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ORIGINAL CONTRIBUTION

Electrospinning and characterization of medium-molecular-weight poly(vinyl alcohol)/high-molecular-weight poly(vinyl alcohol)/montmorillonite nanofibers

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Abstract Submicron fibers of medium-molecular-weight poly(vinyl alcohol) (MMW-PVA), high-molecular-weight poly(vinyl alcohol) (HMW-PVA), and montmorillonite clay (MMT) in aqueous solutions were prepared by electrospinning technique. The effect of HMW-PVA and MMT on the morphology and mechanical properties of the MMW-PVA/HMW-PVA/MMT nanofibers were investigated for the first time. Scanning electron microscopy, viscometer, tensile strength testing machine, thermal gravimetric analyzer (TGA), and transmission electron microscopy (TEM) were utilized to characterize the PVA/MMT nanofibers morphology and properties. The MMW-PVA/HMW-PVA ratios and MMT concentration played important roles in nanofiber's properties. TEM data demonstrated that exfoliated MMT layers were well distributed within nanofibers. It was also found that the mechanical property and thermal stability were increased with HMW-PVA and MMT contents.

Keywords Nanofibers · Poly(vinyl alcohol) · Montmorillonite · Electrospinning

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Introduction

Electrospun polymer nanofibers have attracted a great deal of attention among the academic and industrial scientists because it is a simple and effective technique to produce nanofibers. These electrospun nanofibers have great potential applications to filters, sensors, wound dressing, tissue engineering, drug release, etc. due to unique properties such as high specific surface and narrow diameter [1–8]. Larrondo and Manley first revived the technique by electrostatic spinning of polymer melts in 1981 [9]. Since then, several synthetic and natural polymers were electrospun into fibers [10]. Recently, scientists take an interest in mechanically and thermally advanced nanofibers with decreasing fiber diameter for many applications. One of the great advantage of this method is to increase nanofibers properties with the incorporation of inorganic materials into polymer nanofibers, and it can exhibit the more advanced properties than homopolymer nanofibers [11–15]. Moreover, the properties of the nanofibers are determined by not only the properties of individual fibers but also by the distribution and orientation of the fibers [16].

Montmorillonite (MMT) is one of the most useful inorganic material, and it has been attracting great attention due to its remarkable enhancement in mechanical, thermal, and barrier properties of blend nanofibers with small amounts (1–10 wt.%) of MMT fillers added. Fong et al. first reported the electrospinning of polymer/MMT nanofiber [13]. Hong et al. in their experimental showed that PU/O-MMT nanofiber mats were improved Young's modulus and tensile strength [14]. Li et al. reported that nylon-6/MMT nanofibers have higher melting temperature, Young's modulus, and tensile strength than nylon-6 nanofibers [15]. These property improvements are attributed to the nanometric thickness and high aspect ratio of the individual

clay platelets, as well as to the nanocomposite morphology with the platelets being exfoliated and well dispersed.

PVA has been mainly used in fiber and film products for many years due to its excellent physical and mechanical properties. It is highly biocompatible, non-toxic, and hydrophilic polymer [11, 17–19]. And, it is commercially available in a wide range of molecular weights at a low cost. These properties have led to use PVA in many applications, including nanofibers. But, there is remarkable point: Almost all studies about PVA ultrafine fiber used number-average degrees of polymerization [(P_n)s] of 1,700 ± 50, known as medium-molecular-weight poly(vinyl alcohol) (MMW-PVA) [17, 18, 20, 21]. PVA shows different properties due to molecular weight, tacticity, and degree of saponification. MMW-PVA could have handled it easily for electrospinning fabrication than high-molecular-weight poly(vinyl alcohol) (HMW-PVA). MMW-PVA is not only more soluble but also has some degree of mechanical and thermal stability for many applications.

Recently, our group studied several cases of electrospun PVA blend nanofibers in aqueous solution to make improved nanofibers. Blends of PVA with chitosan oligosaccharide by electrospinning technique show properties changes with homo-PVA nanofibers [22]. We got mechanically and thermally improved PVA blend nanofibers as well as the best condition of PVA blend nanofibers such as electrospinning instrument parameters, including electric voltage and tip-target distance, and also solution parameters like polymer concentration and feed mass ratios. Also, we reported MMW-PVA/HMW-PVA blend nanofibers [23]. It showed that HMW-PVA was required for obtaining improved nanofibers. In this work, we prepared MMW-PVA/HMW-PVA/MMT nanofibers in aqueous solutions. In our above previous works, we confirmed those materials, in which HMW-PVA and MMT had important factors influencing the nanofiber properties [22, 23]. Here, we evaluated the role of MMT contents and blend ratios of two different molecular weights of MMW-PVA and HMW-PVA to electrospun nanofibers properties. Nanofibers were investigated using field-emission scanning electron microscopy (FE-SEM), thermal gravimetric analyzer (TGA), viscometer, transmission electron microscopy (TEM), and mechanical measurements, and the related characterizations were also discussed.

Experimental

Materials

MMW-PVA with P_n = 1,700 [fully hydrolyzed, degree of saponification (DS)=99.9%] was obtained from DC Chemical, Seoul, Korea, and HMW-PVA with P_n = 4,000 [fully hydrolyzed, DS = 99.9%] was synthesized in our laboratory, and synthesis protocol has been published elsewhere [24]. MMT was purchased from Kunmine Indusries, Japan. Doubly distilled water was used to prepare all polymers solutions.

Preparation of PVA/MMT blend nanofiber

MMT powder was dispersed in doubly distilled water under magnetic stirring for 1 h at room temperature, and then the PVA-17 and PVA-40 were added in the solution. The solution was heated in a water bath at 80 °C under magnetic stirring for 2 h followed by cooling to room temperature. The PVA-17/PVA-40/MMT blend solution was prepared at total solid concentration of 7.5% with different mass ratios (10/0, 9/1, 7/3, and 5/5) and different concentrations of MMT (1%, 3%, 5%, and 10%).

Electrospinning of PVA/MMT blend submicron fibers

During electrospinning, PVA-17/PVA-40/MMT blend solutions were put in a syringe and then applied with high voltage power (CHUNGPA EMT, Seoul, Korea; model CPS-60K02VIT). The applied voltage was adjusted to 15 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 15 cm distance to the needle tip. The above spinning conditions were found, being the best condition to make PVA-17/PVA-40 blend nanofiber from our previous work [23].

Characterizations

The morphology of electrospun PVA-17/PVA-40/MMT nanofibers was investigated with a FE-SEM (JEOL, model JSM-6380, Japan) after gold coating and viscosity of blend solution measured by viscometer (Brookfiled, model LVDV-1+ viscometer, USA) used 61 spindles. Tensile strength was determined by the ZWICK Z005 materials testing machine (Zwick GmbH, Germany). The thermal behavior of PVA blend nanofibers were studied with TGA techniques (model Q-50) from TA instruments, USA. TEM analysis was conducted on a H-7600 model machine (HITACHI, LTD) with an accelerating voltage of 100 kV.

Results and discussion

Morphology

Changing the polymer mass ratios of PVA-17/PVA-40 and the MMT contents in the composite could alter the fiber

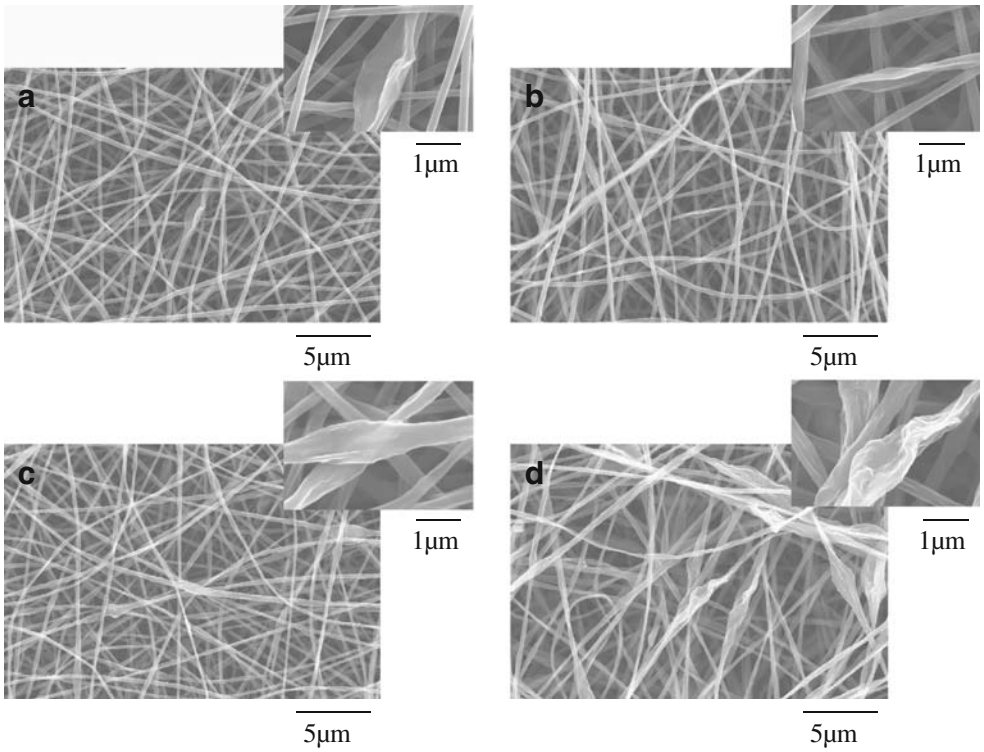

Fig. 1 SEM images of PVA-17/PVA-40/MMT nanofibers that electrospun with various MMT mass ratios of **a** 1, **b** 3, **c** 5, and **d** 10 wt.%. (PVA-17/PVA-40 = 10/0, applied voltage = 15 kV, polymer concentration = 7.5 wt.%, and TCD = 15 cm; *inset* high magnification of some specific beads morphology)

diameter and morphology very effectively, as shown in Figs. 1, 2, 3, and 4. PVA-17/PVA-40 concentration (7.5 wt.%) and instrument parameters such as applied voltage of 15 kV and tip to collector distance of 15 cm were determined as an optimum condition by our recent report in the absence of MMT. This condition was the best to make homogeneity and ultrafine PVA-17/PVA-40 nanofiber. In the present study, we made a series of nanofiber using various PVA-17/PVA-40 mass ratios (10/0, 9/1, 7/3, and 5/5) and MMT contents (1, 3, 5, and 10 wt.% based on

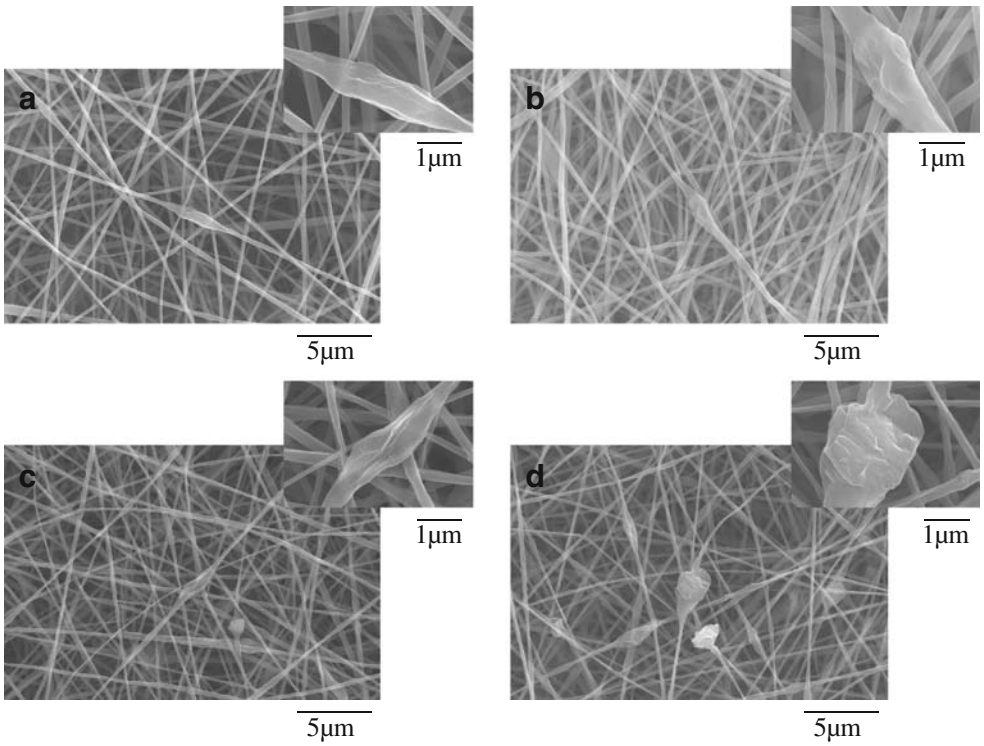

Fig. 2 SEM images of PVA-17/PVA-40/MMT nanofibers that electrospun with various MMT mass ratios of **a** 1, **b** 3, **c** 5, and **d** 10 wt.%. (PVA-17/PVA-40 = 9/1, applied voltage = 15 kV, polymer concentration = 7.5 wt.%, and TCD = 15 cm; *inset* high magnification of some specific beads morphology)

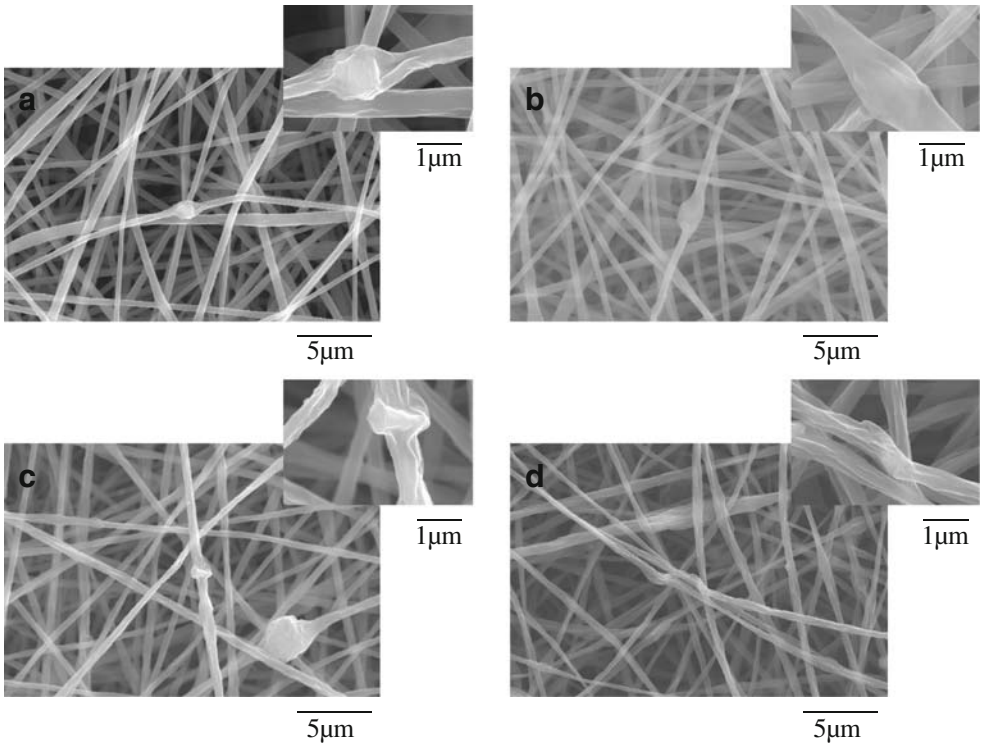

Fig. 3 SEM images of PVA-17/PVA-40/MMT nanofibers that electrospun with various MMT mass ratios of **a** 1, **b** 3, **c** 5, and **d** 10 wt.%. (PVA-17/PVA-40 = 7/3, applied voltage = 15 kV, polymer concentration = 7.5 wt.%, and TCD = 15 cm; *inset* high magnification of some specific beads morphology)

the total solid contents). It should be noted here, when the PVA-17/PVA-40 mass ratios in the blend solutions are lower than 5/5, that the viscosity of the solution is too low to be electrospun, and it was hardly working by this aqueous solution.

Figures 1, 2, 3, and 4 show dramatic morphological changes as the mass of polymers and concentration of MMT change. The obtained nanofibers were ranged from 200 to 700 nm. The average diameters of the PVA-17/PVA-40/MMT nanofibers were increased with the increasing

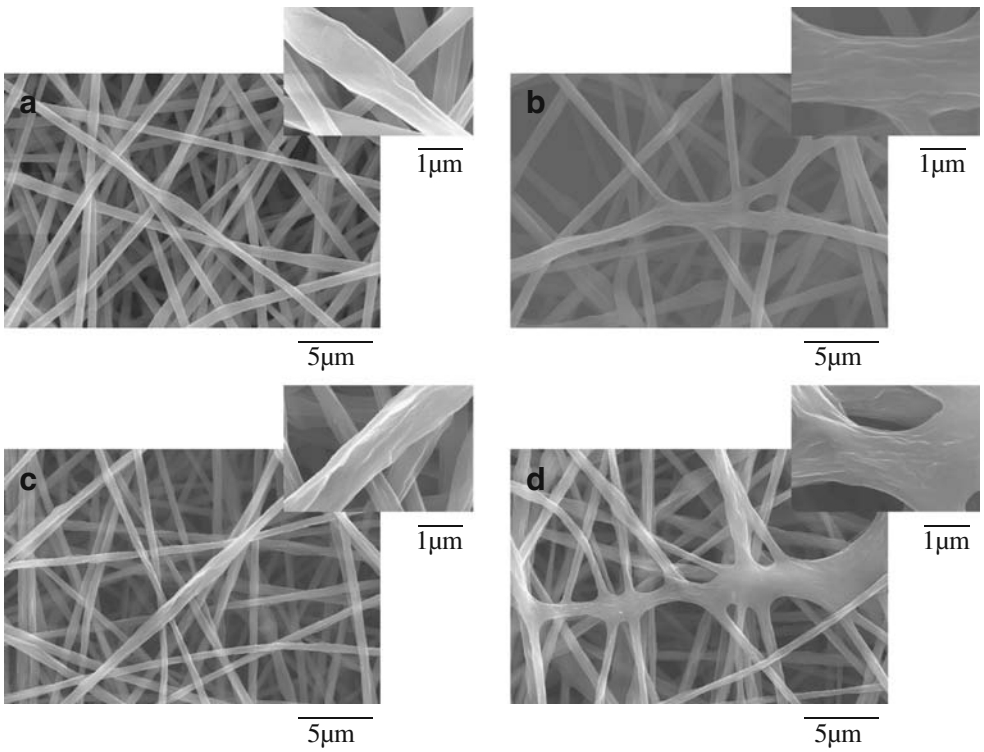

Fig. 4 SEM images of PVA-17/PVA-40/MMT nanofibers that electrospun with various MMT mass ratios of **a** 1, **b** 3, **c** 5, and **d** 10 wt.%. (PVA-17/PVA-40 = 5/5, applied voltage = 15 kV, polymer concentration = 7.5 wt.%, and TCD = 15 cm; *inset* high magnification of some specific beads morphology)

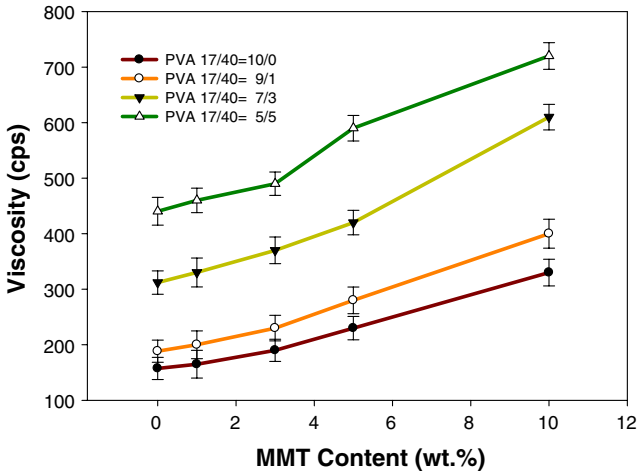

Fig. 5 Viscosity data of eletrospun PVA-17/PVA-40/MMT nanofibers with various MMT mass ratios. (Applied voltage = 15 kV, polymer concentration = 7.5 wt.%, and TCD = 15 cm)

content of HMW-PVA. It is known that the diameter of fibers and the formation of beads were strongly influenced by the viscoelasticity of the solution [25]. By increasing MMT concentration, nanofibers were aggregated, and the homogeneity of the nanofibers was decreased (a to d), suggesting that the homogenous nanofibers could be obtained only at low MMT concentration.

Figure 5 shows viscosity of PVA-17/PVA-40/MMT solutions. According to the addition of HMW-PVA and MMT in the solution, viscosity is increased. The viscosities of the blend solutions also suggest that there might present hydrogen bonding between clay and PVA. As in our experiments, MMT is fully delaminated in water, so the specific surface is increased to maximum, and likewise, the interaction is present between the polymer and MMT particles in aqueous solution. At the same time, the viscosity of the solution is increased. Although high viscosity makes uniform fiber, its diameter also increases. It can be concluded from the above discussions that the PVA-17/PVA-40 mass ratios and MMT contents in the blend solutions are two important parameters, which have remarkable effects on the morphology of electrospun submicron fibers of PVA/MMT blend.

Tensile strength

Some of the fascination with the behavior of polymer comes from the large changes in physical properties and the wide range of mechanical behaviors displayed at easily accessible conditions [26]. Figure 6 shows that the tensile strength of PVA-17/PVA-40/MMT nanofibers when electrospun with various conditions is non-linear even at a small deformation. It is found that the tensile strength of the PVA-17/PVA-40/MMT blend nanofibers is increased with increasing the weight percentage of HMW-PVA and with the MMT contents up to 5 wt.% and then slightly decreased for 10 wt.% of MMT. This result indicates that both HMW-PVA and clay have reinforcement effects on the fibers, and HMW-PVA is more effective than MMT. Clay has a maximum value at a concentration of 5 wt.% (10.4, 11.3, 11.8, and 13.8 MPa) because of the combination effect of molecular chain orientation and well-exfoliated MMT layer structure inside the nanofiber; therefore, the tensile strength values of electrospun fibers increases as the clay concentration is increased. The reason for the slightly decreased tensile strength at 10 wt.% MMT seems to be related to the aggregation of large amount of MMT particles in the polymer matrix at high concentration condition.

Thermal properties

Thermal stability of electrospun PVA/MMT nanofiber was measured using TGA. Tests were conducted at a heat rate of 10°C/min from ambient to 600°C under nitrogen gas atmosphere. Figure 7 shows TGA thermograms of different decomposition temperatures with various PVA-17/PVA-40 mass ratios and MMT contents. PVA is pyrolyzed in the absence of oxyzen and undergoes dehydration and depolymerization at over 200 and 400°C. Three weight loss peaks were observed in the TGA curve for PVA-17/PVA-40. In Fig. 7a, PVA-17/PVA-40/MMT nanofibers exhibit an onset degradation temperature, higher than that of pure PVA-17/PVA-40.

Figure 7b–d shows the similar thermogram trend for PVA-17/PVA-40/MMT blend nanofibers with the 9/1, 7/3, and 5/5 mass ratios, respectively. However, by careful comparison, it was found that higher mass ratio of HMW-PVA has a higher thermal stability. Also, it was found that

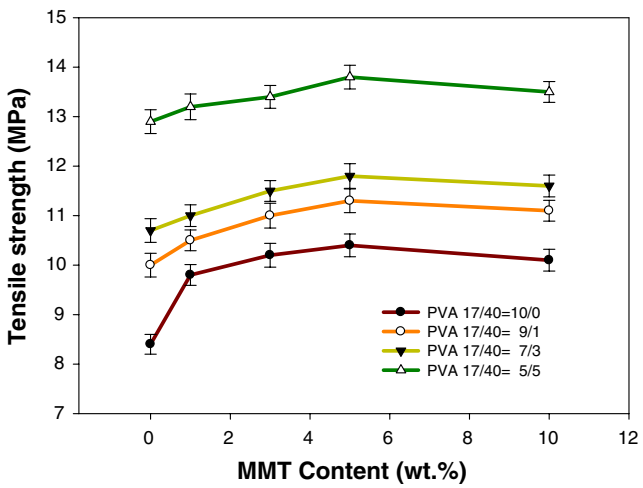

Fig. 6 Tensile strength of eletrospun PVA-17/PVA-40/MMT nanofibers with various MMT mass ratios. (Applied voltage = 15 kV, polymer concentration = 7.5 wt.%, and TCD = 15 cm)

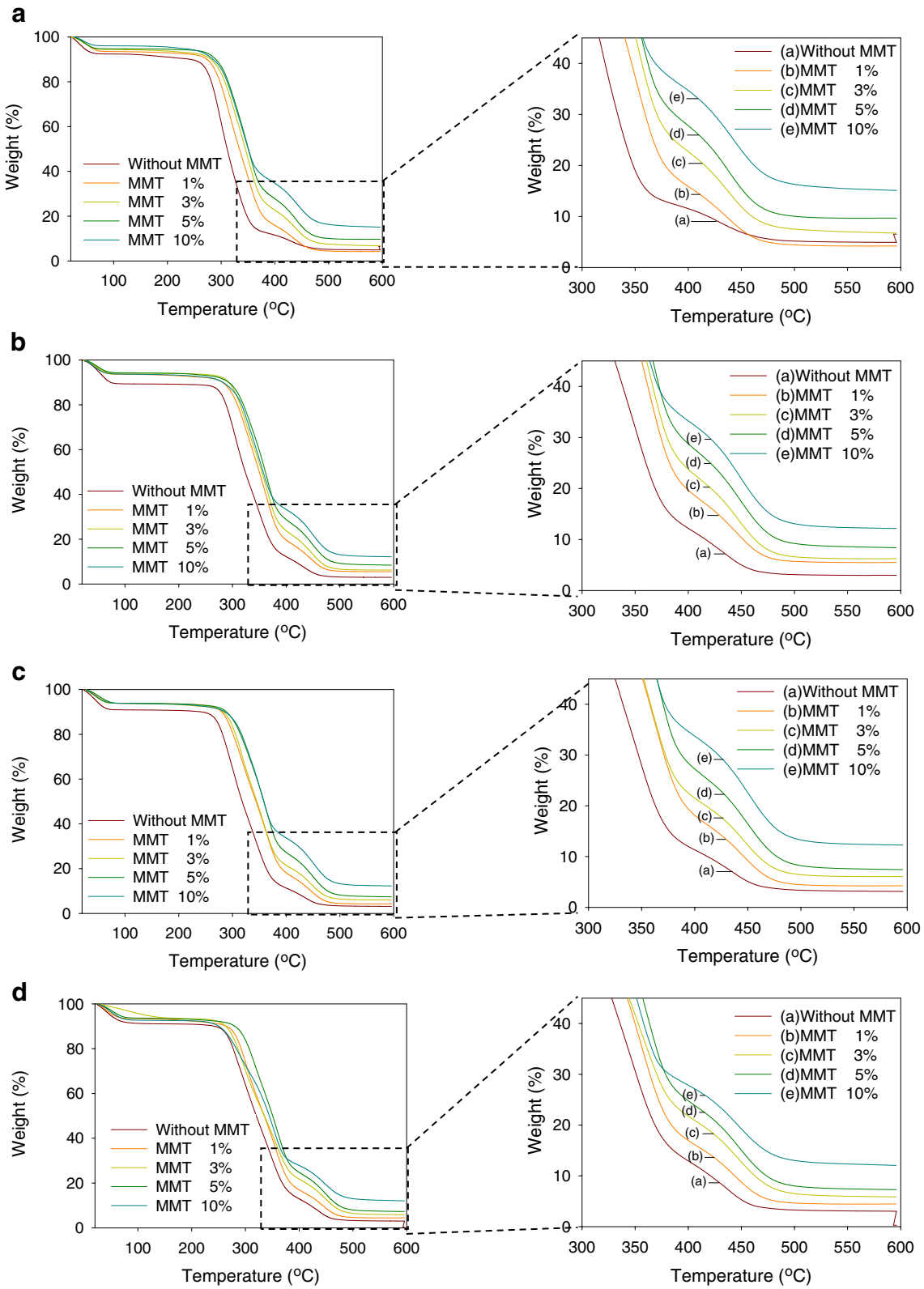

Fig. 7 TGA data of eletrospun PVA-17/PVA-40/MMT nanofibers with various PVA mass ratios of **a** PVA-17/PVA-40 = 10/0, **b** PVA-17/PVA-40 = 9/1, **c** PVA-17/PVA-40 = 7/3, and **d** PVA-17/PVA-40 = 5/5. (Applied voltage = 15 kV, polymer concentration = 7.5 wt.%, and TCD = 15 cm)

the thermal stability was increased gradually with high MMT contents. In enlarged thermograms, we can easily confirm the trend of thermal stability. Higher thermal stability of HMW-PVA and high MMT contents rate might be attributed to its higher chain compactness due to the interaction between the PVA and clay. Incorporation of high temperature nanoparticles such as carbon nanotubes, metals, and clay have also shown to increase thermal decomposition temperatures [27–31]. Thus, we concluded that using high mass of HMW-PVA and MMT could increase thermal stability.

TEM images

TEM analysis of these electrospun nanofibers revealed the distribution of the MMT clay within the PVA matrix. The TEM image in Fig. 8 indicates the nanosize MMT in the nanofibers electrospun from the solution containing 5 wt.% MMT, which appears the highest tensile strength. It can be clearly observed that each silicate platelet forms a dark line in the nanofiber. The size of the dark line is about 2–10 nm thick, indicating the good dispersion and exfoliation of MMT layers in the nanofibers. All of the samples show the same results that the majority of MMT platelets are exfoliated, and they are well distributed within the fiber matrix and oriented along the fiber axis. This clearly indicates the feasibility of electrospinning of the 2-D platelet structures and the potential to achieve proper alignment of these clays along the fiber axis, which is critical for nanocomposite fiber fabrication [13].

Conclusion

This work was directed to the mechanically and thermally advance nanofibers by electrospinning. PVA-17/PVA-40/MMT nanofibers could be fabricated by the electrospinning method in aqueous solutions. The mass ratios of two polymers and concentration of MMT are important factors influencing the electrospinnability of the PVA-17/PVA-40/MMT solutions, the morphology, and the mechanical and thermal properties of the electrospun submicron fibers. Mass ratios of the HMW-PVA and MMT determined the results: Viscosity, tensile strength, and thermal stability are increased as HMW-PVA and MMT are increased. TEM result shows that the majority of MMT platelets are exfoliated, and they are well distributed within the fiber matrix and oriented along the fiber axis. These exfoliated MMT nanoparticles improved the tensile strength and thermal stability of the electrospun nanofibers. The electrospun PVA nanofibers have great potential for the applica-

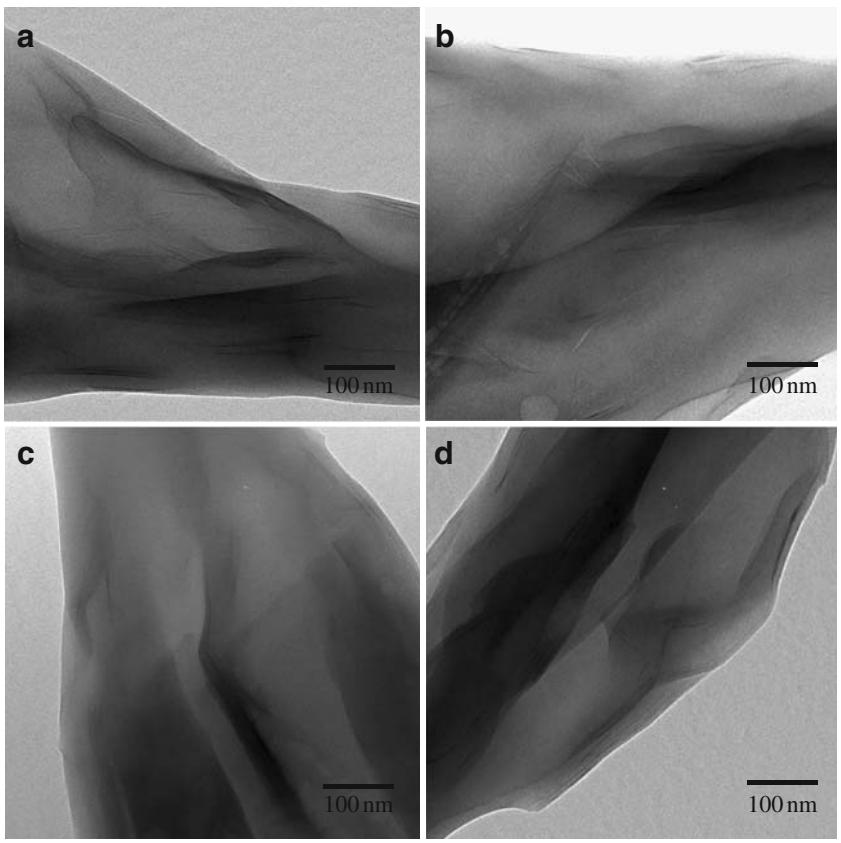

Fig. 8 TEM images of eletrospun PVA-17/PVA-40/MMT nanofibers with various PVA mass ratios of **a** PVA-17/PVA-40 = 10/0, **b** PVA-17/PVA-40 = 9/1, **c** PVA-17/PVA-40 = 7/3, and **d** PVA-17/PVA-40 = 5/5. (Applied voltage = 15 kV, MMT concentration = 5 wt.%, polymer concentration = 7.5 wt.%, and TCD = 15 cm)

tion where both mechanical and biocompatible properties are required such as fiber reinforcement materials.

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