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Branched nanofibers for biodegradable facemasks by double bubble electrospinning

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Abstract:
World health organization (WHO) data shows that air pollution kills an estimated seven million people worldwide every year. A nanofiber based biodegradable facemask can keep breath from smoke and other particles suspended in the air. In this study, we propose branched polymeric nanofibers as a biodegradable material for air filters and facemasks. Fibers have been elecrospun using double bubble electrospinning technique. Biodegradable polymers, PVA and PVP were used in our experiment. Two tubes, each filled with one of the polymers, were supplied with air from the bottom to form bubbles of polymer solutions. DC 35-40 kV was used to deposit the fibers on an aluminum foil. Results show that the combination of polymers under specific conditions produced branched fibers with average nanofibers diameter of 495nm. FT-IR results indicate the new trends in the graph of composite nanofibers.

Keywords: polymeric nanofibers, electrospinning technique, Biodegradable polymers, aluminum foil

1.0. Introduction:

As compared to a microscopic level with the matter in the visible scale, there is minimal difference in the particles' properties. But when particles are formed with dimensions of 1–100 nm, the properties of the materials change strikingly. That is the scale where the behavior and attributes of particles are governed by so-called quantum effects. The material properties are scale-dependent, and so is every natural phenomenon [1,2]. Electrospun nanofibers have several advantages over the conventional fibers including high surface area to volume ratio, adaptable surface morphology, tailorable porosity and improved mechanical performance. So, it has become an area of interest for many industries involved in tissue engineering, filtration, drug delivery, energy storage, sensors, smart dressing, oil-water separation or hydrophilic/phobic surfaces [3–5]. Electrospinning is the simplest way to produce superfine fibers with diameters ranging from a few micrometers down to 10 nanometers by forcing polymer solutions or melts through a needle and collected on a surface with the help of an electric field [6,7]. Bubble electrospinning and bubbfil spinning are comparatively newer techniques for producing nanofibers with higher throughput [8,9].

With the ability to fabricate nanostructures from various types of raw materials, ranging from natural and synthetic polymers to composites (consisting of organic and inorganic components), an increasing number of scientists are attracted to this highly effective technique for the preparation of various nanostructures, which can find applications in almost every field. Electrospun nanofibers have also played a pivotal role in the area of biomaterials [7]. The importance of electrospun nanofibers in biomedical field can be determined from the fact that numerous articles are being published on a regular basis highlighting its importance in the area of biomedical engineering using biocompatible and biodegradable (natural or synthetic) polymers. Electrospun nanofibers scaffolds can be tailored in accordance with the purpose of their use. Such hybrid nanofibers scaffolds play an important role in providing a familiar environment to the cells, which ultimately results in their better attachment, proliferation, and differentiation [10].

A wide range of polymers can be used in bubble electrospinning. Poly (vinyl alcohol) (PVA); a water soluble, biodegradable and ecofriendly polymer which has been a source of interest in nanofibers production for many years [11]. PVA is prepared via polymerization of vinyl acetate monomers, and then alcoholysis [12]. It has a wide range of practical applications due to the excellent physical and chemical properties. Moreover, PVA molecular chain contains a large number of hydroxyl groups, which could be used to adsorb heavy metal ions in wastewater by hydrogen bonding and crosslinking [13].

On the other hand, poly (vinyl pyrrolidone) (PVP) is an important synthetic polymer. It has been used as a film forming agent, viscosity enhancement agent, lubricator and in hair sprays, mousse, gels, lotions and solutions. It has found a widespread use in cosmetic market as skin care products, hair-drying reagents, shampoos, eye makeup, lipsticks, deodorants, sunscreen products and dentifrices due to its low chemical toxicity and biocompatibility. It is one of the most important materials used in detergents, paints, electronics and biological engineering [14].

The significant advantages of dual polymer spinning are that the properties of the final product can be tailored to the requirements of the applications, which is hard to achieve alone by one polymer. However, the manifestation of superior properties depends upon the spinning conditions of both polymers. Blending can, however, have profound and sometimes unexpected effects on thermal stability, which cannot simply be predicted on the basis of behavior of the components and their relative proportions [15].

In this study, PVA/PVP composite branched nanofibers were produced as promising materials for biodegradable facemasks [16,17]. Double bubble electrospinning technique was used in order to synthesize nanofibers due to the fact that this technique of electrospinning is relatively cost-effective and an easy one for nanofiber fabrication.

2.0. Experimental method

2.1. Materials

Poly vinyl pyrrolidone (PVP, Mw 130,000 g/mol) and polyvinyl alcohol (PVA, Mw 80,000 g/mol) were purchased from Beijing Lark Branch Co. Ltd. (Beijing, China) and Shanghai Aladdin Biochemical Technology Co., Ltd., (Shanghai, China), respectively. The solvents; pure alcohol and distilled water were obtained from Shanghai Chemical Co., Ltd., (Shanghai, China) and Soochow University’s lab, respectively. All the chemicals were used as received without further purification. The PVP and PVA polymers were dissolved into a solvent mixture of pure alcohol/ distilled water with the weight ratio of 9:1 and distilled water, respectively. The PVP solution concentration was adjusted to 15 wt % and mechanically stirred for 2 hours at room temperature. The PVA concentration was adjusted to 9 wt% and mixture was stirred in water bath for 2 hours at 80^{o}C temperature. PVA solution was used after cooling it to room temperature.

2.2. Preparation of PVA/PVP nanofibers

A schematic of the double bubble electrospinning apparatus is shown in Figure 1. It consists of two solution tubes, both solutions are positively charged and a grounded collector is placed on the top. An air injection tube attached to the bottom of both solutions to provide air from the air pump for bubbles formation [18].

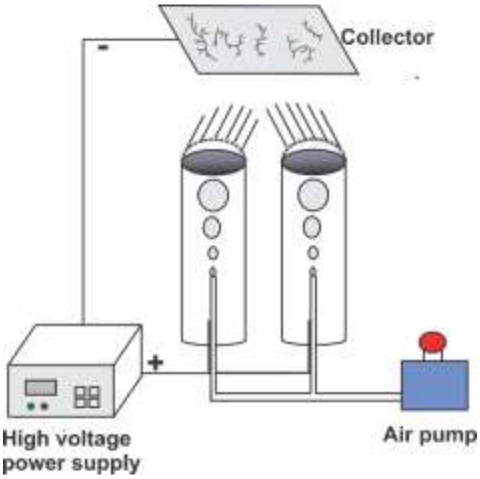

Figure 1: Schematic diagram of double bubble electrospinning for branched fibers

In bubble formation process, the air was firstly supplied to each solution tube with uniform rate using an air pump. PVA and PVP spinning solutions were transported to separate tubes using a metering pump. Bubbles formed on the head of the tube when the air from the air chamber was pressed upwards through the spinning solution. Both tubes containing spinning solutions were connected to the positive polarity of the high-voltage DC power supply. The collector plate was set above the spinning unit at a distance of 18cm and connected to the ground terminal of the power supply. When the charged bubbles formed on the head of tubes, they ruptured into multi-jets and then were stretched by the electric field into nanofibers. These nanofibers were collected on the aluminum foil [9].

The internal diameter of each tube was 1.4cm. The distance between positively charged bubbles and grounded collector was adjusted to 18cm. In order to form a uniform web of fibers, bubbles formation frequency was tried to match by adjusting the air pressure separately. An applied voltage of 35–40 kV, spinning solution flow rate of 16–48 mL/h and airflow rate of 1000–1400 mL/min were used in the process of electrospinning the nanofibers web.

2.3. Characterization

The morphology of the samples was observed using a scanning electron microscope (SEM) (Hitachi S-4800, Hitachi, Tokyo, Japan). All the samples were sputter coated with gold using an E-1045 (Hitachi, Tokyo, Japan) for 90s before observing. The fiber diameters were measured using the image processing software, ImageJ (Image Pro-Express, Version 5.0.1.26, Media Cybernetics Inc.), which is a public domain Java image processing program.
FTIR spectra of nanofiber membranes (NFMs) were obtained on a Fourier transform infrared (FTIR) spectroscopy (Nicolet5700, Thermo Nicolet Company, Waltham, MA, USA) with the wave number ranging from 500 to 4000 cm^{-1}.

3.0. Results and Discussion

3.1. Spinning Mechanism

In spinning process after applying the voltage, the bubbles formed on the top of both tubes experienced an electric field force, air pressure inside and outside of the bubble and the surface tension. When the electric field force overcomes the surface tension, polymer bubbles deform and eventually ruptures to from multiple jets of nanofibers. Then these nanofibers of two different polymers are collected on the same collector.
In bubble electrospinning, multiple fragments of various forms are formed from a broken bubble. The interaction of fast moving fragments give rise to the branched nanofibers. Consider a fragment of a ruptured bubble as illustrated in Figure 2, we suppose the width of the fragment is *L* and thickness is *h.* This thin film fragment has a strong trend to curl and become a cylindrical fiber with radius *R* and circumference *L* due to the calculus of variation [19].

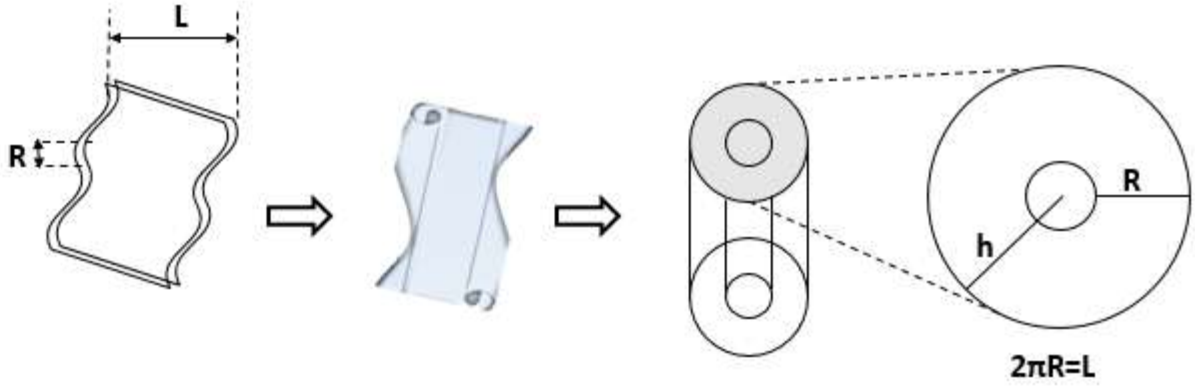

Figure 2: Tendency of polymer debris to form cylindrical fiber

$$R = \frac{L}{2\pi} \quad (1)$$

$$r = R - h \quad (2)$$

When R - h = 0, a cylindrical fiber is formed due to the natural tendency of a film to curl. Fragments of different sizes originating from two polymer bubbles could interact while moving towards the collector. Intermingling of fragments formed branched fibers due to the miscible nature of both polymers.

3.2. Morphology Characterization

The morphology of the PVA/PVP fibers produced via double bubble electrospinning was examined using SEM micrographs. Figure 3 shows the SEM image of PVA/PVP branched nanofibers. There seen elongated and bifurcated electrospun nanofibers with average diameter of 495nm. Standard deviation was calculated as 265nm. Higher value of standard deviation is due to the electrospinning of two polymers having different rheological properties such as, conductivity, viscosity and surface tension. At specified spinning parameters, both solutions have different spinning rates and quality of fibers. Therefore, branched fibers with hierarchical structure have achieved.

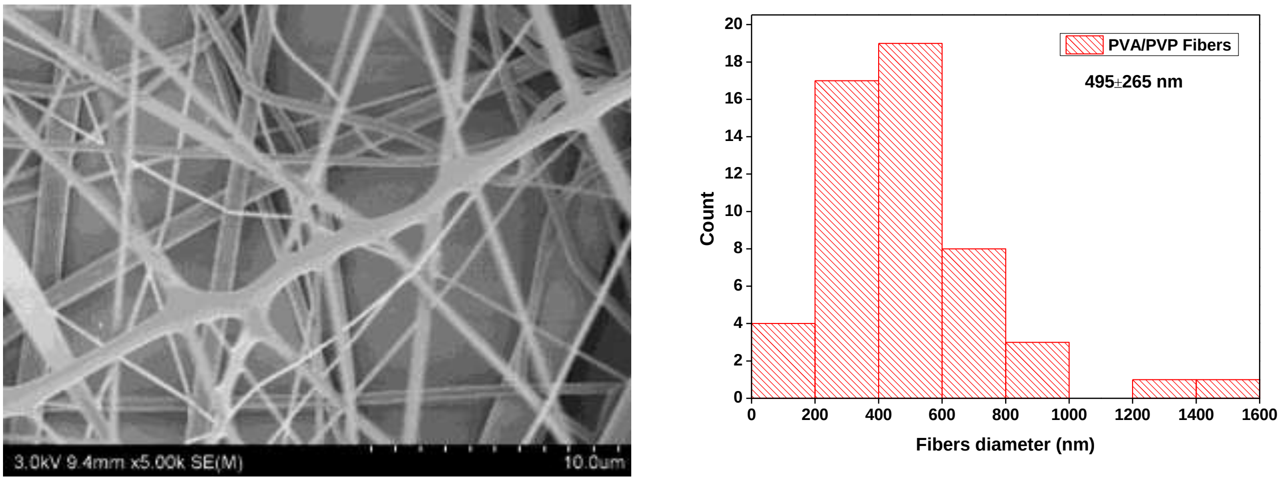

Figure 3: Branched nanofibers and their diameter distribution

Fibers produced from double bubble electro spinning are cylindrical in shape and branched in structure. When bubble film ruptured, it got stretched due to the electrical force and formed a cylindrical fiber before reaching to the collector. Meanwhile, ruptured films originating from bubbles had a strong trend to attract nearby tiny fragments due to the geometric potential [20–23]. As the fragments are tiny and have high surface to volume ratio, their surface induced force is also high. Combination of such polymers under specific conditions could give rise to the branched structure. This type of hierarchal structure is highly useful as a filtration media such as facemasks. Moreover, biodegradable nature of polymers make it environment friendly.

4.0. Fourier-Transform Infrared (FTIR) Spectroscopy

Figure 4 shows FT-IR transmission spectra of the PVP, PVA and PVP/PVA mesh fibers recorded at room temperature in the region 4000–500 cm^{-1}. The spectra exhibit bands characteristic of stretching and bending vibrations of the fibers. FT-IR transmission bands positions and the assignments of all prepared samples are listed in Table 1. From the spectra, for pure PVA, the broad band at about 3295 cm^{-1} is assigned to O–H stretching vibration of hydroxyl group. The band corresponding to CH$_2$ asymmetric stretching vibration occurs at about 2937 cm^{-1}. The band at about 1091 cm^{-1} corresponds to C–O stretching of acetyl groups present on the PVA backbone. The vibrational band at about 1632 cm^{-1} corresponds to C=O stretching of PVP/PVA fibers [15].

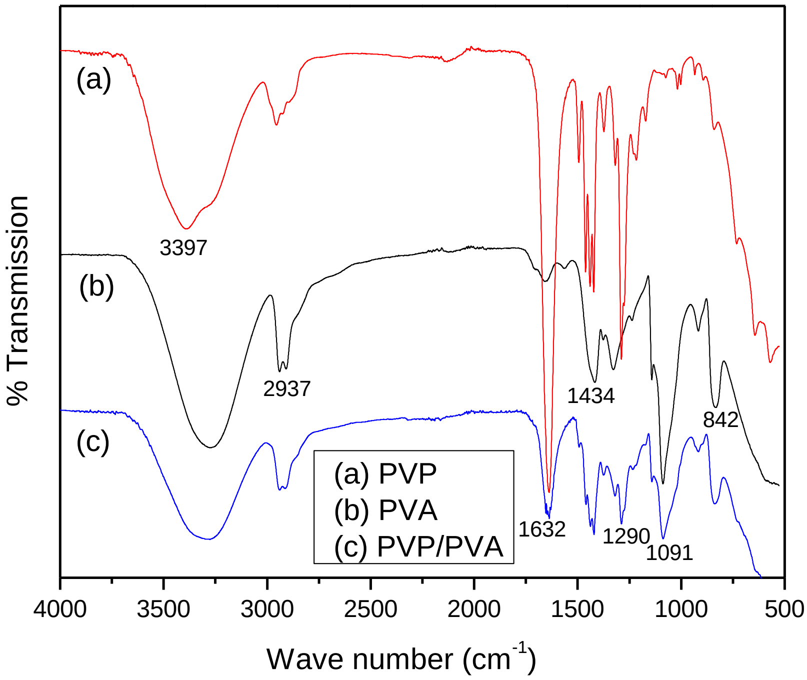

Figure 4: FT-IR Transmission spectra of PVA fiber, PVP fiber and PVP/PVA mesh fibers

On the other hand, for pure PVP, small transmission band at about 1500 cm^{-1} is assigned to the characteristic vibration of C=N (pyridine ring) [24].

Table 1: FT-IR Transmission bands positions and their assignments [24–26].

Vibrational frequency (cm^{-1})	Band assignment
3397	O–H stretching
2937	CH_2 asymmetric stretching
1632	C=O stretching
1434	C=C (pyridine ring)
1290	C–H wagging
1091	C–O stretching
842	Out-of-plane rings C–H bending

In case of PVA/PVP, FT-IR spectra shows shifts in some bands and change in the intensities of other bands comparing with pure films. This indicates the considerable interaction between the polymers.

5.0. Conclusion

In this study, a novel method has been described for the production of biodegradable branched composite nanofibers web. Two polymers, PVA and PVP, were electrospun simultaneously by double bubble electrospinning technique. Branch-like structure of nanofibers was achieved at 35-40kV DC current. Average diameter of fibers was 495nm with 265nm standard deviation. FT-IR studies were characterized by certain bands that have been assigned to PVP and PVA fibers, and indicated the presence of both polymers. Such type of fiber-web can be used in selective filtration such as facemasks, photochemical and thermal devices due to the combination of unique polymers at nanoscale. This method can be applied to different polymer combinations without complexity.

6.0. References

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