environment. First, the two-dimensional cross-sectional geometry of the structure designed by Solidworks software is imported into COMSOL Multiphysics. In order to simplify the calculation, only one spider silk structure is used for simulation. The two-dimensional transient calculation model of the fluid flow and moisture transport module in the air is adopted, and moist air is selected as the water vapor to simulate the moist air in the real environment. The designed spider silk structure is placed in a rectangle with external boundary conditions, and the rectangular boundary is set as an open boundary. The fluid flow in the external environment is set to laminar flow, and the diffusion coefficient between the humid air and the environment is set to 2.6 × 10⁻⁵ m²/s. Establish corresponding grids to couple heat, humidity and water flow.

3. Results and discussion

The typical spider web structure is shown in Figure 1a. The spider web is made of random nanowires coated with glycoprotein liquid on the surface, which can lure and stick to prey (Figure 1a). Studies have found that there are periodic spindle knots on spider silks able to achieve directional fog collection [2]. The difference in Laplace pressure and surface energy gradient at the spindle junction and junction can promote the condensation and coalescence of the mist on the spider web and its directional transport (Figure 1b) [11,12,13,14,25]. Inspired by the principle of spider web water collection, we used light-curing 3D printing technology to fabricate an artificial spider web water collection device, and obtained a set of spider web structures with multiple sizes and different curvatures (Figure 1c-d). The water collection capacity of 3D printed spider webs was studied in saturated humid air with 95% relative humidity at room temperature. Figure 1e shows a self-made mist collection device in the laboratory, including a humidifier, iron bracket and glassware. When the artificial spider web is placed in a high humidity environment, water droplets can condense on the spider silk and gradually gather and grow (Figure 1f).

Firstly, we use COMSOL multiphysics software to simulate the moisture flow on the wet surface of various bionic spider web models. In order to simplify the calculation, only a single spider silk is selected for calculation in a humid cylindrical space with a diameter and a height of 20 mm Figure 2a show the simulation results of the moist air flow velocity on the surface of the spider silk. It can be seen from the simulation...
results that the velocity distribution around the spider silk varies with the shape of the spindle knot on the spider silk. Because the existence of the spindle knot blocks the free flow of air, the air velocity is low near the spider silk. When the spindle shape is triangular, the fluid velocity near the spider silk is lower than that of the elliptical and trapezoidal spindles. And the curvature of the connection of the spindle knot is changed from a smooth cylindrical shape to a variable curvature connection, so that the air flow rate near the spider silk is reduced. The spindle knot is further designed into an asymmetric structure, and minimize the flow velocity near the optimized convex-concave spindle knot. Figure S1, S2 (Supporting Information) shows the specific optimization route of this work.

Figure 2b shows the simulation result statistics of the highest point of the liquid water concentration of each model. It can be seen that the spider silk with convex-concave spindle knots and multi-curvature connection can get the most liquid water, and the liquid water concentration reaches 77 mol/m². See Figure S4 (Supporting Information) for the specific simulation results of each model.

The ability of spider silk to trap mist is related to the maximum droplet volume that can be suspended by the combination of the spindle knot and the connection, and three-phase contact line (TCL) affects the size of suspended droplets [2, 26, 27, 28], as shown in Figure 3a, three types of spider webs with different spindle knot combinations in three cycles are designed, including one ellipse knot (spindle), two ellipse knots of the same size (Double-spindle), and two ellipse knots of different sizes (‘spindle). From the optical photos of the water droplets hanging on the spider web (Figure S3, Supporting Information), it is obvious that the water droplets hanging on the printed spider silk of different sizes of elliptical knots are the largest. From the curve of the water collection volume of the fog trapping experiment with time, it can be seen that the spider webs of different sizes of elliptical knots.

Figure 1. Inspiration from Spider Silk Biomimetic Water Collection and 3D Printing Biomimetic Preparation. (a) Schematic diagram of natural spider web and SEM image of natural spider silk [2]; (b) Natural spider web collects water in a humid environment, and the effect of water droplets hanging on the spider silk; (c) Schematic diagram of 3D printed spider web; (d) 3D printed spider web Physical image; (e) Schematic diagram of artificial spider web simulating a water collection device in a high humidity environment; (f) Artificial spider web hangs water droplets on spider silk after a period of spraying.

Figure 2. Bionic Simulation of Water-collecting Behavior on Spider Silk. (a) The 10pcs models designed in this paper use COMSOL software to simulate the two-dimensional results of the flow velocity in the flow field; (b) The statistics of the highest point of the liquid water concentration on each model.
knots of different sizes in the cycle. We placed the spider webs with printed spider webs are all triangular-pointed and there are two spindle the least. In the following experimental study, the spindle knots of the 3D trapezoidal spindle is the smoothest [26]. So the water collection is greater than that of the elliptical-shaped spindle knot, and the top of smoother, so the Laplacian pressure of the triangular-shaped spindle knot has a greater curvature, while the elliptical-shaped tip is trapezoidal shapes. The reason is that the tip of the triangular-shaped condensed water droplets (Figure 3c). When the spider web is 90° perpendicular to the desktop (parallel to the humidifier nozzle), the water collection area on the natural spider silk only occurs at the surface and the water collection capacity in 2 h is nearly doubled. Because the TCL length of spider webs with elliptical knots of different sizes is longer than two elliptical knots of the same size and one elliptical knot. Therefore, the suspended droplets on the spindles of different sizes are larger than those on the other two types of spindles, so the water-collecting ability is better. The spindle knots on the natural spider silk are elliptical. The 3D printing technology used in this article can design and rapidly shape the spindle knots of different shapes to explore the influence on the water collection performance of the spider web. As shown in Figure 3b, three shapes of spindle knots are designed, and the cross-sectional shapes are elliptical (spindle), trapezoidal (trapezoid) and triangular (triangle). It can be seen from the graph of the water collection volume of mist trapped over time that the water collection volume of spider webs with a triangular spindle-shaped section is 10–15% higher than the water collection volume of elliptical and trapezoidal shapes. The reason is that the tip of the triangular-shaped spindle knot has a greater curvature, while the elliptical-shaped tip is smoother, so the Laplacian pressure of the triangular-shaped spindle knot is greater than that of the elliptical-shaped spindle knot, and the top of the trapezoidal spindle is the smoothest [26]. So the water collection is the least. In the following experimental study, the spindle knots of the 3D printed spider webs are all triangular-pointed and there are two spindle knots of different sizes in the cycle. We placed the spider webs with triangular spindle knots at multiple inclination angles (90°, 45° and 0°) and kept the same distance from the humidifier nozzle to determine the effect of the way the spider webs are placed on the collection of condensed water droplets (Figure 3c). When the spider web is 90° perpendicular to the desktop (parallel to the humidifier nozzle), the water collection is the highest within 2 h.

The water collection area on the natural spider silk only occurs at the spindle knots and joints. The two driving forces are the Laplace pressure caused by the change in the curvature of the spindle knot, and the surface free energy gradient caused by the change in the roughness of the spindle knot at the connection make small droplets transport and converge [29, 30, 31]. The small droplets adhering to the middle of the joint cannot be transported quickly and efficiently. Therefore, as shown in Figure 3d, the connecting filaments between adjacent spindles were treated with different curvatures, and the surface of the spider web was treated with plasma hydrophilic treatment. It is generally believed that the chemical factors and roughness of the surface will have an effect on the surface tension and adhesion of water, and the hydrophilic surface is more conducive to water collection [12, 32, 33, 34]. From Figure 3d, the water collection capacity of the spider web at the variable-curvature joint reaches 3.9196g, which is 65% higher than that of the spider web with constant curvature because of the small droplets adhering to the middle of the joint. Also due to the Laplace pressure generated by the curvature change of the joint moving in the direction of the large spindle knot, the speed of the liquid droplets will be faster and the water collection will increase. Water transportation on spider silk requires a lot of tiny droplets to adhere to the joints and spindles, so that transportation and convergence occur. The contact angle of the small droplets on the hydrophobic surface is large, and the length of the TCL when suspended is very short. During transportation, It is easy to drip and difficult to gather into large droplets. The hydrophilic surface will make small droplets adhere to the surface of spider silk, forming a water film, which will speed up the transportation of droplets and increase the water collection capacity. The size of the spider web we printed is 10 times the size of the actual spider silk. Comparing the water-collecting performance of the two in Figure S5(Supporting Information), our spider silk increases the volume of the single largest water droplet by 34% in the same time.

Based on the above discussion, we can conclude that the optimal design is two triangular spindle knots of different sizes, and the curvature of the junction changes. In addition, we observe that the spindle knots on Figure 3. Effects of Redesign and Optimization of The Spindle on Spider Silk on Water-harvesting Properties. (a) The curve of the water collection of spider silk with different spindle combinations over time during the 3D printing cycle; (b) The curve of the water collection of spider silk with different spider knot shapes of 3D printing over time; (c) The curve of artificial spider web versus time The water collection volume affected by different desktop placement angles changes with time; (d) The curve of the water collection volume of the spider silk with different curvatures at the 3D printed spider knot connection over time; (e) The spider silk collection with different spider knot shapes after the curvature of the connection is optimized. The curve of water volume change with time; (f) The optimal model of artificial spider web (‘convex-concave’) water collection volume changes with different cycles. The inset is the water collection optical photo of the optimal model under this group of comparisons.
the natural spider web are elliptical and the cross section is a convex arc. Here we can consider designing a concave arc and designing an asymmetrical surface. Using the optimization results discussed earlier, four types of spider webs are designed, which are double-concave arc spindle knot (‘Double-concave’-optimization 1), convex-concave arc spindle knot (‘Convex-concave’-optimization 2), semi-flat and semi-concave arc spindle knot (‘Flat-concave’-optimization 3), and triangular spindle knot (‘Triangle’-optimization 4), as shown in Figure 3e. It can be seen from the change curve of the water collection volume of the mist capture that in the time range from 0-120min, the surface of the optimized 2 spider web with the most efficient water collection capacity, and the water collection volume reaches 4.7g. Specifically, the water collection on the surface of the spider webs of optimization 2 is 25%, 18%, and 9% higher than that of optimization 1, 3, and 4, respectively. This difference stems from different fog flow fields and the directional movement of water droplets on a structured surface with multi-branched spines. For the bionic surface, it is ideal to advocate the ability to maintain strong robustness. 

**Figure 3f** shows that after 10 fog collection cycles of the optimized 2 spider web, the water collected on the spider web surface can be stabilized above 4.5g. Therefore, the surface shows excellent robustness and applicable functions.

Based on the water collection principle of spider silk, it is necessary to make full use of the force generated between the structures to drive the movement of small droplets on the surface of the spider silk fiber. Therefore, we optimize the curvature and spindle knots of the joints on the spider silk, as shown in **Figure 4**, we optimized the elliptical spindle knot into a triangular shaped spindle knot with a cross-sectional apex angle of 120°, and the curvature of the connection was also optimized. First, the mist condenses into tiny droplets on the spindle knots and joints on the spider silk. Due to the change in curvature, the resulting Laplace pressure difference makes the tiny droplets have a driving force at the joints, not only On the spindle knot, the triangle-shaped spindle knot has a more obvious curvature change than the elliptical shape. The periodic spindle knots are arranged in two different sizes, making the three-phase contact line (TCL) of the largest suspended droplet longer. The tiny droplets on the joint and the surface of the large spindle will move to the large spindle and condense into large droplets S1, S3, S5, while the tiny droplets on the surface of the small spindle and the junction will move towards the small spindle. Move and condense into small droplets S2, S4. Since the Laplacian pressure at the high curvature portion is greater than the Laplace pressure at the low curvature portion [35], the small droplet S4 will converge toward the large droplet S5 to form a droplet S7. As more and more small droplets converge, the droplets S1 and S3 gradually become larger. The small droplet S2 will first converge with one of the large droplets, and finally converge with three droplets to form a larger droplet S6. When the gravity of the droplet is greater than the adhesion force, it will drop. The entire water collection system can go through the cycle of condensation→coalescence→transportation→transfer→dripping to achieve an efficient mist trapping effect [12,36]. Form the Figure S2(Supporting Information), We can see that there are stair effects (not smooth) on the printed spider web, from the point of view of the water collection mechanism, the roughness on the spindle is greater than that on the joint due to the uneven shape of the spindle. Forces generated by the induced surface energy gradient due to surface roughness differences drive droplets to move from less hydrophilic regions (junctions with relatively lower surface energy) to more hydrophilic regions (spindle knots with higher surface energy).

At the same time, we compared the effects of different reported spindle structures and different preparation methods on the water-collecting performance. As shown in **Figure 5a**, the spider silk of our semi-convex and semi-concave multi-dimensional spindle is 16% higher than the best model reported for water-collecting performance [11,37].
4. Conclusion

In conclusion, we have demonstrated the production process of artificial spider webs with spider silk as a reference through 3D printing technology. Using a combination of finite element analysis and experimental verification to optimize the size of the spindle knot and the curvature of the joint on the spider silk, design spider webs of different shapes and arrangements, hydrophilic surfaces and optimized curvature structures of 3D printed spider webs and others Compared with the structure, it has a more significant water collection effect. The mechanism has three aspects: First, the flow field around the optimized structure more significantly increases the effective deposition area, which is conducive to the condensation of moist air on the surface of the spider silk; second, the condensed water droplet is transported along the curvature of the spine. It is faster because the Laplace pressure on both sides of the droplet is different; third, the hydrophilic surface will make the small droplet adhere to the surface of the spider silk, and the three-phase contact line of the droplet will become longer and form on the surface. The water film will accelerate the transportation speed of the droplets, thereby increasing the water collection capacity. 3D printing technology can be quickly manufactured and mass-produced, and the optimized artificial spider web may have a certain effect on alleviating the water shortage problem in desert areas.

Declarations

Author contribution statement

Chi Guo: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Chengguan Wang: Performed the experiments; Analyzed and interpreted the data; Wrote the paper. Qi Huang, Zhi Wang: Performed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper. Xiaojing Gong: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper. Seeram Ramakrishna: Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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