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Carbon Nanotube Embedded Multi-Functional Polymer Nanocomposites

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1. Introduction

Polymer nanocomposites represent a new alternative to conventionally filled polymers which have significant commercial potential. Polymer nanocomposites are a class of materials in which nanometer scaled inorganic nanomaterials are dispersed in an organic polymer matrix in order to improve the structures and properties of the polymers effectively. An advanced morphologies and improved properties are expected from the polymer nanocomposite materials due to the synergetic effect of the comprising components which could not be obtained from the individual materials. The incorporation of a small amount of inorganic materials such as metal nanoparticles, carbon nanotubes (CNTs), clay into the polymer matrix significantly improve the performance of the polymer materials due to their extraordinary properties and hence polymer nanocomposites have a lot of applications depending upon the inorganic materials present in the polymers [34; 41; 58; 63].

There are many types of nanocomposites such as polymer/inorganic particle, polymer/polymer, metal/ceramic, and inorganic based nanocomposites which have attracted much interest to the scientists [59]. These types of polymer nanocomposites have diverse field of applications such as optics, electrical devices, and photoconductors, biosensors, biochips, biocompatible thin coatings, biodegradable scaffolds, drug delivery system and filter systems [81; 29; 30; 35; 46; 49; 51].

There are so many methods to produce polymer nanocomposites such as simple mixing of required inorganic materials with polymers [38], in-situ polymerization of monomers inside the galleries of the inorganic host [31], melt intercalation of polymers [53; 54] etc. On the other hand, to blend polymers directly with inorganic materials, microwaves, latex-colloid interaction, solvent evaporation, spray drying, spraying a polymer solution through a small orifice and Shirasu Porous Glass (SPG) membrane emulsification technique are employed [1; 7; 33; 36; 44; 59].

Electrospinning is one of the most important techniques for preparing polymer nanocomposite nanofibers that has attracted great interest among academic and industrial scientists. Electrospinning is a very simple, low cost, and effective technology to produce polymer nanocomposite nanofibers which have exhibited outstanding physicochemical properties such as high specific surface area, high porosity and resistance against microorganism. These nanofibers are widely used as separation filters, wound dressing materials, tissue engineering, scaffold engineering, drug delivery, sensors, protective clothing, catalysis reaction, etc. [3; 16; 19; 26; 28; 32; 38; 43; 47; 55; 56; 57; 59; 64]. Electrospraying is as the same as electrospinning and widely used to prepare polymer nanocomposite nanoparticles. The main distinguishable characteristics between electrospinning and electrospraying is the solution parameter that is low concentrated polymer solution is used during electrospraying.

Suspension polymerization is also another synthetic method to produce a whole range of polymer/inorganic nanocomposites. It is low cost, effective, and easy to manipulate and control particle size. In suspension polymerization technique there are some variables which have great effect on the polymerized microspheres. These variables include the type and amount of initiator and suspending agent, the polymerization temperature, the monomer to water ratio, and the agitation speed [14; 11; 17; 18; 25].

Fabrication of polymer nanocomposites with various morphologies by using different technique such as, electrospinning, electrospraying, and in-situ suspension polymerization has been discussed in this article. Inorganic nanomaterials such as, carbon nanotube (CNTs), gold (Au) and silver (Ag) nanoparticles, and inorganic clay, montmorillonite (MMT), were incorporated within the polymer, poly (vinyl alcohol) (PVA), matrix using the method mentioned above. These nanocomposites were characterized by field emission-type scanning electron microscope (FE-SEM), transmission electron microscopy (TEM), optical microscopy, and differential scanning calorimetry (DSC). The anti-bacterial performance of polymer nanofibers was also discussed.

2. Background

Inorganic nano-structured materials and their nano-composites have potential applications in microelectronics, optoelectronics, catalysis, information storage, textile, cosmetics and biomedicine. For instance, TiO_2 , silver, gold, carbon nanotubes (CNTs), nano-clay and their nanocomposites are widely used in diverse fields for their anti-microbial, UV protecting,

photo-catalyst, electrical conductive and flame retardant characteristics [4; 5; 6; 10; 15; 22; 39; 48; 52; 62].

Semi-crystalline structure, good chemical and thermal stability, high biocompatibility, non-toxicity, and high water permeability have made poly(vinyl alcohol) (PVA) the promising candidate for a whole range of applications especially in the medical, cosmetic, food, pharmaceutical and packaging industries [24; 27; 28; 42]. The outstanding physicochemical properties and unique structures of carbon nanotubes (CNTs) have made them attractive material for a whole range of promising applications such as supports for inorganic nanomaterials, central elements in electronic devices, building blocks for the fabrication of advanced nano devices and catalyst. They also have anti-microbial activity [39; 22].

Metal nanoparticles have potential application in diverse field of modern science [6]. Gold nanoparticles have novel biomedical applications for their anti-bacterial, anti-fungal, and electrical conductive characteristics. Antibacterial effectiveness against acne or scurf and no tolerance to the antibiotic have caused their commercial usage in soap and cosmetic industries [5; 15; 37; 60; 62]. Excellent structure depended physicochemical properties of silver nanoparticles have expanded their potential applications such as a photosensitive components, catalysts, chemical analysis, antibacterial and disinfectant agents. Silver nanoparticles have excellent resistance against microorganisms. Introducing Ag nanoparticles into polymer matrix improve the properties and expand the applications of polymer nanocomposites [6; 13; 38; 45; 59].

As an inorganic materials, MMT has been widely used in polymer nanocomposites to improve their mechanical, thermal, flame-retardant, and barrier properties. A small amount of MMT is effective enough to promote performance of polymer composites. It is regularly used for packaging and biomedical applications [9; 38; 50].

3. Experimental

3.1. Materials

PVA with P_n (number-average degree of polymerization) = 1,700 [fully hydrolyzed, degree of saponification = 99.9%] was collected from DC Chemical Co., Seoul, Korea. MMT was purchased from Kunimine Industries Co., Japan. Hydrogen tetrachloro aurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), tetra-n-octylammonium bromide (TOAB), sodium borohydride (NaBH_4), 4-(dimethylamino)pyridine (DMAP), polyvinylpyrrolidone (PVP, $M_w = 10,000$) were purchased from Sigma-Aldrich, toluene from Junsei, MWNT (CM-95) from ILJIN Nanotech Co. Ltd., and aqueous silver nanoparticle dispersion (AGS-WP001; 10,000 ppm) with diameters ca.15–30 nm was purchased from Miji Tech., Korea. All of these chemicals were used as received. Gold (Au) nanoparticles were synthesized following the method described elsewhere by reducing gold salt between water/toluene interfaces and stabilized by TOAB in toluene. Finally to obtain highly polarized Au nanoparticles, an aqueous 0.1M DMAP solution was added to the as-made Au nanoparticles of the same volume [2; 12]. Doubly distilled

water was used as a solvent to prepare all the solutions. Vinyl acetate (VAc) purchased from Aldrich was washed with aqueous NaHSO_3 solution and then water and dried with anhydrous CaCl_2 , followed by distillation in nitrogen atmosphere under a reduced pressure. The initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) (Wako) was recrystallized twice in methanol before use [21] PVA with a number-average molecular weight of 127,000 and a degree of saponification of 88% (Aldrich) was used as a suspending agent.

3.2. Electrospinning nanocomposite nanofibers

The electrospinning was performed following our previous work [38]. Our group has optimized the best condition to make PVA blend nanofiber such as polymer concentration, electric voltage applied to create Taylor cone of polymer solutions, tip-collector distance (TCD), and solution flow rate etc. [20; 23; 26; 27; 38]. The polymer blend solution was contained in a syringe. During electrospinning, a high voltage power (CHUNGPA EMT Co., Korea) was applied to the polymer solution by an alligator clip attached to the syringe needle. The applied voltage was adjusted to 15 kV. The solution was delivered through the blunt needle tip by using syringe pump to control the solution flow rate. The fibers were collected on an electrically grounded aluminum foil placed at 15 cm vertical distance to the needle tip. The electrospinning process is shown schematically in Figure 1.

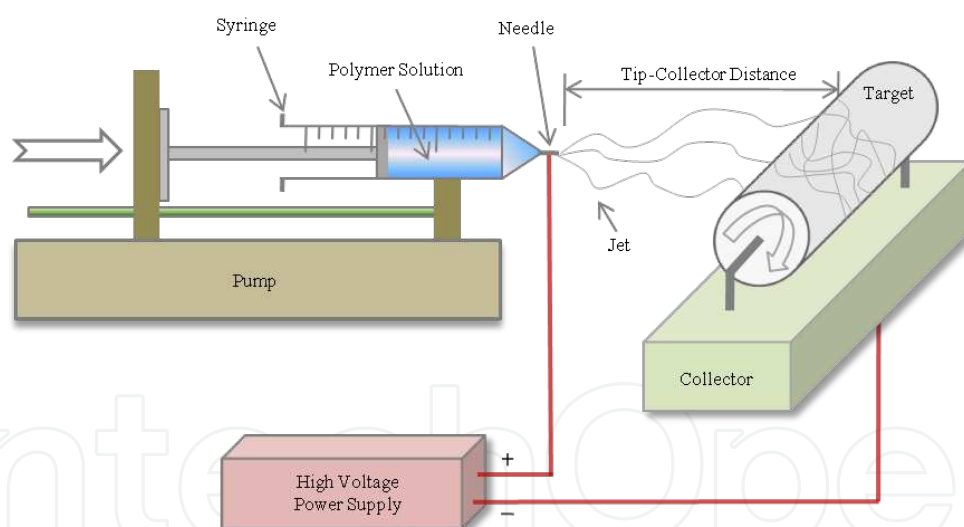


Figure 1. Schematic representation of electrospinning process

3.3. Electrospaying nanocomposite nanoparticles and nanosphere

The principle and apparatus setting of electrospaying and electrospinning techniques is the same. The most important variable distinguishing electrospaying and electrospinning is solution parameter such as polymer molecular weight, concentration and viscosity, etc. Our group has optimized the suitable conditions for electrospaying to prepare nanoparticles and nanosphere. During electrospaying 15-30 kV power was applied to the PVA solution to

fabricate PVA/MWNT nanoparticles and PVA/MWNT/Ag nanospheres and the solution concentration was fixed at 5 wt% of PVA, 1 wt% of MWNTs and 1 wt % of Ag nanoparticles. The nanoparticles and nanospheres were collected on an electrically grounded aluminum foil placed at 15 cm vertical distance to the needle tip.

3.4. Suspension polymerization and saponification of nanocomposite microspheres

Vinyl acetate (VAc) was polymerized through suspension polymerization method to prepare PVAc/MWNT nanocomposite microspheres following the procedure described elsewhere [21]. Monomer and MWNTs were mixed together prior to suspension polymerization. Suspending agent, PVA, was dissolved in water under nitrogen atmosphere and ADMVN was used as an initiator. After 1 day cooling down of the reaction mixture, the collected PVAc/MWNTs nanocomposite microspheres were washed with warm water. To produce PVAc/PVA/MWNT core/shell microspheres, the saponification of PVAc/MWNT nanocomposite microspheres was conducted in an alkali solution containing 10 g of sodium hydroxide, 10 g of sodium sulfate, 10 g of methanol and 100 g of water following the method reported by [21]. PVAc/PVA/MWNT core/shell microspheres were washed several times with water and dried in a vacuum at 40 C for 1 day.

3.5. Anti-bacterial test

Resistance of PVA/MWNT-Au nanofibers against *Staphylococcus aureus* (ATCC6538) were performed following the conditions described in a report published by [38]. Samples were prepared by dispersing the nanofibers in a viscous aqueous solution containing 0.01 wt.% of neutralized polyacrylic acid (Carbopol 941, Noveon Inc.). A mixed culture of microorganism, *Staphylococcus aureus* (ATCC6538) was obtained on tryptone soya broth after 24 h incubation at 32 C. Then, 20 g of samples were inoculated with 0.2 g of the microorganism suspension to adjust the initial concentration of bacteria to 10⁷ cfu/g. Then, the inoculant mixed homogeneously with the samples and was stored at 32 C.

3.6. Characterization

Field-emission scanning electron microscopic (FE-SEM) images were obtained using JEOL, JSM-6380 microscope after gold coating. The transmission electron microscopy (TEM) analysis was conducted on an H-7600 model machine (HITACHI, LTD) with an accelerating voltage of 100 kV. The thermal properties were studied with differential scanning calorimeter (DSC) (Q-10) techniques from TA instruments, USA under the nitrogen gas atmosphere. The core/shell structure of PVAc/PVA/MWNT nanocomposite microspheres was examined using an optical microscope (Leica DC 100). The degree of saponification (DS) of PVAc/PVA/MWNT nanocomposites microspheres was determined by the ratio of methyl and methylene proton peaks in the ¹H-NMR spectrometer (Varian, Sun Unity 300) [21]. The antibacterial performance was investigated to examine the biological function of PVA/MWNT/Au nanofibers by KSM 0146 (shake flask method) using ATCC 6538 (*S. aureus*) [38].

4. Results and discussion

4.1. PVA/MWNT-Au nanocomposite nanofibers

4.1.1. Morphology

Figure 2 shows the FE-SEM images of pure PVA and PVA/MWNT-Au nanocomposite nanofibers and they are compared each other. The high magnification images are shown in the insets of each respective image. It can be seen from Fig. 2 that the average diameter of PVA/MWNT-Au nanocomposite nanofiber is increased compared to pure PVA nanofiber due to the incorporation of MWNT-Au nanocomposites into PVA nanofiber. The average diameter of pure PVA nanofibers is estimated ca. 300 nm whereas that of the PVA/MWNT-Au composite nanofiber is ca. 400 nm. Moreover, the PVA/MWNT-Au nanofibers are found quite smooth and bead free as like as pure PVA nanofiber. This result indicates that MWNT-Au nanocomposites have expanded the morphology of PVA nanofiber and they have been embedded well within the PVA nanofiber.

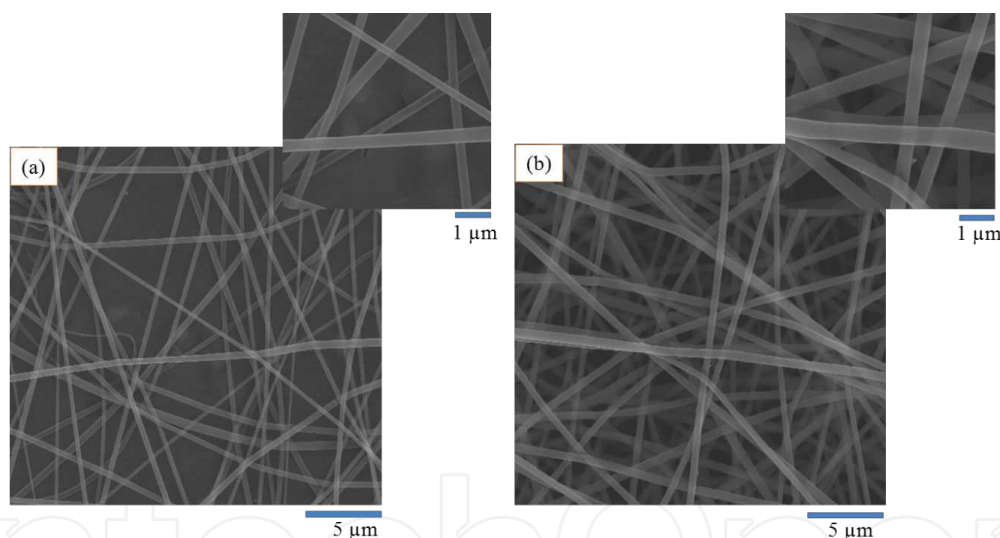


Figure 2. FE-SEM images of (a) pure PVA and (b) PVA/MWNT-Au nanocomposite nanofibers (PVA solution concentration = 10 wt%, TCD=15 cm, and applied voltage=15 kV; inset: high magnification morphologies of related images).

The detailed morphologies of the PVA/MWNT-Au nanocomposite nanofibers are investigated by transmission electron microscopy (TEM). Figure 3 demonstrates the TEM images of pure PVA and PVA/MWNT-Au composite nanofiber. Distributions of Au nano particles on the sidewalls of MWNTs and the structures of MWNT-Au composites are reported in our previous publication [40]. MWNT-Au nanocomposites are found unaltered into the polymer matrix comparing with our previous work [40]. A single isolated MWNT-Au nanocomposite is clearly seen in Figure 3 (b). This TEM image reveals that Au nanoparticles are remaining attached on the sidewalls of MWNTs and MWNT-Au nanocomposites are distributed along

the PVA nanofiber which supports the smooth and uniform morphology of PVA/MWNT-Au composite nanofiber observed in the SEM images.

Moreover, this TEM image confirms that composites of MWNTs and Au nanoparticles were embedded well within the PVA nanofiber rather than cramming MWNTs and Au nanoparticles randomly. This might be a unique architecture of polymer nanofiber containing CNTs decorated with metal nanoparticles. However, some MWNT-Au composites were clustered together which is shown in Fig 3(c). This image indicates that in a polymer matrix MWNT-Au composites can be distributed randomly within the entire length of nanofiber.

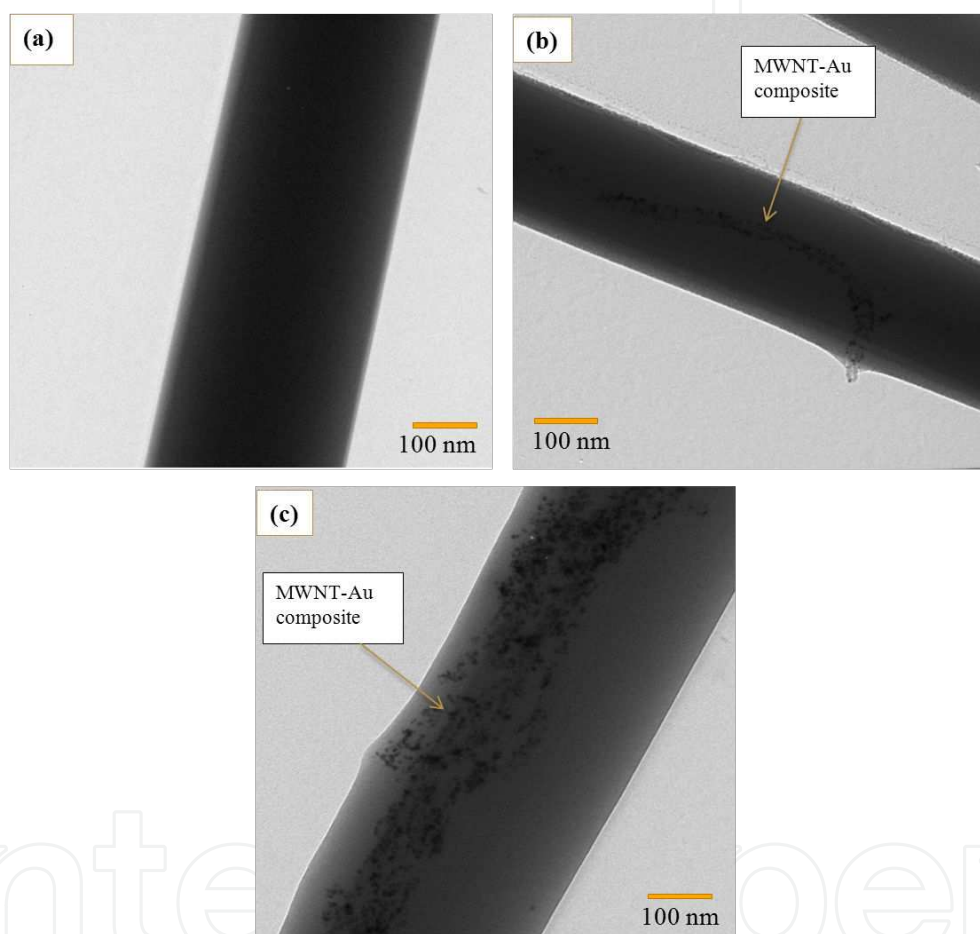


Figure 3. TEM images of (a) pure PVA nanofiber, and (b)-(c) PVA/MWNT-Au nanocomposite nanofibers. A single isolated (b) and an aggregated (c) MWNT-Au composites are clearly visible inside the fibers in which the Au nanoparticles are strongly attached to the surface of MWNTs. (PVA solution concentration= 10 wt%, TCD=15 cm, and applied voltage=15 kV.)

4.1.2. Thermal properties

Pyrolysis of PVA in nitrogen atmosphere undergoes dehydration and depolymerization at temperatures greater than 200 and 400 C, respectively. The actual depolymerization temperature depends on the structure, molecular weight, and conformation of the polymer [26]

Thermo gravimetric analysis (TGA) was conducted in nitrogen atmosphere to investigate the thermal stability of electrospun PVA/MWNT-Au nanocomposite nanofibers and the data were compared with pure PVA nanofibers. Figure 4 shows the TGA thermograms of pure PVA and PVA/MWNT-Au nanocomposite nanofiber at different decomposition temperature. Though the change is unclear but it can be assumed from the TGA thermograms that the thermal property of PVA/MWNT-Au nanocomposite nanofibers is different from pure PVA nanofiber [26]. This result suggest that incorporating MWNT-Au nanocomposites can cause a change in thermal stability of PVA/ MWNT-Au nanocomposites nanofiber.

4.1.3. Antibacterial efficacy

CNTs and Au nanoparticles both have strong inhibitory and antibacterial effects as well as a broad spectrum of antimicrobial activities [5]. In this work, we have investigated the antibacterial efficacy of PVA/MWNT-Au nanocomposites nanofibers. The data obtained from the resistance of nanocomposite nanofiber against bacteria were compared with those of pure PVA nanofiber. The antibacterial test was performed in viscous aqueous test samples and shown in Fig. 5. The performance of nanofiber against bacteria was evaluated by counting the number of bacteria in the sample with the storage time at 32 °C. As shown in Fig. 5, pure PVA nanofibers are not effective enough to prevent the growth of bacteria and hence, a number of bacteria in the test samples remaining constant for a long time. On the other hand, PVA/MWNT-Au nanocomposites nanofibers exhibit a remarkable inhibition of bacterial growth completely. This result indicates that only a small amount of MWNT-Au nanocomposites have improved anti-bacterial efficacy of PVA nanofibers and can make PVA nanofibers more efficient against bacteria. These features might have a potential medical applications.

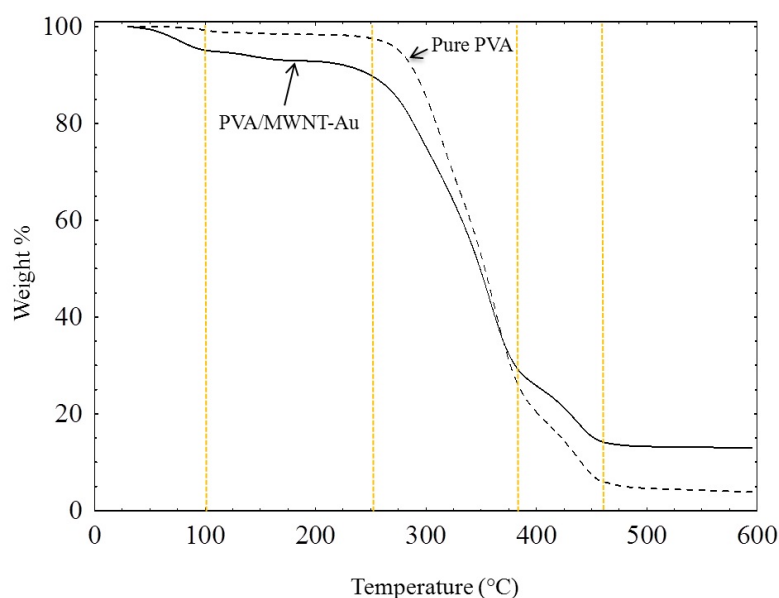


Figure 4. TGA thermograms of pure PVA and PVA/MWNT-Au composites nanofibers (PVA solution concentration = 10 wt%, TCD=15 cm, and applied voltage=15 kV)

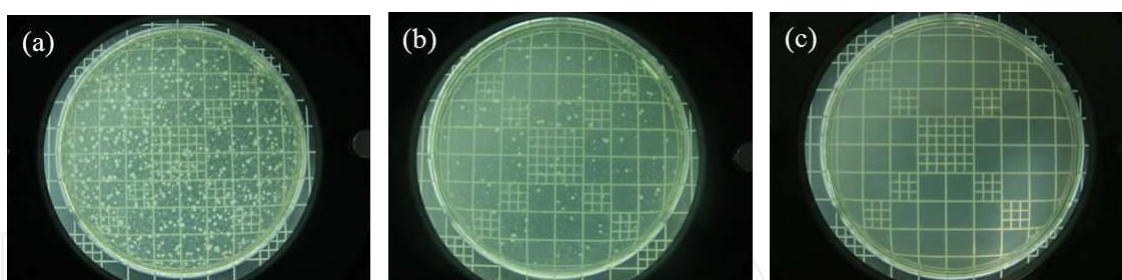


Figure 5. Anti-bacterial performance test of (a) blank, (b) pure PVA and (c) PVA/MWNT-Au nanocomposites nanofibers against the bacteria, *Staphylococcus aureus*. (PVA solution concentration = 10 wt%, TCD=15 cm, and applied voltage=15 kV)

4.2. PVA/MWNT/Ag nanocomposite nanoparticles and nanospheres

4.2.1. Morphology

Nanoparticles and nanospheres of PVA/MWNTs and PVA/MWNT/Ag nanocomposites were prepared by electrospraying technique following the method described in our previous report. Morphologies of these nanoparticles and nanospheres are investigated by transmission electron microscopy and they were compared each other. Figure 6 shows the TEM images of PVA/MWNT nanocomposite nanoparticles. It can be seen from the TEM images that CNTs were crammed into PVA nanoparticles with a random manner and the CNTs were embedded within the particles rather than sticking on the surfaces of the nanoparticles. The incorporation of CNTs into the PVA nanoparticles expanded the morphologies of the nanocomposite nanoparticles. The shapes were lengthened and crinkled and the sizes were increased. This results suggest that CNTs have an effect on the morphologies of PVA nanoparticles.

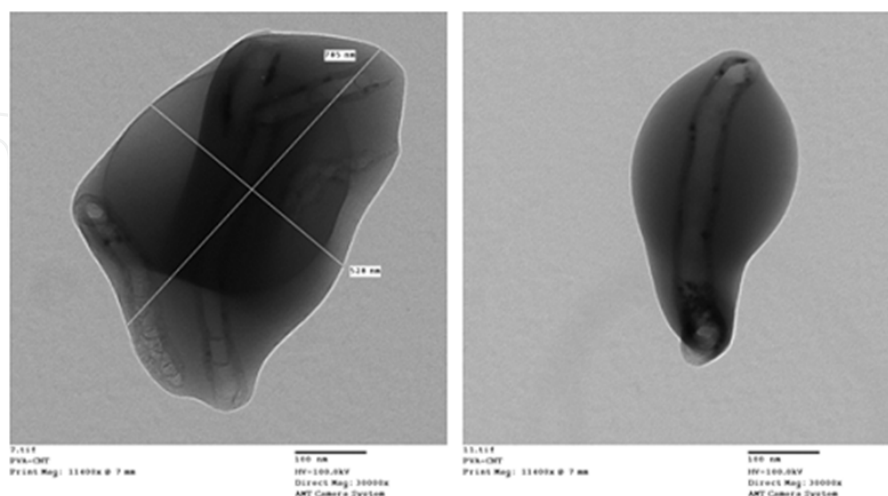


Figure 6. TEM images of the PVA/CNT nanoparticles using electrospraying (PVA solution concentration = 5 wt%, MWNTs concentration = 1 wt%, TCD=15 cm, and applied voltage=15 kV)

To prepare multifunctional nanocomposites, PVA/MWNT/Ag nanocomposites nanospheres were also prepared by electrospraying. TEM images in Figure 7 exhibit the morphologies of PVA/MWNT/Ag nanocomposites nanospheres.

A spherical morphology rather than particulates was obtained. Ag nanoparticles are distributed uniformly within the nanosphere together with CNTs but the Ag nanoparticles were not attached with the surfaces of CNTs. Moreover, Ag nanoparticles did not agglomerate within the nanosphere.

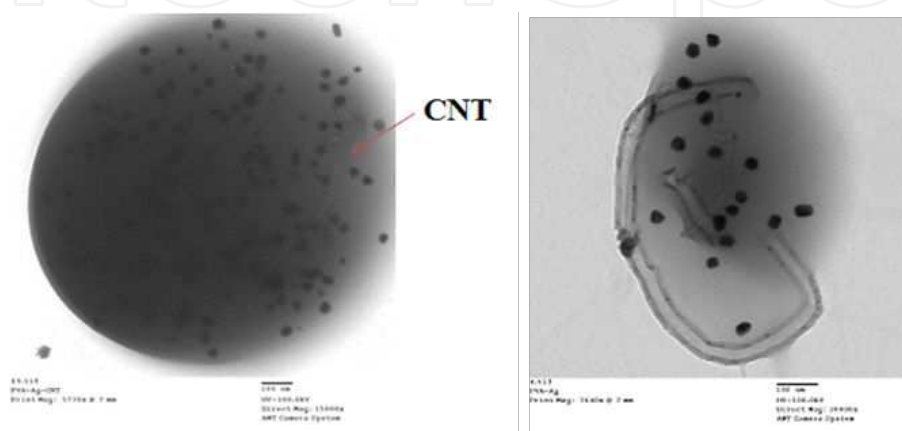


Figure 7. TEM images of the PVA/CNT/Ag nanosphere using electrospraying (PVA solution concentration = 5 wt%, MWNTs concentration = 1 wt%, Ag concentration = 1 wt.%, TCD= 15 cm, and applied voltage = 15 kV).

4.3. PVA/MWNT/Ag/MMT nanocomposite nanofibers

4.3.1. Morphology

Multifunctional nanocomposites nanofibers composed of PVA, MWNTs, Ag nanoparticles and clay, MMT, were also prepared in aqueous medium by electrospinning. Figure 8 represents the TEM images of PVA/MWNT/Ag/MMT multifunctional nanocomposites nanofibers electrospun from 5 wt% MMT solutions containing different amounts of carbon nanotubes (CNTs) (none, 0.1, and 0.5 wt%). PVA forms very smooth nanofibers but the addition of MMT clay and Ag nanoparticles into the polymer matrix increases the diameters of the nanofibers. The addition of MMT crinkled the fibers shape and may planes with many edges developed on surfaces of the nanofibers [38; 61]. It can be seen from Figure 8 (b) and (c) that CNTs were embedded along the fiber directions. Ag nanoparticles were uniformly distributed within the fibers and on the fiber cross-section [38]. It can be clearly seen that the increase of CNTs amount increased the diameter of the nanofibers and expanded the morphology of the multifunctional nanocomposite nanofibers.

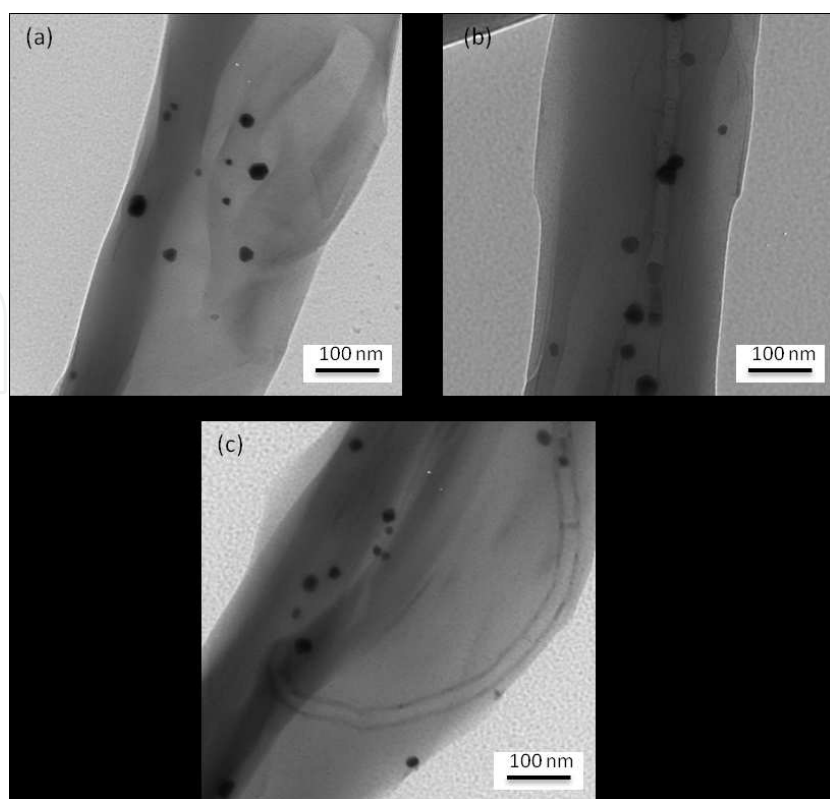


Figure 8. TEM images of electrospun PVA/MWNT/Ag/MMT multifunctional composite nanofibers with different CNT contents of 0 wt% (a), 0.1 wt% (b), and 0.5 wt% (c) (Polymer concentration = 10 wt%, MMT concentration= 5 wt%, Ag concentration = 1 wt%, TCD= 15 cm, and Applied voltage= 15 kV).

4.3.2. Thermal properties

Thermal properties of electrospun PVA/MWNT/Ag/MMT multifunctional composite nanofibers were measured using Differential Scanning Calorimetry (DSC) in nitrogen atmosphere. Figure 9 shows the DSC thermograms of electrospun PVA/MWNT/Ag/MMT multifunctional composite nanofibers containing different CNT contents (none, 0.1 and 0.5 wt%). A large endothermic peak was observed at 224 C in the DSC curve obtained from only PVA nanofibers (Figure 9a).

The peak of PVA/MMT/Ag was moved to higher temperature i.e 226.5 C while their was no CNTs (Figure 9b). This result indicates that Ag content increased the thermal stability [38]. With the addition and increase of CNTs content into the PVA/MMT/Ag nanocomposite nanofibers, the peaks of PVA/MWNT/Ag/MMT composite nanofibers in Figure 9 (c) and (d) shifted to 228 and 229 C, respectively. These results indicate that the addition of carbon nanotubes (CNTs) improves the thermal properties of PVA/MWNT/Ag/MMT composite nanofibers. Moreover, the increased amount of CNTs increase the thermal stability of PVA/MWNT/Ag/MMT composite nanofibers. These results suggest that the incorporation of CNTs into the multifunctional PVA composite nanofibers might increase their thermal stability significantly.

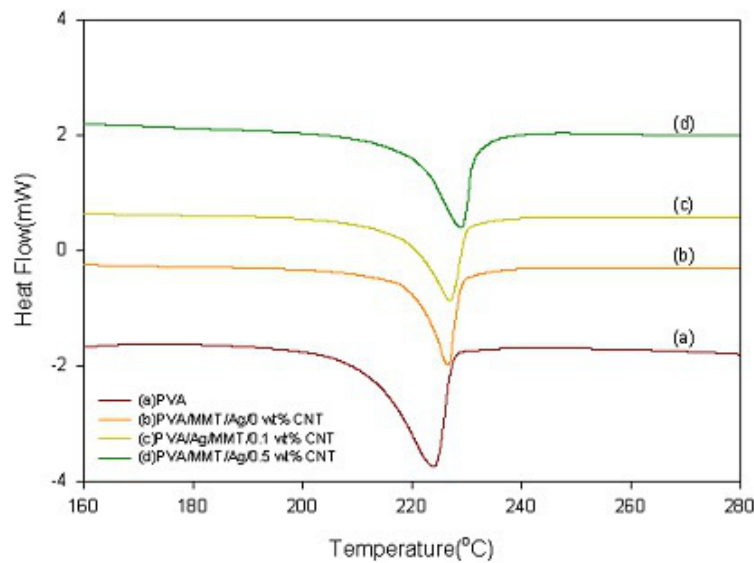


Figure 9. DSC data of electrospun PVA nanofibers (a), and PVA/MWNT/Ag/MMT multihybrid nanofibers with different CNT contents of 0 wt.% (b), 0.1 wt.% (c), and 0.5 wt.% (d) (Polymer concentration = 10 wt.%, MMT concentration= 5 wt.%, Ag concentration = 1 wt.%, TCD= 15 cm, and Applied voltage= 15 kV).

4.4. PVAc/PVA/MWNT microspheres

4.4.1. Morphology

Figure 10 represents the FE-SEM images of the PVAc/MWNT microspheres prepared by suspension polymerization [21]. It can be seen from Fig. 10 that sizes of the PVAc/MWNTs microspheres are not uniform. A single microsphere is enlarged and its rough surface is observed where as the surface of the PVAc microspheres is smooth [21]. The roughness of the surface was caused by the presence of MWNTs which is clearly seen in the highly magnified image in Figure 10. To understand the surface morphology of the PVAc/MWNT microspheres better, their fracture surface was investigated by SEM which is represented in Figure 11. The rough surface shown in the enlarged images confirms that the MWNTs were evidently incorporated within the PVAc microspheres by suspension polymerization.

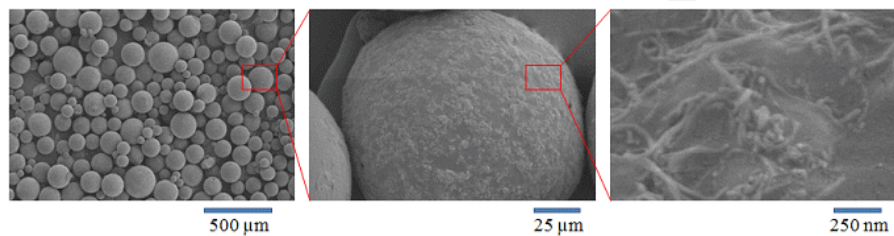


Figure 10. SEM images of the PVAc/MWNT microspheres prepared by suspension polymerization. A single PVAc/MWNT microsphere and its surfaces are enlarged with different magnifications

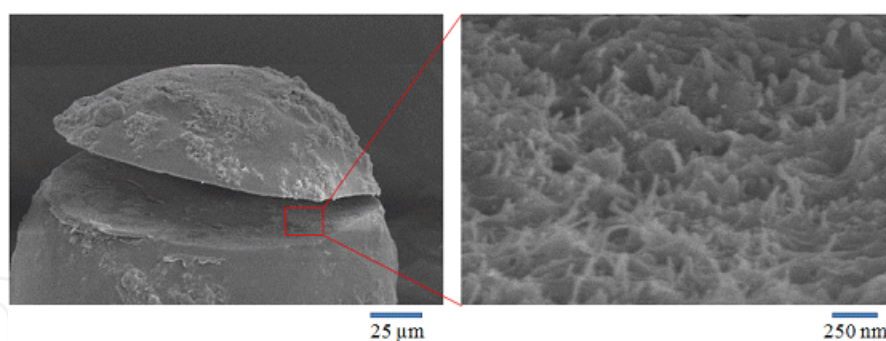


Figure 11. SEM images of the fracture part of a PVAc/MWNT microsphere prepared by suspension polymerization

4.4.2. Optical micrographs

PVA/MWNT nanocomposite microspheres were prepared by heterogeneous saponification following the method reported in our previous work [21]. The spherical shapes of PVAc/MWNT nanocomposite particles were maintained during saponification process by dispersing PVAc/MWNT nanocomposite particles in aqueous alkali solution with very gentle agitation. The optical micrographs of PVAc/PVA/MWNT nanocomposite microspheres prepared by heterogeneous saponification are presented in Figure 12. It can be seen from the micrographs that composite microspheres with a PVAc core and PVA shell structure were obtained and MWNTs were distributed throughout the core/shell microsphere.

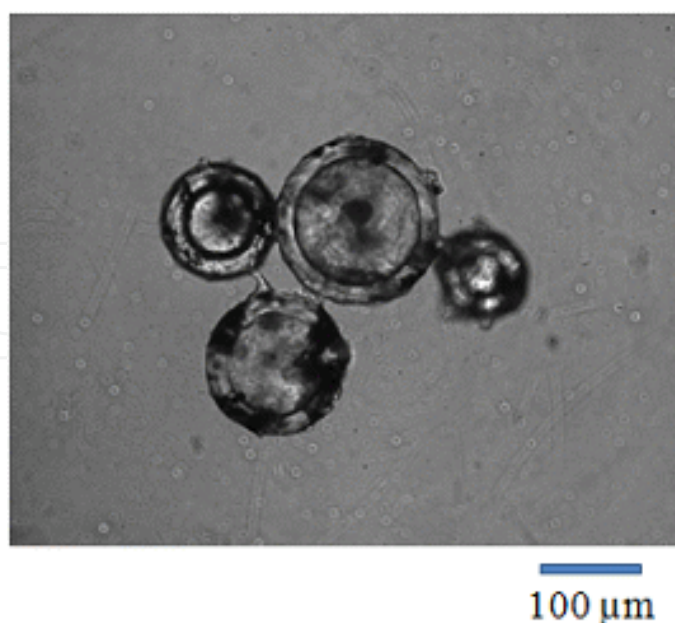


Figure 12. Optical micrograph of the PVAc/PVA/MWNT core/shell microspheres (The saponification times and DS value was 4 h and 18%.

5. Conclusions

Polymer nanocomposites of different types and structures have been successfully prepared and characterized by FE-SEM, TEM, TGA, DSC, optical microscopy and antibacterial efficacy test. PVA/MWNT-Au, and PVA/MWNT/Ag/MMT nanocomposites nanofibers were prepared by electrospinning from aqueous solution. Electrospinning technique was employed to prepare PVA/MWNT/Ag nanoparticles and nanospheres. PVAc/PVA/MWNTs core/shell microsphere were prepared by saponification of PVAc/MWNTs microsphere prepared by suspension polymerization. Au nanoparticles were remaining attached with MWNTs within the PVA/MWNT-Au nanofibers. MWNT-Au nanocomposites expanded the morphologies and improved the properties of PVA/MWNT-Au nanofibers. MWNT-Au nanocomposites showed significant performance against bacteria. MMT and MWNTs increased the diameters of the PVA/MWNT/Ag/MMT nanocomposites nanofibers. Silver nanoparticles were distributed well within the PVA/MWNT/Ag nanocomposites nanoparticles. The results obtained in this study may help to fabricate polymer nanocomposite in order to improve their properties and expand their applications in the field of modern science.

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References

- [1] Berkland, C., Kim, C., & Pack, D. W. (2001). Fabrication of PLG microspheres with precisely controlled and monodisperse size distributions. *J. Control. Release*, 73(1), 59-74, 0168-3659.
- [2] Brust, M., Schiffrin, D. J., Bethell, D., & Kiely, C. J. (1995). Novel gold-dithiol nano-networks with non-metallic electronic properties. *Adv. Mater.*, 7(9), 795-797, 0935-9648.
- [3] Choi, J. S., Lee, S. W., Jeong, L., Bae, S. H., Min, B. C., & Youk, J. H. (2004). Effect of organosoluble salts on the nanofibrous structure of electrospun poly(3-hydroxybutyrate-co-3-hydroxyvalerate). *Int. J. Bio. Macromol.*, 34(4), 249-256, 0141-8130.
- [4] Chu, H., Wei, L., Cui, R., Wang, J., & Li, Y. (2010). Carbon nanotubes combined with inorganic nanomaterials: Preparations and applications. *Coordin. Chem. Rev.*, 254(9-10), 1117-1134, 0010-8545.
- [5] Dastjerdi, R., & Montazer, M. (2010). A review on the application of inorganic nano-structured materials in the modification of textiles: Focus on anti-microbial properties. *Colloid Surface B*, 79(1), 5-18, 0927-7765.
- [6] Feldheim, D. L., & Foss, C. A. (2000). Metal Nanoparticles: Synthesis, Characterization and Applications,. Dekker, New York,, 978-0824706043.
- [7] Fischer, H. R., Gielgens, L. H., & Koster, T. P. M. (1999). Nanocomposites from polymers and layered minerals. *Acta Polym.*, 50(4), 122-126, 0323-7648.
- [8] Fleming, M. S., Mandal, T. K., & Walt, D. R. (2001). Nanosphere-microsphere assembly: methods for core-shell materials preparation. *Chem. Mater.*, 13(6), 2210-2216, 0897-4756.
- [9] Gates, W. P., Komadel, P. K., Madefova, J., Bujdak, J., Stucki, J. W., & Kirkpatrick, R. J. (2000). Electronic and structural properties of reduced-charge maontmorillonites. *Appl. Clay Sci.*, 16(5-6), 257-271, 0169-1317.
- [10] Georgakilas, V., Gournis, D., Tzitzios, V., Pasquato, L., Guldi, D. M., & Prato, M. (2007). Decorating carbon nanotubes with metal or semiconductor nanoparticles. *J. Mater. Chem.*, 17(26), 2679-2694, 0959-9428.
- [11] Giannetti, E., & Mazzocchi, R. (1986). High conversion free-radical suspension polymerization: End groups in poly(methyl methacrylate) and their influence on the thermal stability. *J. Polym. Sci. Pol. Chem.*, 24(10), 2517-2551, 0087-624X.
- [12] Gittins, D. I., & Caruso, F. (2001). Spontaneous Phase Transfer of Nanoparticulate Metals from Organic to Aqueous Media. *Angew. Chem. Int. Ed.*, 40(16), 3001-3004, 1433-7851.
- [13] Glaus, S., Calzaferri, G., & Hoffmann, R. (2002). Electronic properties of the silver-silver chloride cluster interface. *Chem.-A Eur. J.*, 8(8), 1785-94, 0947-6539.

- [14] Gotoh, Y., Igarashi, R., Ohkoshi, Y., Nagura, M., Akamatsu, K., & Deki, S. (2000). Preparation and structure of copper nanoparticle/poly(acrylic acid) composite films. *J. Mater.Chem.*, 10(11), 2548-2552, 0959-9428.
- [15] Grace, A. N., & Pandian, K. (2007). Antibacterial efficacy of aminoglycosidic antibiotics protected gold nanoparticles: a brief study. *Colloids Surf. A*, 297(1-3), 63 -70 , 0927-7757.
- [16] Han, X. J., Huang, Z. M., He, C. L., Liu, L., & Wu, Q. S. (2006). Coaxial electrospinning of PC(shell)/PU(core) composite nanofibers for textile application. *Polym. Composite.*, 27(4), 381-387, 0272-8397.
- [17] Hatchett, D. W., Josowicz, M., Janata, J., & Baer, D. R. (1999). Electrochemical formation of au clusters in polyaniline. *Chem. Mater.*, 11(10), 2989 -2994 , 0897-4756.
- [18] Huang, C. J., Yen, C. C., & Chang, T. C. (1991). Studies on the preparation and properties of conductive polymers. III. Metallized polymer films by retroplating out. *J. Appl. Polym. Sci.*, 42(8), 2237-2245, 0021-8995.
- [19] Huang, Z. M., Zhang, Y. Z., Kotaki, M., & Ramakrishna, S. (2003). A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Compos. Sci. Technol.*, 63(15), 2223 -2253 , 0266-3538.
- [20] Ji, H. M., Lee, H. W., Karim, M. R., Cheong, I. W., Bae, E. A., Kim, T. H., Islam, S., Ji, B. C., & Yeum, J. H. (2009). Electrospinning and characterization of medium-molecular-weight poly(vinyl alcohol)/high-molecular-weight poly(vinyl alcohol)/montmorillonite nanofibers. *Colloid and Polymer Science*, 287(7), 751-758, 0303-402X.
- [21] Jung, H. M., Lee, E. M., Ji, B. C., Deng, Y., Yun, J. D., & Yeum, J. H. (2007). Poly(vinyl acetate)/poly(vinyl alcohol)/montmorillonite nanocomposite microspheres prepared by suspension polymerization and saponification. *Colloid Polym. Sci.*, 285(6), 705-710, 0303-402X.
- [22] Kang, S., Herzberg, M., Rodrigues, D. F., & Elimelech, M. (2008). Antibacterial Effects of Carbon Nanotubes: Size Does Matter! *Langmuir*, 24(13), 6409-6413, 0743-7463.
- [23] Karim, M. R., Lee, H. W., Kim, R., Ji, B. C., Cho, J. W., Son, T. W., Oh, W., & Yeum, J. H. (2009). Preparation and characterization of electrospun pullulan/montmorillonite nanofiber mats in aqueous solution. *Carbohydrate Polymers*, 78(2), 336 -342 , 0144-8617.
- [24] Krumova, M., López, D., Benavente, R., Mijangos, C., & Pereña, J. M. (2000). Effect of crosslinking on the mechanical and thermal properties of poly(vinyl alcohol). *Polymer*, 41(26), 9265-9272, 0032-3861.
- [25] Lee, J. E., Kim, J. W., Jun, J. B., Ryu, J. H., Kang, H. H., Oh, S. G., & Suh, K. D. (2004). Polymer/Ag composite microspheres produced by water-in-oil-in-water emulsion polymerization and their application for a preservative. *Colloid Polym. Sci.*, 282(3), 295 -299 , 0303-402X.
- [26] Lee, H. W., Karim, M. R., Park, J. H., Ghim, H. D., Choi, J. H., Kim, K., Deng, Y., & Yeum, J. H. (2009a). Poly(vinyl alcohol)/Chitosan Oligosaccharide Blend Sub-micro-

meter Fibers Prepared from Aqueous Solutions by the Electrospinning Method. *J. Appl. Polym. Sci.*, 111(1), 132-140, 0021-8995.

- [27] Lee, H. W., Karim, M. R., Ji, H. M., Choi, J. H., Ghim, H. D., Park, J. H., Oh, W., & Yeum, J. H. (2009b). Electrospinning Fabrication and Characterization of Poly(vinyl alcohol)/ Montmorillonite Nanofiber Mats. *J. Appl. Polym. Sci.*, 113(3), 1860-1867, 0021-8995.
- [28] Li, D., & Xia, Y. (2004). Electrospinning of nanofibers: reinventing the wheel? *Adv. Mater.* 0935-9648 , 16(14), 1151-1170.
- [29] Luna-Xavier, J. L., Bourgeat-Lami, E., & Guyot, A. (2001). The role of initiation in the synthesis of silica/poly(methylmethacrylate) nanocomposite latex particles through emulsion polymerization. *Colloid Polym. Sci.*, 279(10), 947-958, 0303-402X.
- [30] Matsumoto, H., Mizukoshi, T., Nitta, K., Minagawa, M., Tanoika, A., & Yamagata, Y. (2005). Organic/inorganic hybrid nano-microstructured coatings on insulated substrates by electrospray deposition. *J. Colloid Interf. Sci.*, 286(1), 414 -6 , 0021-9797.
- [31] Messersmith, P. B., & Giannelis, E. P. (1993). Polymer-layered silicate nanocomposites: In situ intercalative polymerization of ϵ -caprolactone in layered silicates. *Chem. Mater.*, 5(8), 1064-1066, 0897-4756.
- [32] Min, B. M., Lee, G., Kim, S. H., Nam, Y. S., Lee, T. S., & Park, W. H. (2004). Electrospinning of silk fibroin nanofibers and its effect on the adhesion and spreading of normal human keratinocytes and fibroblasts in vitro. *Biomaterials*, 25(7-8), 1289 -1297 , 0142-9612.
- [33] Mu, L., & Feng, S. S. (2001). Fabrication, characterization and in vitro release of paclitaxel (Taxol®) loaded poly(lactic co-glycolic acid) microspheres prepared by spray drying technique with lipid/cholesterol emulsifiers. *J. Control. Release*, 76(3), 239-254, 0168-3659.
- [34] Okamoto, M., Morita, S., Taguchi, H., Kim, Y. H., Kotaka, T., & Tateyama, H. (2000). Synthesis and structure of smectic clay/poly(methyl methacrylate) and clay/polystyrene nanocomposites via in situ intercalative polymerization. *Polymer*, 41(10), 3887-3890, 0032-3861.
- [35] Okuda, H., & Kelly, A. J. (1996). Electrostatic atomization-experiment, theory and industrial applications. *Phys. Plasmas.*, , 5, 1070-664X, 3, 2191 -2196 .
- [36] Oriakhi, C. O., & Lerner, M. M. (1995). Poly(pyrrole) and poly(thiophenb)/clay nanocomposites via latex-colloid interaction. *Mater. Res. Bull.*, 30(6), 723-729, 0025-5408.
- [37] Park, S. H., Oh, S. G., Munb, J. Y., & Han, S. S. (2006). Loading of gold nanoparticles inside the DPPC bilayers of liposome and their effects on membrane fluidities,. *Colloid Surf. B*, 48(2), 112 -118 , 0927-7765.
- [38] Park, J. H., Karim, M. R., Kim, I. K., Cheong, I. W., Kim, J. W., Bae, D. G., Cho, J. W., & Yeum, J. H. (2010). Electrospinning fabrication and characterization of poly(vinyl

- alcohol)/montmorillonite/silver hybrid nanofibers for antibacterial applications. *Colloid Polym. Sci.*, 288(1), 115-121, 0303-402X.
- [39] Popov, V. N. (2004). Carbon nanotubes: properties and application. *Mater. Sci. Eng. R*, 43(3), 61-102, 0927-796X.
- [40] Rabbani, M. R., Ko, C. H., Bae, J. S., Yeum, J. H., Kim, I. S., & Oh, W. (2009). Comparison of some gold/carbon nanotube composites prepared by control of electrostatic interaction. *Colloid Surf. A*, 336(1-3), 183 -186 , 0927-7757.
- [41] Ramos, J., Millan, A., & Palacio, F. (2000). Production of magnetic nanoparticles in a polyvinylpyridine matrix. *Polymer*, 41(24), 8461 -8464 , 0032-3861.
- [42] Ren, G., Xu, X., Liu, Q., Cheng, J., Yuan, X., Wu, L., & Wan, Y. (2006). Electrospun poly(vinyl alcohol)/glucose oxidase biocomposite membranes for biosensor applications. *React. Funct. Polym.*, 66(12), 1559-1564, 1381-5148.
- [43] Reneker, D. H., & Chun, I. (1996). Nanometre diameter fibres of polymer, produced by electrospinning. *Nanotechnology*, 7(3), 216 -223, 0957-4484.
- [44] Rosca, I. D., Watari, F., & Uo, M. (2004). Microparticle formation and its mechanism in single and double emulsion solvent evaporation. *J. Control. Release*, 0168-3659 , 99(2), 271 -80 .
- [45] Rujitanaroj, P. O., Pimpha, N., & Supaphol, P. (2008). Wound-dressing materials with antibacterial activity from electrospun gelatin fiber mats containing silver nanoparticles. *Polymer*, 49(21), 4723 -4732 , 0032-3861.
- [46] Salata, O. V., Hull, P. J., & Dobson, P. J. (1997). Synthesis of nanometer-scale silver crystallites via a room-temperature electrostatic spraying process. *Adv. Mater*, 9(5), 413 -417 , 0935-9648.
- [47] Sangamesh, G. K., Syam, P. N., Roshan, J., Hogan, M. V., & Laurencin, C. T. (2008). Recent Patents on Electrospun Biomedical Nanostructures: An Overview. *Recent Patents Biomed. Eng.*, 1(1), 68 -78 , 1874-7647.
- [48] Schartel, B., Pötschke, P., Knoll, U., & Abdel-Goad, M. (2005). Fire behaviour of polyamide 6/multiwall carbon nanotube nanocomposites. *Eur. Polym. J.*, 41(5), 1061 -1070 , 0014-3057.
- [49] Sinha, V. R., Bansal, K., Kaushik, R., & Trehan, A. (2004). Poly- ϵ -caprolactone microspheres and nanospheres: an overview. *Int. J. Pharmaceut*, 278(1), 1-23, 0378-5173.
- [50] Svensson, P. D., & Staffan, Hansen. S. (2010). Freezing and thawing of montmorillonite-A time-resolved synchrotron X-ray diffraction study. *Appl. Clay Sci.*, 49(3), 127 -134 , 0169-1317.
- [51] Tiarks, F., Landfester, K., & Antonietti, M. (2001). Silica nanoparticles as surfactants and fillers for latexes made by miniemulsion polymerization. *Langmuir*, 17(19), 5775 -5780 , 0743-7463.

- [52] Unger, E., Duesberg, G. S., Liebau, M., Graham, A. P., Seidel, R., Kreupl, F., & Hoenlein, W. (2003). Decoration of multi-walled carbon nanotubes with noble- and transition-metal clusters and formation of CNT-CNT networks. *Appl. Phys. A*, 77(6), 735-738, 0947-8396.
- [53] Usuki, A., Kato, M., Olada, A., & Kurauchi, T. (1997). Synthesis of polypropylene-clay hybrid. *J. Appl. Polym. Sci*, 63(1), 137-138, 0021-8995.
- [54] Vaia, R., Vasudevan, S., Krawiec, W., Scanlon, L. G., & Giannelis, E. P. (1995). New polymer electrolyte nanocomposites: Melt intercalation of poly(ethylene oxide) in mica-type silicates. *Adv. Mater.*, 7(2), 154-156, 0935-9648.
- [55] Vasita, R., & Katti, D. S. (2006). Nanofibers and their applications in tissue engineering. *Int. J. Nanomedicine*, 1(1), 15-30, 1176-9114.
- [56] Wang, X., Drew, C., Lee, S. H., Senecal, K. J., Kumar, J., & Samuelson, L. A. (2002). Electrospun nanofibrous membranes for highly sensitive optical sensors. *Nano Lett.*, 2(11), 1273-1275, 1530-6984.
- [57] Wu, L. L., Yuan, X. Y., & Sheng, J. (2005). Immobilization of cellulase in nanofibrous PVA membranes by electrospinning. *J. Membr. Sci.* - 0376-7388, 250(1-2), 167-173.
- [58] Wu, W., He, T., & Chen, J. F. (2006). Study on in situ preparation of nano calcium carbonate/PMMA composite particles. *Mater. Lett.*, 60(19), 2410-2415, 0167-577X.
- [59] Yeum, J. H., Park, J. H., Kim, I. K., & Cheong, I. W. (2011). Electrospinning Fabrication and Characterization of Water Soluble Polymer/Montmorillonite/Silver Nanocomposite Nanofibers out of Aqueous Solution. *Advances in Nanocomposites-Synthesis, Characterization and Industrial Applications*, Intech Publishers,, Croatia,, 483-502, 978-9-53307-165-7.
- [60] Yonezawa, T., & Kunitake, T. (1999). Practical preparation of anionic mercapto ligandstabilized gold nanoparticles and their immobilization,. *Colloids Surfaces A*, 149(1-3), 193-199, 0927-7757.
- [61] Zhang, Z., & Han, M. (2003). One-step preparation of size-selected and well-dispersed silver nanocrystals in polyacrylonitrile by simultaneous reduction and polymerization. *J. Mater. Chem*, 13(4), 641-643, 0959-9428.
- [62] Zhang, Y., Peng, H., Huanga, W., Zhou, Y., & Yan, D. (2008). Facile preparation and characterization of highly antimicrobial colloid Ag or Au nanoparticles. *J. Colloid Interface Sci.*, 325(2), 371-376, 0021-9797.
- [63] Zhu, Z. K., Yin, J., Cao, F., Shang, X. Y., & Lu, Q. H. (2000). Photosensitive polyimide/silica hybrids. *Adv. Mater.*, 12(14), 1055-1057, 0935-9648.
- [64] Zussmas, E., Theron, A., & Yarin, A. L. (2003). Formation of nanofiber crossbars in electrospinning. *Appl. Phys. Lett*, 82(6), 973-975, 0003-6951.

