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전기방사법을 이용한 폴리(비닐 알코올)/ 수분산 폴리우레탄/몬모릴로나이트 나노복합섬유의 제조 및 특성분석

김인교 · 염정현†
경북대학교 기능물질공학과
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Electrospinning Fabrication and Characterization of Poly(vinyl alcohol)/ Waterborne Polyurethane/Montmorillonite Nanocomposite Nanofibers

In Kyo Kim and Jeong Hyun Yeum†
Department of Advanced Organic Materials Science & Engineering, Kyungpook National University, Daegu 702-701, Korea
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초록: 전기방사법을 이용하여 폴리(비닐 알코올)(poly(vinyl alcohol), PVA)/수분산 폴리우레탄(waterborne polyurethane, WBPU)/montmorillonite clay(MMT) 나노복합섬유를 제조하고 특성을 분석하였다. Scanning electron microscopy(SEM), transmission electron microscopy(TEM), X선 회절, thermal gravimetric analyzer(TGA)의 분석장비들을 이용하여 제조된 나노복합섬유의 형태와 구조적, 열적특성을 확인한 결과, 평균직경이 600~900 nm인 나노복합섬유들이 성공적으로 제조되었으며, MMT가 나노섬유 내에 완전박리되어 기존의 고분자 나노섬유에 비해 열적성질이 향상되었음을 확인할 수 있었다. 본 연구를 통해 제조된 나노복합섬유는 친수성이고 생체친화적인 재료들을 이용하여 제조되었으며, 의료 분야를 비롯하여 의류 및 산업용 코팅제, 필터 등의 분야로 이용이 가능할 것으로 보인다.

Abstract: Poly(vinyl alcohol) (PVA)/waterborne polyurethane (WBPU)/montmorillonite clay (MMT) nanocomposite nanofibers were prepared using electrospinning technique of aqueous solutions. Scanning electron microscopy, transmission electron microscopy, X-ray diffraction and thermal gravimetric analyzer were used to characterize the morphology and properties of the nanocomposite nanofibers. Since PVA, WBPU and MMT are hydrophilic, non-toxic and biocompatible materials, these nanocomposite nanofibers can be used for filter and medical industries as wound dressing materials, antimicrobial filters, etc.

Keywords: poly(vinyl alcohol)(PVA), waterborne polyurethane(WBPU), montmorillonite(MMT), nanocomposite, nanofiber.

Introduction

Polymer nanocomposites with montmorillonite clay (MMT) have been attracting great attention due to MMT-filled polymer composites which exhibit remarkable improvement in material properties and with a low percentage of MMT filler content. The main advantages of these nanocomposites are improved thermal and mechanical properties, reduced flammability and better barrier properties compared to unfilled polymers. 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.[1] Today, efforts are being conducted globally; using almost all types of polymer matrices to produce MMT based nanocomposites for packaging and medical applications.[2-4]

Polyurethane is widely used as functional polymers in the medical field as their properties can be tailor-made by adjusting their compositions.[5-7] It has excellent performance but the preparation of these materials requires a large amount of volatile organic solvent which enters the atmosphere during the drying stage. Hence the development of waterborne polyurethane (WBPU) formulations has been motivated by environmental considerations.[8,9] However, WBPU has low

†To whom correspondence should be addressed.
E-mail: jhyeum@knu.ac.kr

viscosity; it is difficult to make WBPU nanofiber from it.

One of the simplest ways for preparing polymer nanocomposite is electrospinning which is widely used for making nanofiber. This technique has received exceedingly great concern from academic and industrial scientists since it is economical, simple, and effective technology to produce polymer nanofibers. They showed remarkable properties such as high specific surface areas and porosities, so these nanofibers can be expected to have potential applications in many fields such as separation filters, tissue scaffold, protective clothing, catalysis reaction, wound dressing materials, sensors, etc.[10-14]

Recently, our group has reported several cases of electrospun PVA blend nanofibers made by electrospinning technique. Blend with chitosan oligosaccharide, WBPU, pullulan, different molecular weight of PVA, MMT, and silver nanoparticles respectively or together.[15-22] During these processes, it has been optimized under the best condition to make PVA blend nanofiber such as electrospinning instrument parameters and solution parameters.

In this study, the PVA nanocomposite nanofibers containing different amounts of WBPU and MMT were successfully prepared using the electrospinning technique. All materials in this study are non-toxic and biocompatible and they can be used in coatings, adhesives, binders, air filters, protective textiles, sensors and medical industries such as wound dressing materials, antimicrobial filters, etc.. The effects of WBPU and MMT on PVA nanofiber formation and the properties were investigated using field-emission scanning electron microscope (FE-SEM), transmission electron microscopy (TEM), reflection type X-ray diffraction (XRD), and thermogravimetric analysis (TGA).

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, Korea and WBPU (solid content = 35%, M_w = 18000) was purchased from Cytec Industries Inc., Korea. MMT was purchased from Kunimine Industries Co., Japan. Doubly distilled water was used as a solvent to prepare all solutions.

Preparation of PVA/WBPU/MMT Blend Solutions. At first, MMT (1, 3, 5, and 10 wt%) powders were dispersed in distilled water under magnetic stirring for 1 h at room temperature. After the MMT was dispersed, PVA was added to all solutions. The solutions were heated in a water bath at 80 ℃ under magnetic stirring for 2 h followed by cooling to room temperature. After dissolved, the required amount of the WBPU was added into all solutions under magnetic stirring for another 2 h at room temperature. The total polymer concentration of blend solution is 15 wt% and PVA/WBPU mass ratio is 7/3. This content of WBPU in PVA hybrid nanofibers revealed the best electrospinnability and properties in our previous report which was predominant reason for using same amount of WBPU in this experiment.[22]

Electrospinning of PVA/WBPU/MMT Nanofiber. During electrospinning, a high voltage power (CHUNGPA EMT Co., Korea) was applied to the PVA/WBPU/MMT blend solutions contained in a syringe via an alligator clip attached to the syringe needle. The applied voltage was adjusted at 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 vertical distance to the needle tip. The above spinning conditions were found being the best condition to make PVA blend nanofiber in our previous reports.[15-22]

Characterizations. The morphology and properties characterization of electrospun PVA/WBPU/MMT nanofiber was observed 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 1.2°/min ranging 1.5° to 35° (2θ). The average diameter of the electrospun fibers was measured by Adobe Photoshop 5.0 software from the FE-SEM images. TEM analysis was conducted on a model H-7600 machine (HITACHI) and accelerating voltage of 120 kV and the thermal behavior of PVA/WBPU/MMT nanofibers was studied with TGA techniques (model Q-50) from TA instruments, USA at the rate of 10 ℃/min from room temperature to 600 ℃ under the nitrogen gas atmosphere.

Results and Discussion

Morphology. The FE-SEM images of PVA/WBPU/MMT nanocomposite nanofibers prepared from aqueous solutions at 7/3 blend ratio of PVA/WBPU containing different amounts of MMT (0, 1, 3, 5 and 10 wt%) are shown in Figure 1. The inset on each image is the enlarged FE-SEM image of PVA/WBPU/MMT nanofibers respected images.

It is found that nanocomposite nanofibers with average diameters of around 600~900 nm were obtained. By increasing MMT concentration from none to 10 wt%, the prepared nanofibers have a rough surface and this is common phenomenon of polymer/MMT clay nanocomposites.[17-21] The effects of the MMT loading on the nanofibers average diameter have been elucidated in Figure 2. It indicates a slightly increase in the fiber diameter when MMT concen-

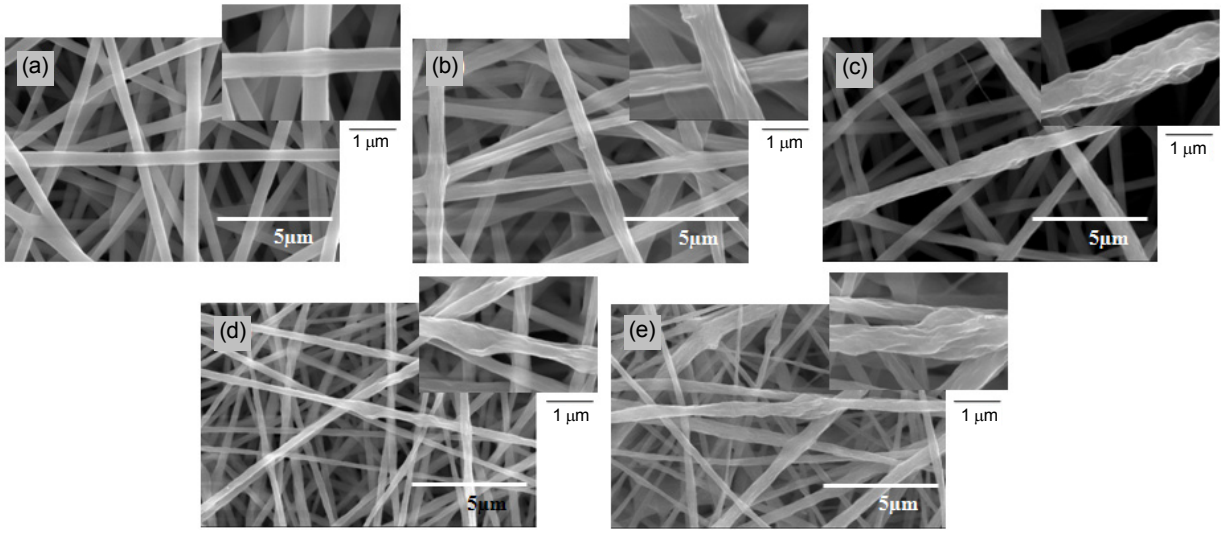

Figure 1. FE-SEM images of (a) pure PVA/WBPU nanofibers and PVA/WBPU/MMT nanofibers prepared with different MMT contents of (b) 1; (c) 3; (d) 5; (e) 10 wt%(inset: high magnification morphologies of related images).

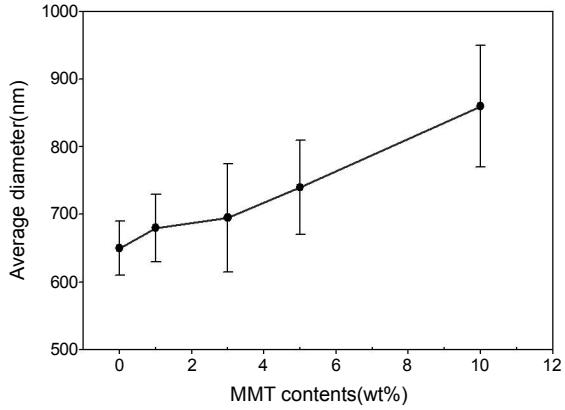

Figure 2. Effects of MMT loading on the average diameter of nanofibers.

tration was increased but fibers homogeneity decreases with increasing of MMT contents from 0 to 10 wt%. TEM images (Figure 3) present an actual image of clay platelets to permit identification of internal morphology of nanocomposites. It can be clearly observed that each silicate platelet forms a dark line in the nanofibers. The size of the dark line is about 2 ~10 nm thick which indicates good dispersion and exfoliation of MMT layers in the nanofibers.

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 X-ray diffraction. Generally intense reflection in the range of 3~9° (2θ) indicates 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-

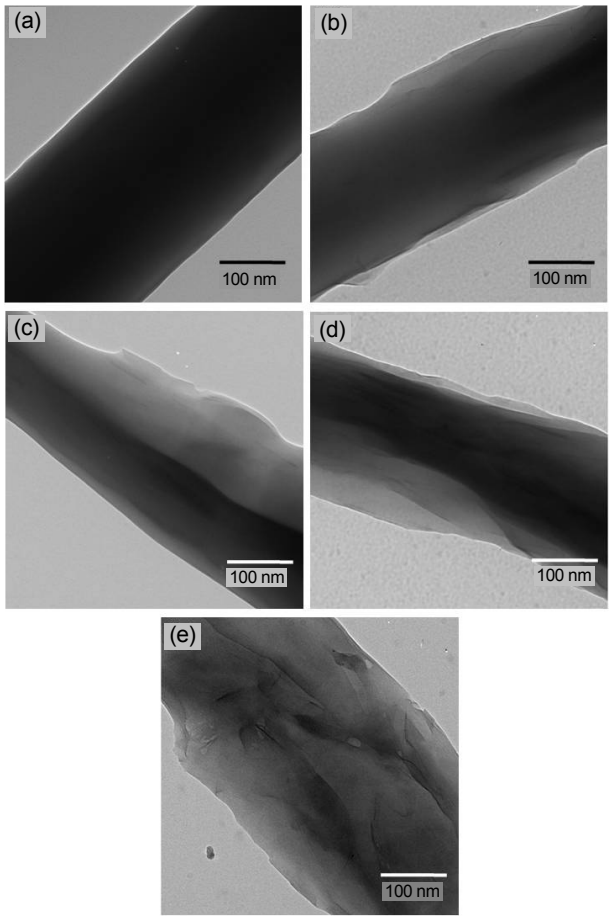

Figure 3. TEM images of (a) pure PVA/WBPU nanofibers and PVA/WBPU/MMT nanofibers prepared with different MMT contents of (b) 1; (c) 3; (d) 5; (e) 10 wt%.

9°(2θ) could be observed.[23,24] Figure 4 shows the XRD patterns of electropsun PVA/WBPU/MMT nanofiber mats with 0, 1, 3, 5 and 10 wt% of MMT contents. The pure PVA/

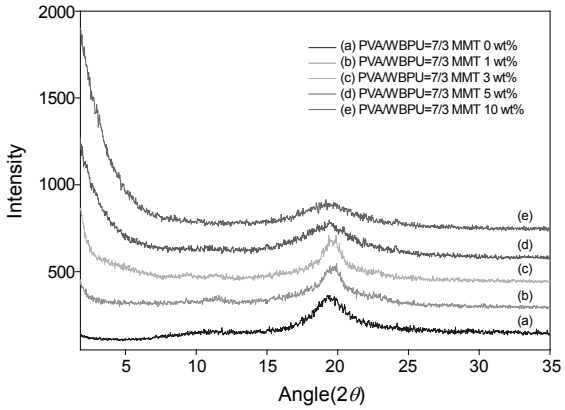

Figure 4. XRD data of (a) eletrospun pure PVA/WBPU nanofibers and PVA/WBPU/MMT nanofibers prepared with different MMT contents of (b) 1; (c) 3; (d) 5; (e) 10 wt%.

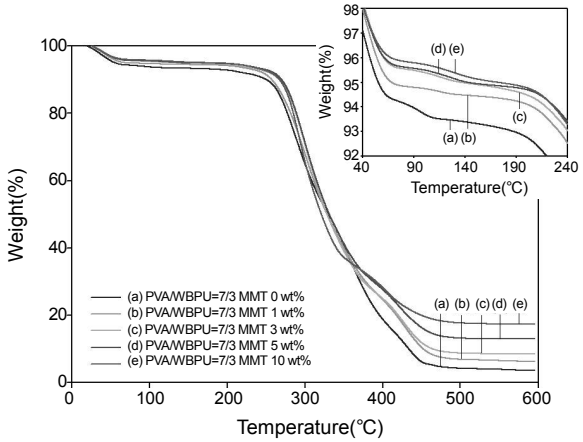

Figure 5. TGA data of (a) pure PVA/WBPU nanofibers and PVA/WBPU/MMT nanofibers prepared with different MMT contents of (b) 1; (c) 3; (d) 5; (e) 10 wt%.

WBPU fiber mat exhibits a significant crystalline peak at 19.3°, which is owing to the occurrence of string inter- and intra-molecular hydrogen bonding. The XRD diffraction pattern of WBPU indicates that it is a typical amorphous material. With the TEM images (Figure 3), XRD results exhibit that MMT is well dispersed in the PVA/WBPU nanofiber, and MMT is predominantly exfoliated.

Thermal Stability. Thermal stability of electrospun PVA/WBPU/MMT nanofibers was measured using TGA in nitrogen atmosphere. Figure 5 shows TGA thermograms of different decomposition temperatures with MMT contents of 0, 1, 3, 5, and 10 wt%. The most below curve of TGA data [Figure 5(a)] represents the PVA/WBPU nanofibers and the most upper curve [Figure 5(e)] is for composite nanofibers with 10 wt% of MMT. All the curves show the same trend of PVA/WBPU thermal stability; three weight loss peaks are observed in Figure 5 and rapid change in mass occurs in the range of 225~450 ℃. The increased thermal stability of MMT content might be attributed to its well chain compactness due to the interaction between polymer matrix and MMT clay.

Conclusions

PVA/WBPU/MMT nanocomposite nanofibers could be successfully fabricated by the electrospinning method in aqueous solutions and characterized by FE-SEM, TEM, XRD and TGA. Uniform PVA/WBPU/MMT nanofibers with an average diameter of nanometer-scale (600~900 nm) could be prepared from PVA/WBPU (7/3) blend solution containing different amount of MMT contents (1~10 wt%). The study shows that the introduction of MMT results in improvement of thermal stability of the polymer matrix. XRD patterns and TEM micrographs suggest the coexistence of exfoliated MMT layers over the studied MMT contents.

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