


A Hydrophilic/Hydrophobic Composite Structure for Water Harvesting from the Air

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ABSTRACT

The freshwater shortage is one of the world's most pressing challenges needs to be addressed rapidly. To overcome this challenge, harvesting water from the air has emerged as a simple and cost-effective approach. Traditional wire meshes have been already used for atmospheric water harvesting from the fog. In foggy areas, the wire meshes are placed perpendicular to wind and water droplets in fog carried by the wind are trapped and deposited on the surface of meshes. The purpose of this study is to improve the water harvesting capacity of the traditional wire mesh by modifying its surface using a nature-inspired composite structure consisting of hydrophilic and hydrophobic zones. Hydrophilic zones were obtained by electrospinning or electrospaying of the polyamide 6 (PA6) / chitosan (CH) blend, and hydrophobic zones were attained by electrospaying of polycaprolactone (PCL). The water harvesting capacity of the resulting meshes was tested and compared with each other. The highest water harvesting capacity was achieved with the PA6/CH nanofiber coated wire mesh as 87 mg / cm²/h. This mesh collected twice as much water compared to the uncoated mesh. However, its water collection rate decreased when nanofiber surface reached the saturation level. The addition of hydrophobic PCL particles onto PA6/CH nanofibers significantly reduced the amount of water captured. When both PA6/CH and PCL were electrospayed on the wire mesh in particle form water harvesting capacity slightly increased, but it was still poor compared to uncoated mesh.

1. INTRODUCTION

In today's world, clean drinking water scarcity is one of the major problems that need to be addressed urgently. It is estimated that nearly 52% of the world's population will live in water-stressed regions by 2050. Unfortunately, only about 2.5% of the water on earth is drinkable, and this rate is decreasing day by day due to increasing environmental pollution and climate change [1,2]. Treatment of wastewater for clean drinking water or obtaining freshwater from seawater are some suggested solutions to reduce the gap between the water supply and demand, but wastewater treatment and desalination of seawater are quite costly with today's technology [3]. This has led people to look for unconventional water resources.

Fog is one of the unconventional water sources, and fog harvesting, which is an ancient practice, is a simple, sustainable, and cheap method to collect water from the air. Fog harvesters are generally made from mesh nets. Water droplets are collected as fog passes through the holes of the mesh by the wind. Although meshes have been the most widely used material for fog harvesting, they have low water collection efficiency [4]. To overcome this limitation, the surface of the mesh can be modified. In recent years, with the development of new and advanced materials, mimicking nature has become very popular. The Namib desert beetle shown in Figure 1 is an insect that lives in an extremely arid desert [5]. This insect uses water vapor in the air to meet its water needs by converting it into liquid form. Due to this feature, it has caught many researchers'

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attention. Parker et al. [6] found that the Namib desert beetle harvests water from thin air through hydrophilic and hydrophobic regions on its back. Several other studies have also revealed that the hydrophilic/hydrophobic structures can be used to capture and condense water from the air [7-10]. Zhai et al. developed a surface consisting of hydrophilic patterns on a superhydrophobic surface to mimic the wing surface of the Namib Desert beetle for water harvesting [7]. Huang et al. produced bio-inspired water harvesters using the electrospinning method. They used polyvinylidene fluoride (PVDF) and expanded graphite (EG) to create bead-on-string nanofibers which are inspired by spider silk [8]. They also fabricated bicomponent nanofibers from polyvinylidene fluoride (PVDF) and polyacrylonitrile (PAN) which are inspired by the Namib Desert beetle [9]. While PVDF provided hydrophobicity PAN and EG created hydrophilic segments of the nanofibrous material. Garrod et al. fabricated hydrophilic-hydrophobic patterned surfaces using pulsed plasma deposition of a hydrophilic polymer array on a superhydrophobic background [10]. The main role of the hydrophilic surfaces in water harvesters is that hydrophilic surfaces promote the nucleation of water droplets since hydrophilic materials attract water molecules in the air. On the other hand, hydrophobic or superhydrophobic surfaces are preferred in water harvesters since water droplets are able to slide over these surfaces, which makes their removal easy [11,12].



Figure 1. Namib desert beetle [5]

Wire mesh has been used traditionally for water harvesting. Ghosh et al. used stainless steel wire meshes inside the cooling tower to harvest water from the rising fog stream. They found that the water harvesting efficiency of meshes was mainly affected by the shade coefficient of the mesh, effective dripping length of water droplets along the mesh, and the inclination angle of the mesh regarding the vertically rising fog stream [13]. Knapczyk-Korczak et al. used a raschel mesh coated with electrospun polyamide 6 nanofibers to condense water from the fog. It was reported that the coated mesh had a water harvesting capacity of three times higher than the uncoated one [14].

In this study in order to improve the water harvesting capacity of the traditional wire mesh hydrophilic and hydrophobic zones were created on the mesh surface. To obtain hydrophilic zones polyamide 6 and chitosan were chosen. Polyamide 6 is a hydrophilic polymer with good mechanical properties [15]. Chitosan is widely used in many areas due to its antimicrobial properties [16]. Polyamide 6 and chitosan are either electrospun or electrospayed to form nanofibers or nano or micro size particles. To obtain a hydrophobic zone on the surface, PCL, which is a hydrophobic polymer, was preferred [17]. It was electrospayed in the form of nano or microparticles. Instead of polymer coating, nano size fibers or particles were preferred in this study since they have the advantage of providing a large surface area for catching small water droplets.

2. MATERIAL AND METHOD

2.1 Material

Polyamide 6, chitosan (medium molecular weight), and polycaprolactone (average Mn 80,000) were used as polymers. Acetic acid (100%), formic acid (98–100%), and dimethylformamide were used as solvents. All chemicals and solvents were purchased from Sigma Aldrich. Single-layer woven stainless steel wire mesh with a mesh count of **3.5 (openings/cm)** and a wire diameter of 1 mm was purchased from the local market.

2.2 Method

Three different surfaces were created for water harvesting experiments, and the untreated wire mesh was used as control. To produce hydrophilic zones nanofibers were produced from the hydrophilic polyamide 6 (PA6) and chitosan (CH) blend by the electrospinning method. Also, nano/micro-sized hydrophilic particles were produced from the same polymer blend using the electrospaying method. In order to obtain hydrophobic zones, polycaprolactone (PCL), which is a hydrophobic polymer, was electrospayed onto either wire mesh or nanofiber coated wire mesh. Both electrospinning and electrospaying methods utilize the electrical field to produce nano-sized fibers or particles. Electrospinning/electrospaying processes were carried out using a high voltage power supply (ISEG), a syringe pump (NE-300, New Era Pump Systems), and an aluminum foil-coated copper plate as the collecting surface. A 5 mL plastic syringe and a 0.8 mm (21 Gauge) internal diameter needle were used in all studies.

First, optimal solution and process parameters were determined for electrospinning and electrospaying to attain uniform bead-free nanofibers and uniform spherical nano or micro size particles. For electrospinning of hydrophilic nanofibers, PA6 / chitosan blend solutions with a concentration of 13.5% (w/v) were prepared by dissolving PA6 and chitosan polymers at a weight ratio of 8:1 (w/w) together in a formic acid/ acetic acid solvent mixture in the ratio of 3:2 (v/v), respectively. The distance between the needle tip to the collector was set to 10 cm and

electrospinning was performed at a flow rate of 0.2 mL/h and applied voltage of 17 kV. To obtain hydrophilic particles, PA6 / chitosan blend solutions with a concentration of 6% (w/v) were prepared using the same polymer blend ratio and solvent mixture. The distance between the needle tip to the collector was set to 10 cm and electrospaying was performed at a flow rate of 0.6 mL/h and applied voltage of 22 kV. For electrospaying of hydrophobic particles, a PCL solution with a concentration of 8% (w/v) was prepared by dissolving PCL in dimethylformamide (DMF), and it was electrospayed at a flow rate of 0.6 mL/h. The applied voltage was 10 kV, and the distance from the needle tip to the collector was 20 cm. After the determination of process and solution parameters, wire meshes were coated for water harvesting experiments. For this purpose, PA6/CH nanofibers were directly electrospun on a wire mesh (Sample 2), PCL particles were electrospayed on the PA6/CH nanofibers coated wire mesh (Sample 3) and also both PCL and PA6/CH were electrospayed on a wire mesh (Sample 4). Table 1 summarizes the wire meshes used in water harvesting experiments. The main purpose was to create hydrophilic and hydrophobic zones on wire mesh. Hydrophilic zones were formed either by PA6/CH nanofibers or PA6/CH nanoparticles. Hydrophobic zones were produced by PCL nanoparticles.

Table 1. Wire meshes used in water harvesting experiments

Code	Sample Content
Sample 1	Uncoated wire mesh
Sample 2	Wire mesh coated with electrospun PA6/CH nanofibers
Sample 3	Wire mesh coated with electrospun PA6/CH nanofibers and electrospayed PCL particles
Sample 4	Wire mesh coated with electrospayed PCL and PA6/CH particles

The water harvesting capacity of coated wire meshes was measured using the experimental setup shown in Figure 2. Mesh samples were cut into rectangular pieces of 10 cm x 17 cm. A conventional ultrasonic cool mist humidifier was used to create fog. The test sample was placed at a distance of 5 cm from the outlet of the humidifier. A beaker was placed under the sample to collect condensed water. Ambient conditions were kept constant at 25 °C and 40 % RH for each trial. Cold water mist was sent on the samples for a total of 3 hours. At the end of each hour, the water collected in the beaker was weighed.

3. RESULTS AND DISCUSSION

3.1 Characterization

The optimal solution and process parameters were determined for electrospinning and electrospaying prior to coating of wire meshes. Figure 3 (a) and (b) show the scanning electron microscope (SEM) images of PA6/CH nanofibers and particles obtained during optimization study, respectively. No bead formation was detected in the fiber structure. PA6/CH particles consisted of smooth spherical ones and irregular granular ones. PCL was successfully sprayed in spherical form (Figure 3c). Average fiber and particle diameters were determined as $101 \text{ nm} \pm 24$, $515 \text{ nm} \pm 376$ for PA6/CH, and $2.5 \text{ } \mu\text{m} \pm 0.525$ for PCL, respectively. Figure 3 (d) shows the scanning electron microscope (SEM) image of the PCL sprayed onto PA6/CH nanofibers. In this case, it was observed that some PCL particles were not in the expected smooth spherical form.

Wire meshes were modified by coating them with hydrophilic and hydrophobic polymers for water harvesting from the fog. Figure 4 (a) shows the wire mesh coated with PA6/CH nanofibers and PCL particles, respectively. Nanofibers covered the holes of the mesh and the wire mesh looked like it was covered by a film. Figure 4 (b) illustrates the wire mesh coated with both PCL and PA6/CH particles. In this case, a white coating covered the wires. The holes were open.



Figure 2. Experimental setup for water harvesting capacity test

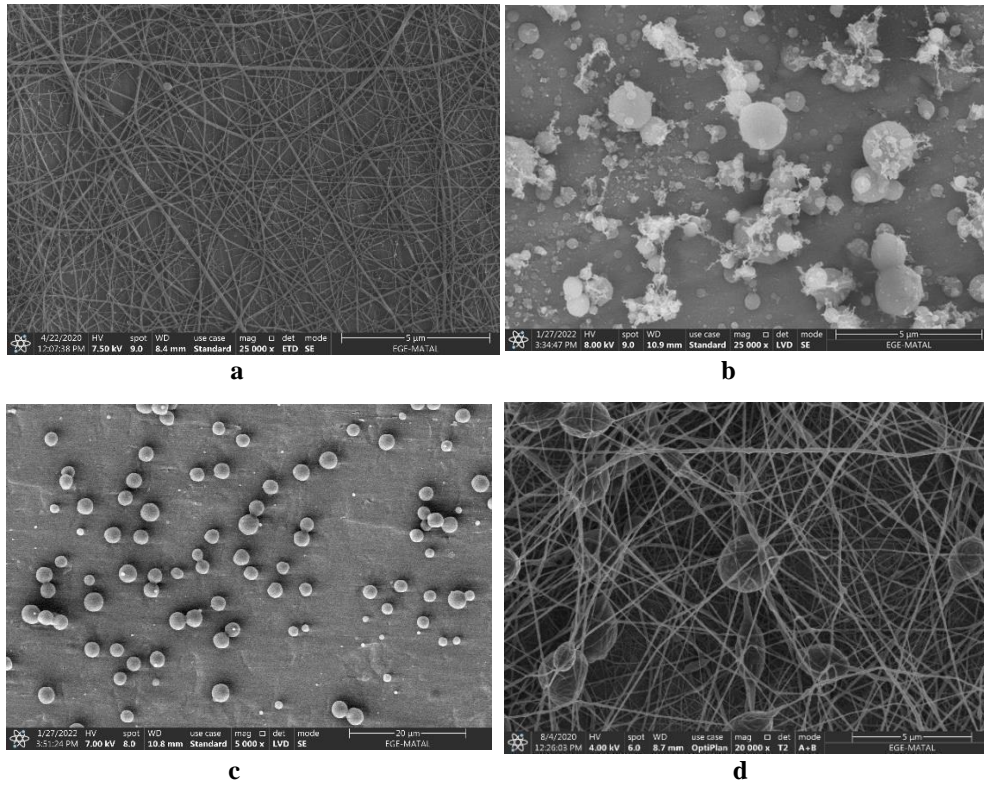


Figure 3. SEM images of (a) PA6/CH nanofibers (b) PA6/CH particles (c) PCL particles (d) PCL sprayed onto PA6/CH nanofibers

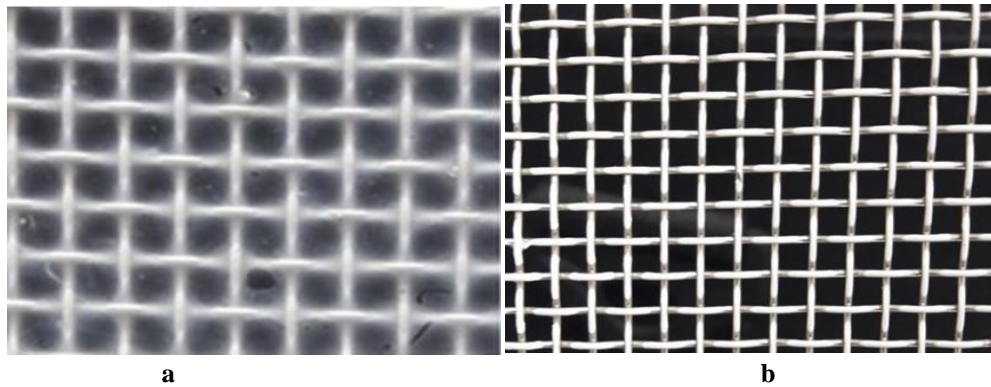


Figure 4. Coated wire mesh (a) Sample 3 (b) Sample 4

3.2 Water harvesting from wire mesh

Figure 5 shows the water harvesting from the fog with a coated mesh. As fog passed through the wire mesh, water droplets formed on the surface. Figure 6 illustrates mesh samples during water harvesting experiments. It was clearly seen that the water droplets condensed on nanofibers in case of PA6/CH nanofibers coated wire mesh (Figure 6b). The nanofiber surface increases the effective area for catching the water droplets [14]. When PCL particles were sprayed onto PA6/CH nanofibers a decrease in the water capturing performance of the mesh was observed (Figure 6c). This can be explained by the reduction of the hydrophilic area on the mesh surface.

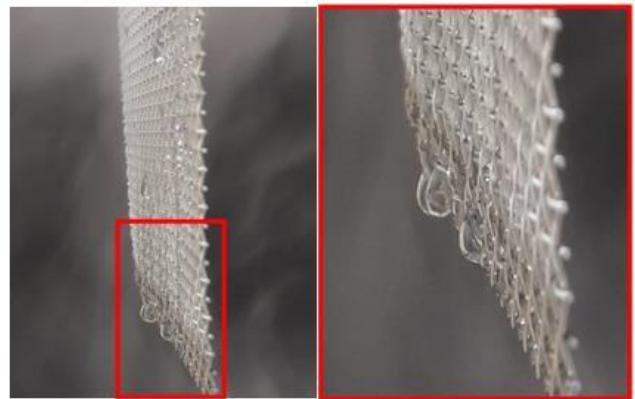


Figure 5. Water harvesting from coated mesh

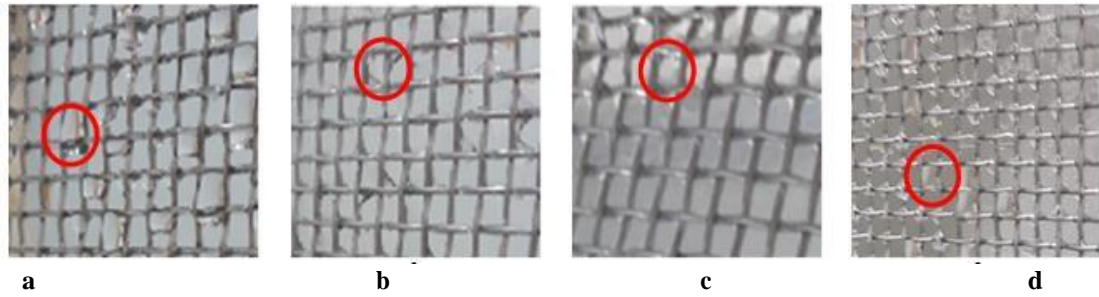


Figure 6. Water harvesting from (a) Uncoated wire mesh, (b) PA6/CH nanofiber coated wire mesh, (c) PCL sprayed onto PA6/CH nanofiber coated wire mesh, (d) PCL and PA6/CH sprayed onto the wire mesh

The water harvesting efficiency of samples was calculated at the end of the first hour according to the equation given by Huang et al.[8]. The results are given in Table 2. Huang et al. defined water harvesting efficiency as the weight of water per unit area per hour [9]. The highest water collection efficiency was obtained as 87 mg/cm²/h with Sample 2. It was observed that the water harvesting capacity of the PA6/CH nanofiber coated wire mesh was two times higher than the uncoated wire mesh at the end of the first hour. After coating with hydrophilic nanofiber, the surface area of the wire mesh increased significantly. This increase led to higher water harvesting capacity. The addition of PCL to the nanofiber-coated surface (Sample 3) reduced the water harvesting capacity about five times compared with nanofiber-coated one. When both PA6/CH and PCL were in particle form (Sample 4) water harvesting capacity was increased slightly compared to Sample 3. It is likely that hydrophobic PCL particles masked the effect of hydrophilic PA6/CH.

Table 2. Water harvesting efficiency

Code	Efficiency (mg / cm ² /h)
Sample 1	45
Sample 2	87
Sample 3	17
Sample 4	25

Water harvesting capacities of the meshes versus time was given in Figure 7. The increase in the water harvesting capacity of Sample 2 slowed down after the first hour. Our experiments were conducted at a relatively low fog flow speed due to the experimental setup. It is believed that the hydrophilic nanofiber surface reached saturation level after a certain period of time. A high fog flow speed could be able to shake the captured water between nanofibers and we probably would not see this slowing down trend. With the addition of PCL, the water harvesting capacity of the mesh dropped drastically. Since PCL is hydrophobic, the addition of PCL particles to the surface reduced the hydrophilic areas which play the main role in catching the water. When both PA6/CH and PCL were in particle form (Sample 4) water harvesting capacity of the mesh was slightly better than Sample 3.

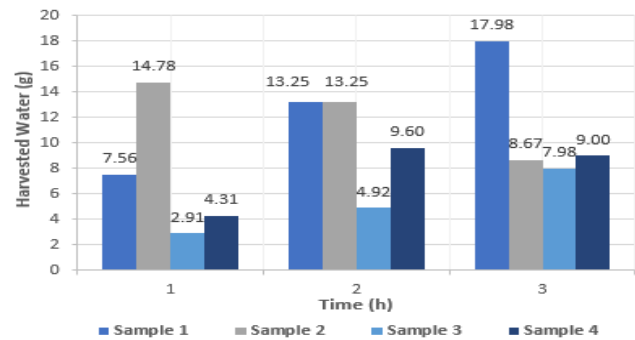


Figure 7. Water harvesting capacities of meshes with changing time

4. CONCLUSION

This study focused on increasing the water harvesting capacity of traditional wire meshes. For this purpose, hydrophilic nanofibers and hydrophilic/hydrophobic nano or microparticles were incorporated on the surface of a wire mesh. Wire meshes are effective tools to capture and condense water from fog. It was observed that the water harvesting capacity of a wire mesh can be controlled by modifying the mesh surface with hydrophilic and hydrophobic polymers. The coating of the mesh surface with hydrophilic nanofibers significantly increased the water harvesting capacity due to increasing surface area. However, when the nanofibers reached the saturation level the water capturing efficiency decreased. Water harvesting capacity was decreased sharply by the addition of hydrophobic particles onto hydrophilic nanofibers. Hydrophobic particles masked the hydrophilic zone and reduced the water capturing ability of the mesh. From these results we can conclude that the wire mesh covered with the hydrophilic nanofiber web was more effective in capturing water droplets from the fog, however, it seems that a new strategy is necessary to collect the captured water droplets from the mesh. In our experiments, gravity was the main force responsible for water collection. In addition to gravity force, applying a mechanical force such as shaking the mesh at regular time intervals might provide better outcomes. Additionally, the sustainability of the nanofiber coated mesh needs to be addressed in order to use it in practical applications.

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