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Transport properties of electrospun nylon 6 nonwoven mats

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Abstract

In this work, we evaluate the physical properties of nylon 6 nonwoven mats produced from solutions with formic acid. Nonwoven electrospun mats from various solutions with different concentration are examined regarding their morphology, pore size, surface area, and gas transport properties. Each nonwoven mat with average fiber diameters from 90 to 500 nm was prepared under controlled electrospinning process parameters. From the results, it was observed that the fiber diameter was strongly affected by the polymer concentration (polymer viscosity). In additional the results showed that the pore size, Brunauer–Emmett–Teller (BET) surface area, and gas transport property of electrospun nylon 6 nonwoven mats were affected by the fiber diameter.

Keywords: Nylon 6; Electrospinning; Nanofibers; Gas transport; Pore size

1. Introduction

Nylon is the first commercialized synthetic fiber, which is used throughout the world such as wearing apparel, brush bristles, and carpet. Nylon has been widely used as an important engineering plastic and synthetic fiber because of its good mechanical properties [1,2]. They have been produced by traditional methods like melt, dry, and wet spinning and are available in staple, tow, monofilament, and multifilament form [1,3]. Fiber diameters produced by these methods range from 10 to 500 μm [4]. Recent work has been focused on trying to prepare ultra-fine fibers with excellent mechanical properties and smooth fibers like skin. In recent years electrospinning is received attention as a useful method to prepare fibers ranging from 50 to 500 nm in diameter [4–7]. The electrospinning process was introduced by Formhals [8] in 1934. In this technique the morphology of the fibers depends on the various parameters such as solution concentration, applied electric field strength, tip-to-collector distance, etc. [9–11]. Nonwoven mats composed of electrospun fibers with submicron diameter have a large surface area per unit mass and very small pore size, so are of interest in a wide variety of applications such as filtration, membrane, reinforcing fibers in composite materials, biomedical devices, and scaffold for tissue engineering [2,5,12,13]. The crystallinity of nanocomposites by electrospinning method was reported by Fong et al. using nylon 6 and nylon 6-montmorillonite [14].

In this work, we describe the interrelationship between the morphology and pore size, surface areas, and gas transport property of different nylon 6 solutions prepared from formic acid.

2. Experimental procedure

2.1. Preparation of polymer solution

Nylon 6 (Unitika Co., Japan) with relative viscosity of 3.2 was used as received. Various polymer solution

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concentration ranging from 15 to 30 wt.% were prepared by dissolving the polymer in formic acid (Showa Ltd., Japan). The electrospun nonwoven mats were dried in a vacuum oven at room temperature for five days to remove the residual solvent.

2.2. Polymer solution properties

Surface tension was measured by tensiometer (K10ST, Krűss Co., Germany) with the Wilhelmy plate method. The platinum plate was cleaned every time by butane torch. Solution viscosity and electric conductivity were determined by a rheometer (DV III, Brookfield Co., USA) and electric conductivity meter (CM-40G, TOA electronics Co., Japan) at 25 °C, respectively.

2.3. Electrospinning process

The experimental set-up used for electrospinning process is shown in Fig. 1. A variable high voltage power supply (CPS-60 K02v1, Chungpa EMT Co., South Korea) was used as a power supply. The polymer solution was placed in a 5 ml syringe to which a capillary tip of 1 mm diameter was attached. The positive electrode of a high voltage power supply is connected to a copper wire immersed in the polymer solution. The negative electrode was connected to a metallic collector wrapped with aluminum foil. In order to make nonwoven mats, the collector was moved in both rotation and traverse. The velocity of rotation and traverse were fixed at 2 and 30 m/min, respectively. The tip-to-collector distance and applied electric field strength were fixed at 5 cm and 15 kV, respectively.

2.4. Morphology

The morphology of electrospun nylon 6 nonwoven mats was observed by scanning electron microscopy (SEM, GSM-5900, JEOL Co., Japan) the diameter of electrospun nylon 6 fibers was measured with an image analyzer (Image-proplus, Media Cybernetics Co., USA).

2.5. Pore size analysis and BET surface area

The pore size and Brunauer–Emmett–Teller (BET) surface area was measured by using a porosimeter (autoporeIV9500, micromeritics Co., USA), and a surface area analyzer (ASAP 2010, micromeritics Co., USA), respectively. The pore size was measured by using mercury and the intrusion pressure range was within 0.1–60,000 psi. The samples were degassed overnight in vacuum at 150 °C and N_2 gas was used to BET surface area. The relative pressure range p/p_0 of 0.05–0.2 was used for calculating the BET surface area.

2.6. Gas permeability analysis

Gas permeabilities at steady state were determined by using a gas permeation analyzer (GPA-2001, B.S. Chem. Co. Ltd., South Korea) at 25 °C, using N_2 gas 0.5–2 atm. pressure. All specimens with area 14.7 cm^2 were prepared in the form of circle shape by die cutting from electrospun nylon 6 nonwoven mats.

3. Results and discussion

3.1. Properties of polymer solutions

It is well known that the morphology of electrospun fibers depends on various processing parameters and environmental conditions such as temperature and humidity [9,10,15,16]. The optimal electrospinning condition, the parameters such as polymer concentration, applied electric field strength, and tip-to-collector distance, etc. were examined. It was not easy to make nonwoven mats with some electrospinning conditions. First, the solution viscosity (it can be controlled by the polymer concentration for a given molar ratio) was too

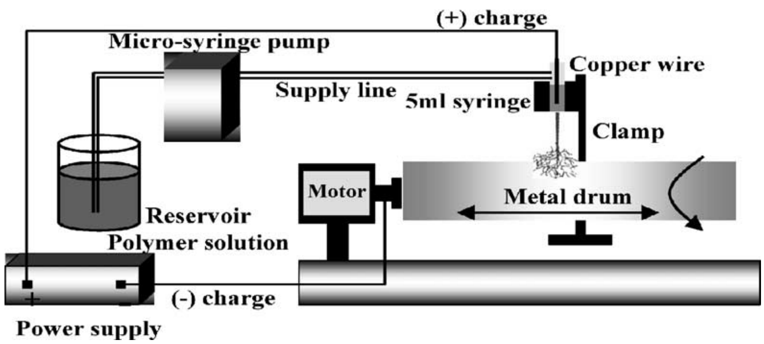

Fig. 1. Experimental set-up for the electrospinning device.

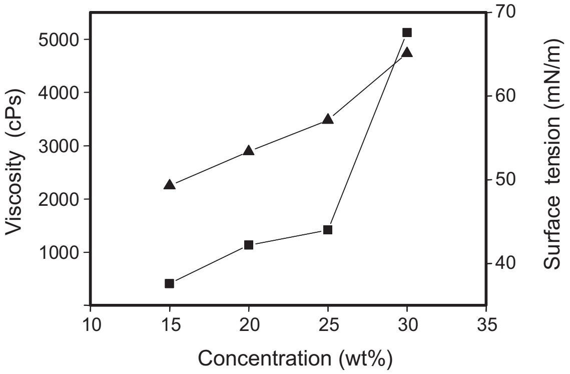

Fig. 2. Solution viscosity and surface tension as a function of polymer solution concentration (■, viscosity; ▲, surface tension).

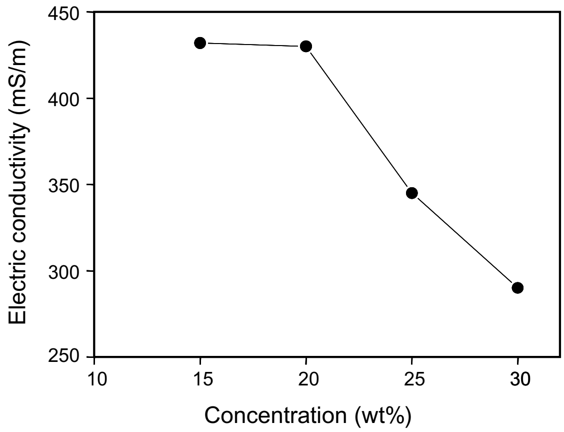

Fig. 3. Electric conductivity as a function of polymer solution concentration.

low to make nonwoven mats below 15 wt.%. So, many beads and drops were formed. Generally, the beads-on-a-string was regarded as "by-product" in electrospinning. It was observed in electrospun nylon 6 nonwoven mats prepared from below 15 wt.%. The viscosity, net charge density and surface tension of solution are key parameters of the formation of the beads-on-a-string. Second, the solvent was not almost evaporated due to shorter tip-to-collector distance. With the tip-to-collector distance increases, electrospinning did not facilitated to collecting at metallic collector because of a relatively low electric field formed between capillary tip and collector. From the results of preliminary experiments, electrospinning facilitated under following conditions: (i) tip-to-collector distance was 5 cm and (ii) the applied electric field strength was 15 kV.

The viscosity and surface tension of solutions depend on the polymer–solvent system used. Fig. 2 shows the viscosity and surface tension of solution dissolved in formic acid; they were 400–5550 cps and 49–68 mN/m, respectively. These values increased with increasing of concentration. Specifically, the viscosity increased from 1400 to 5100 cps for solution concentration from 25 to 30 wt.%.

The electric conductivity of polymer solutions was 200–430 mS/m (in Fig. 3). The electric conductivity was decreased with increase in concentration due to high dielectric constant (58.5, at 15 °C) and dipole moment (1.41 Debye) of formic acid [17].

3.2. Morphology of electrospun nonwoven mats

Figs. 4 and 5 show the macro- and micro-morphology of electrospun nonwoven mats, respectively. It has been observed that beads were disappeared and the fiber diameters were increased with increasing polymer concentration.

The beads can be removed as controlling the viscosity and electric conductivity of the polymer solution [9,11].

Fig. 6 indicates the distribution of electrospun fiber diameter. The fiber distribution is becoming gradually broader with increasing concentration. The average fiber diameter increases from 90 to 480 nm for 15–30 wt.% nylon 6 solution. The average fiber diameters have a similar tendency to viscosity and surface tension. Thus the polymer concentration has a significant effect on the final diameter of electrospun nylon 6 fiber.

3.3. Pore size and BET surface area of electrospun nonwoven mats

Electrospun nonwoven mats composed of submicrometer size fibers have high porosity and very small pore size. Generally, porosity can be controlled from nearly nonporous polymer coating, to very porous [13].

The porosity (determined by mercury porosimetry) depends on fiber diameter and pore size. Mercury porosimetry is the most popular method adopted for the characterization of relatively large pores, in particular macropores. Mercury intrusion measurements are extremely simple in principle, although a number of experimental complications need to be considered [18]. In the usual procedure, the small specimens were dried to empty the pores from any existing fluid. The samples were then weighed, transferred to a chamber, which were then evacuated, and mercury was introduced to surround the specimen [3,19,20].

Fig. 7 shows the pore size distribution of electrospun nylon 6 nonwoven mats as a function of polymer concentration. The pore site shifted toward large values with increasing polymer concentration, indicating that the pore size depends on the fiber diameter. The average

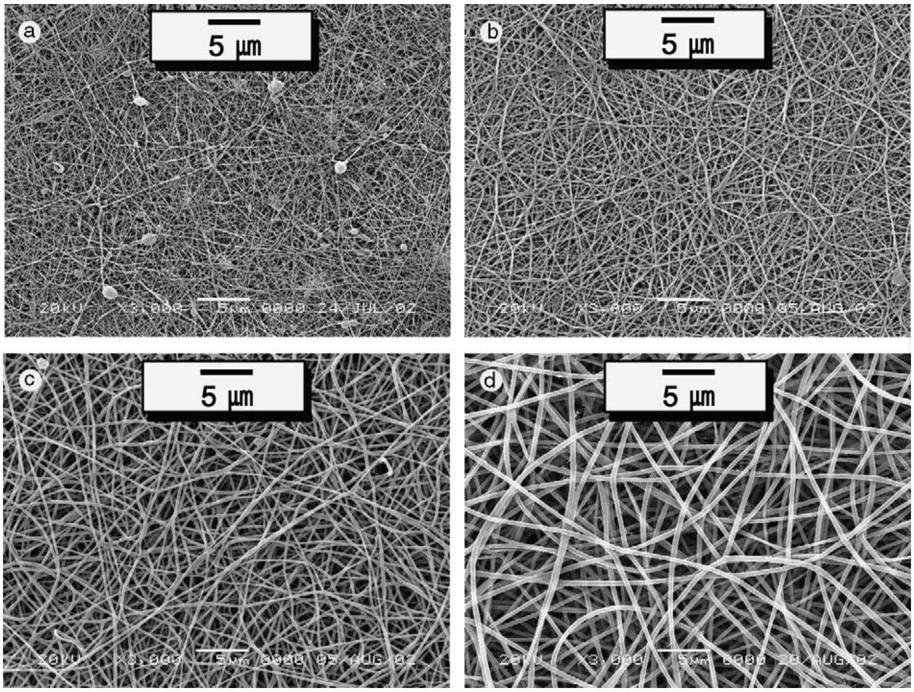

Fig. 4. Macro-SEM photos of electrospun nylon 6 nonwoven mats as a function of concentration. Solution concentrations were (a) 15, (b) 20, (c) 25, and (d) 30 wt.%. The applied electric field and tip-to-collector distance were 15 kV and 5 cm, respectively.

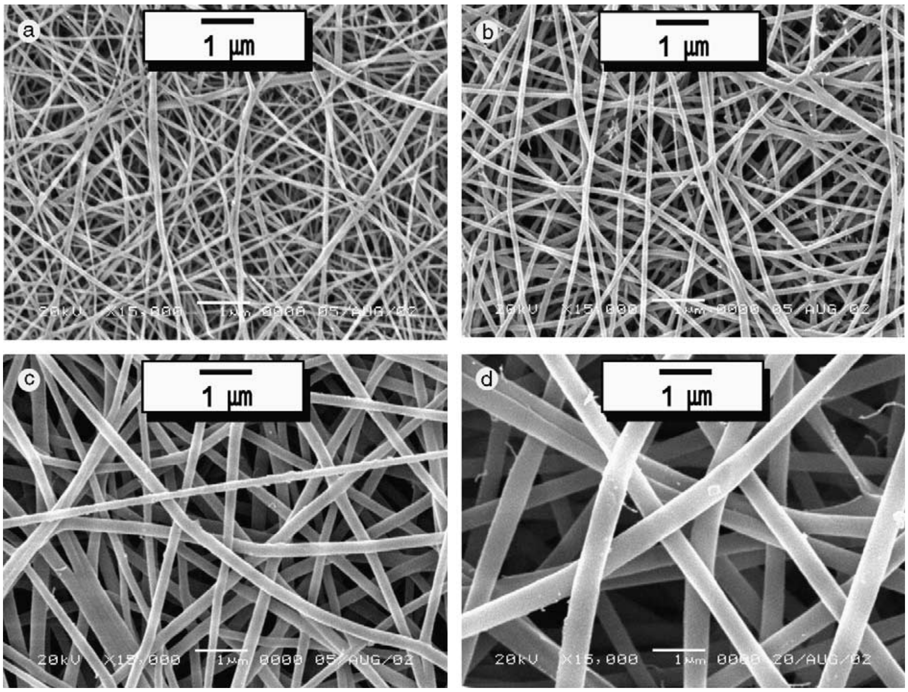

Fig. 5. Micro-SEM micrographs of electrospun nylon 6 nonwoven mats as a function of concentration. Solution concentrations were (a) 15, (b) 20, (c) 25, and (d) 30 wt.%. The applied electric field and tip-to-collector distance were 15 kV and 5 cm, respectively.

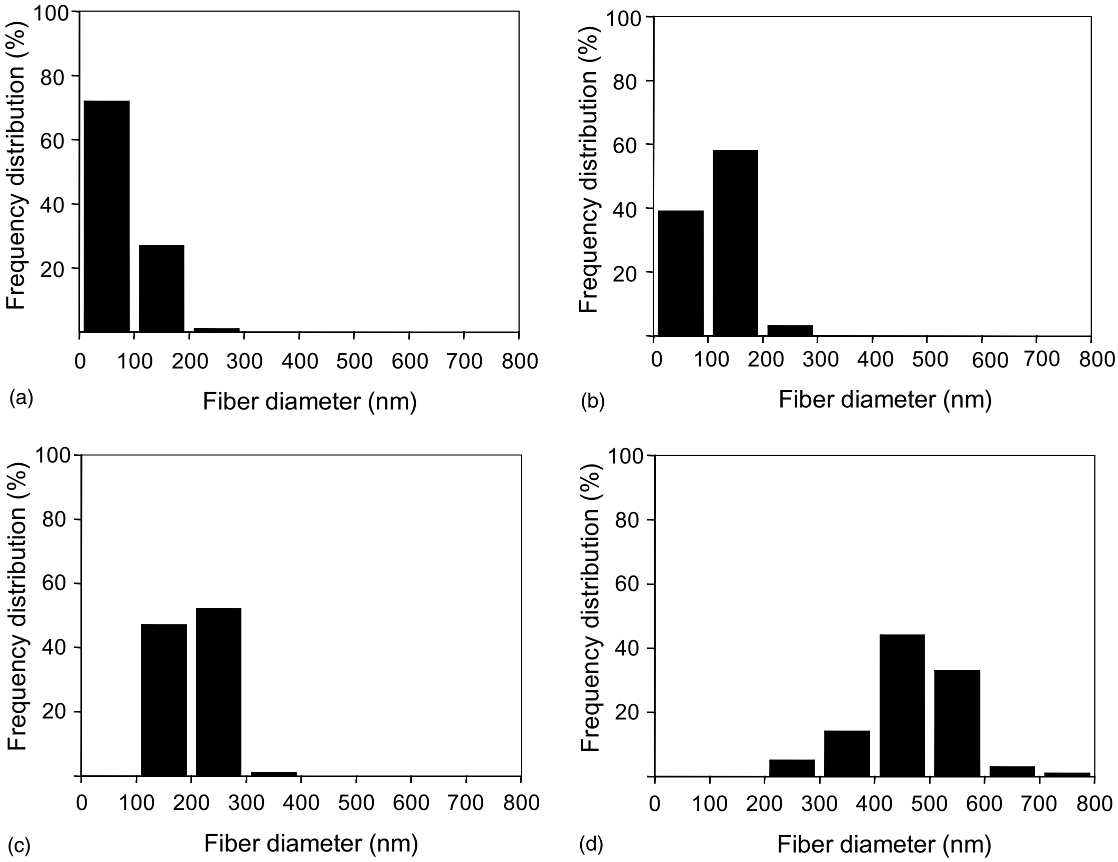

Fig. 6. Fiber diameter distributions of electrospun nylon 6 nonwoven mats as a function of polymer concentration. Solution concentrations were (a) 15, (b) 20, (c) 25, and (d) 30 wt.%.

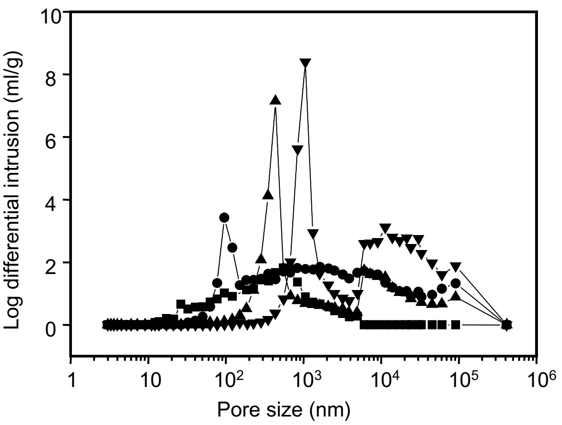

Fig. 7. Pore size distributions of electrospun nylon 6 nonwoven mats as a function of polymer concentration (■, 15 wt.%; ●, 20 wt.%; ▲, 25 wt.%; ▼, 30 wt.%).

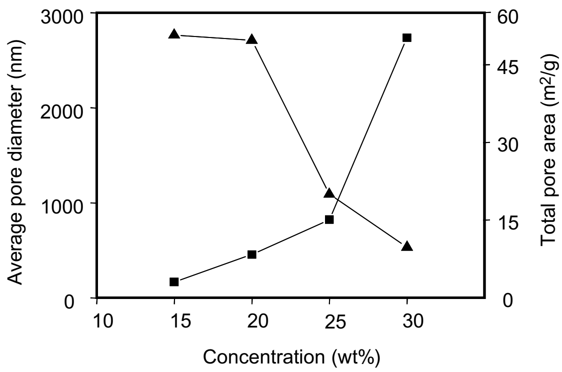

Fig. 8. Average pore diameters and total pore areas of electrospun nylon 6 nonwoven mats as a function of polymer concentration.

pore size and the total pore area of electrospun nonwoven mats are displayed in Fig. 8. The average pore diameters were calculated using $4V/A$ (V, volume; A, area). The result ranged from 167 to 2737 nm for concentrations of 15–30 wt.%. Also, the total pore area

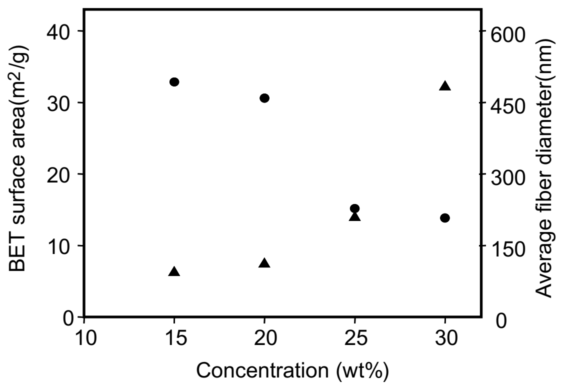

Fig. 9. BET surface areas and average fiber diameters of electrospun nylon 6 nonwoven mats as a function of polymer concentration (●, BET surface area; ▲, average fiber diameter).

varied between 51 and 9 m^2/g for concentrations of 15–30 wt.%.

The porosity of electrospun nylon 6 nonwoven mats ranged from 25% to 80% for concentrations of 15–30 wt.% (not shown data). The average pore diameters have a similar tendency to the average fiber diameter, but the values of the total pore areas have an opposite trend as the average fiber diameter. Thus, it has been concluded that pore size and total pore area values depend on the fiber diameter.

The interrelationship between BET surface area and average fiber diameter as a function of polymer concentration is shown in Fig. 9. The value of each BET surface areas [33 m^2/g (15 wt.%), 31 m^2/g (20 wt.%), 15 m^2/g (25 wt.%), and 14 m^2/g (30 wt.%)] are smaller than that of inorganic particles. However, these values are higher than the currently available textile fibers [14].

3.4. Gas transport properties

Fig. 10 shows that the mass flow rate of nylon 6 nonwoven mats for N_2 decreased with increasing pressure of gas. On the other hand, the gas permeability increased with increasing polymer concentration. It could be regarded as gas permeability of electrospun nonwoven mats depended on fiber diameter and pore size.

The gas flow rate range was from 11,000 to 25,000 cc/min and permeability range varied from 3.7×10^7 to 1.7×10^7 barrer (1 barrer $= 10^{-10} \times 10^{-3}$ STP/cm^2 s cmHg). As mentioned above, gas flow rate and permeability of 30 wt.% were higher than those of the nonwoven mats prepared from 15 to 25 wt.%, because of the thick fiber diameter, so it had larger pores.

4. Conclusions

Nonwoven electrospun mats have been prepared from various solutions with different concentrations. The mats were examined regarding their morphology, pore size, surface area and gas transport properties. It has been observed that the diameter of electrospun fiber was affected by viscosity of the polymer solutions. The diameter of the fiber is average and average pore size increased from 90–500 to 170–2700 nm, for increasing concentration of solution from 15 to 30 wt.%. Further, BET surface area was high for 15 wt.% solution.

It has been concluded that the fiber diameter was affected by the polymer solution concentration. The other parameters such as pore size, BET surface area and gas transport property were also depended on the fiber diameters.

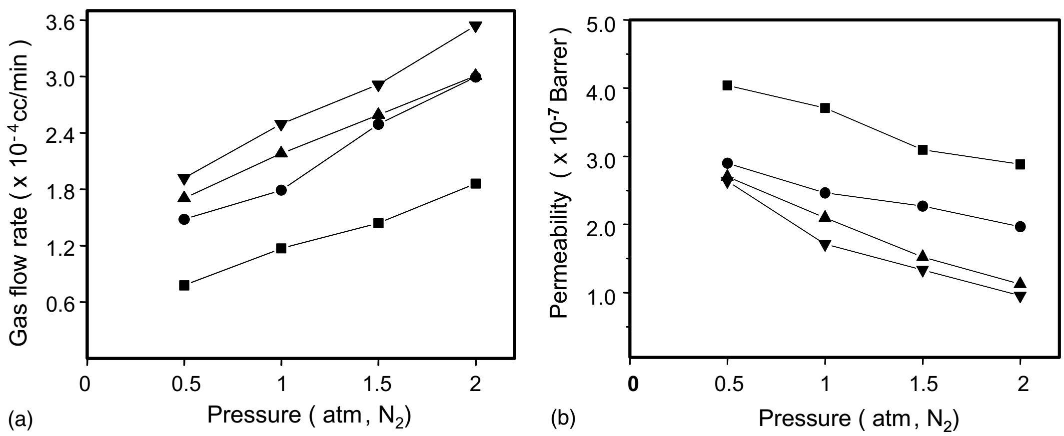

Fig. 10. Gas flow rate (a) and permeability (b) of electrospun nylon 6 nonwoven mats as a function of pressure of N_2 gas (■, 15 wt.%; ●, 20 wt.%; ▲, 25 wt.%; ▼, 30 wt.%).

References

[1] Zimmerman J, Mark HF, Bikales NM. In: Encyclopedia of polymer science and engineering, vol. 6. New York: Wiley; 1988. p. 802–39.

[2] Bergshoef MM, Vancso GJ. Transparent nanocomposites with ultrathin, electrospun nylon-4,6 fiber reinforcement. Adv Mater 1999;11:1362–5.

[3] Gaylord NG, Piatzer NA. Copolymer, polymer blends, and composites. In: Advances in chemistry series, vol. 142. Washington, DC: American Chemical Society; 1975. p. 76.

[4] Ziabicki A. Fundamentals of fibre formation: the science of fiber spinning and drawing. New York: Wiley; 1976.

[5] Deitzel JM, Kosik W, Mcknight SH, Beak Tan NC, Desimone JM, Crette S. Electrospinning of polymer nanofibers with specific surface chemistry. Polymer 2002;43: 1025–9.

[6] Ding B, Kim HY, Lee SC, Shao CL, Lee DR, Park SJ, et al. Preparation and characterization of a nanoscale poly(vinyl alcohol) fiber aggregate produced by using electrospinning method. J Polym Sci, Polym Phys 2002;40:1261–8.

[7] Dai H, Gong J, Kim HY, Lee DR. A novel method for preparing ultra-fine alumina-borate oxide fibers via an electrospinning technique. Nanotechnology 2002;13:674–7.

[8] Formhals A. US Patent 1,975,504, 1934.

[9] Fong H, Chun I, Reneker DH. Beaded nanofibers formed during electrospinning. Polymer 1999;40:4585–92.

[10] Bognitzki M, Czado W, Frese T, Schaper A, Hellwig M, Steinhart M, et al. Nanostructured fibers via electrospinning. Adv Mater 2001;13:70–2.

[11] Lee KH, Kim HY, La YM, Lee DR, Sung NH. Influence of a mixing solvent with tetrahydrofuran and *N,N*-dimethylformamide on electrospun poly(vinyl chloride) nonwoven mats. J Polym Sci, Polym Phys 2002;40:2259–68.

[12] Doshi J, Reneker DH. Electrospinning process and applications of electrospun fibers. J Electrostat 1995;35:151–60.

[13] Gibson PW, Schreuder-Gibson HL, Riven D. Transport properties of porous membranes based on electrospun nanofibers. AIChE J 1999;45:190–5.

[14] Fong H, Liu W, Wang CS, Vaia RA. Generation of electrospun fibers of nylon 6 and nylon 6-montmorillonite nanocomposite. Polymer 2002;43:775–80.

[15] Reneker DH, Chun I. Nanometer diameter fibers of polymer, produced by electrospinning. Nanotechnology 1996; 7:216–23.

[16] Deitzel JM, Kleinmeyer J, Harris D, Beck Tan NC. The effect of processing variables on the morphology of electrospun nanofibers and textiles. Polymer 2001;42:261–72.

[17] John AD. LANGE'S handbook of chemistry. 15th ed. New York: McGraw-Hill; 2001. p. 5.118.

[18] León y León CA. New perspectives in mercury porosimetry. Adv Colloid Interface Sci 1998;76–77:341–72.

[19] McEnaney B, Mays TJ, Patrick JW. Porosity in carbons: characterization and applications. New York: Halsred Press; 1995. p. 93.

[20] Scatterfield CN. Heterogeneous catalysis in industrial practice. 2nd ed. New York: McGraw-Hill; 1991. p. 131.