

Electrospinning Fabrication and Characterization of Poly(vinyl alcohol)/Montmorillonite Nanofiber Mats

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ABSTRACT: Poly(vinyl alcohol) (PVA)/montmorillonite clay (MMT) nanofiber mats have been fabricated by the electrospinning technique. The PVA/MMT nanofiber mats were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), Fourier transform infrared (FTIR), and mechanical measurements. The study showed that the introduction of MMT results in improvement in tensile strength, and thermal stability of the PVA matrix. XRD

patterns and SEM micrographs suggest the coexistence of exfoliated MMT layers over the studied MMT contents. FTIR revealed that there might be possible interaction occurred between the MMT clay and PVA matrix. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1860–1867, 2009

Key words: poly(vinyl alcohol); nanofiber mats; montmorillonite; electrospinning

INTRODUCTION

Recently, poly(vinyl alcohol) (PVA)/montmorillonite clay (MMT) hybrid nanocomposites have attracted great interest due to MMT-filled polymer composites often exhibit remarkable improvement in material properties with only a low percentage of MMT fillers added. One of the major findings that have stimulated the interest in MMT-filled nanocomposites is the work by Okada et al.¹ They reported that with only a small amount of layered silicate (MMT) added into nylon-6, pronounced improvements in thermal and mechanical properties can be obtained. Subsequently, Vaia et al.² reported that it is possible to melt-mix polymers with layered silicates, without the use of organic solvents. Today, efforts are being conducted globally, using almost all types of polymer matrices to produce MMT-based nanocomposites. The main advantages of these nanocomposites are improved thermal and mechanical properties, reduced flammability and better barrier properties comparing with unfilled polymer. The composite studies focus on the method of their preparation,

structure characterization, mechanical and thermal properties, and processing.

PVA is a water-soluble polymer produced industrially by the saponification of poly(vinyl ester) or poly(vinyl ether), with good chemical and thermal stability.³ PVA is highly biocompatible and is non-toxic. It can be processed easily and has high water permeability.⁴ PVA solutions can form physical gels from various types of solvents. These properties have led to the use of PVA in a wide range of applications in medical, cosmetic, food, pharmaceutical, and packaging industries. PVA-containing solutions have been processed by numerous techniques including sol-gel processing, phase separation and freeze-thaw cyclic treatments to produce a variety of structures. Ultrafine PVA fibers, which may have different potential applications, cannot be produced by conventional spinning techniques. Through the processes, such as melt spinning, dry or wet spinning, fibers with diameters ranging from 5 to 500 μm are generally obtained.⁵ Moreover, a great interest in polymer-clay composites inspired by the pioneering work by researchers at Toyota, which has demonstrated an improvement in both physical and mechanical properties.^{6,7} Clay consists of nano layers with thickness around 1 nm and platelet aspect ratio of ~ 1000 . Incorporation of clay may increase the mechanical properties of PVA/MMT, improve the tensile strength, and reduce the release of plasticizer from PVA/MMT.

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Electrospinning is a very simple and effective approach to produce nanofibers, including aligned nanofibers and crossbar structures with the diameters ranging from micrometers to few nanometers scale, which may have been found attractive for various applications in biomedical engineering, filtration, protective clothing, catalysis reaction, and sensors.^{8–10} In a typical electrospinning process, a high voltage is applied to create electrically charged jets of polymer solutions. The jets dry and form nanofibers, which are collected on a target as non-woven mat. The principle of the electrospinning method is quite simple; the electrostatic field stretches the polymer solution into fibers at the same time as the solvent evaporates. However, the process is difficult to control and several variables have an influence on the properties of the end product. Furthermore, the quality of the fibers is typically inconsistent, for example, the fiber deposition may be uneven or the distribution of fiber diameter may be large. Research on PVA/MMT nanofiber mats by electrospinning technique has not been a focus in enormously. No reports are available yet on the morphology and crystalline structure of PVA/MMT nanofiber mats by electrospinning technique.

In this study, it has been demonstrated for the first time, ultrafine PVA/MMT nanofiber mats can be fabricated by using the electrospinning technique. The PVA/MMT nanofiber mats were investigated using scanning electron microscopy (SEM), Fourier transform infrared (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), mechanical measurements and the related characterizations were also discussed.

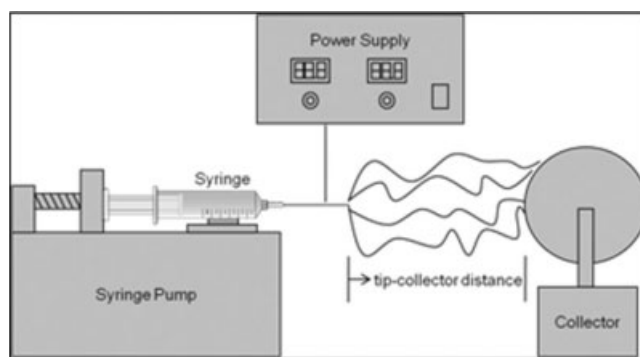
EXPERIMENTAL

Materials

PVA with P_n (number-average degree of polymerization) = 1700 [fully hydrolyzed, degree of saponification (DS) = 99.9%] was obtained from DC Chemical Co., Seoul, South Korea and Montmorillonite (MMT) was purchased from Kunimine Industries Co. Japan. Doubly distilled water was used as a solvent to prepare all solutions.

Preparation of PVA/MMT blend solutions

The PVA solutions (5–12.5 wt %) were prepared in doubly distilled water at 80°C under magnetic stirring for 2 h, and then cooled to room temperature. MMT powder was dissolved also in the doubly distilled water under magnetic stirring for 1 h at room temperature. The PVA/MMT blend solutions were prepared by mixing of bulk PVA (7.5 wt %) and different amount of MMT (1, 3, 5, and 10 wt %)



Scheme 1 Schematic representation of the electrospinning technique.

aqueous solutions at room temperature with gently stirred for another 2 h.

Electrospinning of PVA/MMT nanofiber mats

During electrospinning, a high voltage power (CHUNGPA EMT Co., Seoul, Korea; model CPS-60K02VIT) was applied to the PVA/MMT solution contained in a syringe via an alligator clip attached to the syringe needle. The applied voltage was adjusted at 5–20 kV. The solution was delivered to the blunt needle tip via syringe pump to control the solution flow rate. Fibers were collected on an electrically grounded aluminum foil placed at 5–20 cm vertical distance to the needle tip. Schematic instrumentation of electrospinning process has been shown in Scheme 1.

Characterizations

The morphology and properties characterization of electrospun PVA/MMT fibrous mats (average thickness = ~ 50 μm) was observed with a field-emission scanning electron microscope (JEOL, model JSM-6380) after gold coating, a FTIR (Bruker IFS 120HR), and an X-ray diffraction (XRD) (Philips model X'Pert APD). The average fiber diameter of the electrospun fibers was measured by Adobe Photoshop 5.0 software from the FE-SEM images. The thermal behavior of PVA/MMT fibers was studied with TGA techniques (model Q-50) from TA instruments, USA at the rate of 10°C/min from room temperature to 600°C under the nitrogen gas atmosphere. A mechanical property (tensile strength; test speed = 100 mm/min; samples height = 1 cm, length = 8 cm, and thickness = 30–70 μm) was determined by the ZWICK Z005 (ZWICK materials testing machine, Germany).

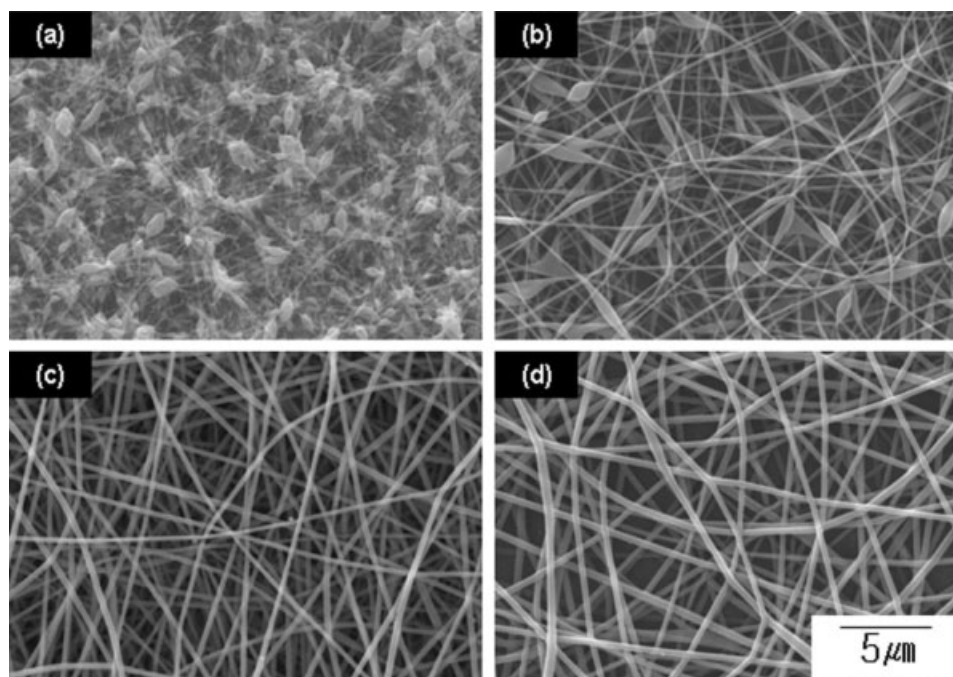


Figure 1 FE-SEM images of bulk PVA nanofiber mats syntheses by using various voltages of (a) 5 kV, (b) 10 kV, (c) 15 kV, and (d) 20 kV (PVA solution concentration = 7.5% and TCD = 15 cm).

RESULTS AND DISCUSSION

Parameters and morphology of PVA/MMT nanofiber mats

Because both polymer and filler used in this study have hydrophilic character, the modification of MMT for component mixing was not necessary. As was described in literature,¹¹ the solution dispersion method of PVA/clay nanocomposite preparation is often used and successful. Such method combined with vigorous stirring was also used in this work to prepare solutions for electrospinning method. Morphology of electrospun nanofiber can be affected by the electrospinning instrument parameters including electric voltage, tip-collector distance (TCD) and solution parameter such as polymer concentration, feed mass ratio, and surface tension.¹² To obtain the suitable electrospinning conditions for thinner and uniform PVA fibers, it was conducted a series of experiments on various conditions for optimizing the solution concentrations.

Applied voltage

A series of experiments were carried out when applied voltage was varied from 5 to 20 kV at an optimum PVA solution concentration of 7.5 wt % with the tip to target distance of 15 cm as shown in Figure 1. The morphological structure can be slightly altered by changing the applied voltage. At low voltage (5 kV), beads were observed numerously [Fig.

1(a)], and increasing the voltage with 10 kV, beads and fibers were seen [Fig. 1(b)]. At high voltage (20 kV), we found nonuniform PVA ribbon-like fibers with larger diameter [Fig. 1(d)]. The best result of uniform PVA fibers were obtained by the applied voltage of 15 kV with the average diameter of ~ 250 nm as shown in Figure 1(c). In an electrospinning process, a polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field. Charge is induced on the liquid surface by an electric field. Mutual charge repulsion causes a force directly opposite to the surface tension. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone. When the electric field reaches a critical value at which the repulsive electric force overcomes the surface tension force, a charged jet of the solution is ejected from the tip of the Taylor cone. The effects of the applied voltage on the nanofibers average diameter have been illustrated in the Figure 2.

Tip to target distance

Tip to target distance had also a significant effect on the electrospun PVA fibers as shown in Figure 3. Four different tip to collector distances (e.g. 5, 10, 15, and 20 cm) were studied and found that at a 15-cm tip to collector distance is the ideal one to synthesize the submicron PVA fibers [Fig. 3(c)].

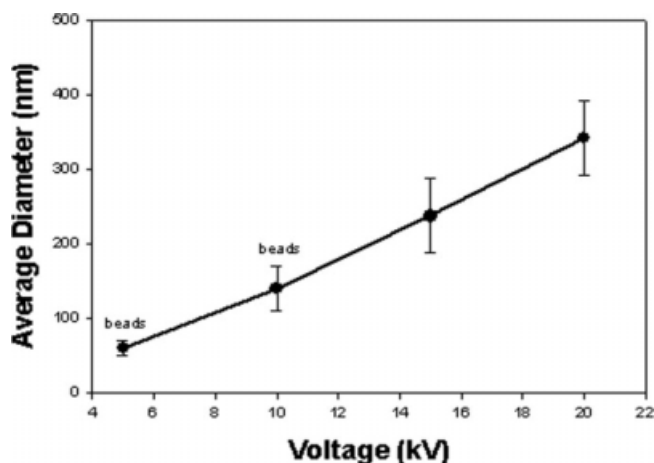


Figure 2 Effects of the applied voltage on the nanofibers average diameter (PVA solution concentration = 7.5% and TCD = 15 cm).

PVA solution concentration

Changing the polymer concentration could alter the fiber diameter and morphology very effectively, as shown in Figure 4. In a fixed applied voltage (15 kV) and tip to collector distance (15 cm), we used 5, 7.5, 10, and 12.5 wt % of PVA solution concentration. We found that at a 7.5% PVA concentration is ideal condition to obtain thinner and uniform PVA fibers.

MMT contents

MMT contents were important parameters which had effects on the morphology of electrospun PVA

fibers. Figure 5 shows the nanofibers including various quantities of MMT. The diameter of fibers and the formation of beads were strongly influenced by the viscoelasticity of the solution.¹³ The diameter of PVA/MMT nanofibers increases but fibers homogeneity decreases with increasing of MMT contents from 1 to 10 wt %. The effects of the MMT loading and polymer solution concentration on the nanofibers average diameter have been elucidated in the Figure 6.

Tensile strength

Figure 7 shows the tensile strength of PVA/MMT nanofibers with different MMT contents. It was found at low (1 and 3 wt %) and high (10 wt %) MMT contents, the tensile strength was lower than 5 wt % of MMT in the nanofiber mats. The maximum tensile strength was found at about 10.4 MPa for 5 wt % MMT content. This result indicates that PVA was strengthened by the introduction of MMT, due to strong interfacial interaction between MMT and PVA matrix in accordance with the work reported in the case of polyimide/MMT.¹⁴ Also, in accordance with that reported by Chen et al.¹⁵ regarding the role of clay as a reinforcing agent in PVA matrix for maleic anhydride modified polypropylene (MAPP)/organoclay nanocomposites. They referred the improvement in mechanical properties due to the interfacial bonding between layered silicates and PVA, which leads to exfoliation of clay among the polymer matrix.

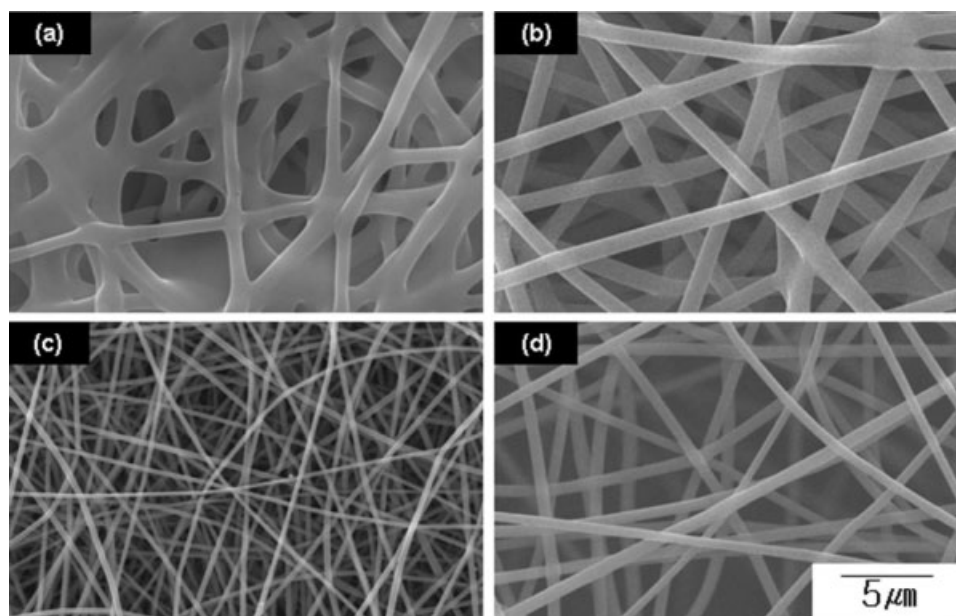


Figure 3 FE-SEM images of bulk PVA nanofiber mats syntheses by using different distances between tip and collector of (a) 5 cm, (b) 10 cm, (c) 15 cm, and (d) 20 cm (PVA solution concentration = 7.5% and applied voltage = 15 kV).

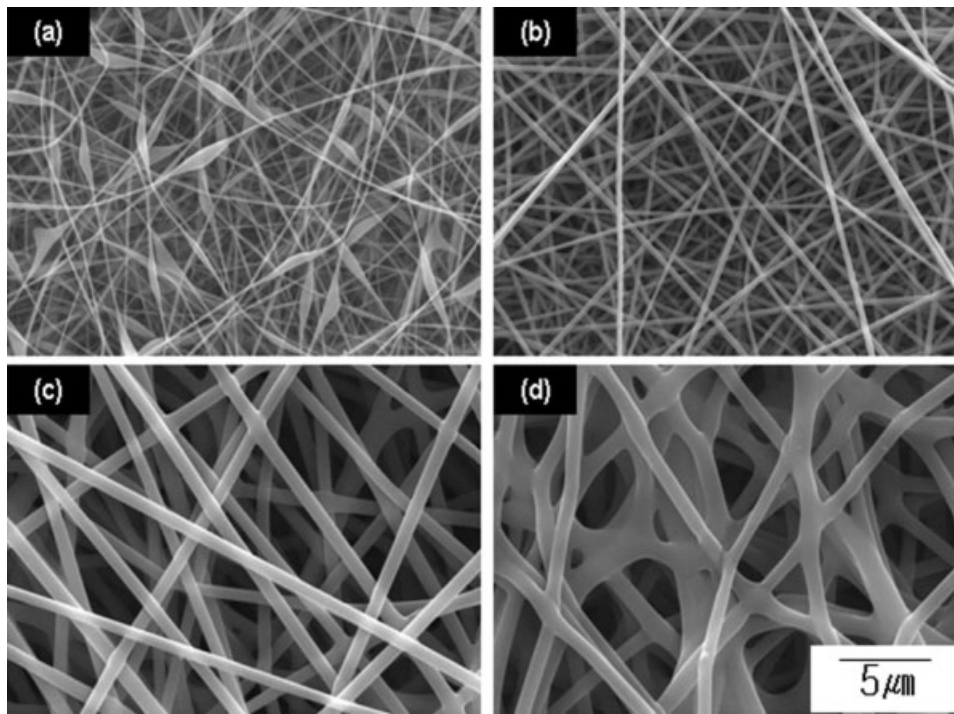


Figure 4 FE-SEM images of bulk PVA nanofiber mats syntheses by using different PVA concentrations of (a) 5 wt %, (b) 7.5 wt %, (c) 10 wt %, and (d) 12.5 wt % (TCD = 15 cm and applied voltage = 15 kV).

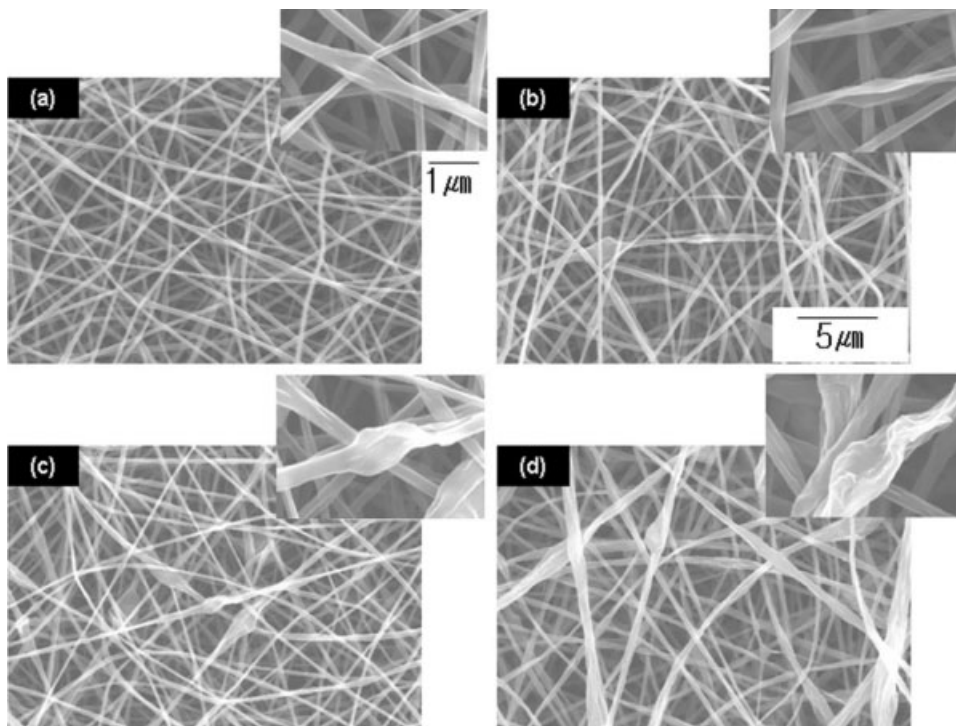


Figure 5 FE-SEM images of PVA/MMT nanofiber mats prepared with different clay contents of (a) 1 wt %, (b) 3 wt %, (c) 5 wt %, and (d) 10 wt % (PVA solution concentration = 7.5%, TCD = 15 cm, and applied voltage = 15 kV; inset: high magnification morphology of related images).

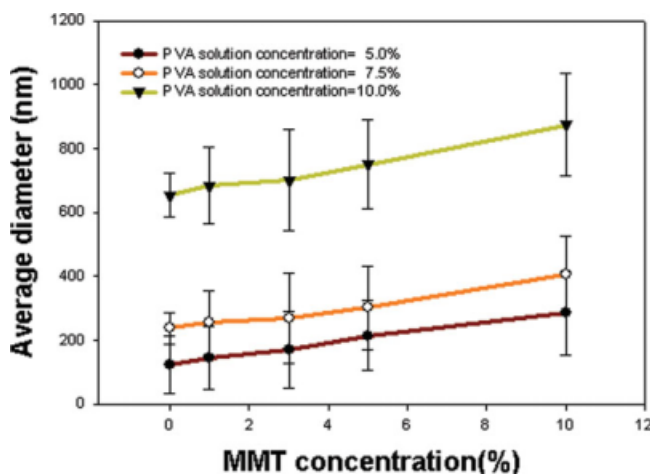


Figure 6 Effects of the MMT loading and polymer solution concentration on the nanofibers average diameter (applied voltage = 15 kV and TCD = 15 cm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Thermal stability

Thermal stability of electrospun PVA/MMT nanofibers was measured using TGA in nitrogen atmosphere. Figure 8 shows TGA thermograms of different decomposition temperature with MMT content of 1, 3, 5, and 10 wt %. The most below curve of the TGA data [Fig. 8(a)] represented the pure PVA and the most upper curve [Fig. 8(e)] was for mass ratio of 10 wt % of MMT, i.e. the highest mass ratio of MMT content was used in our work. Figure 8(b–d) was displaying three middle mass ratio of MMT contents at the same trend of thermal stability like the Figure 8(a,e). Within up to 225°C, there is increased in thermal stability from the pure PVA nanofibers to PVA/MMT (10 wt %) nanofibers. The

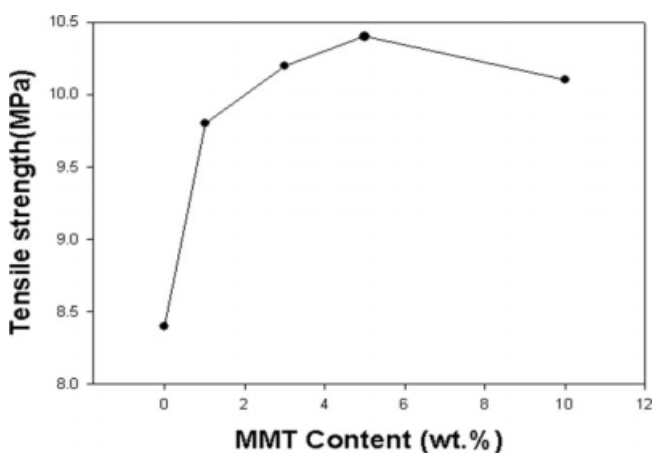


Figure 7 Tensile strength of electrospun PVA/MMT nanofiber mats with various MMT contents (TCD = 15 cm, applied voltage = 15 kV, and PVA solution concentration = 7.5%).

higher thermal stability of high MMT content rate might be attributed to its higher chain compactness due to the interaction between the PVA and the clay.

XRD data

The spacing between clay platelets, or gallery spacing, is an indicator of the extent of intercalation/exfoliation of clay platelets within a polymer matrix and can be observed by using XRD. Generally intense reflection in the range of 3–9° (2 θ) indicates an ordered intercalated nanocomposites. In exfoliated nanocomposites, on the other hand, where single silicate layers (1-nm thick) are homogeneously dispersed in the polymer matrix, and XRD patterns with no distinct diffraction peak in the range of 3–9° (2 θ) could be observed.^{16,17} Figure 9(a,b) shows the XRD patterns of bulk clay and PVA and PVA/MMT nanofiber mats with various MMT contents, respectively. Here, the XRD patterns do not observe any diffraction peak in 3–9°, indicating the possibility of having exfoliated silicate the layers of clay dispersed in PVA [Fig. 9(b)]. There is an intense peak appearing near 19.4°, corresponding to a *d* spacing of 4.52 for PVA.¹⁸

FTIR spectra

FTIR spectra give additional information about the structure of nanofiber mats studied. In Figure 10, examples of spectra of bulk PVA, bulk MMT, and PVA/MMT (1 and 10 wt % of MMT) nanofiber mats at 600–3600 cm⁻¹ range are shown. Bulk MMT spectrum [Fig. 10(a)] is composed of broad hydroxyl and silanol bands at 3200–3700 and 900–1200 cm⁻¹, respectively.¹⁹ Pure PVA exhibits typical bands for

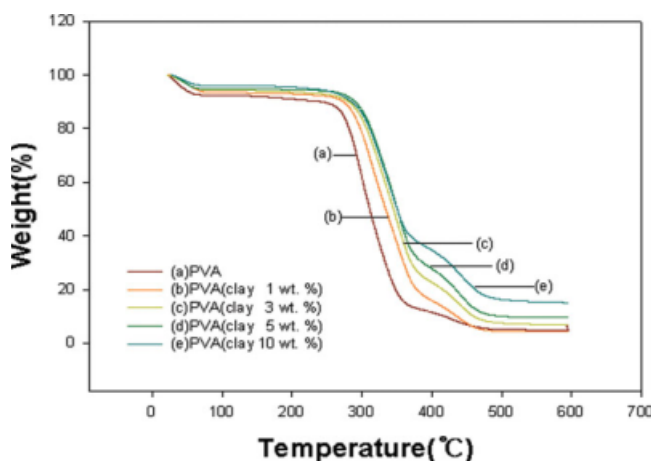


Figure 8 TGA data of electrospun PVA/MMT nanofiber mats with various PVA/MMT mass ratios (TCD = 15 cm, applied voltage = 15 kV, and PVA solution concentration = 7.5%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

vinyl polymers [Fig. 10(d)]. Bands at $2800\text{--}3000\text{ cm}^{-1}$ are due to stretching vibrations of CH and CH_2 groups and bands attributed to CH/ CH_2 deformation vibrations are present at $1300\text{--}1500\text{ cm}^{-1}$ range. Also very intensive, broad hydroxyl band occurs at $3000\text{--}3600\text{ cm}^{-1}$ and accompanying C—O stretching exists at $1000\text{--}1260\text{ cm}^{-1}$. Low-intensive carbonyl band, resulting of residual acetate groups, is detected at 1732 cm^{-1} in PVA spectrum. All these bands are also present in PVA composites with MMT [Fig. 10(b,c)]. The presence of carbonyl groups in PVA arises from production of polymer. PVA is obtained from poly(vinyl acetate) by hydrolysis, thus, it is always polluted by residual acetate groups resulting of not complete process. The small shifts of absorption maximum and alteration of band shape are results of changes in the nearest surrounding of functional groups. These observations are illustrated in Figure 10 for bands in region $1000\text{--}1700\text{ cm}^{-1}$. For example, band at 1457 cm^{-1} in spectrum of pure PVA occurs at 1435 cm^{-1} for PVA and 1 wt % MMT and at 1436 cm^{-1} for PVA and 10 wt % MMT.

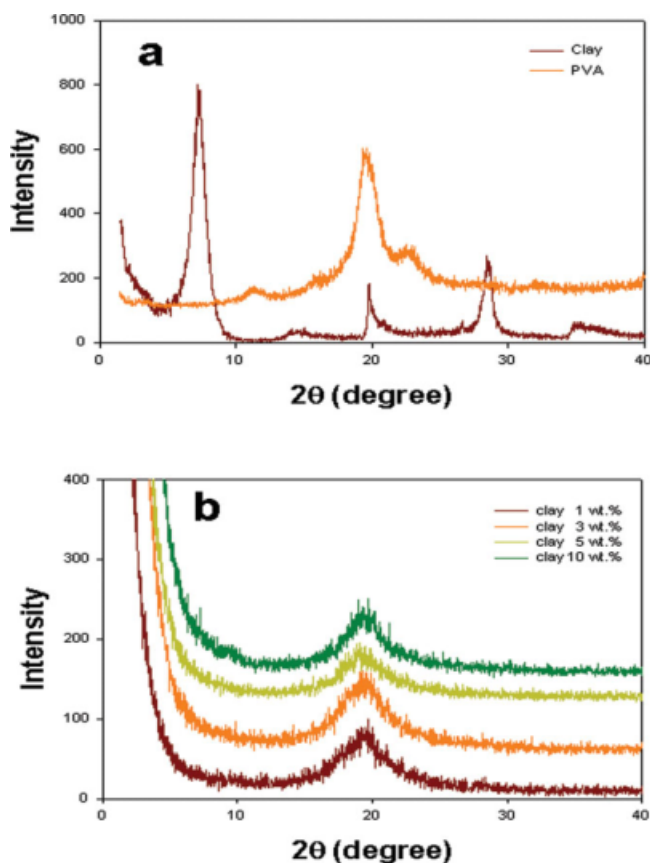


Figure 9 XRD data of bulk clay and PVA (a) and eletrospun PVA/MMT nanofiber mats with various PVA/MMT mass ratios (b) (TCD = 15 cm, applied voltage = 15 kV, and PVA solution concentration = 7.5%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

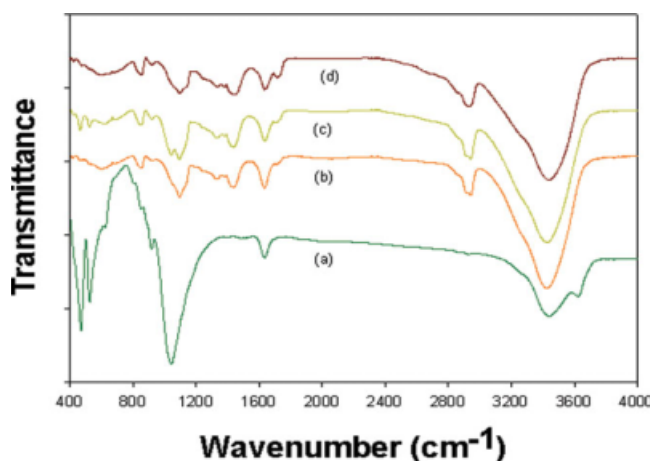


Figure 10 FTIR data of bulk MMT powder (a), bulk PVA powder (d), and eletrospun PVA/MMT nanofiber mats with 1 wt % MMT (b) and 10 wt % MMT (c) (TCD = 15 cm, applied voltage = 15 kV, and PVA solution concentration = 7.5%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Neighboring band situated at 1095 cm^{-1} in PVA spectrum is shifted to 1093 and 1092 cm^{-1} in PVA and 1 wt % MMT and PVA and 10 wt % MMT, respectively. Thus, the FTIR spectroscopy supplied also evidences of possible interactions between PVA matrix and MMT clay, which were suggested earlier.

CONCLUSIONS

Ultrafine PVA/MMT clay nanofiber mats could be fabricated by the electrospinning method in aqueous solutions. The polymer concentration, applied voltages and tip-to-collector distances were the main important factors influencing the electrospinnability of the bulk PVA solutions and the morphology of the electrospun nanofiber mats. Uniform PVA/MMT fibers with an average diameter of nanometer-scale ($\sim 250\text{ nm}$) could be prepared from the 7.5 wt % of PVA containing different amount of MMT contents (1–10 wt %). The study showed that the introduction of MMT results in improvement in tensile strength, and thermal stability of the PVA matrix. XRD patterns and SEM micrographs suggest the coexistence of exfoliated MMT layers over the studied MMT contents. FTIR revealed that there might be possible interaction occurred between the MMT clay and PVA matrix.

References

- Okada, A.; Kawasumi, M.; Usuki, A.; Kojima, Y.; Kurauchi, T.; Kamigaito, O. In *MRS Symposium Proceedings*; Pittsburgh, 1990; Vol. 171, p 45.
- Vaia, R. A.; Ishii, H.; Giannelis, E. P. *Chem Mater* 1993, 5, 1694.

3. Shao, C.; Kim, H.; Gong, J.; Ding, B.; Lee, D.; Park, S. *Mater Lett* 2003, 57, 1579.
4. Yeum, J. H.; Kwak, J. W.; Han, S. S.; Kim, S. S.; Ji, B. C.; Noh, S. K.; Lyoo, W. S. *J Appl Polym Sci* 2004, 94, 1435.
5. Deitzel, J. M.; Kleinmeyer, J.; Harris, D.; Beck Tan, N. C. *Polymer* 2001, 42, 261.
6. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Polym Chem* 1993, 31, 983.
7. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Polym Phys* 1994, 32, 625.
8. Reneker, D. H.; Chun, I. *Nanotechnology* 1996, 7, 216.
9. Li, D.; Xia, Y. *Adv Mater* 2004, 16, 1151.
10. Cui, W.; Li, X.; Zhou, S.; Weng, J. *J Appl Polym Sci* 2007, 103, 3105.
11. Chiellini, E.; Corti, A.; D'Antone, S.; Solaro, R. *Prog Polym Sci* 2003, 28, 963.
12. Greiner, A.; Wendorff, J. H. *Angew Chem Int Ed Engl* 2007, 46, 5670.
13. Fong, H.; Chun, I.; Reneker, D. H. *Polymer* 1999, 40, 4585.
14. Biswas, M.; Ray, S. S. *Adv Polym Sci* 2002, 155, 167.
15. Chen, L.; Wong, S. C.; Pisharath, S. *J Appl Polym Sci* 2003, 88, 3298.
16. Barber, G. D.; Calhoun, B. H.; Moore, R. B. *Polymer* 2005, 46, 6706.
17. Zhu, J.; Wang, X.; Tao, F.; Xue, G.; Chen, T.; Sun, P.; Jin, Q.; Ding, D. *Polymer* 2007, 48, 7590.
18. Yu, Y.-H.; Lin, C.-Y.; Yeh, J.-M.; Lin, W.-H. *Polymer* 2003, 44, 3553.
19. Krishnamoorti, R.; Vaia, R. A. *Polymer Nanocomposites Synthesis, Characterization and Modeling*; ACS: Washington DC, 2002.