

PREPARATION AND CHARACTERIZATION OF ELECTROSPUN WOOL KERATIN/POLYETHYLENE OXIDE NANOFIBERS FOR AIR FILTRATION APPLICATIONS

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In this work, the wool keratin/polyethylene oxide (PEO) nanofibers used for air filtration were prepared and characterized. Keratin proteins were first extracted from wool fibers by sulphitolysis, and then blended with PEO to improve the processability of keratin. Keratin/PEO nanofibers were produced by the electrospinning of the blend aqueous solutions. The rheological and conductive characteristics of the keratin/PEO blend solutions were studied, and correlated with the morphological and structural properties of the electrospun nanofiber membranes. Furthermore, the keratin/PEO nanofiber membranes were composited with polypropylene nonwoven fabric with the aim of being used as filtration materials. The observations by scanning electron microscopy showed that the morphological structures and diameter distributions of the keratin/PEO nanofibers were affected by the content of keratin. The filtration tests revealed that the filtration efficiency of the nanofiber nonwoven composites was greatly higher than that of polypropylene nonwoven fabric, and increased with the prolongation of electrospinning time. This study points out that keratin/PEO nanofibers can be used as promising materials for air filtration.

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1. Introduction

Keratin is a structural protein of ectodermal cells and presents in feathers, wool, hair, nails and so on [1]. Keratin has good skin-friendly performance, and can not cause skin allergy because its basic component unit is amino acids. Keratin has good biocompatibility and degradability [2,3], and it can be used in biological fields such as tissue engineering and wound materials [4,5]. In addition, keratin materials also can adsorb toxic substances, such as heavy metal ions, formaldehyde and other hazardous volatile organic compounds [6,7], so their possible applications can be foreseen in water purification and air cleaning [8]. Thus, keratin materials are expected to be applicable for a high-performance protective mask, which effectively intercepts particulate matter less than 2.5 microns (PM 2.5) and viruses that exist in the air.

The current shortage of keratin is one of the most serious problems. Keratin materials, which exist on earth, have been mostly exploited, so the existing keratin materials can no longer meet the current and future human needs. Moreover, the waste of the old products and inferior materials with abundant keratin is a direct threat to the natural environment [9]. Therefore, the recovery and reasonable utilization of keratin are two important ways to develop new keratin products, and have become a hot research topic in recent years. Current research on wool keratin is mainly focused on the following four areas: extraction method [10,11], fiber forming [12], film forming [13], and biological applications [14]. The intramolecular disulfide bonds of keratin make the peptide chains to form a three-dimensional network structure, so keratin is difficult to dissolve [3,15]. Mechanical method, oxidation, acid-base method, metal salt method, ionic liquid dissolution and reduction are six different ways to extract keratin [16–18], and their common purpose is to destroy the disulfide bonds to make keratin dissolve in water [19]. Keratin obtained

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by most of these approaches has the following characteristics: poor structural stability, relatively low molecular weight, and low extraction rate. Out of these approaches, the reduction method is optimal because the obtained keratin solution is more stable, and the resulting protein has relatively higher molecular weight. In previous researches, this method was often used to extract keratin powder.

Electrostatic spinning is an efficient technology to manufacture the nanofibers of many polymers [20–23]. Under a high-voltage electrostatic field, the melt or liquid of polymers with electrical charge is injected, stretched and split, and ultimately nanofibers are formed on metal receiving board or drum [24]. The resulting nanofibers have the characteristics of small diameter, high specific surface area, and high porosity [25]. The keratin composite nanofibers prepared by electrospinning have the properties of general nanofibers as well as the adsorption property of keratin. Therefore, keratin composite nanofiber membranes can effectively filter small substances in the air. The filtration efficiency of nanofibers is much better than that of conventional fibers. However, nanofiber membranes are easily broken because of their low strength, and often need to be combined with other materials for making filter materials. Nanofiber membranes are worth to be considered as air filter materials in conjunction with a substrate, such as non-woven material and woven fabric. Wang et al. prepared polyimide nanofiber membrane/carbon woven fabric composite, and found that the maximum filtration efficiency of the nanocomposite non-woven material containing the nanofiber with an average diameter of 190 nm reached 99.99% for PM 2.5, while the maximum pressure drop was only 251.86 Pa after continuously testing for 25 min under a constant flow rate of 20 L/min [26]. This suggests that nanofiber membranes have a good prospect in the field of air filtration.

Keratin is not suitable for spinning alone due to its low viscosity, and it often needs to prepare a spinning solution in combination with a high viscosity polymer. Polyethylene oxide (PEO), a water-soluble polymer, has crystalline, thermoplastic, non-toxic characteristics. Because the aqueous solution of PEO is a pseudoplastic liquid and has excellent rheological properties, it can be often mixed with the materials having low viscosity to prepare composite nanofibers, in order to improve their processability spinnability. Keratin/PEO blend materials have been studied by some researchers. Tonin et al. [27] extracted wool keratin by bisulfite, urea and sodium dodecyl sulfate (SDS), and prepared keratin/PEO films by casting. They found that wool keratin showed partial degradation when the extract was performed at 100 °C, whereas keratin extracted at 65 °C was well preserved, and that wool keratin reduced the crystallization temperature, melting point and related enthalpy of PEO. Aluigi et al. [24] and Liu et al. [28] prepared keratin/PEO blend nanofibers, and investigated the properties of the nanofibers. Fan and co-workers employed two-step cross-linking process to prepare water insoluble high-content keratin/PEO nanofibers with high-content keratin for biomedical utilization [22]. However, these studies are not involved in the filtration properties of nanofiber membranes.

This work not only investigated the preparation and performance of keratin/polyethylene oxide (PEO) aqueous solution and keratin/PEO nanofiber membranes obtained by the electrostatic spinning technology, but also discussed the air filtration properties of the nanocomposites prepared using keratin/PEO nanofiber membranes in combination with polypropylene nonwoven fabric.

2. Experimental

2.1. Materials

Wool fiber was purchased by a local wool textile factory. In order to remove the fatty matters on wool surface, the fiber samples were first subjected to soxhlet extraction of petroleum ether [29], and then thoroughly rinsed with deionized water. The purified samples were conditioned at 20 °C and 65% RH for 48 h. Polypropylene nonwoven fabric (weight per square meter 20 g/m²) was commercially obtained.

Polyethylene oxide (PEO) with an average molecular weight of 300,000 was purchased from Sigma-Aldrich (Shanghai) Trading Co. Ltd., China. Sodium sulfide, urea and sodium dodecyl sulfate (SDS) were of analytical reagent grade, and purchased from Sinopharm Chemical Reagent Co. Ltd., China. Dialysis membrane with a molecular weight cutoff of 8000–14000 was

bought from Shanghai Yuanye Bio-Technology Co. Ltd., China.

2.2. Preparation of keratin powder

Keratin was obtained by means of dissolving degreased wool in the solvent consisting of sodium sulfide, urea and SDS according to our previously reported method [30]. Sodium sulfide (1.9 g), urea (42 g) and SDS (0.8 g) were put into a beaker, and then deionized water was added to form 100 ml solution. The prepared solution was stirred in a water bath oscillator at 35 °C until the solutes were totally dissolved. Afterwards, 5 g of degreased wool samples which were cut into small snippets were dissolved in the aforementioned solution at 35 °C for 14 h. After the resulting solution was filtered, the filtrate solution was dialyzed against deionized water in a dialysis membrane at room temperature for 3 days. After dialysis, the dialyzate was poured into a beaker and placed in an oven at 40 °C to concentrate into a smaller volume solution. The concentrated liquid was poured into 50 ml centrifuge tube and placed in the refrigerator at -38 °C until it completely solidified into solid. Then, the solid was placed in a -40 °C freeze dryer for four days and three nights. Finally, the bulky wool keratin powder was obtained.

2.3. Preparation and characterization of keratin/PEO aqueous solution

Wool keratin and PEO were respectively dissolved in aqueous solution at room temperature. Subsequently, the 8% wt blend solutions with the keratin/PEO weight ratios of 10/90, 20/80, 30/70, 40/60, 50/50 were prepared. The rheological performance of the keratin/PEO aqueous solutions was measured by the AR2000 rheometer (TA Instruments, USA) with cone-plate geometry (40 mm diameter and 2° angle) at 25°C. The shear rate was logarithmically increased from 0.1 to 1000 s⁻¹ at 25 °C. The conductivity of the keratin/PEO aqueous solutions was measured by the DDS-11A electric conductivity meter (Shanghai INESA Scientific Instrument Co. Ltd., China).

2.4. Preparation and characterization of keratin/PEO nanofiber membrane

The keratin/PEO aqueous solution was poured into a syringe linked to a capillary pipe with a metallic tip, and then clamped on the top of the constant flow pump. The positive electrode on the high voltage electrostatic generator was connected with the metallic tip of capillary pipe, and the negative electrode was connected with the metal plate which was covered with the aluminum foil paper for receiving the keratin/PEO nanofiber membrane. The experimental parameters were set as follows: spinning voltage 14 kV, receiving distance 24 cm, and spinning flow 0.2 ml/h.

The morphologies of keratin/PEO nanofiber membranes were observed using a Hitachi S-4800 silence emission scanning electron microscopy (SEM). Before observation, small pieces of keratin/PEO nanofiber membranes were coated by gold. The diameter of each nanofiber sample was measured by the Image-pro 5.0 image analysis software, and the average value was calculated from randomly selected 100 measurements. The Fourier transform infrared (FT-IR) spectra of keratin/PEO nanofiber membranes were measured by a Nicolet 5700 FT-IR spectrometer (Thermo Fisher Scientific Inc., USA). Before analysis, the membranes were cut into powders which were mixed with potassium bromide, and pressed into about 1 mm thick slice.

2.5. Preparation and filtration properties of nanofiber nonwoven composites

The 8% wt keratin aqueous solution was blended with 8% wt PEO aqueous solution to prepare the 20/80 keratin/PEO aqueous solution as a spinning solution. The spinning parameters were set as follows: spinning voltage 14 kV, receiving distance 16 cm, and spinning flow 0.2 ml/h. Nanofiber membranes were spun on the polypropylene nonwoven fabric. The nanofiber nonwoven composites consisting of keratin/PEO nanofiber membrane and polypropylene nonwoven fabric were used as filtration materials. The nanocomposite nonwovens having different thickness and filtration properties were obtained by adjusting different spinning times.

Taking the test convenience of filtration performance and the potential application of nanofiber filtration materials into consideration, the three layer filtration material was prepared by covering the aforementioned two layer nonwoven composite with a polypropylene nonwoven, and used for filtration test. The filtration performance of the three layer nanocomposite nonwovens was measured by the 8130 automatic filter tester. According to GB 19083-2010 "Technical

requirements for protective face mask for medical use”, the filtration efficiency of masks was measured in the conditions of a flow rate of 85 L/min, and a sodium chloride aerosol particle size of 75 nm. Filtration efficiency and pressure drop are two important factors to characterize the filtration properties of materials [31]. The filtration efficiency refers to a percent ratio of the airborne particles which can not penetrate through filter materials to total airborne particles. The pressure drop directly reflects the resistance of the airflow through filter materials in a specified condition.

3. Results and discussion

3.1. Properties of keratin/PEO aqueous solutions

The rheological behaviors of the keratin/PEO aqueous solutions with different ratios of keratin/PEO are shown in Fig. 1. Except the pure keratin aqueous solution, all the solutions behaved as typical non-Newtonian, shear-thinning fluids. In the case of the pure keratin aqueous solution, the rheological curve had no obvious change with increasing shear rate, and the viscosity was nearly zero. This is because the structure of keratin is relatively loose, and there are less force and less bound nodes between its molecules, resulting in the less shear rate dependence of the viscosity of its solution. However, at the beginning of the increase of shear rate, the rheological curve of pure PEO aqueous solution showed a relatively gentle downward trend, and it displayed obvious shear thinning phenomenon with further increasing shear rate. This is because with the increase of shear rate, the failure rate of the large molecular entanglement is higher than the rate of reconstruction, and the interaction between the molecules decreases, leading to the decrease of the viscosity [32]. The rheological curves of keratin/PEO aqueous solutions were between those of pure keratin and PEO solutions. As a whole, the rheological curves of the keratin/PEO solutions with high keratin content were closer to that of pure keratin aqueous solution. The blend solutions with a higher proportion of PEO showed strong characteristics of non-Newtonian fluid, and enhanced pseudoplastic nature. Therefore, the rheological properties of the blend solutions depended on the proportion of keratin and PEO components. Thus, it can be said that the addition of PEO improves the rheological properties of keratin solution.

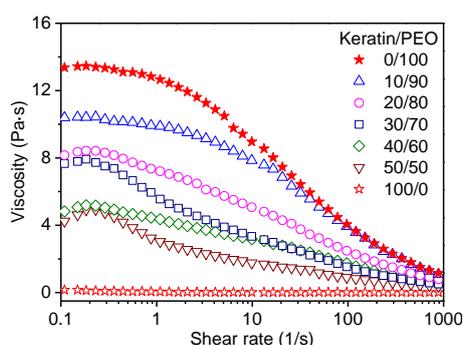


Fig. 1. Rheological behaviors of the keratin/PEO aqueous solutions

The viscosity is an important factor for the electrospinning of keratin/PEO blend solution and fiber formation. Fig. 2 shows the zero shear viscosity and conductivity of keratin/PEO aqueous solutions. The zero shear viscosity was estimated from the rheological curves in Fig. 1. The conductivity of the keratin/PEO solutions were between that of pure keratin and PEO aqueous solutions. With increasing keratin proportion, the conductivity of the blend solution increased due to the fact that the keratin molecules contain a large number of polar amino acids [24]. The zero shear viscosity of the blend solution decreased with increasing keratin content. In the electrospinning process, the solution having appropriate conductivity and viscosity is propitious to the formation of fiber jet, and the drawing of nanofibers under the action of electric field force [33]. Therefore, in the following study PEO was added to keratin aqueous solution to improve the

viscosity and electrospinning ability of keratin solution.

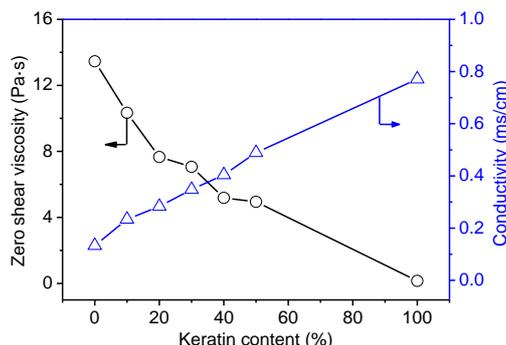


Fig. 2. Zero-shear viscosity and conductivity of the keratin /PEO aqueous solutions as a function of keratin content

3.2. Nanofiber morphologies and diameter distributions

Fig. 3 shows the SEM images and diameter distributions of the keratin/PEO nanofibers. The keratin/PEO nanofibers with 10/90, 20/80 and 30/70 keratin/PEO ratios had a small quantity of tiniest beads, and were relatively smooth and continuous. The 40/60 and 50/50 keratin/PEO nanofibers had a large number of beads and poor continuity. With the increase of keratin content, the diameter of the blend nanofibers became smaller, and the relative variation coefficients (CV) showed an increment trend. In the case of high keratin content, the formation of smaller nanofibers is due to the low viscosity of the keratin/PEO blend solution. Furthermore, the low viscosity of the blend solution leads to the fact that the droplet is hard to form Taylor cone in the needle, resulting in incomplete drawing and the formation of a large number of beads on the receiver board. Thus, the uniformity of nanofibers becomes poor.

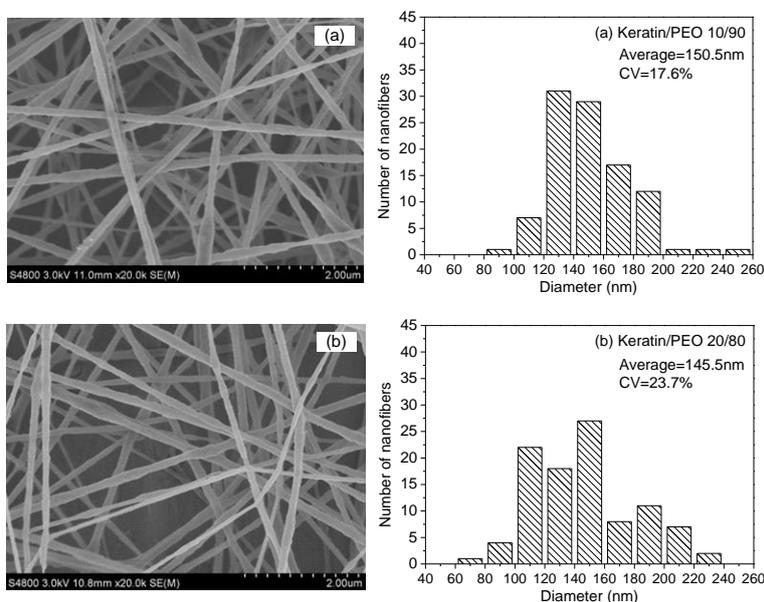


Fig. 3.1 SEM images and diameter distributions of the keratin/PEO nanofibers.
a) keratin/PEO 10/90 b) keratin/PEO 20/80

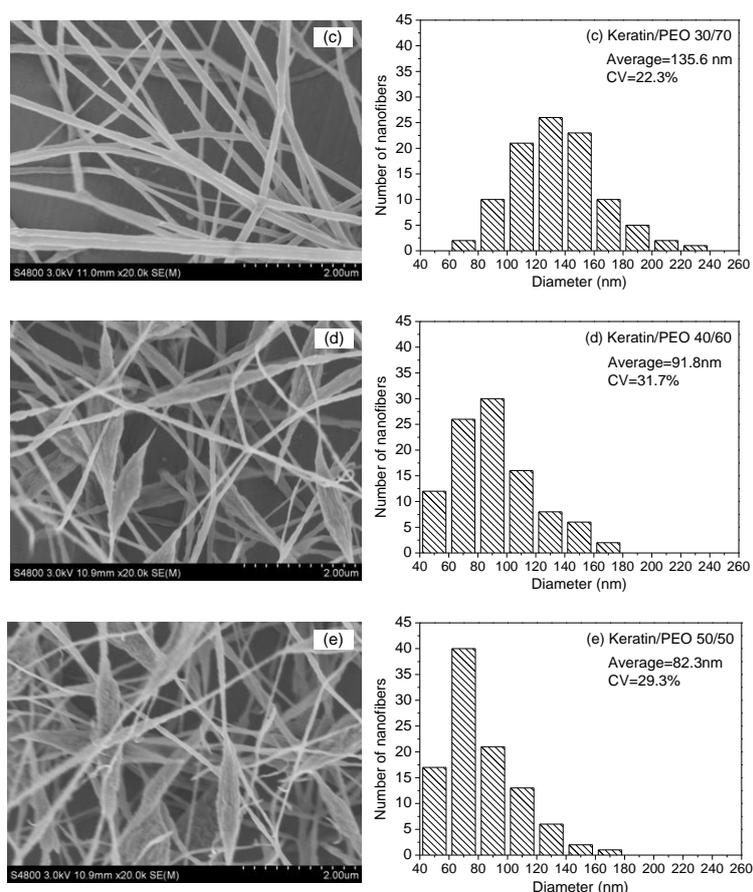


Fig. 3.2 SEM images and diameter distributions of the keratin/PEO nanofibers.
 c) keratin/PEO 30/70 d) keratin/PEO 40/60 e) keratin/PEO 50/50

3.3. FT-IR analysis of keratin/PEO nanofibers

Fig. 4 shows the FT-IR spectra of keratin powder, PEO powder and keratin/PEO nanofibers. Pure keratin had characteristic peaks at 3428, 3137, 1647, 1542, 1395, 1234, and 1072 cm^{-1} . The peak at 3428 cm^{-1} is assigned to the N-H stretching vibration. The absorption peaks at 3137 and 1395 cm^{-1} belong to the stretching and bending vibrations of C-H, respectively. The absorption bands at 1647, 1542 and 1234 are attributed to the amide I (stretching vibration of C=O), amide II (bending vibration of C-N) and amide III (stretching vibration of C-N) of keratin protein peptides, respectively. The weaker absorption peak at 1072 cm^{-1} is assigned to the stretching vibration of S-O [27], which is caused the breakage of the disulfide bond during the wool keratin extraction process. The FT-IR spectrum of pure PEO powder showed characteristic absorptions at 3421, 3153, 1400, and 1103 cm^{-1} . The peak at 3421 cm^{-1} is caused by the hydrogen bonding between the hydrogen and oxygen in the hydroxyl groups of PEO. The bands at 3153 and 1400 cm^{-1} are attributed to the stretching vibration and bending vibration of C-H, respectively. The week peak at 1103 cm^{-1} is assigned to the stretching vibration of C-O-C.

Fig. 4 shows that as the content of PEO in the blends increased, the bands of amide II at 1535 cm^{-1} and amide III at 1223 cm^{-1} as well as the stretching vibration of S-O at 1030 cm^{-1} gradually disappeared. However, the peak of amide I shifted to a lower wavenumber, and the C-O-C absorption peak of PEO became sharper. It is worth noting that as the PEO content increased, the absorption peak of keratin at about 3428 cm^{-1} also shifted to a lower wavenumber and became much broader because of the formation of hydrogen bonding between keratin and PEO molecules. Additionally, with the increase of the PEO content, the structure of keratin/PEO nanofiber membranes gradually resembled the characteristics of PEO.

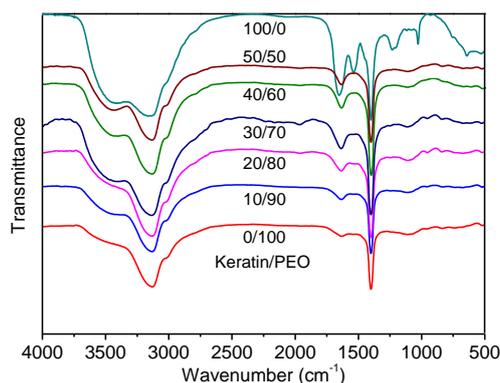


Fig. 4. FT-IR spectra of keratin powder, PEO and the keratin/PEO nanofibers obtained using various ratios of keratin to PEO

3.4. Filtration properties of nanofiber nonwoven composites

The filtration properties of filtration materials are associated with their specific surface area, porosity, fiber diameter, and filter thickness. The nanofiber membrane prepared by electrospinning is composed of fibers and pores, and its pores can effectively intercept the particles whose size is larger than its diameter, and capture particles by virtue of adsorption function. Fig. 5 shows the surface morphologies of the keratin/PEO nanofiber membrane inserted between two polypropylene nonwovens before and after the filtration test. After filtration, a large number of sodium chloride particles distributed on the membrane surface, revealing that the keratin/PEO nanofiber can be used as a filtration membrane material.

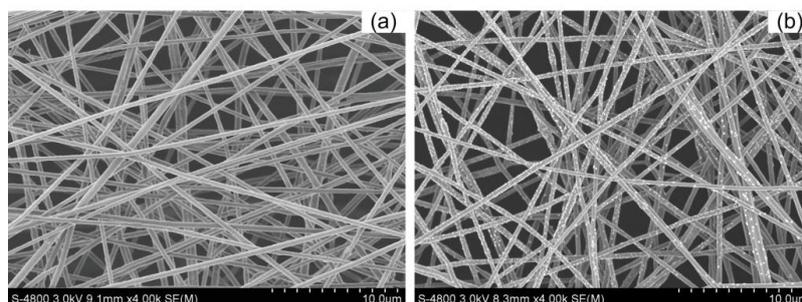


Fig. 5. SEM images of the keratin/PEO nanofiber membrane inserted between two polypropylene nonwovens before and after the filtration test
a) before the filtration test b) after the filtration test

In the present study, the thickness and filtration properties of the keratin/PEO nanofiber membrane inserted between two polypropylene nonwovens were able to be adjusted by the spinning time. An extension of spinning time can increase the thickness of the nanofiber membrane, and reduce the size of the pores between the nanofibers, thus resulting in the improved filtration performance and the increased resistance of air flow through filtration materials. Fig. 6 shows the filtration efficiency and pressure drop of the nanocomposite nonwovens consisting of keratin/PEO nanofiber membrane and polypropylene nonwoven fabric. Two layers of polypropylene nonwoven fabric between which was not inserted by keratin/PEO nanofibers showed poor filtration efficiency at 2.5%, while the filtration efficiency reached 88% after the keratin/PEO nanofiber membrane was composited with them. Polypropylene nonwoven fabric is composed of the fibers with large diameter, and between these fibers there exist larger pores. As a result, particles can easily pass through the fabric, giving rise to low pressure drop and high penetration. However, the composition of polypropylene nonwoven fabric with the keratin/PEO nanofiber membrane can greatly reduce the pore size of the filtration material due to the small

diameter of nanofibers. Therefore, the filtration efficiency of the nanofiber nonwoven composites can be markedly enhanced in comparison with the original nonwoven fabric.

Fig. 6 demonstrates that with the prolongation of electrospinning time, the filtration efficiency of the nanofiber nonwoven composites increased, and meanwhile the pressure drop increased. Obviously, the filtration efficiency of the nanofiber nonwoven composites can be significantly improved by means of an increase in the thickness of the nanofiber membrane which is accompanied by increasing electrospinning time. Thus, it can be concluded that the nanofiber nonwoven composite with high filtration efficiency and appropriate pressure drop should be able to be fabricated by adjusted the diameter of nanofiber and the thickness of nanofiber membrane.

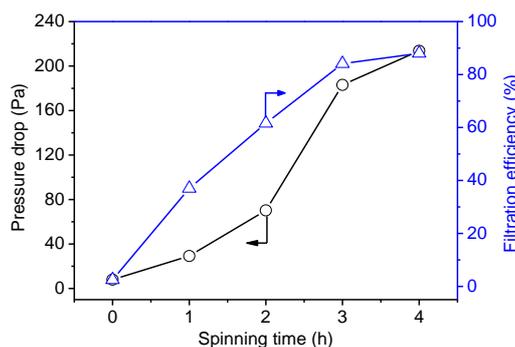


Fig. 6. Filtration efficiency of nanofiber nonwoven composites

4. Conclusions

In this study, keratin was successfully extracted from wool by sulphitolysis, and mixed with PEO to prepare the keratin/PEO aqueous solution used for electrospinning. The rheological, conductivity and spinning tests of the keratin/PEO aqueous solution indicated that the addition of PEO was able to improve the electrospinning ability of keratin. The SEM images and diameter distributions of keratin/PEO nanofibers showed that with increasing keratin content, the surface of keratin/PEO nanofibers was more prone to form beads, and the average diameter of nanofibers became smaller and uneven.

The results of FT-IR analyses indicated the existence of the interactions between keratin and PEO molecules. In the experiments of the composition of keratin/PEO nanofiber membrane with polypropylene nonwoven fabric, the filtration test showed that the filtration efficiency of the nanofiber nonwoven composites was higher than that of polypropylene nonwoven fabric, and increased with the extension of electrospinning time. The filtration efficiency of the composites was able to reach up to 88%. This study reveals that the nanofibrous nonwoven composites can be used as potential candidates for air filtration materials.

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