

## Electrospun Nitrocellulose and Composite Nanofibers

**B. Naderizadeh<sup>a\*</sup>, A. Moghimi<sup>b</sup>, M. Shahi<sup>c</sup>**

<sup>a</sup> *Sama Technical and Vocational Training College, Islamic Azad University, Kermanshah Branch, Kermanshah, P.O. Box 671791-7855, Iran.*

<sup>b</sup> *Department of Chemistry, Imam Hossein University, Tehran, P.O. Box 16575-416, Iran.*

<sup>c</sup> *Department of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, P.O. Box 191367-4711, Iran.*

### Article history:

Received 5/8/2012

Accepted 10/12/2012

Published online 1/12/2012

### Keywords:

Electrospinning

Nanofiber

Nnitrocellulose

Explosive

Antimicrobial activity

### Abstract

Electrospinning was applied to nitrocellulose (NC) solutions in DMF, DMSO and Ethyl methyl keton to obtain NC nanofibers. Electrospinning process was observed when DMF was used as solvent. In comparison to NC/DMF, NC/DMSO solution resulted in the formation of a coating film as indicated by SEM. Two different electrospun nanofibers, smooth nanofibers with 90 to 150 nm diameters and porous nanofibers with 400 to 500 nm diameter, were noticed when EMK was used. Electrospun explosive composite nanofibers were also successfully prepared from NC to modify the properties of NC and their morphology were investigated by SEM. Explosive materials such as nitrotriazolone (NTO), its sodium salt, picric acid and nanosilver were used as the second component of the composites. A reduction in the diameters of the composite nanofibers involving Na-NTO was noticed comparing to the parent NC nanofibers. The diameters of the other explosive composite nanofibers were in the range of 50-300 nm indicating no significant diameter change for NC nanofibers upon the addition of 0.1 wt% NTO and picric acid. Composite nanofibers containing nanosilver particles were also prepared and their antibacterial activities were tested against *E. coli* and *S. aureus*. These nanofibers successfully inhibited the growth of both bacteria.

*\*Corresponding author:*

E-mail address:

b\_naderyzadeh@yahoo.com

Phone: 98 912 5430445

Fax: +98 21 22262563



## 1. Introduction

Electrospinning is an interesting process for producing non-woven fibers with the average diameters in the range of micro-to nanometers while traditional melts spun fibers range in a diameter of about 5 to 200  $\mu\text{m}$  [1, 2]. Electrospinning is a unique, simple, low-cost and effective approach not only for the preparation of polymer nanofibers [3] but also for the ceramic oxide materials [4] and the composite nanofibers involving metals and metal oxides [5-12]. In this process, a continuous filament is drawn from a polymer solution or a melt through a spinneret by high electrostatic forces to deposit it on a grounded-metal collective screen [13]. Electrospinning of a variety of synthetic as well as natural polymer fibers for different applications have also been reported in the literature [14]. A search in the literature indicated that different polymers such as chitosan, dextral, polyacrylonitrile, polyvinyl alcohol, poly(methyl methacrylate), polystyrene, polycaprolactone, poly(vinyl pyrrolidone), biodegradable poly(L-lactide), nylon 6 and cellulose acetate [2-12] do electrospinning as well as different conducting polymers.

Incorporation of nanoparticles in polymer nanofibers has attracted a considerable attention due to possibilities of fabricating suitable materials for applications such as catalysts, drug deliveries, tissue engineering scaffolds, medical gauzes, fiber-based sensors and membranes [3-10,15]. Since the first report on electrospinning method [16], many scientists have used this process to incorporate different species. The appearance of the collected fibers depends on several factors including; viscosity of the solution, average molecular weight of the polymer, surface tension, concentration of solution, gravitational force which is dependent on

solution density, electrostatic force which has been found to depend on the applied electrostatic field and the conductivity of polymer, and ambient parameters such as temperature and humidity [17-20]. One attractive feature of electrospinning is the simplicity and inexpensive nature of the set up. The typical electrospinning set up consist of a syringe pump, a high voltage source and a collector.

A lack of research in the field of electrospun fibers in the literature promoted this research group to prepare and characterize a new class of electrospun explosive nanofibers (EENF). Such explosive fibers are expected to behave differently from the corresponding common fibers and show different properties from the explosive point of view. Also, of interest to us has been the preparation of electrospun explosive composite nanofibers (EECNF) involving both NC and other known explosive materials. In this paper three such explosives *ei.* NTO, Na-NTO and Picric acid have been used and examined. The structure of these components is observed in Fig. 1. The presence of these components in NC electrospun nanofibers are expected to influence the properties of the resulting composites.

## 2. Experimental procedure

### 2. 1. Materials and Instrumentation

Commercially available NC (12.6% N) was obtained from Parcheen Chemical Industries, Tehran. NTO was prepared according to the reported procedure [21], Dimethylsulfoxide (DMSO) 99% was obtained from Fluka. Picric acid, N, N- dimethylformamide (DMF) 99.5% and Ethyl Methyl Keton (EMK) 99% were purchased from Merck.

To characterize the morphology of the electrospun nanofibers, the samples were sputter

coated with gold and examined at different accelerating voltages and Scanning Electron Microscope (SEM) images were obtained by a Philips XL-30. The thermal behavior of the composite nanofibers was studied by STA 1500 from 20 to 700 °C under argon flow with at a heating rate of 10°C/min.

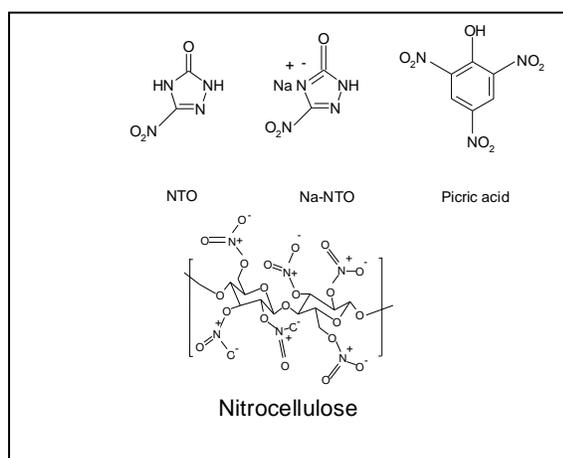


Fig. 1. Chemical structures of NC, NTO, Na- NTO and picric acid

## 2. 2. Synthesis of Na-NTO

The synthetic procedure reported in the literature, with some minor modification, was followed to prepare Na-NTO [22]. NTO (1.3g) was added to a basic solution containing NaOH (0.4g) in water at 60 °C. The yellow color was turned orange and orange precipitate was formed. The precipitate was filtered off and dried.

## 2. 3. Preparation of NC nanofibers and composite nanofibers involving NC

Generally, viscose solutions were prepared by dissolving appropriate amount of dried NC, in an oven at 65 °C for 2h, and additives, if needed, in solvents and transferred into hypodermic syringes. Then, appropriate voltages were applied between two electrodes and the webs of nanofibers were

accumulated on the surface of the aluminum foil, as collector. As the jet accelerated towards the cathode, the solvent evaporated and fibers were deposited on the collector cathode.

### 2.3.1. Preparation of NC electrospun nanofibers

NC electrospun nanofibers were obtained by the preparation of NC solutions, using DMSO, DMF and EMK as solvent. Typically, 1 ml of each solvent was added to a container containing 0.1 g NC and stirred to obtain clear homogeneous solution. The solution was then transferred into a syringe. The voltage applied between the tip of syringe and collector was 18 kV and the distances were 8 cm for DMSO and DMF and 11 cm for EMK.

### 2. 3. 2 Preparation of NTO/NC and Na-NTO/NC electrospun composite nanofibers

For the preparation of NTO/NC electrospun composite nanofibers, NTO compound (0.05g) was added to a solution containing NC (0.5g) in 6 ml EMK and electrospinning was performed at high voltage (20 kV) when the distances between two electrodes was set at 11 cm.

For the preparation of Na-NTO/NC electrospun composite nanofibers, 0.1 g of NC was dissolved in 1 ml EMK and the resulting solution was added to 0.1 g of Na-NTO and stirred until a clear viscose solution was obtained. The resulting solution was then transferred to a syringe. Upon applying high voltage (20 kV) and the 7 cm distance between anode and cathode, a fluid jet was ejected from the capillary.

### 2. 3. 3. Preparation of Picric acid/NC electrospun composite nanofibers

EMK (5 ml) was added to a mixture of NC (0.5 g) and Picric acid (0.05 g) and stirred for about 30

min at room temperature. The homogeneous solution was then transferred to a syringe and the electrospinning was performed at 20 kV and 7.5 cm distance between two electrodes.

### 2. 3. 4. Preparation of Ag/NC electrospun composite nanofibers

The NC nanofibers prepared by the procedure described in part a, was dipped and dried three times in an aqueous solution containing 2000 ppm nanosilver. Also, NC nanofibers were immersed in the same nanosilver solution while irradiating with UV irradiation.

### 2. 4. Antimicrobial Activity Study of Ag/CN Composite Nanofibers

The antimicrobial activities of composite nanofibers impregnated with Ag were examined against Gram- negative Escherichia coli (E. coli) and Gram-positive Staphylococcus aureus (S. aureus). Briefly, sterilized Luria- Bertani (LB) broth was measured (5 ml) into sterile tubes. The impregnated fibers with nanosilver were introduced into the LB broth solution containing E. coli. The mixtures were cultured at 37 °C in a shaking incubator for 24 h. A tube without nanofibers was also tested as blank control. This test was repeated for S. aureus too. 100  $\mu$ L of each microorganism was seeded onto LB agar using a surface spread plate technique. The plates were incubated at 37 °C for 2h.

## 3. Results and Discussion:

### 3. 1. NC electrospun nanofibers

NC was dissolved in DMF and transferred into a syringe. Then, both high voltage and the distance between the syringe needle and aluminum foil collector were adjusted until a jet was ejected from the surface of a charged NC solution indicating the

overcome of applied electric field strength to the surface tension and consequently the electrostatic repulsion on the surface of the fluid. The ejected jet traveled rapidly to the aluminum foil collector target and was collected in the form of solid polymer filament. During the flight time, a series of electrically driven bending instabilities that gives rise to a series of looping and spiraling motions was applied to the jet and therefore fine fibers were obtained (Fig. 2).

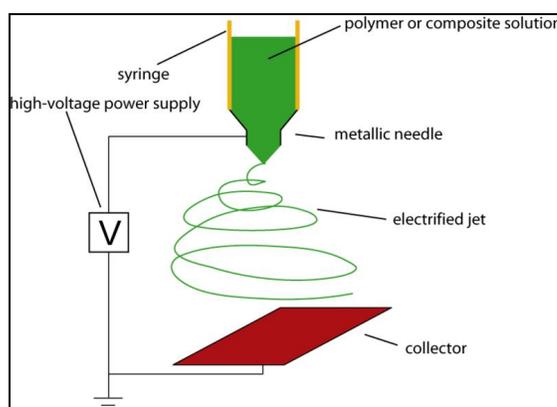


Fig. 2. Schematic illustrations of the electrospinning set-up used

The morphologies of collected NC pads on the Al foil were investigated by SEM. The results, as shown in Fig.3, indicate that electrospinning of the NC solution in DMF produce NC nanoparticles with diameters of 50 nm to about 1 $\mu$ m. In comparison to DMF, the morphology of collected NC was found to be different when DMSO was used as solvent. As can be seen in Fig. 4, a coating film of NC on aluminum surface has been formed. This indicates that DMF could be a good candidate if one plans to prepare NC nanoparticles. The ejected particles might be directed toward a container containing water to dissolve DMSO carrier and prevent coagulation of NC particles. Such a strategy to separate high boiling point

solvent from the jet has been introduced in the literature [23].

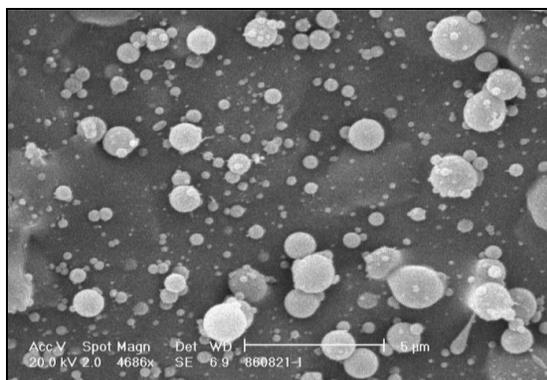


Fig. 3. SEM images of NC/DMF nanoparticles

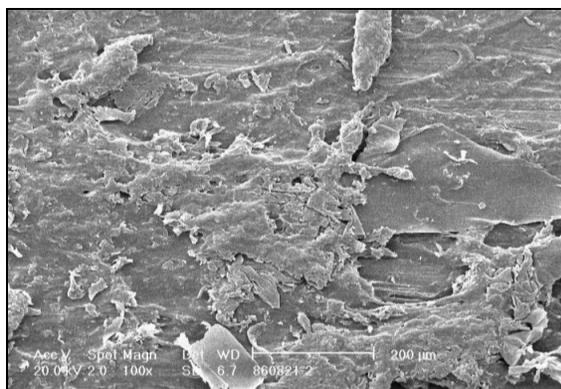


Fig. 4. SEM images of NC/DMSO nanofibers

Fig. 5 demonstrates SEM image of nanofibers electrospun from 10 wt% NC solution in EMK. As is clear two different morphologies could be detected among the generated fibers. The surface of the nanofibers with 90-150 nm diameters appears smooth while some pores are visible on the surface of the fibers with greater diameters range from 400 to 500 nm. So, among three solvents used, EMK was found as an appropriate solvent for the preparation of NC nanofibers.

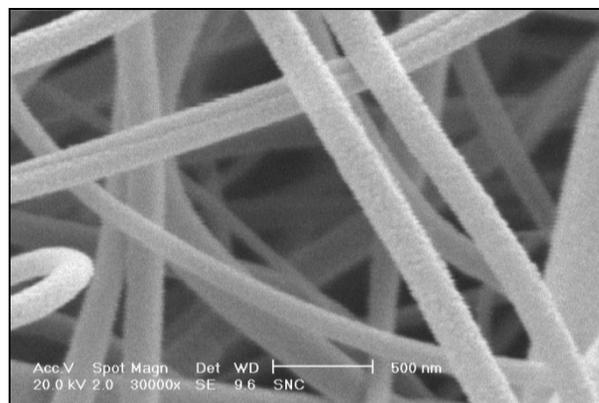


Fig. 5. SEM images of NC/EMK nanofibers

### 3. 2. NC\ NTO and NC/ Na-NTO Electrospun Composite Nanofiber

In order to modify the properties of NC from the explosive properties point of view, the preparation of NC composites involving some known explosives was planned. As the first step NTO, Na-NTO and Picric acid were chosen. So, based on the results discussed earlier, EMK was used to dissolve both NC and Na/NTO and electrospinning was applied to the solution. It has to be noticed that a great deal of caution should be undertaken while working with explosives and a protective shield is needed for safety purpose. The SEM image shown in Fig. 6 presents nanofibers with diameters ranging from 50 to 150 nm. It is seen that the average diameters of composite nanofibers have been decreased in comparison to the Na-NTO free NC nanofibers in Fig. 5. The presence of Na-NTO salt may have increased the solution polarity and conductivity and these led to the formation of nanofibers with reduced average diameters. Combination of NC and picric acid in EMK solvent was also tried and smooth composite nanofibers as shown in Fig. 7 were obtained successfully. However, the range of prepared composite nanofibers (80- 300 nm) is greater than the range of NC nanofibers prepared under the same experimental condition.

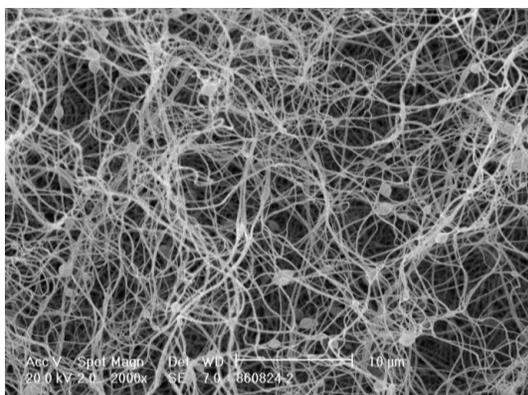


Fig. 6. SEM image of NC/Na- NTO composite nanofibers

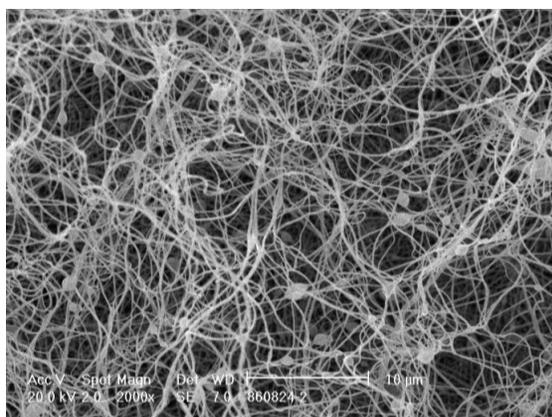


Fig. 7. SEM images of NC/Picric acid composite nanofibers

### 3. 3. Ag/NC Composite Nanofibers

As discussed in pervious section, the second components in each of the composite nanofibers were introduced in the pre electrospinning setup. For the preparation of Ag/NC composite there were possible ways to introduce Ag particles; in situ, encapsulation and immersion of NC nanofibers in to a solution containing nanosilver. The last one, however, was chosen by dipping-drying NC nanofibers three times into an aqueous solution containing 2000 ppm nanosilver.

The antimicrobial activities of the Ag/NC composite nanofibers were examined against *E. coli* and *S. aureus*. The numbers of colonies of *E.*

*coli* and *S. aureus* were significantly reduced in the case of composite after 24h incubation at 37 °C. This not only clarified surface treatment by silver, also indicated the successfully inhibition of growth of mentioned two bacteria.

### 3. 4. DSC Analysis of NC Electrospun Nanofibers

In order to investigate the thermal behavior of NC electrospun nanofibers, the heating temperature range of 25 to 550 °C with heating rate of 10 °C/min and dinitrogen flow of 50 ml/min was chosen. Fig. 8 shows the resulting thermogram with a strong exothermic peak at 212 °C. This exothermic peak is consistent with the results obtained for normal NC and indicating thermal stability of the resulting NC electrospun nanofibers.

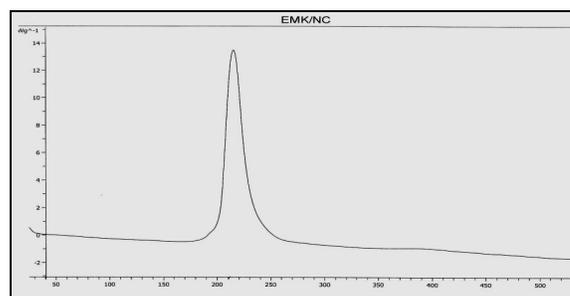


Fig. 8. Thermal analysis of NC nanofibers

### 4. Conclusions

It has been shown that NC can easily be used to prepare electrospun NC nanofibers using EMK as an appropriate solvent. The known explosive materials such as NTO, Na-NTO and picric acid have been added to the dissolved NC in EMK and electrospinning process have been applied to the resulting solution to obtain electrospun explosive composite nanofibers successfully.

The results presented in this research paper will open new research fields both for scientists deal

with electrospun nanofibers and researchers working with explosive materials. The properties of the obtained explosive nanofibers are currently under investigation. The preparation of other EENP as well as EECNP is also in progress.

### Acknowledgment

Financial support by Imam Hossein University is gratefully acknowledged.

### References

- [1] S. Megelski, J.S. Stephens, D.B. Chaisea and J.F. Rabolt. 35 (2002) 8456-8466.
- [2] D.H. Renker and I. Chun. 7 (1996) 216-223.
- [3] a) M.M. Demir, I. Yilgor, E. Yilgor and B. Erman. Polymer. 43 (2002) 3303-3309. b) J.M. Deitzel, J.D. Kleinmeyer, J.K. Hirvonen and N.C.B. Tan, Polymer. 42 (2001) 8163-8170.
- [4] J. Yuh, L. Perez, W.M. Sigmund and J.C. Nino, 37 (2007) 254-259.
- [5] Q.B. Yang, D.M. Li, Y.L. Hong, Z.Y. Li, C. Wang, S.L. Qiu and Y. Wei, Synth. Met. 137 (2003) 973-974.
- [6] W.K. Son, J.H. Youk and W.H. Park, Carbohydr. Polym. 65 (2006) 430-434.
- [7] X. Xu, Q. Yang, Y. Wang, H. Yu, X. Chen and X. Jing, Eur. Polym. J. 42 (2006) 2081-2087.
- [8] S. Li, C. Shao, Y. Liu, S. Tang and R. Mu, J. Phys .Chem .Solids. 67 (2006) 1869-1872.
- [9] C. Shao, H. Guan, Y. Liu, J. Gong, N. Yu and X. Yang, J. Cryst.Grow. 267 (2004) 380-384.
- [10] K.H. Hong, J.L. Park, I.H. Sul, J.H. Youk and T.J. Kang, J. Polym. Sci. B. 44 (2006) 2468-2474.
- [11] Y. Hong, D. Li, J. Zheng and G. ZouIn. 22 (2006) 7331-7334.
- [12] Y. Lu, M. Yu, M. Drechsler and M. Ballauff. 254 (2007) 97-102.
- [13] T. Jarusuwannapoom, W. Hongrojjanawiwat, S. Jitjaicham, L. Wannatong, M. Nithitanakul, C. Pattamaprom, P. Koombhongse, R. Rangkuoan and P. Supaphol, Eur. Polymer. J. 41 (2005) 409-421.
- [14] J.M. Deitzel, J. Kleinmeyer, D. Harris and N.C. Beck Tan, Polymer. 42 (2001) 261-272.
- [15] X. Wang, C. Drew, S.H. Lee, K.J. Senecal, J. Kumar and L.A. Samuelson, Nano Letters. 2 (2002) 1273-1275.
- [16] A. Formhals, US Patents. 1,975,504, 1934.
- [17] Q.P. Pham, U. Sharma and A.G. Mikos, Tissue Engineering. 12 (2006) 1197.
- [18] C.J. Buchko, L.C. Chen, Y. Shen and D.C. Martin, Polymer. 40 (1999) 7397-7407.
- [19] H. Fong, I. Chun and D.H. Renker, Polymer. 40 (1999) 4585-4592.
- [20] B. Duan, C.H. Dong, X.Y. Yuan and K.D. Yao, J. Biomat. Sci. Polym. E. 15 (2004) 797-811.
- [21] W. Smith Matthew and D. Cliff Matthew, Report No. DSTO- TR- 0796, (1999).
- [22] G. Singh and S.P. Felix, J. Hazard. Mater. A. 90 (2002) 1-17.
- [23] G. Viswanathan, S. Murugesan, V. Pushparaj, O. Nalamasu, P.M. Ajayan and R.J. Linhardt, Biomacromolecules. 7 (2006) 415-418.