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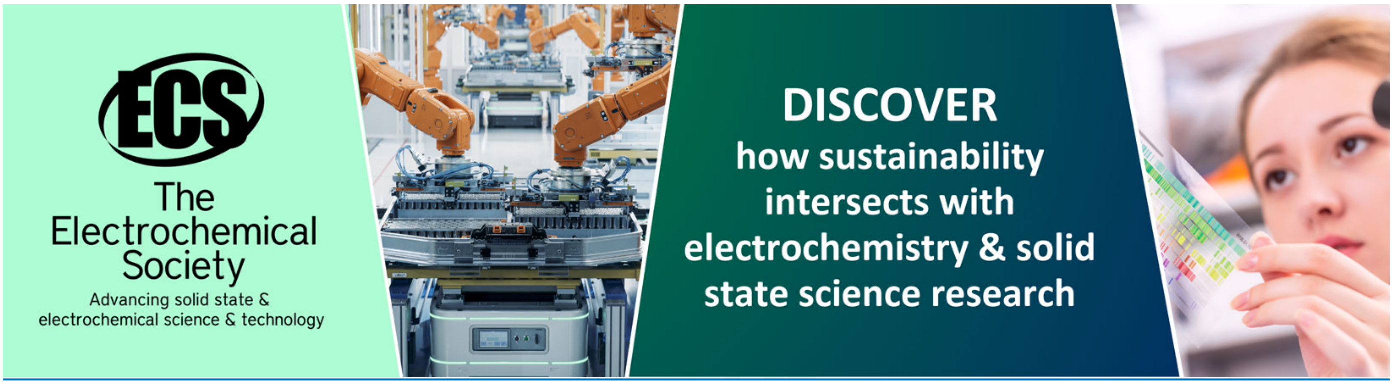

Applications of web produced by hot air assisted melt differential electrospinning method

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Abstract: Melt electrospinning, a technique that has gained increasing attention since it easily can generate continuous ultrafine fibers directly from polymer melts without the use of any solvent. Therefore, it is considered as a safe, cost effective, and environmental friendly technique. However, with all those great advantages, the technique still suffers some drawbacks such as: large fiber diameter and low throughput. The hot air assisted melt differential electrospinning (MDES**)** is a new technique invented by our research team that can solve or eliminate those drawbacks. The most important features of our used apparatus are: Needleless nozzle that could generate multiple Taylor cones around the bottom edge of the nozzle, which can result in a high throughput. The stretching force acting on the jets can be further strengthened by an air current provided by an air pressure gun. Interference between the high voltage supply and temperature sensors could be prevented through the grounding of the nozzle. The ultrafine pp webs produced using the same apparatus was in the micro/nano scale with a diameter of 600nm-6um and a smooth surface. Porosity of the webs ranges from 86.5%-99.4% when different collecting devices are used. The resultant ultrafine webs were applied in three areas: oil sorption, water treatment, and hydrophilic PP membrane. The results were very promising as for oil the sorption capacity was 129.0g/g; for water treatment, the rejection rate for 3um particles was 95%. And for the hydrophilic PP membrane, the water sorption capacity was 12.3 g/g.

Keywords: Melt differential electrospinning (MDES**)**, fiber diameter, oil sorption, water treatment, hydrophilic PP membrane

1. Introduction

With the increasing advancement in science and technology research, electrospinning has been attracting increasing attention, probably due in part to a surging interest in nanotechnology, or interest in its ability for the fabrication of continuous polymeric ultrafine fibers or fibrous structures, it is a high efficient method for producing nano-fibers, which can be classified into two types: solution electrospinning (SES) and melt electrospinning (MES). However, the MES is believed to be an alternative method of SES, because it is more environmental-friendly, low-cost, and high efficient in spinning than the latter[1].When the diameters of the polymeric fibers decreased from micrometers to nanometers, it provided several amazing characteristics such as high surface area to volume ratio, high porosity, flexibility in surface functionalities, and superior mechanical properties. These outstanding properties of electrospun nanofibers make them to be the optimal candidates for a broad range of important applications in widely different areas such as drug carriers, tissue scaffolds, wound dressing, reinforcement materials, filters, protective clothing, electrodes, sensors, catalysts, etc. [2].The origin of electrospinning as a viable fiber spinning technique can be traced back to a hundreds of years ago. The process of electrospinning, also termed as electrostatic spinning, was first conceived by Lord Rayleigh [3] in the late 19th century. In 1902, the first patent for the production of fibers from a solution jet by using electric field was issued to Cooley [4] in the USA. From 1934 to 1944, Formhals published a series of patents [5–9], describing an experimental setup for the production of polymer filaments using an electrostatic force. Since then, the electrospinning truly surfaced as a feasible technique for spinning fibers with small diameters. Following the work of Formhals, the focus changed to developing a better understanding of the electrospinning process. In 1969, Taylor published his work[10] on the shape of the polymer droplet produced at the tip of the needle when an electric field was applied. Taylor found that the pendant droplet developed into a cone when the surface tension was balanced by electrostatic force and the jets were ejected from the vertices of the cone with diameters significantly smaller than the diameter of the needle when the electrostatic force exceeded its surface tension. This conical shape of the jet was later referred as the “Taylor Cone” in subsequent work. In the subsequent years, interest shifted away from the fundamental understanding of the electrospinning process to studying the structural morphology of the electrospun nanofibers and the relationship between the structural features and individual processing parameters. In 1971, Baumgarten[11] reported to make an apparatus to electrospun acrylic fibers with diameters in the range of 500 to 1100 nm. In 1981, LarrondoandMandley[12, 13]successfully produced polyethylene and polypropylene fibers by electrospinning their melts. They found that the fibers electrospun from a melt were relatively larger in diameter than fibers electrospun from a solution. In the early 1990s, several research groups, especially the Reneker group, revived the electrospinning by demonstrating the fabrication of ultrathin fibers from various polymers [14].Since then, the electro-spinning regained an upsurge attention in the research due to the potential applications of these nanofibers in various areas. Up to date, over a hundred synthetic and natural polymers have been successfully electrospun into fibers with diameter ranging from a few nanometers to several micrometers[15].In recent years, the research interest on electrospinning has been quickly shifted from the fabrication of nanofibers to the application of these resultant electrospun nanofibers with various functionalities. Some of these applications have reached the industrial level. Moreover, the results on the application areas showed that electrospinning is a versatile technique with broad applications in biomedical applications, as tissue engineering scaffolds, in wound healing, drug delivery, filtration, as affinity membrane, in immobilization of enzymes, small diameter vascular graft implants, healthcare, biotechnology, environmental engineering, defense and security, and energy storage and generation and in various researches that are ongoing[16-20]

2. Melt electrospinning

Melt electrospinning is a promising approach which has several advantages over solution electrospinning. Even though much of the research ,industrlization, and commercial development to date has been in solution electrospinning, but once the complications associated with Melt electrospinning method such as : relative thick fiber diameter, high viscosity and device complexity for high temperatures and high voltage were solved, this solvent-free method will open the doors to new horizons in modeling electrospinning without any risk of solvent evaporation, and complicated process for the solvent recycling as well as mass production of micro-nano fibers .It can be seen from literatures that many researchers focused on improvement of electrospinning equipment, fibers made from special materials and structure, and on nano scale fibers based on test results or microscopic images. In 1981 Larrondo and Manley[21–23] confirmed the feasibility of polymer MES according to their experiments when they established a simple device and electrospun PP fiber with diameter of about 50μm successfully by extruding the melt with a piston. Moreover, the formation and properties of fibers, the flow field during spinning process and the deformation of melt droplets were analyzed in detail. In 2004, Lyons[24] summarized the theoretical model of MES in his doctoral dissertation, In the same year, he published an article and pointed out that the electric field strength and polymer molecular weight have an important effect on the morphology and diameter of MES fibers.[25] Eduard [26]presented a gas-assisted polymer melt electrospinning process where under the investigation condition in electrospinning of polylactic acid (PLA) melt, air drag produced an additional 10% thinning compared to the un-assisted melt electrospinning process. Christopher[27] made Poly (butylene terephthalate), polypropylene, and polystyrene fiber by a single orifice melt blowing apparatus. They produced nanofibers with average diameters less than 500 nm. Ogata N, et al from university of Fukui in Japan designed a melt electrospinning setup that could produce 1μm fiber with laser heating source. Although the indirect flash heating system had some advantages, but laser equipment was of high energy consumption and risk. Shimada N, et al followed to heat a membrane with customized linear laser source, by which a line of Taylor cones was obtained and a row of jets were produced. This method increased the productivity comparing with the point laser source, but the yield was relatively low. Michal Komarek and Lenka Martinova from technical university of Liberec, Czech Republic invented two melt electrospinning devices, One is a “rod” style spinning head; another is a slot-shaped spinning head. The later one gave inspiration about the design of the melt electrospinning apparatus, yet it didn’t combine the screw continuous extrusion device, and the melt distribution at the slot was poor. In addition, the number of the fibers was limited when using a slot only. W. M.Yang research group from Beijing university of chemical technology, China, utilized typical materials commonly used in fiber manufacturing industry such as PP, PE, PA, PET, PLA,PCL, PES etc., to make fibers through self-designed MES equipment. The effect of voltage and temperature on fiber morphology was studied, and a few micron-grade fibers were achieved.[28, 29]

3. Design and Features of the melt differential electrospinning Setup

The hot air assisted melt differential electrospinning is a new technique invented by our research team that can solve or eliminate the drawbacks of melt electrospinning technique. It is a technique that provides a differential electrostatic melt spinning nozzle, through which a shunt within the nozzle cone can produce a plurality of individual fibers，functioning to resolve the key difficulties of device using single orifices, the self-designed apparatus consists of six major parts as shown in (Figure 1) : power supply of high-voltage, heating system, an air pressure gun, a copper circular ring functioning as electrode A, a needleless cone-shaped nozzle, and a collecting device. The power supply device secures a maximum output of 100 kV and a maximum current output of 2 mA. The electric heating ring with a power of 300 W was custom-built. The function of hot air can be summarized into three main points: Preserving heat of runner, accelerating thinning of flying jets, and keeping the environmental temperature high, that's higher than the softening point which will increase the action time of electric force and reduce fiber diameter (Figure 2 and Figure 3).

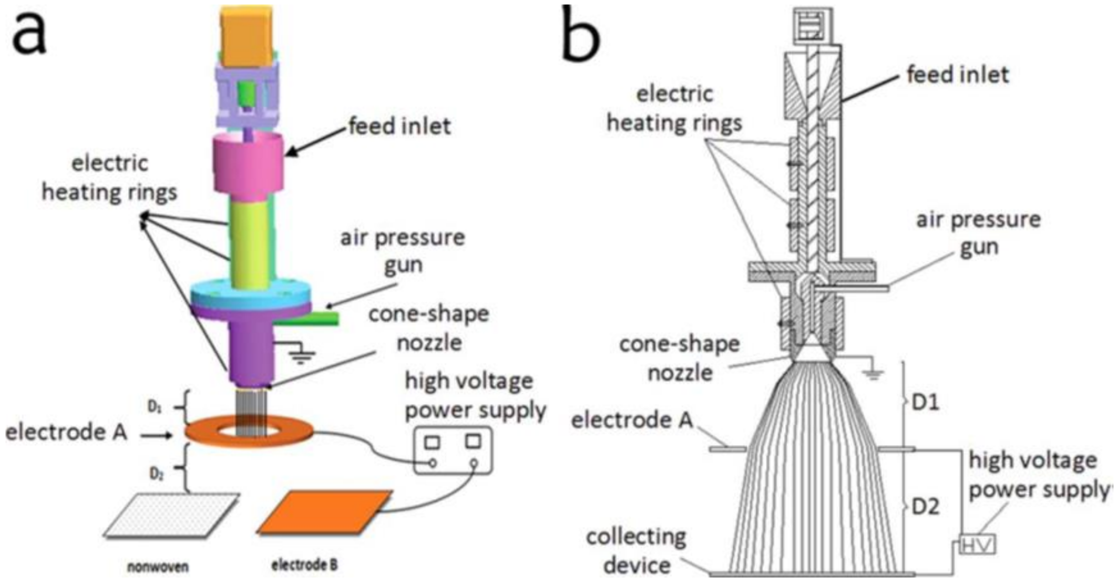

Figure 1. Schematics of a self-designed needleless MDES apparatus.

The unique features of the apparatus are: the generation of multiple Taylor cones around the bottom edge of the nozzle, resulting in a high throughput; the air current driven by an air pressure gun further strengthened the stretching force acting on the jets. More importantly, it could contract the flying jets with the pressure difference between the air current and the atmosphere to prevent the polymer jets from being attracted by the inner circle of electrode A; and two kinds of collecting devices were applied, namely, the nonwoven and electrode B. The nozzle was grounded to prevent any kind of interference between the high-voltage supply and temperature sensors;

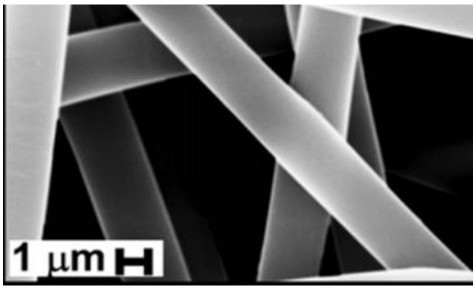

Figure 2. Un-assisted: 1-2 μm

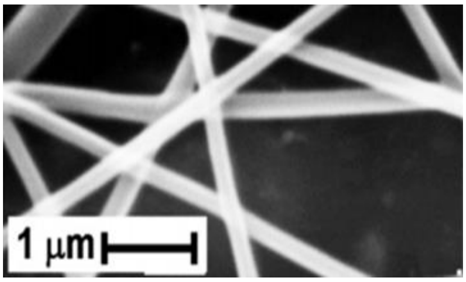

Figure 3. Hot air assisted: 0.2-0.8 μm

With all those features, the device has the advantages of simple structure, capability of spinning thin fibers, high spinning efficiency, and the ultrafine PP webs produced are in the micro/nano scale with a diameter of 6um-600nm and a smooth surface. Porosity of the webs ranges from 86.5%-99.4% when different collecting devices are used.

4. Applications of web produced by hot air assisted MDES

Since the early 1980's, electrospun polymer nanofibers have already been proposed for many different applications. Reviewing the number of patents, we can see that approximately two-thirds of all electrospinning applications are in the medical field. Of the remaining patents, one-half deals with filtration applications, and all other applications share the remaining half [30]. But most of applications were using solution electrospun fibers, and the use of melt electrospun fibers in many applications is still limited, some groups started to research the feasibility of using melt electrospun fibers in different applications. The web fabricated by hot air assisted melt differential electrospinning method was applied experimentally in three areas of research, and gave promising results. The areas were:

4.1. *Sea Oil-Spill Cleanup applications*

Polypropylene (PP), a synthetic polymer and general purpose plastic, has great mechanical behavior, together with other excellent properties, like nontoxicity, processibility, and low cost, PP has been widely used in many applications, but have not been used in oil sorption as melt electrospun produced fiber before. Ultrafine polypropylene (PP) webs as oil sorbents used in this application were produced via the melt-differential-electrospinning self– designed apparatus and characterized by SEM and contact-angle analysis. PP webs of various diameters and porosities were obtained by the manipulation of the applied electrical field. The effects of the fiber diameter and porosity on the oil-sorption capacity and oil retention behavior were investigated. The experimental results showed that for web diameter on the microscale, the porosity played an important role in determining the oil-sorption capacities. The maximum oil-sorption capacity of the resulting PP webs with regard to the kinds of oil used (motor – peanut) were 129 and 80 g/g, respectively; these values were approximately six to seven times higher than that of the commercial PP nonwoven for the corresponding oils. The high oil-sorption capacity of the melt-electrospun PP webs was attributed to its small fiber diameter, high porosity, olephilicity, and hydrophobicity. Additionally, the great mechanical performance of the resulting webs ensured their reusability and recoverability. They could be reused up to seven times while still maintaining a sorption capacity of around 80 g/g, and above 97% of the sorbed oil could be recovered, which indicated excellent reusability and recoverability.(Figure 4)[31]

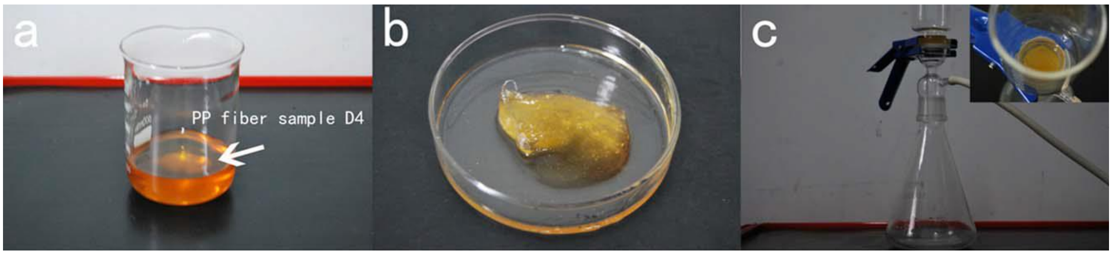

Figure 4. Oil sorption / desorption process

4.2. Fabricated oriented fiber membranes for microfiltration applications

The main aim of this study was to explore the influence of arrangement for oriented fibers on filtration efficiency. The melt-differential-electrospinning self–designed technique was used to fabricate oriented fiber membranes for this application. During the experiment, Polypropylene (PP) with a melt flow rate of 2000 g/10min was used. Electrospinning was carried out in a humidity of 25% at 24 C^0, and the nozzle temperature was set at $240C^0$. The PP melt were electrospun at the condition of single-electrode with a feed rate of 15 g/h controlled by a pump. A cylinder collector (diameter: 100mm, maximum rotating speed: 1400 rpm) was used to get the oriented fibers and was placed 260mm off the effects of the nozzle (Figure 5).

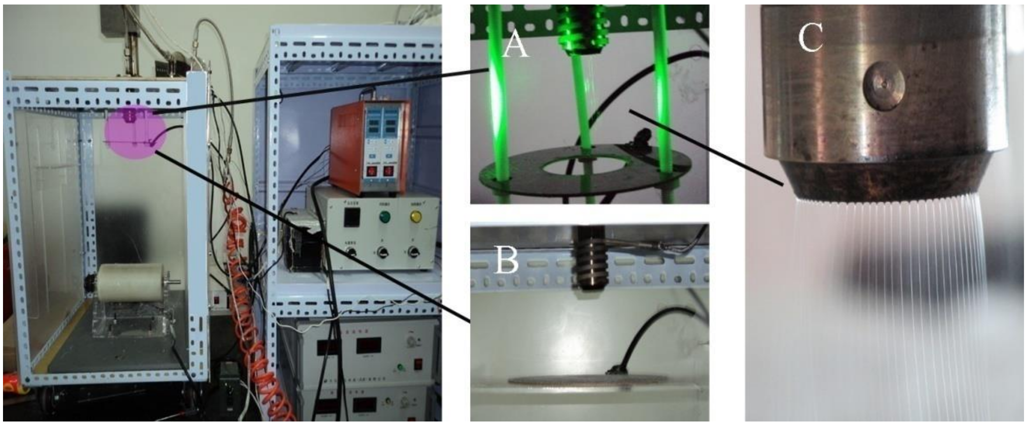

Figure 5. Images of melt electrospinning apparatus: (A) single electrode as receiver, (B) ring electrode with a cylinder collector, (C) melt jet.

The oriented PP fibers were stacked under different azimuthal angles based on the horizontal datum of 0 degrees to obtain a series of filtration membranes (Figure 6), and used these samples to do orthogonal experiments. Then, six prepared PP membranes were treated by hot-pressing at $90C^0$, along with the one untreated original membrane. The oriented fiber membrane were 100 mm in diameter and Characterized by scanning electron microscopy (SEM, HITACHI S4700, Japan) after gold coating to examine the morphology of electrospun PP fiber filtration membrane, and the fiber diameter was measured by the image analysis software (Image J 2X). A micrometer was used to measure the thickness of the membranes.

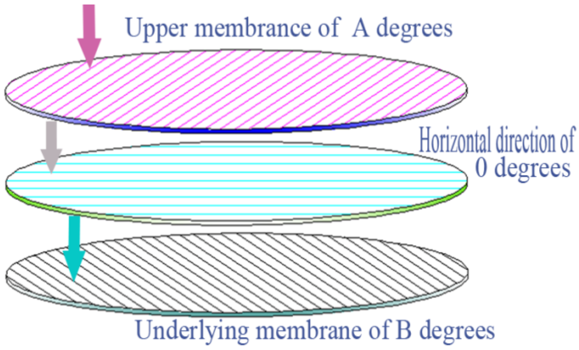

Figure 6. Schematic diagram of sample under different azimuthal angles

The mechanical properties of membranes were assessed by a material testing system (Instron5565, Instron Co.) at a loading velocity of 10 mm/min. And the thermal properties of membranes were evaluated by differential scanning calorimetry(DSC, Q2000, TA Instruments) at a heating rate of 10C^0/min under nitrogen atmosphere from 30 to 250C^0. The contact angle between the electrospun PP membrane and water was measured by using a contact angle analysis system (OCA20, Dataphysics). Two microliters of deionized water were dropped on the surfaces of samples. Image of solid/liquid interface was captured by a charge-coupled device camera. The contact angle data of PP membrane (Figure 7) illustrate that the oriented PP membrane showed a high water contact angle of (127. 9°) than the random PP membrane of (124.4°), which may be due to the smaller pore size of oriented membrane than that of the original membrane.

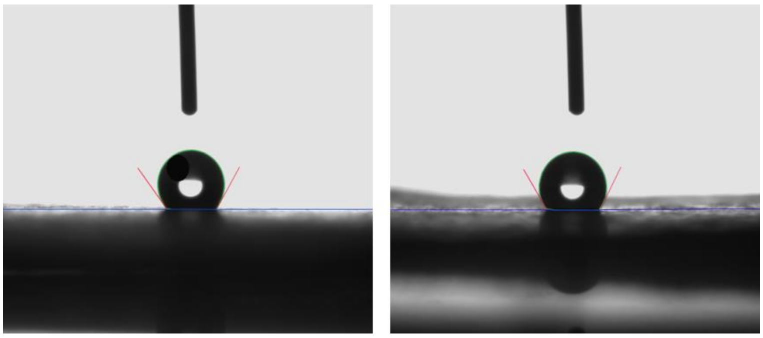

Figure 7. Contact angle of (a) oriented PP membrane (127. 9°) and (b) random PP membrane (124.4°)

The particle rejection test used 300 nm-3μm carbonate particles to prepare 1% wt of the original solution. The concentration of the solution was examined by UV spectrophotometer (UV-9000). The rejection efficiency indicates the rejection performance of one particle which is a very important indicator during the actual filtration. The results of the rejection efficiency of different membranes to the particles showed that rejection of all membranes after hot-pressing treatment could reach more than 90%, while the original membrane exhibited only 75% rejection. This conclusion shows that hot-pressing process made the film more dense and fiber surface much more attached. Also, when the interval angle of adjacent membranes was smaller, the filtration efficiency was greater. And the results demonstrated that electrospun oriented membranes showed more efficiency in rejecting the 300 nm

-3μm particle, and still maintained the same permeate flux as that of the original membrane. The electrospun oriented fiber membranes also showed good overall mechanical performance.

4.3. Hydrophilic PP membrane

The hydrophilic modification of PP and the transfer mechanism of water have been studied by many researchers, but few research works about the production of hydrophilic modified PP ultra-thin fibers by melt electrospinning and hydrophilic performance of these fibers have been reported. In this study, pure ultra-fine PP fibers and PP blending fibers have been fabricated by the melt-differential-electrospinning self– designed apparatus In order to study the modification effect of the different hydrophilic modification methods. Different kinds of hydrophilic agents (Nano Calcium Carbonate，SDBS，Arstar-7008)as additives and (emulsifier OP-10，TF-629,TF-629C) as coating respectively were mixed with Polypropylene (PP) (melt flow rate of 2000 g/10min),and the mixtures spun under specific spinning conditions(spinning temperature: 230℃；top plate voltage : 30kv；bottom plate voltage : 65kv；distance between sprayer and top plate: 50mm；distance between top and bottom plates: 120mm).Experiments were done to determine Water absorption capacity, and Water delivery rate where mathematical equations have been applied to calculate the average for both. Fiber diameter and surface morphology of elecrospun fibers are examined by scanning electron microscopy (SEM). Image processing software (Image J 2X) is applied to calculate the average fiber diameters. The water contact angle of fibers is measured by a contact angle meter. Images of solid/liquid interface are captured by a charge-coupled device camera, and the average contact angle value is obtained by measuring the same sample at five different positions. Our results showed that the method of melt-differential-electrospinning can produce mass blending ultra-fine fibers with considerable production efficiency (effective output is about 9g/h) , and diameters of which mainly range from 2 to 6μm. In addition, after adding or coating with hydrophilic agents, the contact angles decrease in different extent and hydrophilicity enhanced. Adding additives alone Arstar-7008 has better effect in hydrophilic modification of PP than that of nano-Calcium Carbonate and analytic pure SDBS. Arstar-7008, composed of 60% PP and 40% additives, can dramatically enhance the hydrophilic performance of PP so that PP fibers can absorb and deliver water repeatedly and constantly. The average water absorption capacity was 12.30g/g, and the average water delivery rate was 1.69(g/min*g). The fibers produced by melt electrospinning have better texture. With comparison among several hydrophilic agents as coatings, TF-629 enhances the hydrophilic performance of PP fibers most. Coatings can easily infiltrate into water and wick fast and high, whereas this kind of modifier has poor sustainability, which means they can easily fall off or be soluble in water. When using additives and coatings.

5. Conclusions

From the experimental work done, we can conclude that the fibers or webs produced by the melt-differential-electrospinning, could be efficiently used in many environmental engineering applications, such as oil-spill cleanup , water treatment, and many other applications .

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