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Spider-net within the N6, PVA and PU electrospun nanofiber mats using salt addition: Novel strategy in the electrospinning process

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ABSTRACT

Electrospun nanofibers are promising candidates in the nanotechnological applications due to the advantages of the nanofibrous morphology. Therefore, many attempts were reported to modify the electrospun mats to gain more beneficial properties. In the present study, we are introducing a strategy to synthesize electrospun polymeric nanofiber mats containing spider-net binding the main nanofibers. Addition with long stirring time of a metallic salt having tendency to ionize rather than formation of sol–gel in the host polymer solution reveals to synthesize a spider-net within the electrospun nanofibers of the utilized polymer. Nylon6, polyurethane and poly(vinyl alcohol) have been utilized; NaCl, KBr, $CaCl_2$ and H_2PtCl_6 have been added to the polymeric solutions. In the case of nylon6 and poly(vinyl alcohol), addition of the inorganic salts resulted in the formation of multi-layers spider-network within the electrospun nanofibers mats. The synthesized spider-nets were almost independent on the nature of the salt; the optimum salt concentration was 1.5 wt%. The metallic acid led to form trivial spider-nets within both of nylon6 and poly(vinyl alcohol) nanofibers. In a case of polyurethane, few spider-nets were formed after salt addition due to the low polarity of the utilized solvents. According to TEM analysis, the synthesized spider-net consisted of joints; the later issued from the main nanofibers at Taylor's cone zone. The spider-net improved the mechanical properties and the wetability of the nylon6 nanofiber mats, accordingly a mat having amphiphilic feature has been prepared.

1. Introduction

Simplicity of the electrospinning process, the diversity of the electrospinnable materials, and the unique features of the obtained electrospun nanofibers provide a special interest for both of the technique and the resultant products. The past decades have witnessed tremendous progress in the development of the electrospinning process to widen the applications of the obtained products. However, many technical issues still need to be resolved before electrospinning process becomes more popular and the electrospun nanofibers get strength for industrial level applications. Some researchers have paid attentions to enhance the alignment of the produced nanofibers [1–7]. Others have focused on the morphology of the obtained nanofibers; they have improved the experimental set-up to produce nanofibers with especial features [8–11]. However, no one has tried to modify the internal structure of the electrospun nanofiber mats to improve the entire physical properties of the mat rather than the individual nanofibers.

Generally, the electrospinning is achieved on polymer or polymer/sol–gel solutions to produce pristine or metal-contained polymeric nanofiber mats, respectively. The utilized sol–gel type in the electrospinning process usually consists of polymer and metal precursor. The precursor consists of a metal or metalloid element surrounded by various ligands (appendages not including another metal or metalloid atom). Alkoxides are the most widely used to prepare the sol–gels [12]. Metal alkoxides are members of the family of organometallic compounds, which have an organic ligand attached to a metal or metalloid atom. The metallic precursor in the sol–gel doesn't ionize into cations and anions, instead it hydrolyzes and polycondensates in the final precursor/polymer mixture to

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form the gel network. Therefore, special class of metals can be utilized to produce the electrospinnable polymer/sol–gel mixtures, the metals which have high oxidation numbers are proper candidates, accordingly transition metals are the most widely used [13–17]. However, addition of an inorganic salt possessing tendency to ionize rather than formation of a sol–gel (e.g. the salt of the first group metals) to the polymer solution might lead to dissociation of this salt; especially if the solution contains either a polar solvent or the used solvent could perform ionic reaction with the salt. The librated ions will randomly spread in the polymeric network. In this work, we have studied the effect of presence of an ionized salt in the polymer solutions on the internal morphology of the electrospun nanofiber mats. Three polymers have been utilized; nylon6, poly(vinyl alcohol) (PVA) and polyurethane (PU); formic acid/acetic acid mixture, water and THF/DMF have been utilized as solvents, respectively. Different metallic salts have been used to prepare the salt/polymer solutions; NaCl, KBr and $CaCl_2$. The salt powder has been added to the polymer solution and well mixed. Hydrogen hexacholorplatinate (H_2PtCl_6) solution was invoked also as a metallic compound with low dissociation compared with the other utilized inorganic salts. Interestingly, electrospinning of such salt/polymer solutions resulted in the formation of spider-net within the main electrospun nanofibers, the obtained results indicated that formation and capacity of the spider-net mainly depends on ionization of the used metallic compound.

2. Experimental

2.1. Materials

Nylon6 (N6, relative viscosity 2.5, grade KN20), poly(vinyl alcohol) (PVA, MW = 65 000 g/mol), and polyurethane (PU, MW = 110,000, medical grade), were obtained from Kolon industries, Inc. (South Korea), Dong Yang Chem. Co., (South Korea) and Cardio Tech. Intern. (Japan), respectively. Sodium chloride (NaCl, 99.9% purity) and calcium chloride ($CaCl_2$, 99% purity) were purchased from Showa Co. (Japan). However, potassium bromide (KBr, 99.9% purity) and hydrogen hexacholorplatinate solution (H_2PtCl_6, 8 wt% concentration) were obtained from VWR Co. Ltd. (UK) and Aldrich (USA), respectively. Acetic and formic acids (analytical grade, Showa, Japan) mixture was used as solvent for nylon6. Tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) (analytical grade, Showa, Japan) were used as solvents to dissolve PU without further purification. Distilled water was utilized to prepare PVA aqueous solution.

2.2. Procedure

The used N6 polymer solution was 22 wt%, N6 pellets were dissolved in formic acid/acetic acid mixture (4:1 weight ratio). PU solution (10 wt%) was prepared in stepwise technique, first PU pellets were dissolved in THF, then DMF was added to the solution to adjust the viscosity and simultaneously obtain electrospinnable solution. THF/DMF weight ratio in the final solution was 1:1. However, PVA was dissolved in a sole solvent; water, PVA aqueous solution (10 wt%) was used in this study. In general, the salt powder was added to the polymer solution except in the case of PU, the salt has been first dissolved in 2 ml of DMF then added to the polymer solution. Different amounts of salts have been utilized to study effect of the salt concentration on the internal morphology; the used salt concentrations were 0.5, 1, 1.5, 2 and 2.5 wt% with respect to the polymer solution. Moreover, different dissolution time were utilized; 0.5, 3 and 24 h. The electrospinning process was carried out at 20 kV applied voltage and 15 cm distance between the tip end and the collector, these conditions were identical for all solutions. A rotating steel drum covered by polyethylene sheet was used as a collector. The obtained electrospun nanofiber mats were vacuously dried at room temperature for 24 h to remove the residual solvents.

2.3. Characterization

Surface morphology was studied by field-emission scanning electron microscope (FESEM, Hitachi S-7400, Hitachi, Japan). Viscosity and electrical conductivity were measured by DV III Ultra programmable Rheometer (Brookfieled Co., USA) and EC meter CM 40G Ver 1.09 (DKK TOA Co., Japan), respectively. TEM images were obtained with transmission electron microscope (TEM, JEM-2010, JEOL, Japan) operated at 200 kV, the grid was placed very close to the tip opening for few seconds. Mechanical properties were measured with a universal testing machine (AG-5000G, Shimadzu, Japan), under a crosshead speed of 10 mm/min at room temperature. The samples were prepared in the form of standard dumbbell shapes according to ASTM Standard D 638 via die cutting from the electrospun mats and tested in the machine direction. The samples had diameters of 10 mm and thickness of 0.039 mm. Information about wetability was obtained by the deionized water contact angle measurement using contact angle meter (Digidrop, GBX, France). Deionized water was automatically dropped onto the electrospun mats (the drop diameter is 6 μm).

3. Results and discussion

Electrospinning is widely used for production of many polymeric nanofibers. Moreover, the electrospinning has been also exploited to produce metal oxides [17] or pure metal nanofibers [18–21] by calcination of electrospun mats obtained from completely miscible sol–gel solutions. In this regard, only the transition metals (either pure or in oxidized forms) have been introduced in a nanofibrous morphology. However, according to our best knowledge the first and second group metals have not been introduced in nanofibrous form, this might be due to the inability of these metals to hydrolyze and polycondensate in the polymeric solutions. Nevertheless, the salts of these metals might be utilized to improve the general characteristics of the electrospun nanofiber mats by modification of the internal structure. In this study, many salts and polymers have been used to properly study the influence of salt nature, polymer solution and stirring time on the internal morphology of the electrospun nanofiber mats.

3.1. Effect of metallic salt kind

As it is well known, the first and second groups in the periodic table involve many metals, in this study we have chosen some salts of the most common three metals; NaCl, KBr, and $CaCl_2$. Beside the popularity, these compounds have been selected because they are strong ionic salts and have high dissociation rates especially in the aqueous solutions. Fig. 1 reveals FE SEM images of the nanofiber mats obtained from the electrospinning of N6 solution mixed with the aforementioned salts individually with the same weight percentage (i.e. 1.5 wt% with respect to the polymer solution). As shown in this figure, very clear spider-nets fastening the main nanofibers are observed. High magnification panels reveal that the spider-net fibers grew from the main nanofibers; it can be noticed also in panel E (the marked areas by circles). Moreover, deep sighting in these images concluded that many spider-net layers were formed as shown in panels C, D and F.

To show the impact of the salt nature and because of the metallic salts of some organic acids have tendency to form sol–gel (e.g. nickel acetate and cobalt acetate [22,23]), a weak metallic acid was used; H_2PtCl_6. Theoretically, this acid cannot form a sol–gel in

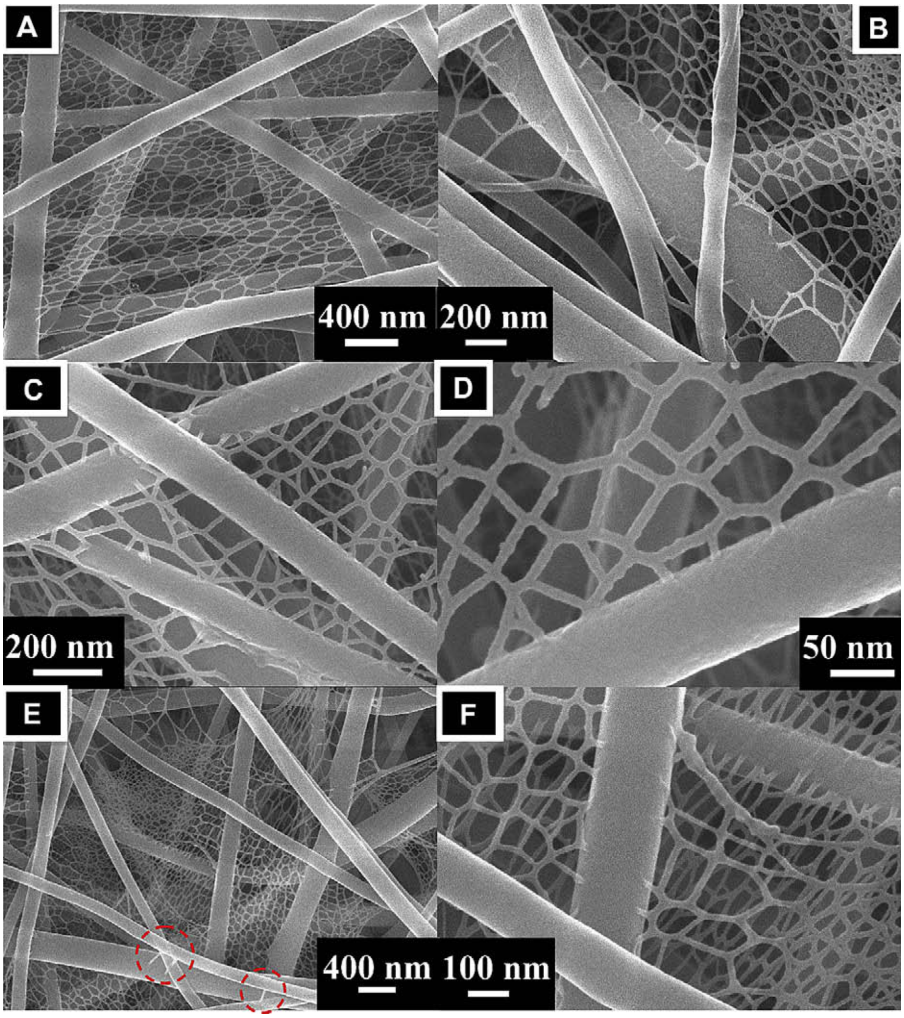


Fig. 1. FE SEM images showing the spider-net in the electrospun nylon6 nanofiber mats containing 1.5 wt% salt, NaCl; (A and B), KBr; (C and D), and $CaCl_2$; (E and F).

the polymeric solution. Fig. 2 shows the obtained FE SEM images for N6 solution containing 1.5 wt% H_2PtCl_6, as can be observed in this figure the synthesized spider-nets are trivial compared with those obtained in the case of using the inorganic salts (Fig. 1). Therefore, one can claim that the expected low dissociation rate of the utilized compound is responsible for the trivial spider-net obtained.

3.2. Effect of polymer solution

As aforementioned in the Experimental section, the utilized N6 has been dissolved in a mixture of acetic acid and formic acid. Therefore, it is expected that the dissociation of the used inorganic salts will be high due to the salt-acid reaction, so the number of the free ions would be high which enhances formation of the spider-net within the electrospun mats as shown in Fig. 1. Poly(vinyl alcohol) is readily soluble in water, so addition of the same utilized salts to the PVA solution resulted in formation of spider-nets as in a case of N6. However, the capacity of the formed spider-net was relatively small compared with the N6 as the salts dissociate physically in the PVA solution rather than chemically in a case of N6. The same salts were added to PU solution in which THF/DMF were utilized as solvents, as it is well known these solvents have

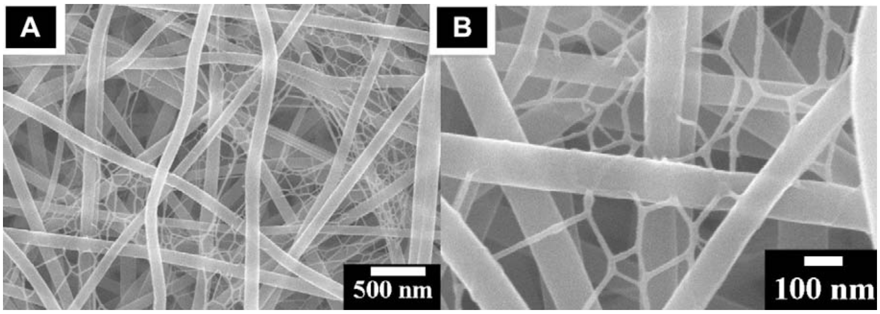


Fig. 2. FE SEM images of N6 with H_2PtCl_6 salt (1.5 wt%) in different magnifications.

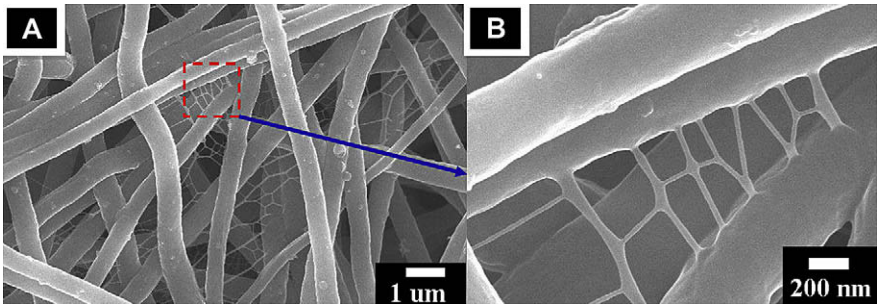


Fig. 3. FE SEM images of electrospun polyurethane nanofiber mat containing 1.5 wt% NaCl.

very low polarity compared with water and do not react with the inorganic salts under the normal conditions. Therefore, it was very difficult to dissolve the salts in the PU solution. The salt powder was premixed with DMF then mixed with PU solution rather than addition of the solid powder to the polymer solution as in case of N6 and PVA. Fig. 3 reveals FE SEM images for the obtained electrospun nanofiber mats when NaCl salt was added to PU solution to form final mixture containing 1.5 wt% NaCl. As shown in this figure, small parts of spider-net were formed due to low ionization of the used salts in the PU solution. Fig. 3B demonstrates high magnification of a specific part in Fig. 3A image, as shown in this figure the spider-net fibers issued from the main PU nanofiber. It is noteworthy mentioning that as in case of N6 and PVA, the synthesized spider-net was not affected by the type of the added metal salt. Moreover, as same as in case of N6; H_2PtCl_6 reveals neglected spider-net. Consequently, the utilized solvent in the polymer solution does have distinct influence on formation of the spider-net. It is noteworthy mentioning that, the spider-net has been also obtained with different polymers and salts unutilized in this study [24].

3.3. *Diameter of the fibers in the synthesized spider-net*

As have been reported by many researchers, addition of salt to the electrospun solution reveals to decrease the average diameter of the obtained nanofibers [25,26], this conclusion has been also observed in this work. For the newly synthesized spider-net, the diameters of some fibers mat have been precisely measured using the FE SEM instruments; the results are demonstrated in Fig. 4. The later reveals the spider-net mat obtained due to addition of NaCl; Fig. 4A and $CaCl_2$; Fig. 4B to N6 solution with the same utilized concentration in Fig. 1. As shown in this figure, the average diameter of the spider-net fibers is almost 15 nm in both salts. According to many FE SEM images which have been obtained from many electrospun nanofiber mats obtained from different formulations, we can say that the average diameter of the nanofiber in the spider-net synthesized within the mats of the utilized polymers (i.e. N6, PVA and PU) is almost independent on both of salt kind and concentration.

3.4. *Effect of salt concentration*

Effect of salt addition on the electrospinning of polymer solution has been previously studied [25,26]. The researchers have concluded that trace amount of salt (especially the monovalent ones) affects the viscosity and electrical conductivity of the polymer solution. With good agreement, addition of the utilized salts to the N6 solution enhanced the electric conductivity of the mixture as shown in Fig. 5 which represents the effect of salt addition on the viscosity and the electric conductivity of N6. As shown in this figure, the electrical conductivity is proportional to the salt amount in the solution, which can be explained as increasing in the amount of the free ions in the solution. Therefore, we think that the liberated ions from dissociation of the metallic salts are responsible for formation of the spider-net. Oppositely, the viscosity sharply decreases due to addition of the salts as could be also concluded by other researchers [27,28]. As can be concluded from Fig. 5, the utilized metallic acid has miniature effect on the electric conductivity of N6 which can be explained as low ionization capacity in the N6 solution as compared with the used inorganic salts. Concerning the spider-net formation within the electrospun nanofiber mats, increase the salt concentration in a case of utilizing of NaCl had distinct impact on the internal morphology of the N6 electrospun mats as microballs was obtained instead of the spider-net when the salt concentration was increased to 2.5 wt%. The scanned FE SEM images for the electrospun mat are presented in Fig. 6A and B. Beyond 2.5 wt% NaCl, the solution was not electrospinnable. For the other utilized metallic salts, the microballs could not be obtained,

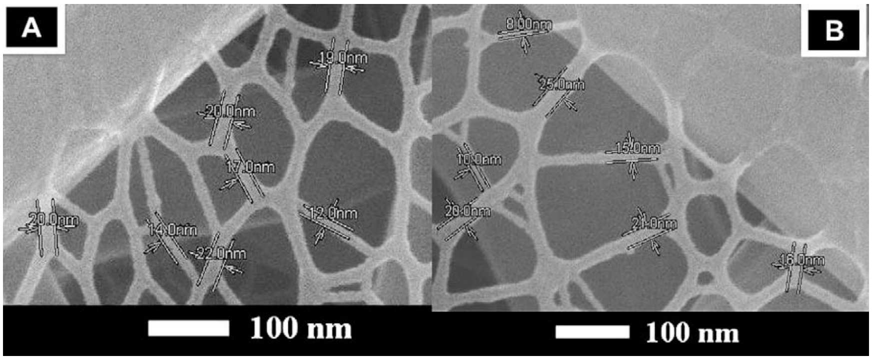


Fig. 4. Diameters of some fibers in the synthesized spider-net in case of NaCl (1.5 wt%)/N6; A and $CaCl_2$ (1.5 wt%)/N6; B.

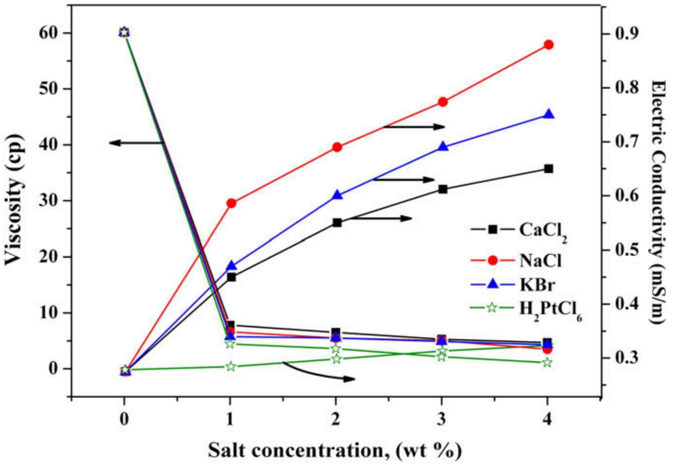


Fig. 5. Effect of the salt addition on the viscosity and electrical conductivity of nylon6 solution.

however the polymer solution could not be also electrospun after the same threshold (i.e. 2.5 wt%). The pristine N6 electrospun nanofiber mats do not contain spider-net or microballs as shown in Fig. 6C which clarifies the influence of the salt addition. For the PVA, the metallic salts could not be completely dissolved in the polymer solution after the threshold. In a case of the utilized metallic acid, both PVA and N6 could be electrospun after the threshold, however the obtained mats became dark yellowish and almost no strong effect on the capacity of the spider-net mats was observed. Therefore, we can say that the optimum salt concentration is 1.5 wt% since the maximum spider-net obtained at this concentration for all the utilized salts.

3.5. *Effect of stirring time*

Addition of salt was found to be relatively more effective to produce small fiber diameter than other process parameters [25,26]. However, in these pervious studies the authors did not give attention to the stirring time, albeit the salt/polymer solution turned into turbidity-free after short time, we have discovered that the time has strong impact. Fig. 7A–C represents the FE SEM images for nanofiber mats obtained from the electrospinning of NaCl/PVA solutions (NaCl 1.5 wt% with respect to the polymer solution) with different stirring times; 0.5, 3 and 24 h, respectively. As shown in Fig. 7A, there are no spider-nets can be observed, however the salt nanoparticles are apparent attaching to the nanofibers. Actually, the main reason behind this is the stirring time. In other words, the utilized stirring time was not enough to completely dissolve the salt in the polymer solution although the solution was clear. This means that the stirring time was not enough to liberate ions on the solution. With relatively little long time (3 h) the spider-net starts to appear as shown in Fig. 7B but also some salt nanoparticles are present. However, with long stirring time (i.e. one day), much spider-net was formed within the main electrospun nanofiber mat as shown in Fig. 7C and no salt nanoparticles could be observed. In a case of N6, the stirring time has also considerable influence as shown in Fig. 7D–F which demonstrate the electrospun nanofiber mats of N6/NaCl (1.5 wt%) after stirring time of 0.5, 3 and 24 h, respectively. As shown in Fig. 7D, some salt nanoparticles are apparent, however spider-net is also present. Formation of spider-net within this short stirring time (0.5 h) indicates fast dissociation of the salt due to embedding of the acidic solvents in the N6 solution. Extending the stirring time into 3 h led to decrease in the amount of the salt nanoparticles as shown in Fig. 7E, however to completely dissolve the salt it needs long stirring time (1 day) as shown in Fig. 7F.

3.6. *Proposed mechanism*

Electrospinning involves the use of a high voltage to charge the surface of the polymer solution droplet and thus to induce the ejection of a liquid jet through a spinneret [20]. Mutual charge repulsion causes a force directly opposite to the surface tension. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the capillary tube elongates to

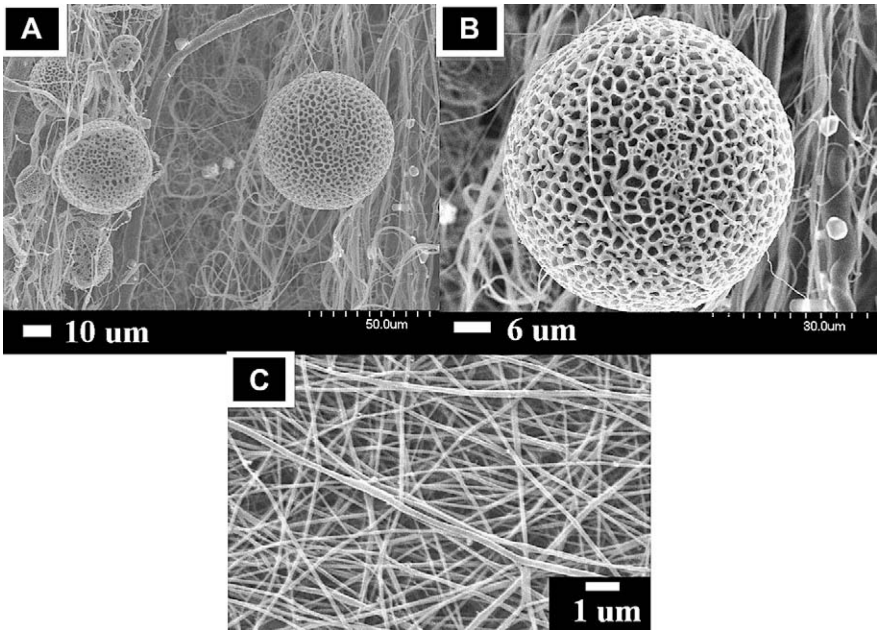


Fig. 6. The microballs obtained when the NaCl concentration in the N6 solution was increased to 2.5 wt%; (A and B), and the pure N6 electrospun mat; (C).

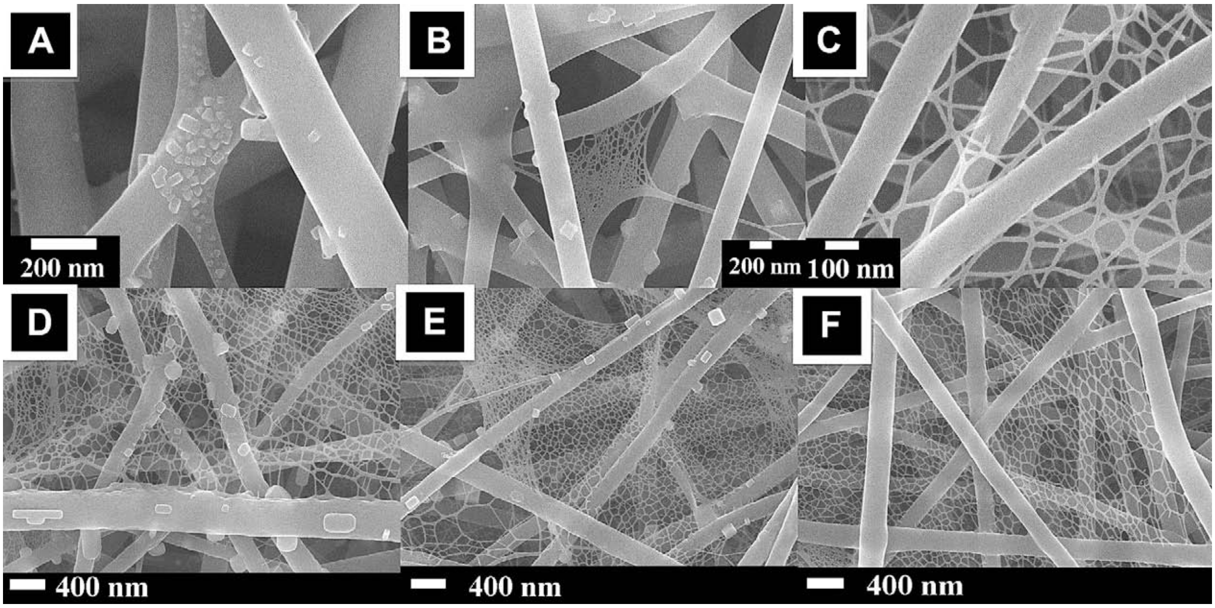


Fig. 7. FE SEM images after different mixing times; 0.5, 3 and 24 h for PVA/NaCl; A, B and C, and for N6/NaCl; D, E and F, respectively. The salt concentration of the salt was 1.5% for both polymers.

form a conical shape known as the Taylor cone [3,29]. Accordingly, if the ions present in the polymeric solution are responsible for formation this spider-net, so this net have to be formed at the place of formation of the main nanofibers; Taylor cone (i.e. tip opening). To precisely confirm that, we have placed a TEM grid very close to the tip end for very short time (a few seconds). Fig. 8 shows the obtained TEM results which affirmed the proposed synthesizing hypothesis. As shown in this figure, the spider-net fibers were issued from the main fibers. According to Fig. 8B, one can say that the spider-net fibers can be considered as joints between the main fibers, moreover according to Fig. 8A it is acceptable to say that the joints do not only synthesized among the main nanofibers but also among pre-formed joints. With considering that the solvent does not immediately evaporate [30,31], which leads to high viscous solution media at such place, formation of the joints was compulsory to keep the ionic balance among these recently pseudo-solid nanofibers since the ions were randomly distributed in original solution and consequently in the newly electrospun nanofibers. To make it more clear and explain the difference between electrospinning of sol–gel and salt/polymer solution, we are suggesting Scheme 1 as conceptual illustration showing the mechanism of forming the spider-net fibers. Scheme 1A represents the nature of sol–gel/polymer solution which has been utilized by many researchers to produce metal oxides nanofibers. Electrospinning of such solution can be illustrated as Scheme 1B, as shown in this build the produced polymeric nanofibers embed the ionically-balanced sol–gel particles which were formed due to hydrolyzing and polycondensation of the utilized precursor, no spider-net had been observed within the electrospun nanofiber mats of such solutions. Therefore, calcination of the electrospun nanofiber mat leads to complete elimination of the polymer and decomposition of the condensated precursor to metal oxide in good nanofibrous shape as so many researchers have concluded [17]. However, it is expected that the utilized salt/polymer solution in the present study might have the semblance demonstrated in Scheme 1C. With long mixing time, the ions randomly spread in the solution and might attach with the polymer chains as figured in the Scheme 1C. Therefore, electrospinning of such solutions can be interpreted as Scheme 1D. As aforementioned, the instantly formed nanofibers at the tip end would contain solvent, and it is expected that these nanofibers are not ionically balanced. Consequently, one can say that the different charges tinny electric poles which are generated in the nanofibers led to synthesize joints between each two different charge poles as demonstrated in Scheme 1D. The electric poles can also present in the recently formed joints which results in creating other connections between these new joints. The

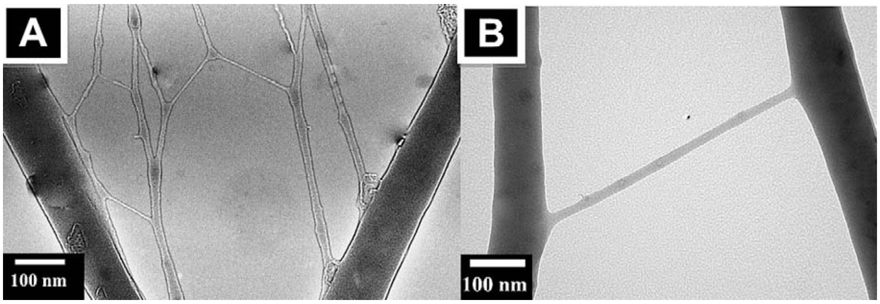
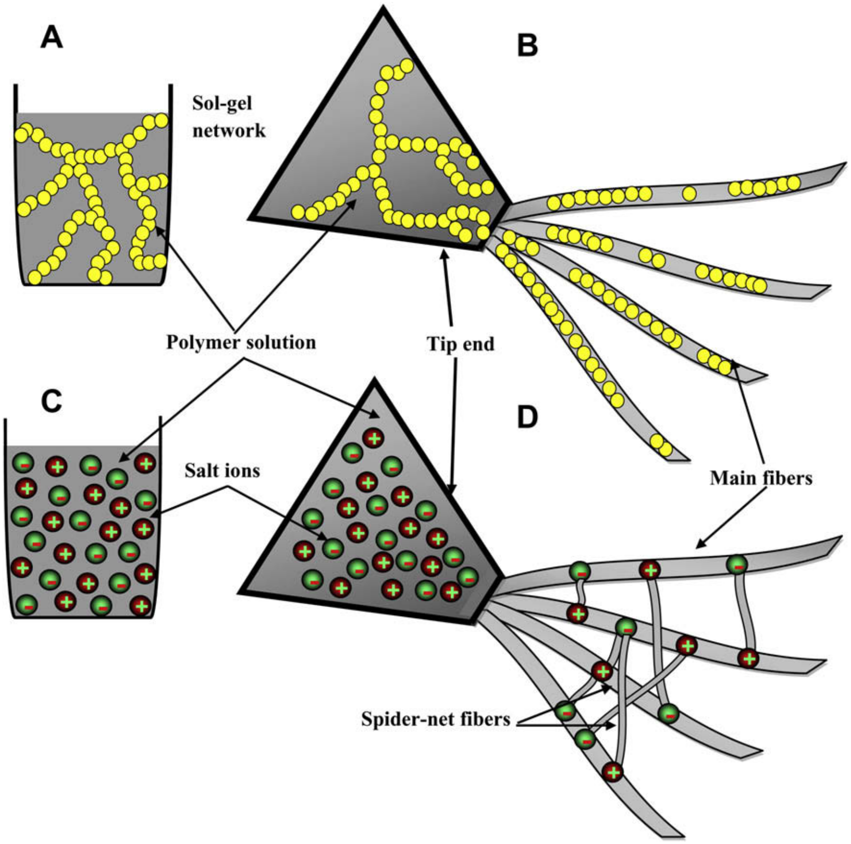


Fig. 8. TEM images of nylon6 with NaCl (1.5 wt%).



Scheme 1. Schematic illustration showing the nature of sol–gel/polymer solution; (A), and mechanism of the corresponding electrospinning process; (B). Also, a conceptual image for a polymer solution consists of an inorganic salt does have tendency to form sol–gel is presented in panel (C), the corresponding behavior of this solution during the electrospinning process is demonstrated in panel (D).

synthesized joints finally shape the observed spider-network within the electrospun nanofiber mats. This hypothesis can be supported by TEM results.

3.7. Applications

We have checked the effect of the formed spider-net within the electrospun nanofiber mats on the mechanical properties and contact angle features, these characteristics strongly influence the application fields of N6. Fig. 9 demonstrates the mechanical properties of pristine N6 and N6 containing NaCl (1.5 wt%) and $CaCl_2$ (1.5 wt%). As shown in this stress–strain curve, the spider-net has a positive effect on the mechanical properties. As in FE SEM results, the average diameter of the main nanofibers as well as the spider-net fibers was not affect by the salt kind; the mechanical properties were also not affected. The formed spider-net plays as connection props which modifies the mechanical properties.

Contact angle is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect. Graphically, Fig. 10 shows the water contact angle after a residence time of 3 s for a pure N6 electrospun nanofiber mats (Fig. 10A), and a mat containing spider-net due to addition of $CaCl_2$ salt to the polymer solution (Fig. 10B). As shown in this figure, a sharp decrease in the contact angle can be observed. In other words, the synthesized spider-net had mutated the hydrophilic nature of the pristine N6 nanofiber mat. This considerable result can be exploited to prepare a single electrospun nanofiber mat with amphiphilic character. This mat was prepared by electrospinning of salt/N6 solution over a pristine N6 mat. Accordingly, the obtained mat has been characterized by measuring the contact angle in both faces, it have two different faces; hydrophobic and hydrophilic. This mat can be utilized in different applications. It is noteworthy mentioning that for PVA and PU polymers, the contact angle property was not investigated because the first is water soluble and the second did not show considerable change in the contact angle as the formed spider-nets are trivial.

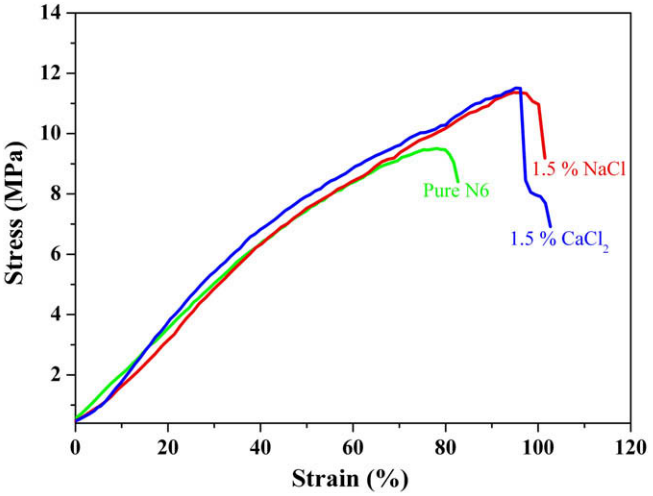


Fig. 9. Effect of the salt addition on the mechanical properties of nylon6 electrospun nanofiber mats.

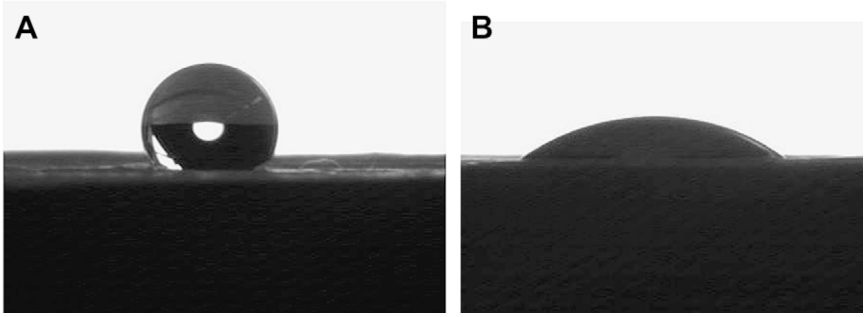


Fig. 10. Contact angle result images (after 3 s) for pure nylon6 nanofiber mat; (A), and $CaCl_2$/nylon6 mat (B).

4. Conclusion

An internal modification of the polymeric electrospun nanofiber mats can be achieved by addition of strong ionic salt to the polymer solution. Ionization of the salt in the polymer solution results in the formation of spider-net within the main nanofibers during the electrospinning process. The formed spider-net mainly depends on the ionization ability of the used salt. The spider-net affects the general properties of the electrospun mat. For instance, the mechanical properties for the commonly used N6 were improved after embedding the spider-net. Moreover, the net had strongly affected the hydrophobicity nature of N6, so single mat with amphiphilic nature could be produced. Finally, the obtained results indicated that the proposed strategy can be generalized to be applicable with many polymers especially those are soluble in polar solvents.

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