

# Nanofibers by Electrospinning of Nylon 6 Doped With Boron

**İbrahim Uslu<sup>1\*</sup>, Ayşenur Altaş<sup>1</sup>, M. Levent Aksu<sup>2</sup>, Faruk Gökmeşe<sup>3</sup>**

<sup>1</sup>Selçuk University, Faculty of Education, Meram Yeniyol, Konya, Turkey

<sup>2</sup>Gazi University, Faculty of Education, Chemistry Education, Ankara, Turkey

<sup>3</sup>Hitit University, Faculty of Arts and Sciences, Department of Chemistry, Çorum, Turkey

## Article Info

### Article history:

Received  
September 15, 2008

Received in revised form  
December 20, 2008

Accepted  
December 25, 2008

Available online  
March 21, 2009

## Key Words

Electrospun,  
Nanofiber,  
Nylon 6,  
Boron doped,  
Boric acid

## Abstract

In this study, Nylon 6 was successfully cross-linked with boron using formic acid as solution. Electrospinning process was performed by putting hybrid nylon 6/boric acid solutions at different applied voltage in a range from 20 to 25 kV using a high voltage power supply. Nylon has been widely used in industry because of its good mechanical properties. The use of boron improves the strength, flame retardant characteristics and flexibility of the nylon 6 fibers.

The structures of the nanofibers synthesized are characterized by the Fourier transformed infrared spectroscopy (FTIR), thermo gravimetric and differential thermal analysis (TG/DTA), differential scanning calorimetry (DSC), atomic force microscopy (AFM), and scanning electron microscopy (SEM).

DSC and TGA analysis revealed that stability of electrospun nylon 6 fiber is higher than non spun sample and increase of boric acid content increases the stability of the polymer. It is observed from the SEM images that the diameters of the fibers decreased with boron content increased. FTIR analysis revealed that all characteristic N-H structures are observed and consistent with literature.

## INTRODUCTION

The objective of this research was to study the cross-linking effects of boron on Nylon 6 nanofibers. Nylon is the first commercialized fiber and used in textiles or composite reinforcement fields [1]. In recent years nylon has been widely used in many other applications because of its good mechanical properties [2-3]. Nylon has been produced by

conventional methods such as melt spinning, dry spinning and wet spinning but average fiber diameters of nylon produced by these methods are in the range of 10 to 500  $\mu\text{m}$ . However with electrospinning process, polymeric fibers can be easily produced in the nano scale range in diameter [1-2]. In this study electrospinning technology has been used to produce nylon 6 fibers.

Electrospinning is a process that uses a high voltage electric field which converts polymeric solution or melts into near nanofibers on the target substrate. This technique became very interesting after 1990s.

\* Correspondence to: İbrahim Uslu,

Selçuk University, Faculty of Education, Meram Yeniyol, Meram, Konya, Turkey

Tel: +90332 323 8220-5490 Fax: +90332 323 8225  
E-mail: iuslu@selcuk.edu.tr

Electrospinning setup consists of four major components. a high-voltage power supply, a spinneret, a syringe pump, and an electrically conductive collector.

Boric acid as a cross-linking agent was added to nylon solution after nylon 6 polymer was fully dissolved in formic acid obtaining a gel like hybrid polymer mixture.

During the experiments, an ordinary metallic needle was used as the spinneret and a piece of aluminum foil served as a fiber collector. The solution for spinning was loaded in a plastic syringe, which was connected to syringe pump so that a constant and adjustable feeding rate of nylon 6/boric acid hybrid solution can be maintained [4-9].

## **EXPERIMENTAL**

### **Measurements and Characterization**

The structures of the nanofibers characterized by the fourier transformed infrared spectroscopy (FTIR) and thermo gravimetric and differential thermal analysis (TG/DTA), differential scanning Calorimetry (DSC), atomic force microscopy (AFM) and scanning electron microscopy (SEM).

### **Preparation of fibers**

Nylon 6 (Merck, Darmstadt, Germany), formic acid (Aldrich, Munich, Germany), boric acid (Merck, Darmstadt, Germany) was purchased and used as received. The electrospinning apparatus used a high voltage power supply (Gamma High Voltage Research, ES 30P-20W/DAM) (200 mA at 30 kV). During electrospinning, a positive high voltage was applied through a copper wire to hybrid nylon 6/boric acid polymeric solutions. Formic acid (HCOOH) was used as a solvent for dissolving the nylon 6. Nylon 6 solution was prepared adding 5 g of nylon 6 into

10 ml formic acid and waited overnight. Solution was always kept closed to prevent the evaporation of formic acid from the solution.

In this study, amine groups of nylon 6 reacts with boric acid in solution form. Extends of cross-linking reaction, namely 0%,10%, 20%, 60%, 80% and 100% were calculated based on trifunctionality of boric acid. For the preparation of 100% cross-linking of Nylon6/boric acid hybrid solution, 0.99 g boric acid in 23 ml formic acid mixed with the nylon 6 solution prepared before.

Electrospinning was performed by putting hybrid nylon 6/boric acid solutions at different applied voltage in a range from 20 to 25 kV using a high voltage power supply.

The ground collection plate was located at a distance from 17 cm to 25 cm from the needle tip. A syringe pump was used to feed polymer solution into needle tip. The viscosity of the hybrid polymer prepared is very important parameter for electrospinning process because syringe pump cannot pump high viscous solutions and clogging of the needle tip may stop the electrospinning process.

As the electrical potential was gradually increased to 20 kV (or 25 kV), a jet was created. The jet, formed by electrical forces, followed a complicated stretching and looping path as it dried and solidified. Nonwoven fabric was formed on the surface of a piece of aluminum foil, which covered the grounded metal sheet. When nanofibers were deposited randomly on the target layer by layer, various diameters of pores (distances between fibers) were formed. After mixture of formic acid/nylon 6 solution and boric acid/formic acid electrospinning was achieved nanofibers were ovened at 70°C after this process. The fabric could easily be peeled off the aluminum foil.

## RESULTS AND DISCUSSION

### FTIR Analysis

Figure 1 and 2 shows the FTIR result of the hybrid polymers. The  $688\text{ cm}^{-1}$  band which is assigned to N-H structure can be easily seen in all of the peaks. Characteristic peaks of  $1530\text{ cm}^{-1}$  (amide C-N stretch + CO-N-H band),  $1630\text{ cm}^{-1}$  (C=O stretch),  $2860\text{ cm}^{-1}$  (symmetric C-H<sub>2</sub> stretch),  $2930\text{ cm}^{-1}$

(asymmetric C-H<sub>2</sub> stretch),  $3080\text{ cm}^{-1}$  (N-H in plane bend),  $3300\text{ cm}^{-1}$  (hydrogen bonded N-H stretch) bands are also exists in all of the peaks. FTIR analysis is not sufficient for the characterization of B-N and B-O-N structure because in literature IR peaks at  $1380$  and  $780\text{ cm}^{-1}$  corresponds to these peaks and they are overlap each other. NMR spectroscopy analysis will be recommended characterization technique at this stage.

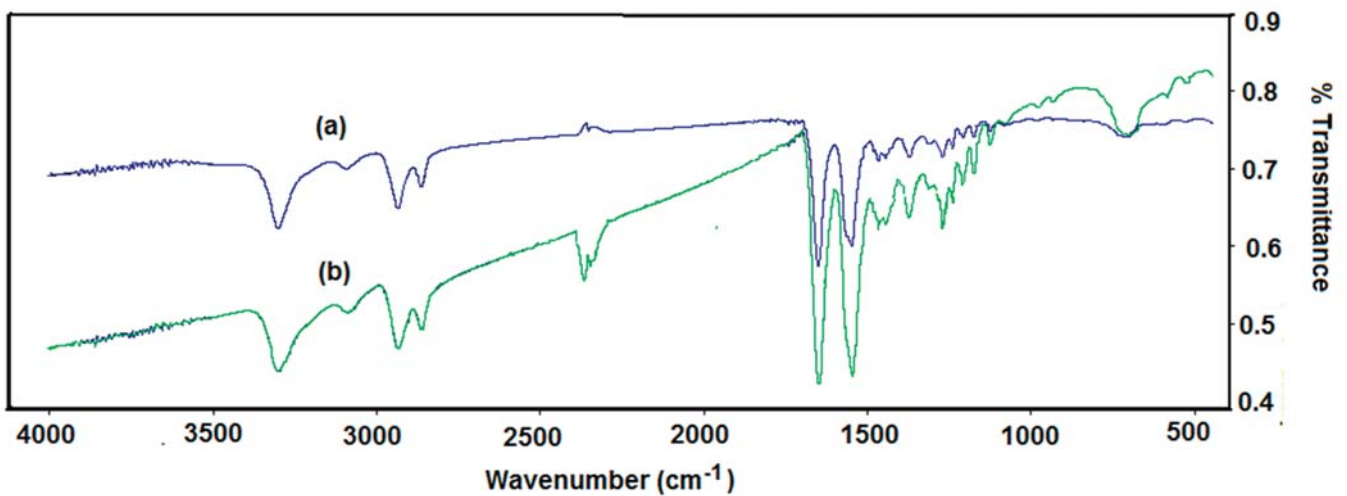


Figure 1. FTIR results of nylon 6 with (a) 10% and (b) 20% extends of cross-linking reaction with boron.

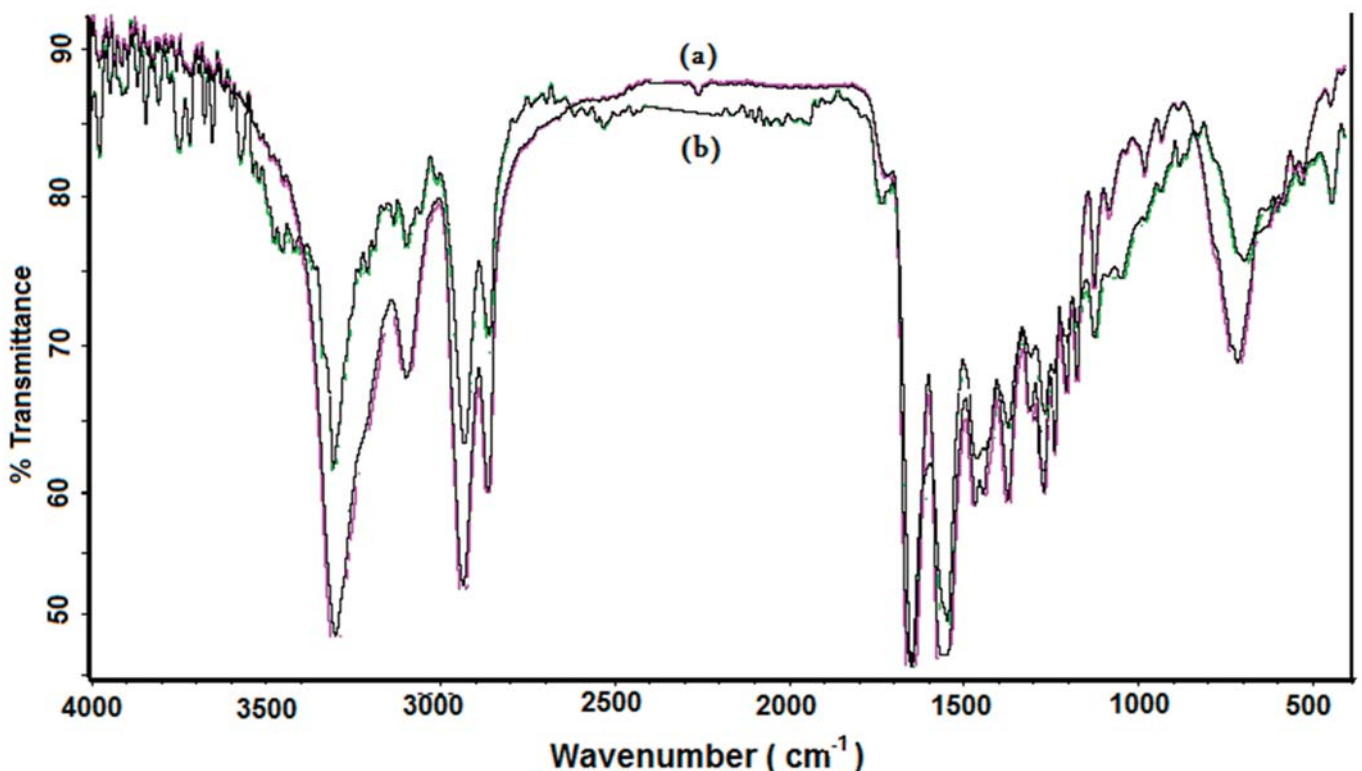


Figure 2. FTIR results of nylon 6 with (a) 60% and (b) 80% extends of cross-linking reaction with boron.

### TGA and DTA Analysis

Figure 3 is the result of the TGA and DTA analysis of the solution form (measured after vacuum drying of the solution) and electrospun 20% hybrid Nylon 6/boric acid polymer fibers. From this figure it is seen that first peak which corresponds to melting temperature of the solution and fiber forms are almost the same but the degradation peak at 30°C is higher in fibers form with respect to solution form. It means that fiber form is a more stabilized than the solution form.

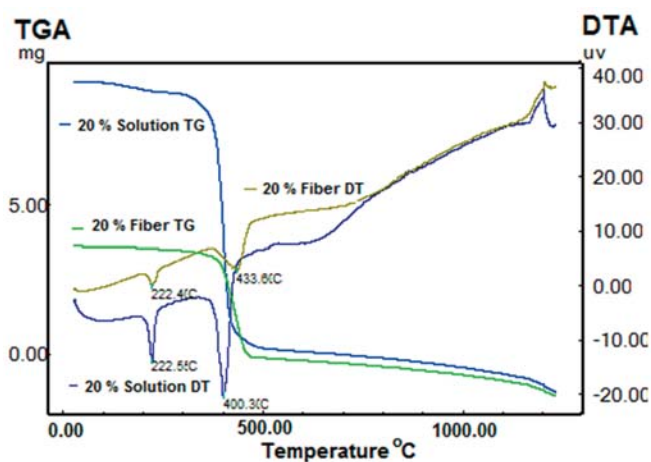


Figure 3. TGA and DTA analysis of the solution form and electrospun 20% hybrid Nylon 6/boric acid polymer fibers.

### Differential Scanning Calorimetry (DSC)

Figure 4 is DSC results of the a) pure non electrospun nylon 6 solution dried in vacuum and b) pure nylon 6 electrospun polymer. For non electrospun nylon 6 fiber the peaks around 420, 450 and 480°C was considered to reflect the decomposition of side chain and main chain of PVA, respectively. It is consistent with literature that stability of electrospun nylon 6 fiber is higher than non spun sample. Degradation peak was broadened and increase to 540°C for electrospun nylon 6 fiber.

Figure 5 is DSC results of the hybrid Nylon 6/boric acid polymer fibers. TGA and DSC results show that increase of boric acid content increases the stability of the polymer. From Figure 4, it is seen that the second peaks which shows the degradation

temperature of the polymer are higher for high boric acid content. There are two degradation peaks at 443 and 506°C for 80% boric acid hybrid polymer and its stability is the highest.

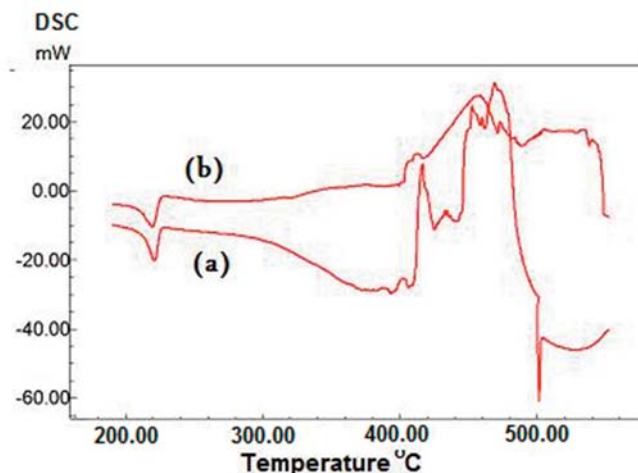


Figure 4. DSC analysis of the (a) solution form and (b) electrospun 20% hybrid Nylon 6/boric acid polymer fibers.

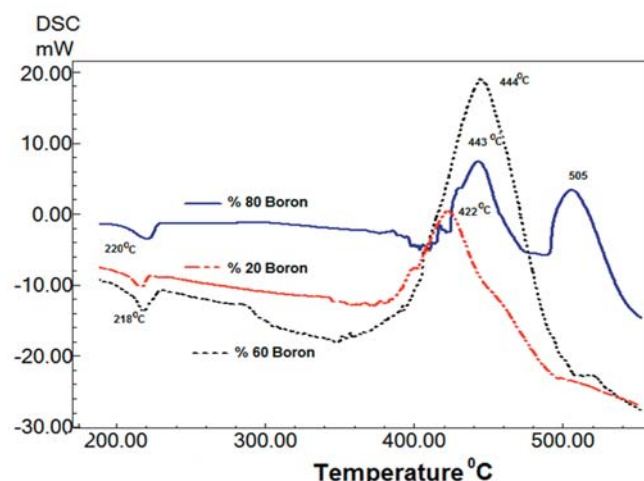


Figure 5. DSC results of the hybrid Nylon 6/boric acid polymer fibers.

### AFM Analysis

Figure 6 shows the appearance of electrospun nylon 6 with 60% extends of cross-linking reaction with boron obtained by AFM. It is observed that fiber diameters ranges are between 100 to 350 nm.

### SEM analysis

The microstructure of fibers was observed by SEM. As can be observed, the fibers have almost uniform diameter without beading. It is observed from the SEM images that the diameters of the fibers decreased with boron content increased.



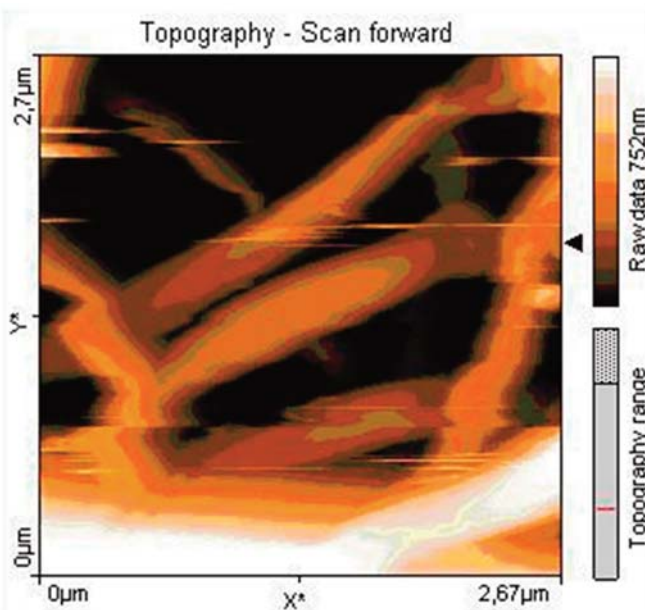
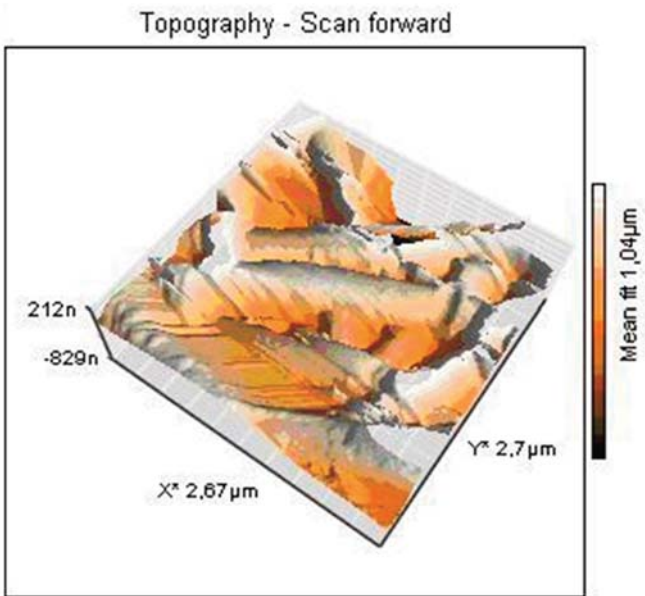
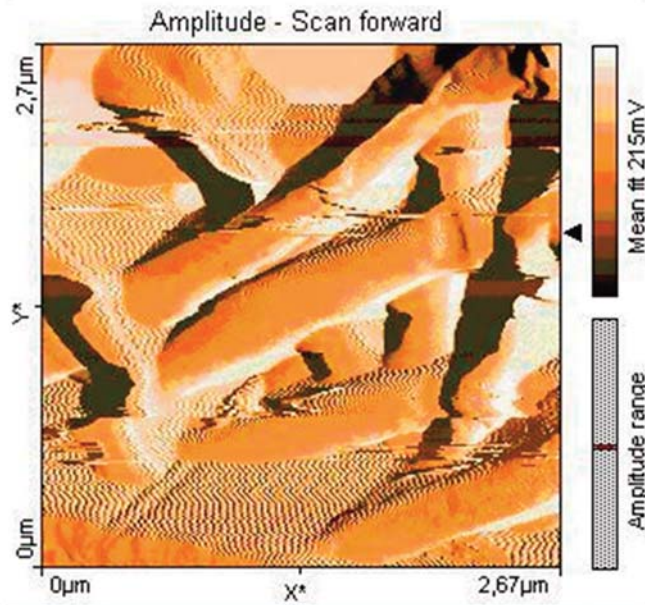


Figure 6. AFM images of electrospun:nylon 6 with 60% extends of cross-linking.

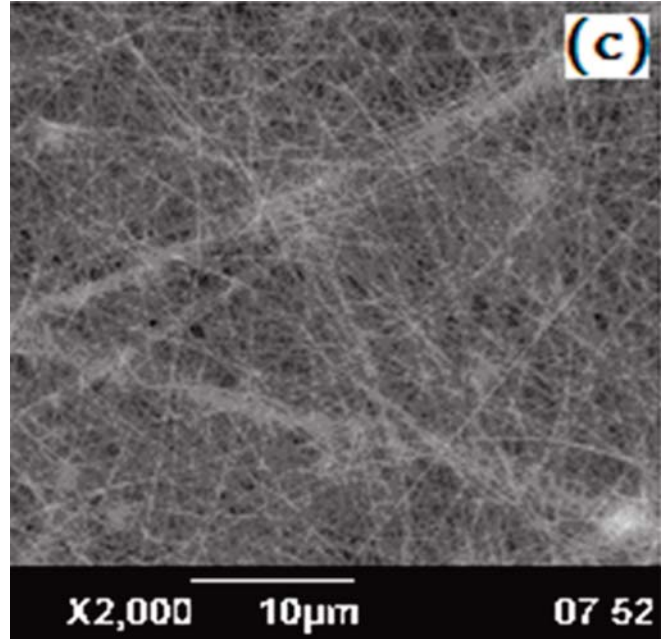
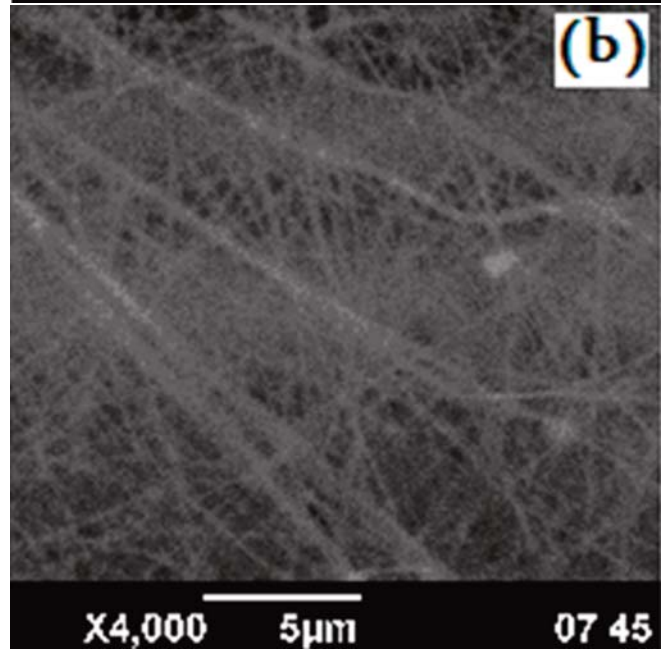
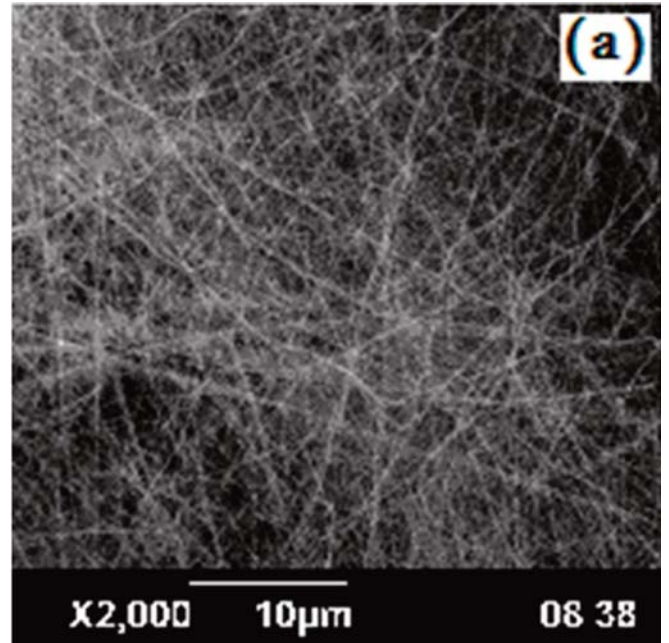


Figure 7. SEM images of:nylon 6 with (a) %20, (b) 60% and (c) 80% extends of cross-linking reaction with boron.

## CONCLUSION

We have successfully electrospun nylon 6 doped with boron by using formic acid as a solvent. A boron containing nylon 6 was easily obtained from the reaction between boric acid and nylon 6.

## ACKNOWLEDGEMENT

The present work is supported financially by the Scientific and Technological Research Council of Turkey (TÜBİTAK) Project by contract 106T630. Special thanks to Prof.Dr. Orhan Atakol for the help on DSC analysis.

## REFERENCES

1. Reneker, D.H.; Chun, I. *Nanotechnology*, 7, 216, 1996.
2. Aoki, I.K.; Ishii, T. *J. Appl. Polym. Sci.*, 14, 1597, 1970.
3. Bankar, V.G.; Spruiell, J.E.; White, J.L. *J. Appl. Polym. Sci.*, 21, 2341, 1977.
4. Murthy, N.S.; Aharoni, S.M.; Szollosi, A.B. *J. Polym. Sci. B.*, 23, 2549, 1985.
5. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurachi, T.; Kamigaito, O.; Kaji, K. *J. Polym. Sci: Polym. Phys.*, 33, 1039, 1995.
6. Kojima, Y.; Matsuoka, T.; Takahasi, H.; Kurachi, T. *J. Appl. Polym. Sci.*, 51, 683, 1994.
7. Fong, H.; *Polymer*, 45, 2427, 2004.
8. Kim, J.S.; Reneker, D.H.; *Polym. Eng. Sci.*, 39(5), 849, 1999.
9. Ryu, Y. J.; Kim, H.Y.; Lee, K.H.; Park, F.C.; Lee, D.R. *European Polym. J.*, 39, 1883, 2003.