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ORIGINAL CONTRIBUTION

Electrospinning and characterization of poly(vinyl alcohol)/chitosan oligosaccharide/clay nanocomposite nanofibers in aqueous solutions

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Abstract Submicron fibers of the composite of poly(vinyl alcohol) (PVA), chitosan oligosaccharide [COS, (1→4)2-amino-2-deoxy-β-D-glucose], and montmorillonite clay (MMT) were prepared using electrospinning method with aqueous solutions. Scanning electron microscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD), thermal gravimetric analyzer, and tensile strength testing machine (Zwick) were utilized to characterize the PVA/COS/MMT nanofiber mats morphology and properties. The PVA/COS ratio and MMT concentration play important roles in nanofiber mat properties. XRD and TEM data demonstrated that exfoliated MMT layers were well-distributed within nanofiber. It was also found that the mechanical property and thermal stability were increased with COS and MMT contents.

Keywords Poly(vinyl alcohol) · Chitosan oligosaccharide · Montmorillonite · Electrospinning · Nanofiber mat

Introduction

Montmorillonite (MMT) has been attracting great attention due to its remarkable improvement in mechanical, thermal, flame-retardant, and barrier properties of polymeric composites with small amounts (1–10 wt.%) of MMT fillers added. 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. Actually, dispersing a hydrophilic MMT in water is not difficult. The hydrophilic MMT is swellable in water. The swelled MMT is very stable in water solution. The high affinity of hydrophilic MMT to water makes it possible to form a hydrogel with only 5–7% MMT (depends on the type of MMT). These gels are usually very stable and no precipitation can be observed in a month. Even for diluted MMT (~1% MMT), the suspension can be stable in water (without polymer) for a few hours after ultrasonification. With water-soluble polymer, the viscosity of the solution is very high. Therefore, the MMT suspension is stable enough during the electrospinning experiments [1–3].

Poly(vinyl alcohol) (PVA) is a semicrystalline hydrophilic polymer with good chemical and thermal stability [4]. PVA is a highly biocompatible and nontoxic polymer [5]. It can be processed easily and has high water permeability. PVA can form physical gels in various types of solvents, which leads to the use of PVA in a wide range of applications in medical, cosmetic, food, pharmaceutical, and packaging industries. Ultrafine PVA fibers, which may have different potential applications comparing with microfibers, cannot be produced by conventional spinning techniques. It is known that electrospinning is a straightforward method to prepare fibers with diameters as small as several tens of nanometers.

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Chitosan, the second most abundant polysaccharide in nature after cellulose, is an *N*-deacetylated derivative of chitin. It is generally regarded as nontoxic, biocompatible, and biodegradable [6]. It has many unique functional properties for different applications like high molecular weight, high viscosity, high crystallinity, and high capacity to hydrogen bond intermolecularly. However, the rigid D-glucosamine structure and high crystallinity in chitosan usually lead to poor solubility of chitosan in common organic solvents as well as in water, such as at physiological pH values (7.2–7.4), restricting its uses, especially in the human body. However, partially depolymerized chitosan products, i.e., low-molecular-weight chitosan (chitosan oligosaccharide [COS]), could overcome these limitations and hence find much wider applications in diversified fields [7]. Nanofibrous chitosan-containing hybrid materials have been electrospun from mixed solutions of chitosan and polyoxyethylene [8, 9], chitosan and silk fibroin [10], chitosan and PVA [11–14], *N*-carboxyethylchitosan and polyacrylamide [15, 16]. Our recent work, which used PVA/COS as the model components in aqueous solutions, demonstrated that the morphology of PVA/COS nanofiber mat could be controlled by electrospinning instrument parameters, such as including electric voltage and tip–target distance, and solution parameters, such as polymer concentration and feed mass ratio [17].

Although many types of chitosan-containing nanofibers were prepared using electrospinning technique, nanoclay-enhanced chitosan-containing nanofibers have not been prepared using the same technique. Because nanoclay has been widely used in various composites to improve the polymer physical properties, the aim of this study is to evaluate the influence of MMT contents on the PVA/COS/MMT nanocomposite nanofibers prepared from aqueous solutions. The PVA/COS/MMT nanofiber mats were investigated using field emission scanning electron microscope (FE-SEM), thermal gravimetric analyzer (TGA), X-ray diffraction (XRD), transmission electron microscopy (TEM), mechanical measurements, and the related characterizations were also discussed.

Experimental

Materials

PVA with P_n=1,700 [fully hydrolyzed, degree of saponification=99.9%] was obtained from DC Chemical, Seoul, South Korea, and COS (average molecular weight above 10,000; 100% water-soluble) was purchased from Kittolife, Kyongki-do, South Korea and used without further purification. MMT was purchased from Kunmine Industries, Japan. Doubly distilled water was used to prepare all polymers solutions.

Preparation of PVA/COS/MMT blend solutions

MMT powder was dispersed in doubly distilled water under magnetic stirring for 1 h at room temperature and then the PVA was 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. COS powder was dissolved in doubly distilled water under magnetic stirring for 2 h at room temperature. The PVA/COS/MMT blend solution was prepared by mixing of PVA/MMT and COS aqueous solution at total solid concentration of 12.5% with different mass ratios (6/4, 8/2, and 10/0) and different concentrations of MMT (1%, 3%, 5%, and 10%).

Electrospinning of PVA/COS/MMT blend nanofiber mats

During electrospinning, high voltage power (Chungpa EMT, Seoul, South Korea; model CPS-60K02VIT) was applied to the PVA/COS/MMT solution in a syringe via an alligator clip attached to the syringe needle. 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 to be the best condition to make PVA/COS blend nanofiber mats in our recent report [17].

Characterizations

The morphology and property characterizations of electrospun PVA/COS/MMT nanofibers were investigated with FE-SEM (JEOL, model JSM-6380) after gold coating and XRD (Philips model X'Pert APD) with the Cu Kα radiation with wavelength of 0.154 nm. The scanning rate was 2°/min ranging from 10° to 30° (2θ). The TEM analysis was conducted on H-7600 model machine (Hitachi) with an accelerating voltage of 100 kV. The samples ultratoming was conducted on a Leica Ultracut UCT machine with samples embedded within an epoxy resin matrix. The ultrathin cut films with thickness about 50–70 nm were directly transferred onto the TEM grid for TEM observation. The fiber diameter was measured from the SEM images. From each image, at least 20 different fibers and 100 different segments were randomly selected for measuring the average fiber diameter by using the Photoshop 5.0 software. Tensile strength was determined by the Zwick Z005 testing machine (Zwick, Germany). The thermal behavior of the PVA blend nanofiber mats was studied with TGA techniques (model Q-50 from TA Instruments, USA).

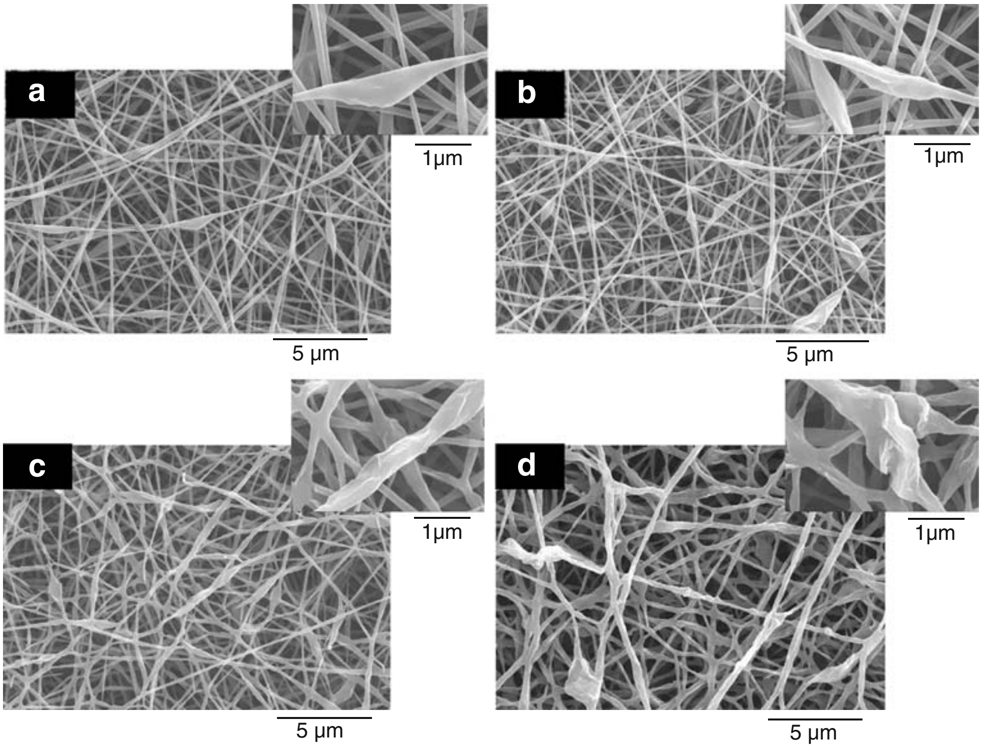

Fig. 1 SEM images of PVA/COS/MMT nanofiber mats that were electrospun with various MMT mass ratios: **a** 1 wt.%, **b** 3 wt.%, **c** 5 wt.%, **d** 10 wt.% (PVA/COS=6/4, voltage=15 kV, concentration=12.5%, TCD=15 cm)

Results and discussion

Morphology

Changing the polymer mass ratio of PVA/COS and the MMT content in the composite could alter the fiber diameter and morphology very effectively, as shown in Figs. 1, 2, and 3. At the operation voltage of 15 kV and tip to collector distance (TCD) of 15 cm, a series of nanofiber mats was made at a fixed total solid content (12.5 wt.%) but various PVA/COS mass ratio (6/4, 8/2, and 10/0) and MMT contents (1 wt.%, 3 wt.%, 5 wt.%, and 10 wt.% based on

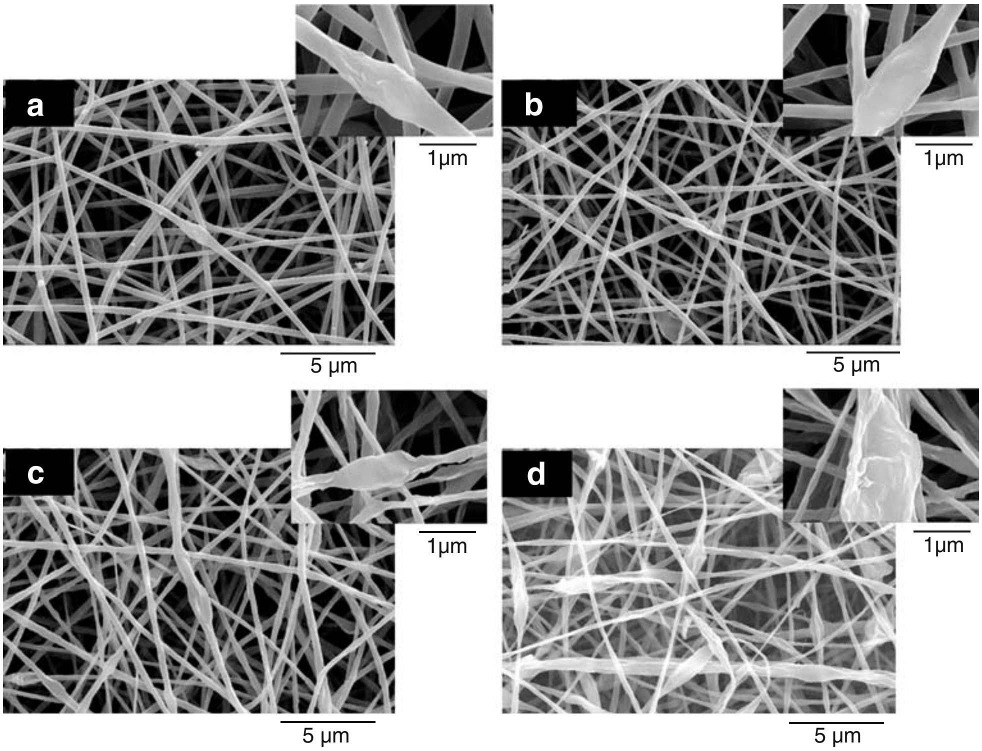

Fig. 2 SEM images of PVA/COS/MMT nanofiber mats that were electrospun with various MMT mass ratios: **a** 1 wt.%, **b** 3 wt.%, **c** 5 wt.%, **d** 10 wt.% (PVA/COS=8/2, voltage=15 kV, concentration=12.5%, TCD=15 cm)

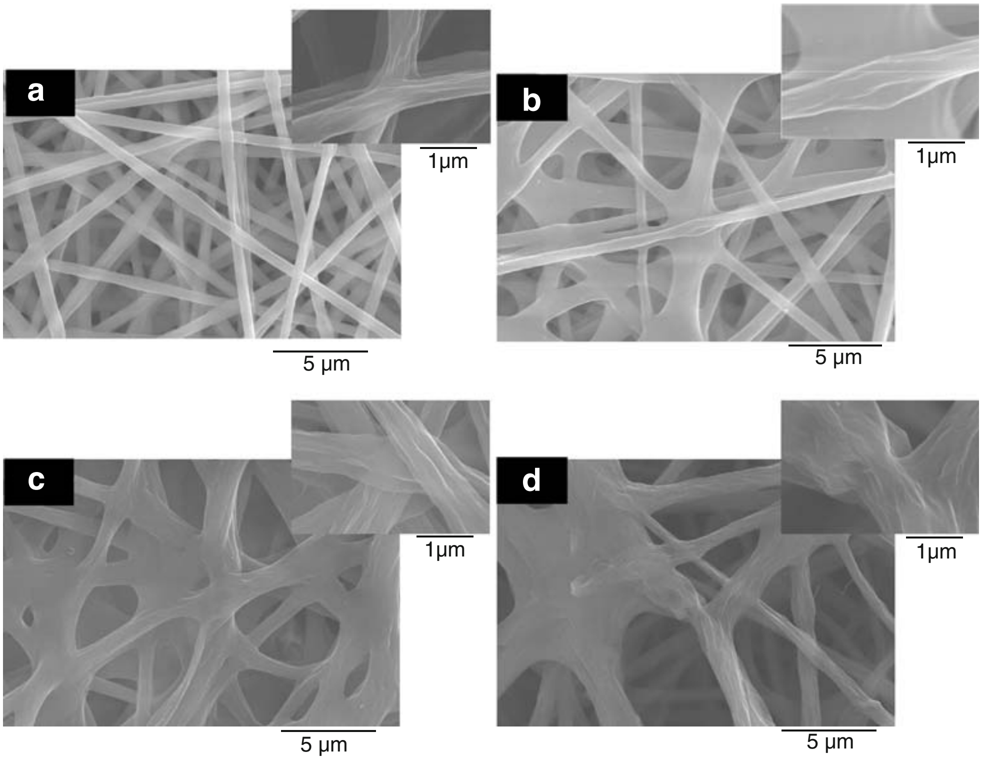

Fig. 3 SEM images of PVA/COS/MMT nanofiber mats that were electrospun with various MMT mass ratios: **a** 1 wt.%, **b** 3 wt.%, **c** 5 wt.%, **d** 10 wt.% (PVA/COS=10/0, voltage=15 kV, concentration=12.5%, TCD=15 cm)

the total solid content). PVA/COS concentration and other parameters were determined by our recent report in the absence of MMT [17]. It should be noted that, when the PVA/COS mass ratio in the blend solutions is higher than 6/4, the viscosity of the solution is too low to be electrospun. Figures 1, 2, and 3 show dramatic morphological changes as the mass of COS and concentration of MMT. It is interesting to note that some small "beads" are presented in some samples. By carefully comparing the SEM images shown in Figs. 1, 2, and 3, we found that the number of beads and fiber diameter show opposite tendency by COS ratio. The maximum bead number and the smallest average diameter of nanofibers were found at a PVA/COS mass ratio of 6/4 (Figs. 1 and 4). It is known that the diameter of the fibers and the formation of beads are strongly influenced by the viscoelasticity of the solution [18]. By increasing MMT concentration, nanofibers were aggregated and the homogeneity of the nanofibers was decreased (Figs. 1, 2, and 3), suggesting that the homogenous nanofibers could be obtained only at low MMT concentra-

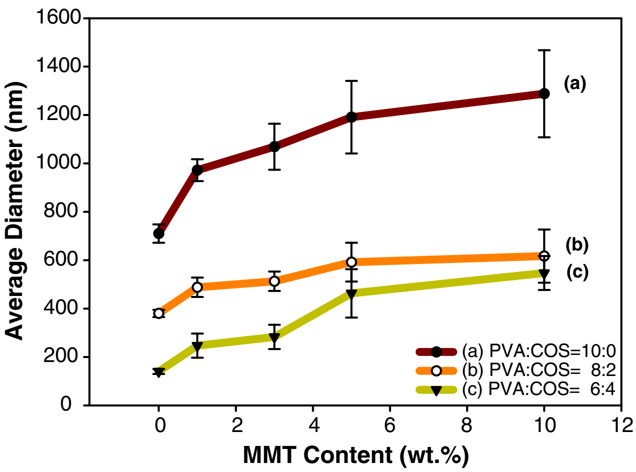

Fig. 4 Average diameter of PVA/COS/MMT nanofiber mats that were electrospun with various conditions (voltage=15 kV, concentration=12.5%, TCD=15 cm)

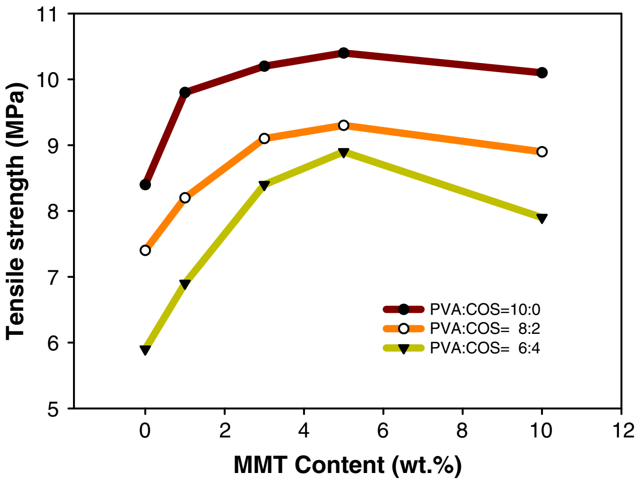

Fig. 5 Tensile strength of PVA/COS/MMT nanofiber mats that were electrospun with various conditions (voltage=15 kV, concentration=12.5%, TCD=15 cm)

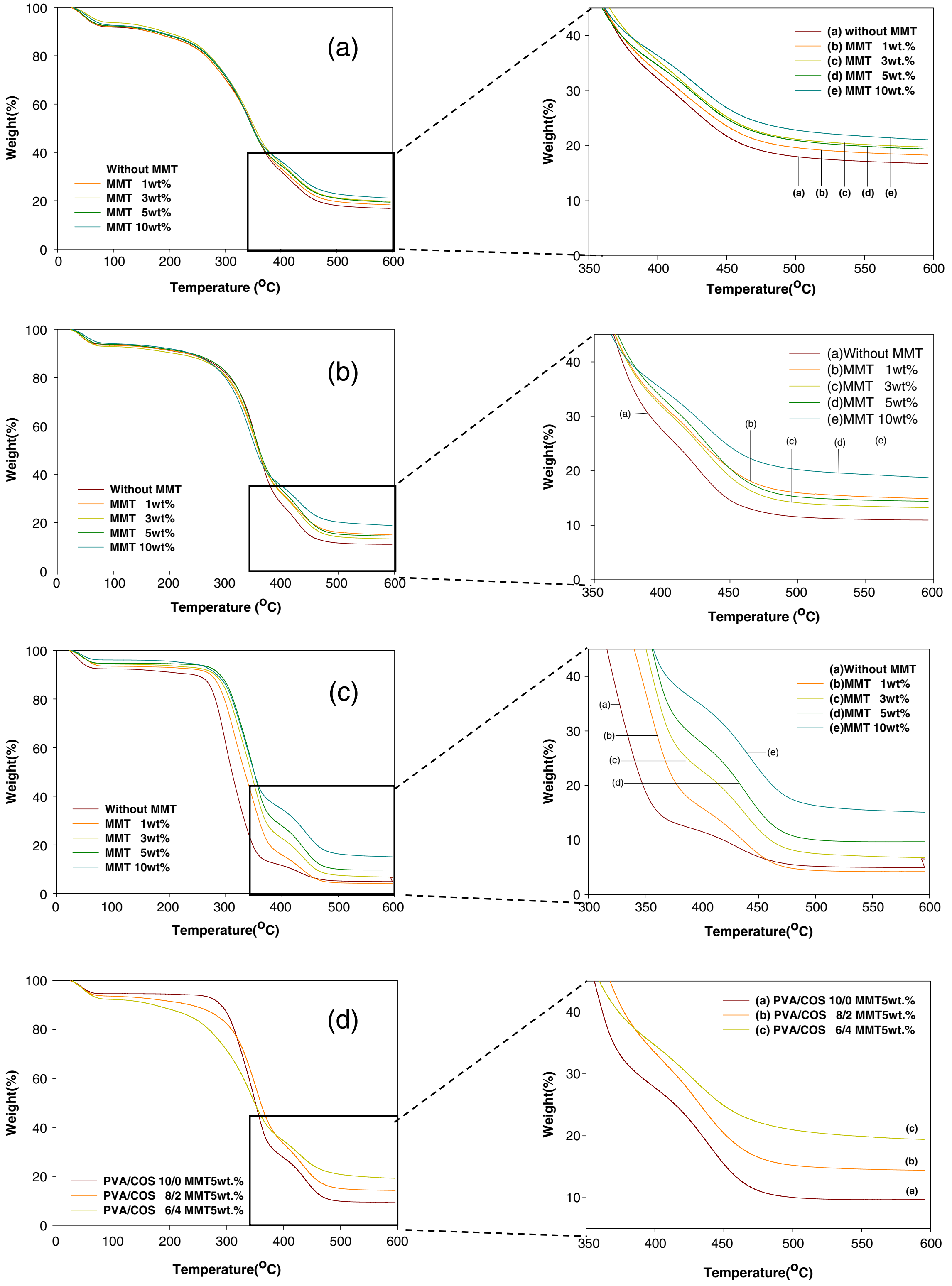

Fig. 6 TGA data of electrospun PVA/COS/MMT nanofiber mats with various MMT mass ratios: **a** PVA/COS=6/4, **b** PVA/COS=8/2, **c** PVA/COS=10/0, **d** PVA/COS/MMT 5 wt.% with different ratios of PVA/COS (voltage=15 kV, concentration=12.5%, TCD=15 cm)

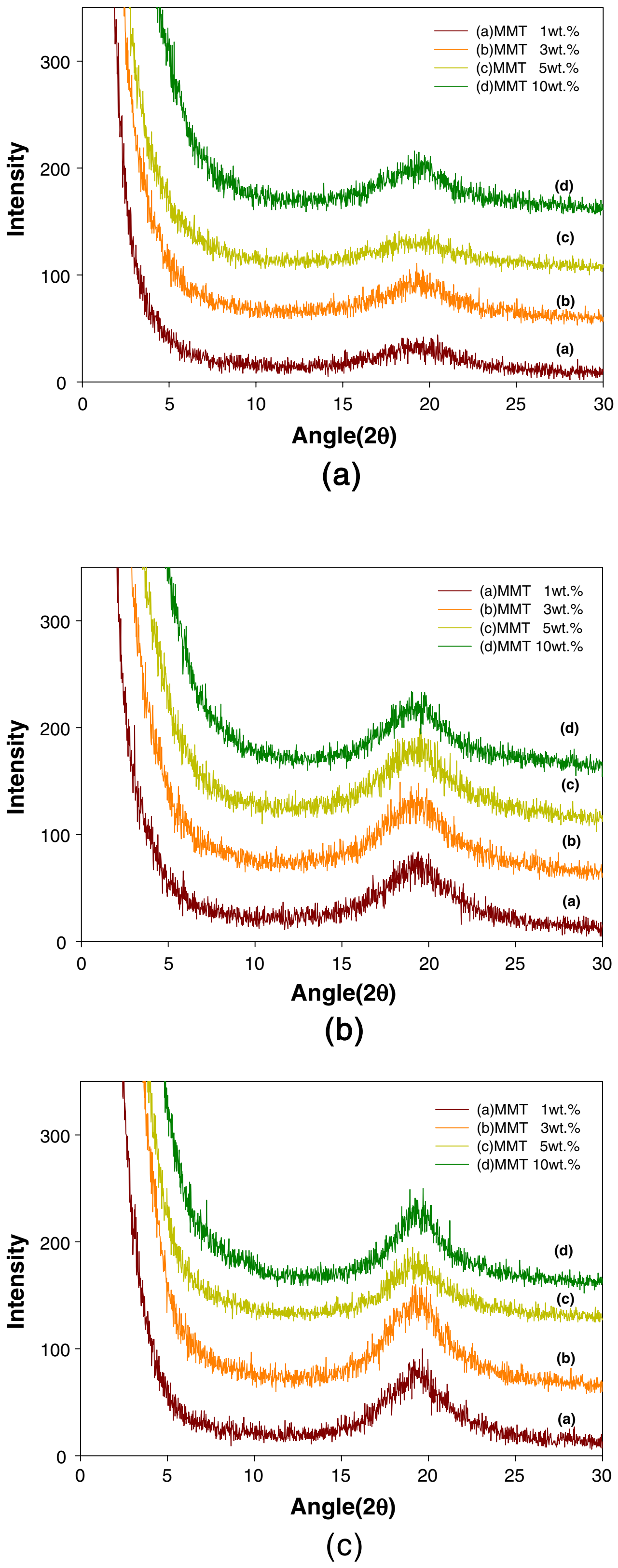

Fig. 7 XRD data of electrospun PVA/COS/MMT nanofiber mats with various MMT mass ratios: **a** PVA/COS=6/4, **b** PVA/COS=8/2, **c** PVA/COS=10/0 (voltage=15 kV, concentration=12.5%, TCD=15 cm)

tion. Figure 4 shows the dependence of the average diameter of the PVA/COS/MMT nanofiber on the PVA/COS ratio and the total MMT content, which indicates a slight increase in the fiber diameter when MMT concentration was increased. It can be concluded that, from the above discussion, the PVA/COS mass ratio and MMT content in the blend solutions are two important parameters which have remarkable effects on the morphology of electrospun submicron fibers of the PVA/COS/MMT blend.

Tensile strength

Figure 5 shows the tensile strength of the PVA/COS/MMT nanofiber mats that were electrospun with various conditions. It was found that the tensile strength of the PVA/COS blend nanofibers is decreased with increasing weight percentage of COS [17], but is increased with MMT contents up to 5 wt.% and then decreased. This result indicates that clay has a reinforcement effect on the fibers. Clay has a maximum value at a concentration of 5 wt.% 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. However, the tensile strength reaches the maximum value at clay concentration of 5 wt.% and further increase in the clay concentration results in a decrease in the tensile strength. This result appears to be related to the aggregation of a large amount of MMT particles in the polymer matrix at high concentration condition [19].

Thermal properties

The thermal stability of electrospun PVA/COS/MMT nanofiber was measured using TGA in nitrogen atmosphere. The TGA thermograms shown in Fig. 6 indicate that the fiber mats with various PVA/COS mass ratios and MMT contents have different decomposition temperatures. Three weight loss peaks were observed in the TGA curve for bulk PVA. Figure 6a, b shows the similar thermogram trend for PVA/COS blend nanofibers with the 6/4 and 8/2 mass ratios. However, by careful comparison, it was found that higher mass ratio of COS has a higher thermal stability (Fig. 6d) [17]. It was also found that the thermal stability was increased with MMT contents. Higher thermal stability of high MMT content rate might be attributed from its higher chain compactness due to the interaction between the PVA and the clay.

XRD data

The pure PVA fiber mat shows a significant crystalline peak at about 19.3°, which is because of the occurrence of strong intermolecular and intramolecular hydrogen bonding [17]. It is well-known that, in a nanoclay–polymer composite, unexfoliated or intercalated MMT usually has a peak in the range 3–9° (2θ). For exfoliated nanocomposites, on the other hand, single silicate layers (1 nm thick) are homogeneously dispersed in the polymer matrix and no distinct diffraction peak in the range of 3–9° (2θ) should be detected [20, 21]. As shown in Fig. 7, as the amount of COS in the PVA/COS blend fibers is increased [(c) to (a)], the diffraction peak at about 19.3° of pristine PVA becomes broad and the intensity of the peak becomes low. Also, there is no diffraction peak in 3–9° (2θ). This suggests that the crystallinity of PVA/COS fibers with higher COS amounts (8/2 and 6/4 mass ratios) is lower in comparison with the electrospun PVA fiber. The TEM image (Fig. 8) confirms that MMT clays are well-dispersed in the nanofiber mats, and they are predominantly exfoliated.

TEM image

The TEM observation reveals the formation of the composite nanofibers and the distribution of the MMT nanoparticles in the nanofiber matrix. The TEM image in Fig. 8b–d indicates the nanosize MMT in the nanofibers electrospun from the solution containing 5 wt.% MMT. It can be clearly observed that each silicate platelet forms a dark line in the nanofiber compare with the pure PVA nanofiber (Fig. 8a). The size of the dark line is about 1–3 nm in width and 100–200 nm in length, indicating the good dispersion and exfoliation of MMT layers in the nanofibers. The TEM results reveal that the majority of the 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

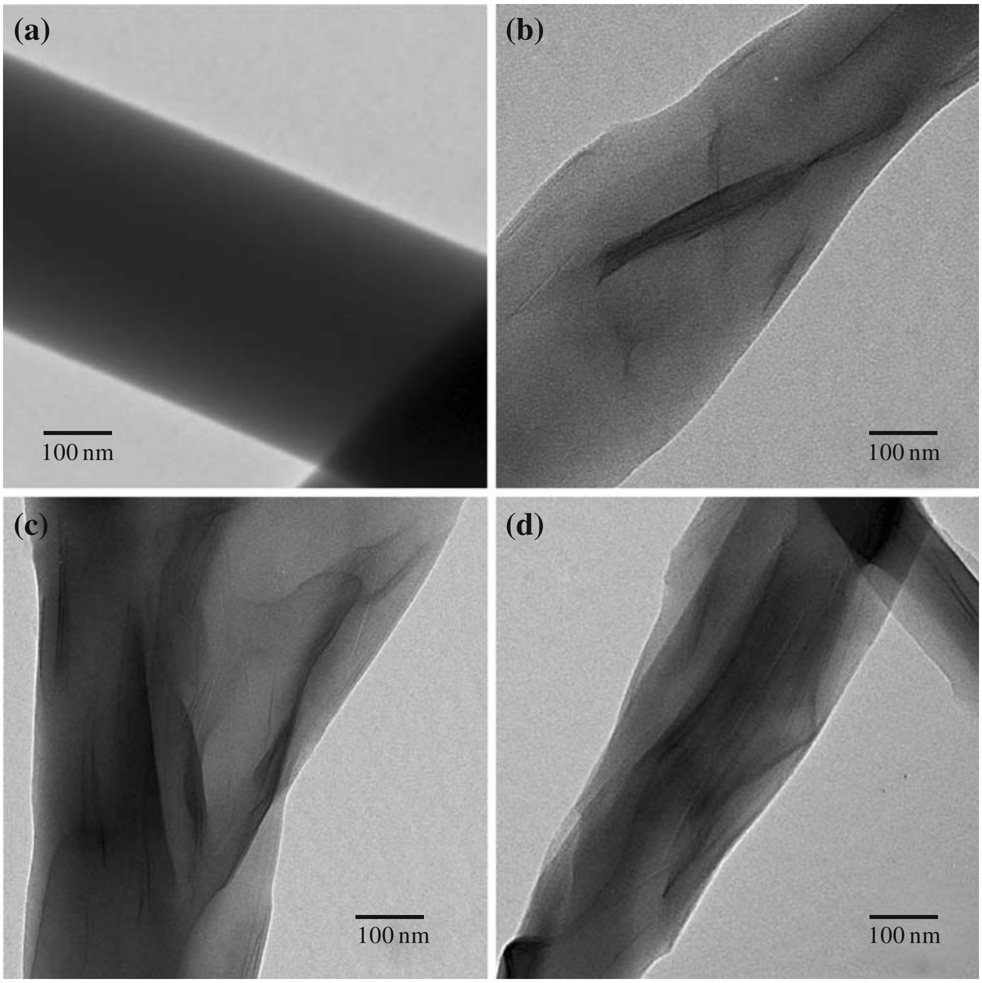

Fig. 8 TEM images of PVA/COS/MMT nanofiber mats that were electrospun with various PVA/COS mass ratios: **a** pure PVA, **b** PVA/COS=6/4, **c** PVA/COS=8/2, **d** PVA/COS=10/0 (MMT=5 wt.%, voltage=15 kV, TCD=15 cm)

these clays along the fiber axis, which is critical for nanocomposite fiber fabrication [22].

Conclusions

Ultrafine PVA/COS/MMT nanofiber mats could be fabricated by the electrospinning method in aqueous solutions. The mass ratio of two polymers and concentration of MMT are important factors influencing the electrospinnability of the PVA/COS/MMT solutions, the morphology, and mechanical as well as thermal properties of the electrospun submicron fibers. As the COS mass ratio increases (PVA/COS=10/0, 8/2, 6/4), the diameter and the tensile strength of nanofiber mats are decreased, but the thermal stability is increased with COS contents. In the presence of MMT in the nanofiber mats, the XRD and TEM results show that the majority of the 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 results obtained in this study may help fabricate high-strength and high-thermal stable electrospun polymer nanocomposite fiber that can be utilized in many industries such as biomedical application, filter, reinforcement in matrix, and protective clothing application [23–28].

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