Fibrous Membranes of Cellulose Acetate and Poly(vinyl pyrrolidone) by Electrospinning Method: Preparation and Characterization

M. M. Castillo-Ortega,[1] J. Romero-García,[2] F. Rodríguez,[1] A. Nájera-Luna,[1] P. J. Herrera-Franco[3]

[1]*Departamento de Investigación en Polímeros y Materiales, Universidad de Sonora, A.P. 130, Hermosillo, Sonora, México*
[2]*Departamento de Materiales Avanzados, Centro de Investigación en Química Aplicada, A.P. 25000, Saltillo, Coahuila, México*
[3]*Unidad de Materiales, Centro de Investigación Científica de Yucatán, calle 43 No. 130 Col. Chuburná de Hidalgo, Mérida, Yucatán, C.P. 97200, México*

Received 11 April 2009; accepted 31 October 2009
DOI 10.1002/app.31722
Published online 5 January 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Fibrous membranes of cellulose acetate (CA), poly(vinyl pyrrolidone) (PVP) and composite membranes of these polymers, were obtained by the electrospinning method. Using systematic method, the optimal conditions for preparation of fibrous membranes were found. Both CA and PVP a concentration of 8% weight was found. The CA was dissolved in a acetone:-water solution, volume ratio 80 : 20 and the PVP is dissolved in ethanol:water solution, ratio volume 85 : 15. The flow rate for both polymers was 1.5 mL h^{-1}. The same applied voltage value and the distance between the needle and collection plate were for polymer both, 15 kV and 15 cm respectively. The morphology of fibrous membranes and composite membranes were evaluated by scanning electron microscopy (SEM). The CA fibers showed ribon morphology, while the PVP fibers were cilindric, in both cases with diameters in the micrometer range. Thermogravimetric analysis showed that CA had a complete degradation to 445°C, while the fibrous membranes PVP required a value of temperature for degradation of up to 571°C. Fibrous composite membrane PVP/CA/PVP shows a higher value of strain at break (%), and a lower value of tensile strength (MPa) compared to CA/PVP/CA. J Appl Polym Sci 116: 1873–1878, 2010

Key words: cellulose acetate; poly(vinyl pyrrolidone); electrospinning

INTRODUCTION

Electrospinning technique is a method thas has been widely used in recent years, because of its simplicity and speed it can be used to prepare polymeric fibers with diameters ranging from nanometer to micrometer scale, for any polymer that is soluble in a volatile solvent. According to a literature review, in 1994, only two publications had been made, but the number of publications have increased so rapidly over time that in the year 2008 there were 1278 research articles already published. In these publications, a large number of applications and different materials have been reported, including nylon, to obtain uniform ultrafine fibers,[1] poly(ethylene) used in tissue engineering and biomedical materials,[2,3] silk for use in biomedicine and tissue engineering,[4,5] poly-(methyl methacrylate) used in nanofibers electroconductive,[6–8] poly(acrylonitrile) to obtain micronanotubes with potential use for the storage of hydrogen, platelet adhesion, lithium batteries,[9–12] cellulose with applications in biomaterials and membranes for the purification of antibodies,[13–17] poly(vinyl alcohol) used in tissue engineering, biomedical materials, bactericides, to study the effect of polarity, for electronic devices and gas sensors[18–24] and other materials.

In the electrospinning process, a continuous strand of a polymer liquid (i.e., solution or melt) is ejected through a nozzle by a high electrostatic force which is deposited ramdomly on a grounded colletor as a nonwoven fiber mat.[25] A candidate material to produce nano and micrometric fibers with possible applications in tissue engineering, controlled release of drugs and as a bactericide is cellulose acetate (CA).[26–37] Also, poly(vinyl pyrrolidone) (PVP) is another material used widely, for the development of nano-fibers with applications in microencapsulation, for the controlled release of drugs and for chemical and biological sensors.[38–43] An interesting possible application is the preparation of cellulose acetate microtubes and/or nanotubes, from the fact

Correspondence to: M. M. Castillo-Ortega (monicac@guaymas.uson.mx).

that PVP is water soluble, there exists the possibility of producing in a coextrusion fashion both the PVP and the CA, and then, after dissolving one of the polymers, we should be left with a tube shapped polymer. The main goal of this work is to show the feasibility and to determine the optimal conditions for the preparation of fibrous membranes of cellulose acetate, PVP and composite membranes of these polymers, via electrospinning, and their morphological, mechanical and thermal characterization.

EXPERIMENTAL

Materials

The materials used were: Cellulose acetate (CA, white powder; 39.7 wt % acetyl content, average $M_n = 50{,}000$), Aldrich. Poly(vinyl-pirrolidone) (PVP, white powder; average $M_w = 360{,}000$), Aldrich. Acetic acid glacial, 99.99%, Sigma. Acetone, 99.7%, Aldrich. Ethanol, 99.6%, Aldrich. All the reagents were used as received.

Fibrous membrane preparation

For the preparation of the fibrous membranes, a careful study of all variables was made. The variables studied were, the concentration of polymer solution, solvent used, applied voltage, flow of the solution, and the distance between the needle and the collector plate. In all cases the needle used had in diameter of 0.8 mm. In the case of fibrous membranes of CA, an acetone-water mixture was used as solvent, varying the polymer concentration in the range of 5 to 10% W. For fibrous membranes PVP, an ethanol-water mixture was used.

The polymer solution was transferred to a plastic syringe of 10 mL capacity and the 0.8 mm diameter needle. Using a syringe pump kdsCientific, the flow velocity was varied in the range of 0.4–5 mL h^{-1}. A high voltage in a range of 10–30 kV was applied to the polymer solution, using a high-voltage power supply, Spellman, model CZE 1000R. Finally the distance between the needle and the collector plate was varied in the range of 8–15 cm. A square plate of aluminum (10 cm $\times$ 10 cm) was used as a collector. To obtain the cellulose acetate microtubes and take advantage of the high solubility in water from PVP, fibrous membranes composite of CA y PVP were made. First, two tubes were formed, one on top of the other, using two adjacent needles, and controlling their flow is way that in the central part was PVP and coated with CA, then, this aasembly was wash and try to dissolve the PVP in water and in this way obtaining microtubes of CA (Method I, M1 CA/PVP/CA). Also, fibers containing PVP at the surface and CA in the centre were made (Method II, M1 PVP/CA/PVP), with the aim of comparing their morphology (diameter) with the fibers prepared above. For both experiments, two syringes with needles of different lengths were placed side-by-side. The longer needle was connected to the syringe containing the polymer that was expected to be at the center of the fiber and the shorter needle, was connected to the syringe containing the polymer supposed to be on the fiber surface. The fibers were washed for 4 h, and then, they were left to dry at room temperature for 12 h. Table I shows the conditions used in preparation of fibrous membranes.

Characterization

The morphology of the fibrous membranes was evaluated using a JEOL 5410LV scanning electron microscopy (SEM), operated at 15 kV. Thermogravimetric analysis (TGA) was carried out on an equipment SDT 2960 simultaneous DSC-TGA TA instruments. The 5 mg samples were warmed up to 600°C at a heating and cooling rate of 10°C min^{-1} under a flow of 20 mL min^{-1} of nitrogen as purge gas was used. Tensile tests were performed on fibrous membranes. Testing was performed using a Universal testing machine (MINIMAT) equipped with a 200 N load cell, and a constant crosshead speed of 1 mm/min. Rectangular samples of the fibrous membranes, 31.75 $\times$ 5.76 mm were cut to allow an initial gage length equal to 12.5 mm. Before testing the samples were conditioned at a 55% relative humidity and room temperature, 28°C.

RESULTS AND DISCUSSION

Electrospinning process: Optimum preparation conditions

The optimal conditions of preparation were found to be those used for the membranes M3 CA and M2 PVP which showed higher homogeneity. Theses conditions are described below.

For both, M3 CA and M2 PVP a concentration of 8% weight was found. The CA was dissolved in a solution 80 : 20 acetone:water in volume. The PVP was dissolved in a solution 85/15 ethanol:water. The flow rate for both polymers was 1.5 mL h^{-1}. The same applied voltage value and the distance between the needle and the collection plate were found for both polymers, 15 kV and 15 cm respectively. Using these experimental conditions, fibrous membranes from CA and PVP which presented a white color were obtained.

TABLE I
Electrospinning Conditions Used in Preparation of Fibrous Membranes of Cellulose Acetate, (CA), Poly(vinyl pyrrolidone), (PVP), and Composite Membranes, CA/PVP/CA, PVP/CA/PVP. Solvent Mixture CA: Acetone: Water. Solvent Mixture PVP: Ethanol: Water

Membrane	Polymer concentration (wt %)	Solvent	Voltage (kV)	Flow rate (mL/h)	Collector distance (cm)
M1 CA	7	Acetic acid	30	5	10
M2 CA	7	80 : 20	30	2.5	10
M3 CA	8	80 : 20	15	1.5	15
M4 CA	10	80 : 20	15	2.5	15
M5 CA	10	80 : 20	15	2.5	10
M6 CA	10	80 : 20	10	1.5	8
M7 CA	12	80 : 20	12	1.0	8
M8 CA	12	80 : 20	12	3.0	8
M1 PVP	8	85 : 15	12	0.4	15
M2 PVP	8	85 : 15	15	1.5	15
Method I					
M1 CA/PVP/CA	8 (both)	80 : 20 CA 85 : 15 PVP	15	1.5	14 CA 15 PVP
Method II					
M1 PVP/CA/PVP	8 (both)	80 : 20 CA 85 : 15 PVP	15	1.5	15 CA 14 PVP

Morphology of fibrous membranes

Figures 1 and 2 show the SEM micrographs for the fibrous membranes M3 CA and M2 PVP, respectively. Membrane M3 CA is composed of fibers with a ribon-like shape, and also have holes and some porosity, while the fibrous membranes M2 PVP have fibers with a cylindrical shape, with diameters varying from 1 to 3 μm. The fiber diameter was determined by image analysis using a commercial image analysis software called software Image Tool versión 3.0 Final. In both polymers, the size of the measured diameters were in micrometer units. The holes observed in fibrous membranes M3 CA suggests the possibility of their application in liquid separation processes.

Figures 3 and 4 show the SEM micrographs from fibrous membrane composite M1 CA/PVP/CA and M1 PVP/CA/PVP, before and after washing with water. In Figure 3(a) shows the existence of cylindrical fibers with values of diameters ranges from 0.6 to 2 μm. After washing, Figure 3(b), clearly shows a decrease in the diameter of the fiber, possibly due to

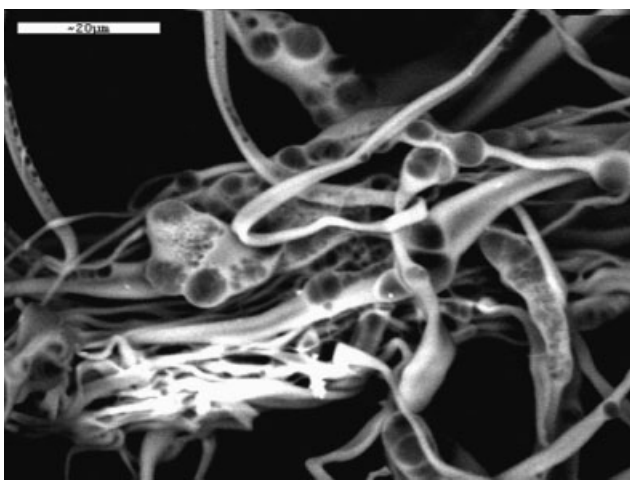

Figure 1 Microphotography by SEM of a fibrous membrane M3 CA, 1500×.

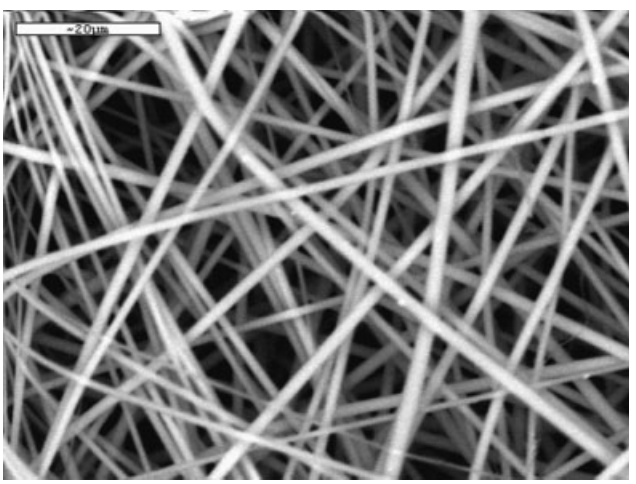

Figure 2 Microphotography by SEM of a fibrous membrane M2 PVP, 1500×.

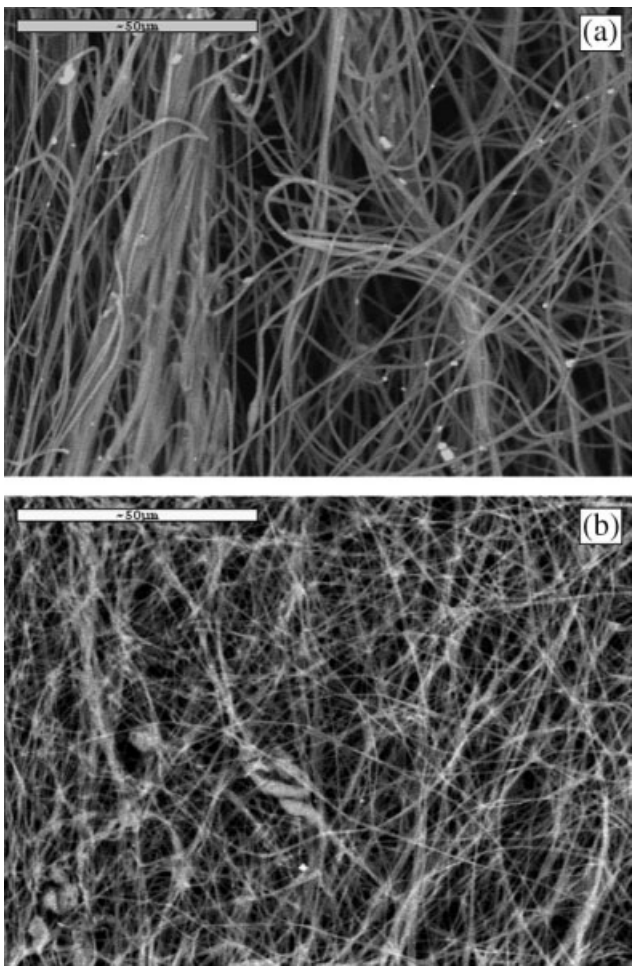

Figure 3 Microphotography by SEM of fibrous membrane composite of PVP is expected at the center and CA on the surface, M1 CA/PVP/CA (a) before washing, (b) after washing, 1000×.

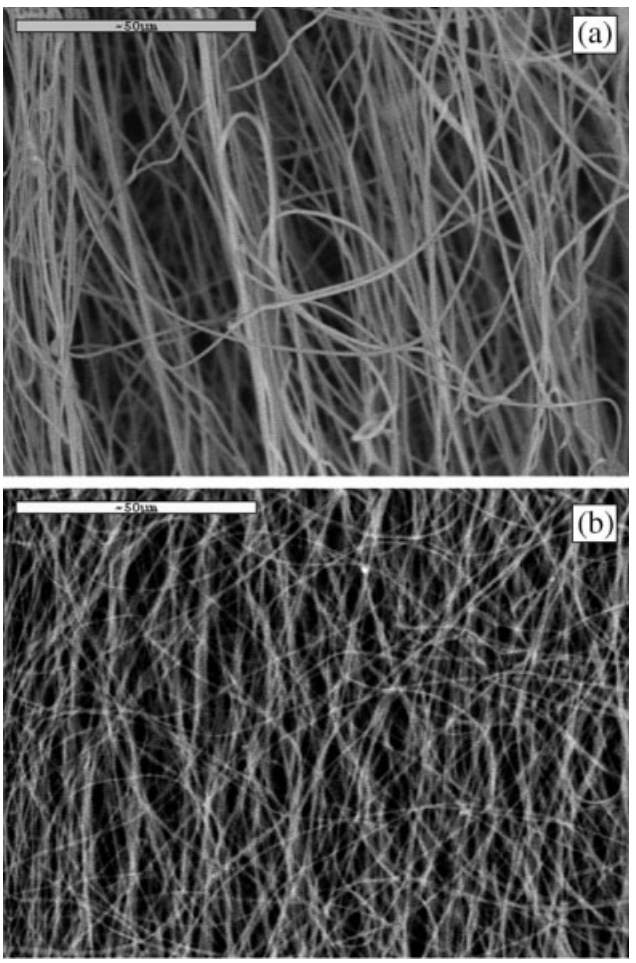

Figure 4 Microphotography by SEM of fibrous membrane composite of CA is expected at the center and PVP on the surface, M1 PVP/CA/PVP (a) before washing, (b) after washing, 1000×.

diffusion of PVP to water. In the case of fibrous membrane composite M1 PVP/CA/PVP (Fig. 4), similar results were found.

Thermogravimetric analysis

Analysis of weight loss as a function of temperature was performed for each type of fibrous membrane, to deduce whether the PVP dissolves in water after washing them. Figure 5(a,b) show the thermograms of fibrous membranes for the M3 CA and M2 PVP membranes respectively. In both cases, the first significant weight loss was at 100°C attributed to the loss of moisture and solvent adsorbed in the fibers. Fibrous membrane M3 CA showed a weight loss of 15%, while the fibrous membranes M2 PVP by 20%, a higher value attributed to the high hygroscopicity of PVP. In the case of CA, a complete degradation to 445°C is observed, while the fibrous membranes PVP required a value of degradation temperature of 571°C.

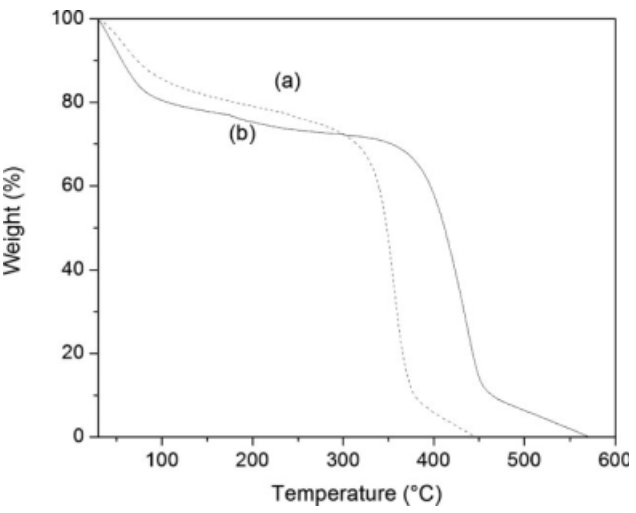

Figure 5 Thermograms of fibrous membranes from (a) M3 CA and (b) M2 PVP.

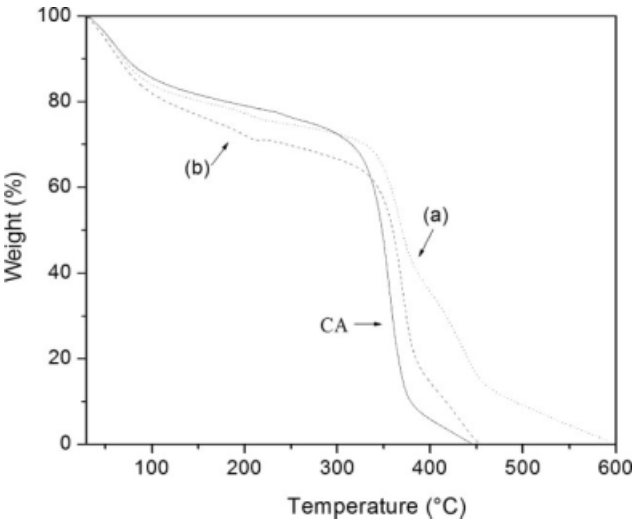

Figure 6 Thermograms of fibrous membranes composite M1 CA/PVP/CA, (a) before and (b) after washing with water.

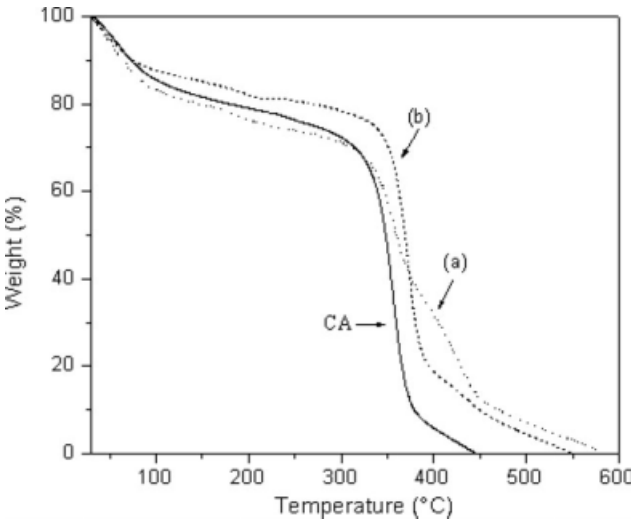

Figure 7 Thermograms of fibrous membranes composite M1 PVP/CA/PVP, (a) before and (b) after washing with water.

Figures 6 and 7 show a comparison of the thermal stability of fibrous CA and PVP composite membranes, (a) before and (b) after washing with water. A thermogram of the fibrous composite membrane M1 CA/PVP/CA is shown in Figure 6(a) shows a weight loss of 2% at 100°C attributed to the loss of moisture and residual solvent; notice that this is an intermediate value of those observed for CA and PVP individually (see Fig. 5). Finally, the total degradation is observed at 590°C, attributed to the PVP. For the thermogram of the fibrous composite membrane, after washing with water [Fig. 6(b)], a temperature of total degradation to 450°C was observed. This is an indication of the absence of PVP in the membrane. This analysis indicates that there exists dissolution of PVP in water when the membrane is washed. A thermogram of the fibrous membrane composite M1 PVP/CA/PVP, (a) before washing, (b) after washing is shown in Figure 7. For the unwashed membranes [Fig. 7(a)], observations similar to those made for the fibrous membrane composite M1 CA/PVP/CA were found. Therefore, the resulting mixture is a blend of these two materials, CA and PVP, without regard of their final morphology. After washing the fibrous membranes, a decrease in the temperature of total degradation is observed, attributed to the elimination of PVP in water. In the case of the fibrous composite membrane M1 CA/PVP/CA, after washing, the temperature of total degradation, tends to the same value observed for CA (Fig. 6), indicating that the PVP dissolves into water during washing. The fibrous composite membrane M1 PVP/CA/PVP, presents a greater thermal stability, with a difference of 30°C after washing with water [Fig. 7(b)]. It also shows that the temperature for total degradation is closer to the temperature of PVP pure, this indicates that the material may contain PVP even after washing.

Tensile tests

Values of tensile strength, Young's Modulus and strain at break are shown in the Table II. Fibrous membranes PVP/CA/PVP shows a higher value of strain at break (%), and a lower value of tensile strength (MPa) compared to CA/PVP/CA. These results suggest that the membrane obtained by Method II (PVP/CA/PVP) is a composite membrane with better mechanical properties due to better interaction between both components. These results are consistent with those obtained in TGA.

CONCLUSIONS

Fibrous membranes of CA, PVP and composite membranes were successfully fabricated via electrospinning.

TABLE II
Values of Tensile Strength, Young's Modulus and Strain at Break of Fibrous Membranes Composite, CA/PVP/CA and PVP/CA/PVP

Membrane	Tensile strength (MPa)	Young's modulus (MPa)	Strain at break (%)
CA/PVP/CA	37.084 ± 5.988	1556. 845 ± 279.225	3.01 ± 0.39
PVP/CA/PVP	17.907 ± 3.36	588.504 ± 92.89	6.25 ± 0.57

Results obtained by TGA indicated that PVP dissolves washing the fibrous membrane composite, M1 CA/PVP/CA. This could be attributted to the fact that PVP is in the center of the fiber, the diffusion of PVP to water, suggesting the formation of microtubes CA. The fibrous membranes of PVP, M2 PVP, showed a morphology of cylindrical fibers, whereas, in the fibrous membrane CA, M3 CA, showed a ribon morphology with holes and porosity, generating interest for further study of this type of fiber, for their potential application in separation systems.

F. Rodriguez thank CONACYT for the granted scholarship.

References

1. Yan, L.; Zhengming, H.; Yandong, L. Eur Polym J 2006, 42, 1696.
2. Trvis, J.; Horst, A. Biomaterials 2008, 29, 1989.
3. El-Refaie, K.; Layman, J.; Watkins, J.; Gary, L. Biomaterials 2003, 24, 907.
4. Byung-Moo, M.; Gene, L.; So-Hyun, S. Biomaterials 2004, 25, 1289.
5. Jingxin, Z.; Yaopeng, Z.; Huili, X. Polymer 2008, 49, 2880.
6. Bazilevsky, A.; Yarin, A.; Megaridis, C. Langmuir 2006, 22, 11384.
7. Mao, P.; Dasong, L.; Ying, C.; Qiang, Z. Langmuir 2006, 22, 9368.
8. Hong, D.; Wayne, E. Langmuir 2006, 22, 11384.
9. Zussman, E.; Yarin, A.; Bazilevsky, A. Adv Mater 2006, 18, 348.
10. Costolo, A.; Lennhoff, J.; Pawle, R. Nanotechnology 2008, 19, 9.
11. Ai-Fu, C.; Xiao-Jun, H.; Zhen-Gang, W. Aust J Chem 2008, 61, 446.
12. Anantha, I.; Padmanabhan, S.; Kalayil, M. J Membr Sci 2008, 325, 683.
13. Zuwei, M.; Kotaki, S. J Membr Sci 2005, 265, 115.
14. Zuwei, M.; Seeram, R. J Membr Sci 2008, 319, 23.
15. Shanshan, X.; Jun, Z.; Aihua, H.; Junxing, L.; Hao, Z.; Charles, H. Polymer 2008, 49, 2911.
16. Audrey, F.; Maria, H.; Pernilla, W. J Appl Polym Sci 2007, 103, 1473.
17. Won, S.; Ji, Y.; Won, P. Biomacromolecules 2004, 5, 197.
18. Milena, I.; Kirilka, S.; Nadya, M.; Nevena, M.; Iliya, R. Carbohydr Res 2006, 341, 2098.
19. Viswanathamurthi, P.; Bhattarai, N.; Kim, H. Y.; Khil, M. S.; Lee, D. R.; Suh, E.-K. J Chem Phys 2004, 121, 441.
20. Ali, K.; Fatih, O.; Ali, D. Text Res J 2008, 78, 532.
21. Yong-Tang, J.; Jian, G.; Xiao-Hua, G.; Hark-Yong, K.; Jiong, D.; Xin-Yuan, S. Carbohydr Polym 2007, 67, 403.
22. Youliang, H.; Dongmei, L.; Jian, Z.; Guangtian, Z. Langmuir 2006, 22, 7331.
23. Eugene, S.; Ulrich, B.; Ronald, D. S. Polymer 2005, 46, 2419.
24. Guan, W.; Yuan, J.; Xianrong, H.; Xiaoqing, Y.; Pelagia-Irene, G.; Michael Dudley, J. Phys Chem B 2006, 110, 23777.
25. Santi, T.; Ittipol, J.; Pitt, S. Polymer 2007, 48, 5030.
26. Won Keun, S.; Ji Ho, Y.; Won, H. P. Carbohydr Polym 2006, 65, 430.
27. Bin, D.; Eiji, K.; Tomokazu, S.; Shiro, F.; Seimei, S. Polymer 2004, 45, 1895.
28. Orawan, S.; Uracha, R.; Pitt, S. Polymer 2008, 49, 4239.
29. Seong, O. H.; Ji, H. Y.; Kyung, D. M.; Yun, O. K.; Won, H. P. Mater Lett 2008, 62, 759.
30. Lifeng, Z.; You-Lo, H. Carbohydr Polym 2008, 71, 196.
31. Lifeng, Z.; Todd, J. M.; Hao, F. J Membr Sci 2008, 319, 176.
32. Pattama, T.; Uracha, R.; Pitt, S. Eur J Pharm Biopharm 2007, 67, 387.
33. Orawan, S.; Praneet, O.; Uracha, R.; Pitt, S. Polymer 2007, 48, 7546.
34. Liang, C.; Lev, B.; Alan Hatton, T.; Gregory, C. R. Polymer 2008, 49, 1266.
35. Bin, D.; Chunrong, L.; Yoshio, H.; Jinho, K.; Oriha, K.; Seimei, S. Nanotechnology 2006, 17, 4332.
36. Young, llY.; Hyun, S. M.; Won, S. L.; Taek, S. L.; Won, H. P. Carbohydr Polym 2009, 75, 246.
37. Changzhong, C.; Linge, W.; Yong, H. Polymer 2007, 48, 5202.
38. Ioannis, S. C.; Sven, G.; Alexandra, J. Polymer 2006, 47, 1597.
39. Dan, L.; Jesse, T. M. C.; Younan, X. Small 2005, 1, 83.
40. Danming, C.; Lili, C.; Junfeng, Z. Synth Met 2008, 159, 537.
41. Jesse, T. M. C.; Manuel, M.; Younan, X. Nano Lett 2006, 6, 162.
42. Bishop, A.; Gouma, P. Rev Adv Mater Sci 2005, 10, 209.
43. Suresh, L.; Shenoya, W.; Douglas Batesa, H. L.; Frischb, G. E. Polymer 2005, 46, 3372.