Nanotechnology Applications in Textile Materials: Plasma and Sol-Gel Techniques

Aysun Akşit[1]*

[1]*Dokuz Eylul University, Textile Engineering Departmen, Buca, Izmir, 35160, Turkey*

Abstract-To overcome the disadvantages of conventional textile finishing processes, for example side effects like decrease in strength, low durability to washing, wastewater load, consumption of water, chemical agents, etc., the new and promising techniques can be used like plasma and sol-gel processes. In this paper these techniques will be discussed.

Earlier methods of improving functional properties focused on simple chemical modification of functional groups of fibers and deposition of active agents on fabrics. Finishing techniques evolved later that used the incorporation of a polymer or copolymer in the fibrous material to impart functional property improvement. Current techniques like plasma and sol-gel techniques use one or more physicochemical and chemical approach to produce textile materials with improved functionality in one or several properties [1]. Plasma and sol-gel methods, which are the important functional property improvements for textiles will be discussed in this paper.

Penetration of nano-sized coatings of sol-gel technique is very good, and very different functional properties can be given to the fabrics in nanosize using very low amount of chemicals. In addition, multifunctional effects can be obtained by combining sol-gel coating and properties of inorganic-organic material properties. Cellulose macromolecules can be cross-linked by means of sol network and the washing durability of the nanosized coating can be increased applying sol-gel coating. Also sol-gel technique can be adapted to continuous lines in textile finishing mills. Accordingly, this technique can be realized in industrial scale. A gel solution (sol) is a medium in which particles in the sizes of 1-100nm are dispersed. A gel is a reticular substance in which submicron holes and polimerized chains are binded together. The sol-gel method causes the gelation of metallic organic and inorganic substances and after that the formation of oxides and other solid compounds by a curing process. Sol-gel process has some advantages when compared to other methods. Firstly, the sol-gel method may be realized in low temperatures by simply controlling the process. Secondly, a highly pure product can be obtained by simply removing solvent. Thirdly, is that the very smooth material can be produced. Finally, it can be used to produce any shape of materials. In our research group, we studied with sol-gel technique for UV protective, self-cleaning, flame retardance, magnetic shielding properties of fabrics and for development of fastness values of direct dyestuffs [2-5].

Plasma is a very reactive material and can be used to modify the surface of a certain substrate (typically known as plasma activation or plasma modification), depositing chemical materials (plasma polymerization or plasma grafting) to impart some desired properties, removing substances (plasma cleaning or plasma etching) which were previously deposited on the substrate. Plasma technologies offer a wide spectrum of possible treatments of materials. Plasma-chemical conversion of the feed gas produces chemically active particles that are able to modify textile surface molecules via chemical reactions after imping on the surface. The radicals generated inside the plasma region must be given the opportunity to move to the reaction place at the textile fiber surface. The main attraction of plasma treatments in industrial processing is the avoidance of chemical effluents. Other advantages include: low cost, rapid reaction times, low amount of chemicals and elimination of water so the plasma polymerization is an ecological and economic process. Plasma polymerization is used in many textile finishing processes to give fabric functional properties such as water-, soil-repellency, wettability, flame-retardancy, etc. [Allan, et al., 2002; Zhang, 2003]. We used plasma technology to give wettability, hydrophobicity to fabrics, to increase their wrinkle recovery angles, for electrical conductivity, flame retardancy, etc [6-8].

*Corresponding author: aysun.cireli@deu.edu.tr

[1] Vigo, T.L. (1994). Textile Processing and Properties. Amsterdam: Elsevier Science B.V.
[2] Akşit A, Onar N, Ebeoğlugil M, Birlik I, Çelik E, Özdemir İ, J Appl Polym Sci, 113, 358/(2009)
[3] Onar N, Akşit A, Ebeoğlugil M, Birlik I, Çelik E, Özdemir İ, J Appl Polym Sci, 114, (2009)
[4] Akşit A, Onar N, J Appl Polym Sci, 109, (2008).
[5] A. Cireli, N Onar, M.F. Ebeoglugil, I. Kayatekin, B. Kutlu, O. Culha, E. Celik, J Appl Polym Sci, 105 (2007).
[6] B Kutlu, A Aksit, M Mutlu, J Appl Polym Sci, 106, (2010).
[7] B Kutlu (Kilic), A Cireli Akşit, M Mutlu, Int J Cloth Sci Tech, 21, (2009).
[8] A Cireli, B Kutlu, M Mutlu, J Appl Polym Sci, 104 (2007).

Modifying textiles with antibacterial effect, friction resistance, UV protection and electrostatic charge decay abilities by an alternative nanotextile technology called MEVVA ion implantation technique

Ahmet Öztarhan[1], Ali Akpek[1], Efim Oks[2], ,Alexey Nikolaev[2]

[1] Biyomühendislik Bölümü, Ege Üniversitesi, İzmir Türkiye

[2] High Current Electronics Institute, Academichesky Ave, Tomsk, Rusya

Abstract- In this study, Ion Beam implantation technology which has been used for surface modification of materials for a long time was used at textile surfaces for the first time. By the help of this technology metal and metal+gas ions implanted to the textile surfaces and gained them unique abilities that can not be held by any other techniques. This study is the first study in the world using MEVVA ion beam implantation technology as an alternative nanotextile technology and obtains a significance step to reach the vision of "infinite antibacterial efficiency"

In first phase of the study, titanium, carbon and crom ions were implanted to a group of Polyester (PES) fabric's surfaces. These fabric's friction coefficients and wear losses were compared with unimplanted PES fabric's friction coefficient and wear loss.
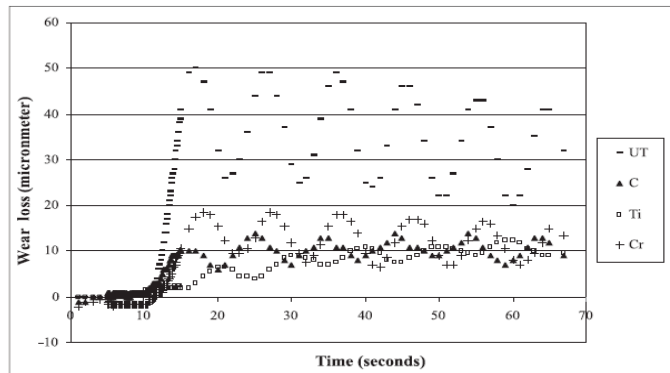
At the end of this phase without analysing any destruction of structural properties of any textiles, Cr, Ti and C ions implanted PES fabrics friction coefficients and wear losses have decreased up to %50

In the second phase of the study, Pb, Ag, Ag+N, Ti+O and Cr+O ions were implanted to the PES fabrics. These implanted PES fabric's UV Protection Factors were compared with unimplanted PES fabric's UV Protection Factor.

No	UV protection Factor (UPF)
Unimplanted	3,87
Pb	15
Ag	**30**
Ag+N	10
Ti+O	10
Cr+O	20

UPF	Protection
15-24	Good
25-39	**Very Good**
40-50, 50+	Excellent

At the end of this phase it has been seen that according to the ion dose and element or compound type, implanted fabric's UV Protection Factors rised up to %700.

In the third phase of the study Cu ions were implanted to the surfaces of PES fabrics with different doses. These implanted fabric's electrostatic charge decay values were compared with unimplanted PES fabric's electrostatic charge decay.

After these researches, it has been focused on antibacterial researches. For this purpose; Ag and Ti+O ions were implanted to the polyester (PES) and cotton based medical textiles to provide them antibacterial ability againist very dangerous pathogenes called Hospital Infections.

Samples	Dose and Energy (ion/cm^2), kV	Charge decay (time to %50 charge)
Unimplanted PES Fabric	-	No Decay after 300 sec
Cu İmplanted PES Fabric-1	$5x10^{15}$,30kV	26 sec
Cu Implanted PES Fabric-2	$1x10^{16}$,30kV	1,5 sec
Cu Implanted PES Fabric-3	$5x10^{16}$,30kV	100 msec

At the end of this phase, it was determined that implanted fabrics electrostatic charge decay were increased significantly.

These medical textiles were tested with AATCC 100-1993 antibacterial test methodology and determined that they all have up to %85 antibacterial efficiency even after 30 washouts. These medical textiles antibacterial ability were also compared with conventional nanotextile based antibacterial medical textiles presented with N and D. Bacteria used in the test was Staphylococcus Aureus. (S.aureus-ATCC 6538)

No	(%) Antibakteriyel Efficiency	
	Before 30 washouts	After 30 Washuts
I1	%99,26	%58,22
İ2	%100	%68,65
I3	%98,95	%83,85
İ4	%97,42	%50,19
I5	%95,80	%72,03
İ6	%97,95	%-27,27
I7	%99,11	%85,62
İ8	%99,08	%1,41
N1	%100	%92,91
N2	%100	%70,82
N3	%100	%71,67
D1	%100	%79,80
D2	%100	%52,16

No	Specification
İ1	Cotton/Ag/$5x10^{15}$
I2	Ag/Cotton/$5x10^{16}$
I3	Ag/PES/$5x10^{16}$
I4	Ag/PES/$5x10^{15}$
I5	TiO_2/Cotton/$5x10^{16}$
I6	TiO_2/Cotton/$5x10^{15}$
I7	TiO_2/PES/$5x10^{16}$
I8	TiO_2/PES/$5x10^{15}$
N1	Ag/Cotton
N2	TiO_2/PES
N3	Ag/Cotton
D1	Secret/Cotton
D2	Secret/PES

*Öktem T., Özdogan E., Namligöz S. E., Öztarhan A., Tek Z., Tarakçioglu I., Karaaslan A., 2006, İnvestigating the Applicability of Metal Ion Implantation Technique (MEVVA) to Textile Surfaces, Textile Research Journal 76: 32p

*Öktem T., Tarakçıoğlu I., Özdoğan E., Öztarhan A., Namlıgöz E.S., Karaaslan A., Tek Z., 2008, Modification of friction and wear properties of PET membrane fabrics by MEVVA ion implantation, Materials Chemistry and Physics, 108, 208–213pp

*Chen X.,Schluesener H J., 2008, Nanosilver: A nanoproduct in medical application, Toxicology Letters 176: 1–12pp

*AATCC Test Method 100-1993, An American National Standard Antibacterial Finishes on Textile Materials

A Study on an Electrospraying Application onto Textile Surface

Cem Gunesoglu[1]*
[1]*Gaziantep University, Textile Engineering Department, 27310, Gaziantep, TURKEY

Abstract- Deposition time is key factor to determine application ease, time and cost of electrospraying. This statistical study investigates the contribution of process parameters of electrospraying on deposition time when conducted for the application of commercially available fluoropolymer resin onto cotton fabric. The results showed that solution viscosity was highly significant on deposition time and any variation in other parameters would cause highly significant changes on deposition time for the solutions with higher viscosity / fluoropolymer resin concentration

Electrospraying process should be well reviewed to consider as a textile application alternative. It is a well-known technique of liquid atomisation via employing electrical forces and has some advantages over conventional mechanical spraying systems with droplets like easy control of charged droplets by electric fields, high deposition efficiency of droplets and smaller droplet size with narrow distribution [1]. A previous study [2] has also demonstrated the success of the electrospraying in the application of commercially available nanoparticles (fluoropolymer) onto textile surface to avoid undesirable agglomeration; it has been also reported that electrospraying would give acceptable finishing performance with very low amount of chemical consumption. Relevant studies determined experimentally the range of physical parameters of liquid which could be atomised by electrical forces. It is concluded that a liquid cannot be electrosprayed when its surface tension is higher than 50 dyn/cm [3 and conductivity doesn't fall within the range of $10^{-1} - 10^{-11}$ S/m [3], $10^{-5} - 10^{-11}$ S/m [4] or $10^{-1} - 10^{-9}$ S/m [5]; additionally viscosity of the liquid, voltage applied, liquid flow rate and electric field were accepted as the other important process parameters which the modes of spraying depend on [1]. There are also experimental equations obtained on mean diameter of droplets [6, 7].

This study is a statistical work on process parameters of electrospraying when conducted for the application of commercially available fluoropolymer resin onto cotton fabric. The aim is simply to perceive the basic relationships between the deposition time of chemical droplets and varying process parameters. Deposition time is considered key factor for the facile process, application time and cost; therefore a statistical approach is made to evaluate the contribution of electrospraying parameters selected as chemical viscosity, electrical voltage, flow rate and syringe-collector distance.

100% cotton RL-knitted fabric was employed in this study. The commercially available fluoropolymer resin F was supplied by Rudolf-Duraner, Bursa / Turkey. The particle size and multimodal size distribution measurements of the chemical were performed with a Brookhaven Instruments 90 Plus (Holtsville, NY / USA) using dynamic light scattering technique to bear if the chemical would be marked as of nano particles. Two different fluoropolymer resin solutions (comprising 5 g/L and 40 g/L F in distilled water, and marked as F1 and F2 respectively) were prepared and the viscosity of the solutions as a process parameter was investigated with an AR 2000ex Rheometer (TA Instrumental, New Castle, DE / USA). Conductivity measurements of the solutions were performed by a multimeter Keithley model 2400 (Cleveland, OH / USA) to determine that the fluoropolymer resin solutions would be electrosprayed theoretically.

The electrospray applications were carried with a previously established setup [12] where fluoropolymer resin solutions was poured into the charged syringe and sprayed onto fabric sample placed on the collector ground electrode. The grounded electrode was a flat aluminum foil which enabled large contact between the sample and the electrode itself. The basic configuration of setup is given in Figure 1.

The syringe – collector distance, the electrical voltage and flow rate were taken as process factors to be investigated, as well as the viscosity of the solution; where the syringe – collector distance had two (3 and 10 cm), electrical voltage value had three (8, 9 and 10 kV), flow rate had five treatment levels (10, 15, 20, 25 and 30 μL/min) respectively. At each combination of factor levels, droplet formation was easy to monitor and time for deposition of 10 droplets onto the samples were measured by simple chronometer: the less the time, the more the facile the process is. The average of four measurements of deposition time was taken as time data.
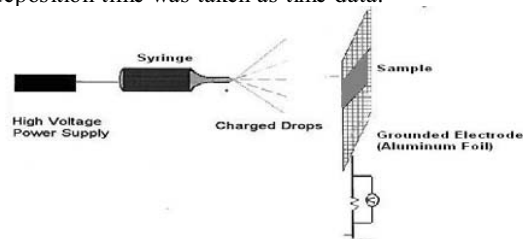

Figure 1. Electrospraying setup.

The contribution of each factor was assessed using a completely randomized two way analysis of variance (ANOVA). The results were evaluated at 5% significance level.

In summary, the results reveal that there was a certain decrease in deposition time as the flow rate and electrical voltage values increase for each sample. However, the ANOVA analysis showed that the contribution of solution viscosity was highly significant and the other parameters had lesser extent than that of viscosity; any variation in process parameters would cause highly significant changes on deposition time for the solutions with higher viscosity / resin concentration.

*Corresponding author: 0Tgunesoglu@gantep.edu.tr

[1]Jaworek, A. et al., Journal of Electrostatistics, 67, 435 – 438 (2009).
[2] Gunesoglu, C., et al., Textile Research Journal, 80 (2), 106-115, (2010).
[3]Smith. D.P.H., IEEE Trans. Ind. Appl. 22 , 527–535, (1986).
[4]Mutoh, M. et al., J. Appl. Phys. ,50, 3174–317, (1979).
[5]Cloupeau,M. B. Prunet-Foch, Sendai, Japan, 22–24.
[6]Ogata, S, et al., Int.Chem. Eng. 18, 488–493, (1978).
[7]De la Mora, J.F. and I.G. Loscertales, J. Fluid Mech. 260 , 155–184, (1994).
[8]Zhang, D., et al., Polymer, 50, 4189 – 4198, (2009).

Characterization of the Crystallization and the Molecular Orientation of Polyester Nanofibers

Sebnem Duzyer[1], Asli Hockenberger[1]* and Ismail Karacan[2]
[1]Department of Textile Engineering, Uludag University, Bursa 16059, Turkey
[2]Department of Textile Engineering, Erciyes University, Kayseri 38039, Turkey

Abstract-Solvent-spun polyester nanofibers by electrospinning technique with different Polyethylene terephthalate (PET) concentrations of 13, 16 and 20% wt were produced. Differential scanning calorimetry (DSC), X-ray diffraction analysis and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FTIR) studies have been carried out to analyze the structural and thermal properties in terms of the degree of crystallization and molecular orientation of polyester nanofibers. Scanning Electron Microscope (SEM) and optical microscopy studies have been performed to investigate the fiber diameter and the fiber diameter distribution of the as-spun polyester nanofibers

Fineness of the textile fiber is very important in terms of many properties; such as surface area, adhesion and mechanical performance. Reduction of the fiber diameter increases the specific surface area. When diameter reaches nano-dimensions, the surface characteristics, then, become very important for the performance. Nanofibers can posses different properties than those of the ones in larger diameters [1]. As the fiber diameter decreases, the surface plays more important role on the properties than those of the bulk material. Nanoscale components have large surface areas, making them ideal for use in filtration, tissue engineering, medical applications and cell growth. Generally, reduction in fiber diameter, increases the fiber spinnability. Crystallization shows an increasing tendency. It is thought that the increase of crystallization leads to the improved mechanical properties.

The aim of this work is to produce nano-scale polyester fibers and to examine the effects of size reduction on the crystallization and molecular orientation of polyester nanofibers. In this study, the scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and X-ray diffraction analysis together with Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FTIR) studies have been carried out. For this purpose, three different Polyethylene terephthalate (PET) concentrations of 13%, 16% and 20%wt polyester nanofibers have been produced. The PET polymer solutions were individually electrospun under constant parameters. Electrospinning parameters were determined in a previous study [2]. SEM and optical microscopy studies were performed to investigate the nanofiber alignment and diameter distribution within the web. Table 1 shows the diameters of the individual fibers. The average diameters of the fiber rage from 820 nm to 3000 nm, depending on polymer concentration.

Table1. Diameter distribution of polyester nanofibers with respect to PET proportion

Material	Min. Dia.(nm)	Max. Dia.(nm)	Average Dia.(nm)
13 wt%	380	1100	820
16 wt%	460	1100	920
20 wt%	1000	5140	3000

DSC analyses were performed to determine glass transition temperature (T_g) and the degree of crystallinity of nanofibers. DSC results show that PET nanofibers produced from 13, 16, 20% wt PET show a Tg of 69.6 °C, 70.2 °C and 66.0 °C, respectively. DSC crystallization results show that the nanofibers produced from 13, 16, 20% wt PET show degree of crystallinity of ~29, 28 and 15%, respectively. (This indicates the presence of the readily crystallizable and oriented amorphous regions.) The internal structure was examined by X-ray diffraction method. The results show that fibers from the various solution concentrations are amorphous. The results also show that nanofibers produced from 20% wt PET consist of non-oriented amorphous structure, nanofibers produced

from 16% wt PET consist of amorphous with partially oriented molecular chains and nanofibers produced from 13% wt PET show higher molecular orientation in amorphous regions. Figure 1 shows the x-ray diffaraction pattern of the samples.
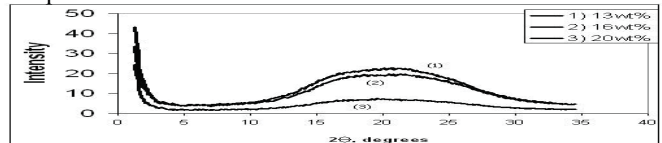

Figure 1. X-ray diffaraction pattern of the polyester nanofibers

Detailed molecular orientation studies were investigated by ATR FTIR method. In the infrared spectrum of PET the 1340 cm^{-1} and 1370 cm^{-1} bands have been assigned to the CH_2 wagging mode in trans and gauche conformers, respectively [3]. Trans conformer generally is in crystalline regions and gauche conformer is in amorphous regions. Since the nanofibers produced from PET are amorphous, the 1370 $^{-1}$ band was investigated in the terms of molecular orientation. ATR FTIR Analyses showed that nanofibers produced from 13, 16, 20% wt PET are ~12.9, 10.41 and 9.87% crystalline, respectively. ATR FTIR analyses also show the molecular orientation of nanofibers. Nanofibers produced from 13, 16, 20% wt PET have a Hermans' molecular orientation ($<P_2>$) value of 0.18, 0.085 and 0.024, respectively. This means that nanofibers produced from 13% wt PET have more oriented amorphous regions. It is found that nanofibers from different Polyethylene terephthalate (PET) concentrations are amorphous but in amorphous regions they have different molecular orientations. In the electrospinning process, the structure of the fiber is formed under the influence of two similtaneous processes namely the evaporation of the solvent and elongation of the fibers. The crystallization of the electrospun fibers are retarded because the rapid solidification of polymer chains hindering the formation of crystalline regions. The results show that nanofibers produced by electrospinning method do not have the tendency to crystallize. They tend to have have oriented amorphous regions in the structure. When PET concentration is reduced, the molecular chains in amorphous regions are found to orient easier. However, an increase in the velocity of the rotating disc collector or annealing may increase the crystallinity.

*Corresponding author: sengonul@uludag.edu.tr

[1] Zussman, E., Burman M., Yarin A L, Khalfin R, Cohen Y., 2006. Tensile Deformation of Electrospun Nylon 6,6 Nanofibers, Journal of Polymer Science: Part B: Polymer Physics 44: 1482-1489

[2] Duzyer S., Hockenberger A., 2008. Characterization of Solvent-Spun Polyester Nanofibers, 4. Nanobilim ve Nanoteknoloji Konferansı, 9-13 Haziran, İstanbul, sayfa 79

[3] Zhang W., Shen D., 1998. The Effects of Thermal Histories on Crystallization of Poly(ethylene ter ephthlate), Polymer Journal, Vol. 30, No: 4, pp 311-314

Effect of Concentration on Electrospun Polyacrylonitrile (PAN) Nanofibers

Umran Ozkoc[1]*, Halil Ibrahim Icoglu[1], Ali Kirecci[1]

[1] Textile Engineering Department, University of Gaziantep, 27310 Gaziantep, Turkey

Abstract-We investigated the concentration effect on morphology of Polyacrylonitrile (PAN) electrospun nanofiber. It is found that as the concentration increases the fiber diameter increases and the bead formation decreases.

Electrospinning is a process that employs electrostatic forces to produce nanofibres with diameter between 50-1000 nm from polymer solution or melt[1-6]. The electrospinning process involves the application of a strong electrostatic field to a capillary connected with a reservoir containing a polymer solution. The high voltage will induce electric charge to the solution and once electric force overcomes the solution surface tension, superfine fibers are produced [7-9]. Polyacrylonitrile (PAN) is the most extensively used polymer in electrospinning because of its excellent properties [10-13].

The morphology of electrospun nanofibres are dependent on a number of processing parameters that include:
(a) the intrinsic properties of the solution such as the type of polymer and solvent, polymer molecula weight, viscosity (or concentration), elasticity, conductivity, and surface tension.
(b) the operational conditions such as the applied voltage, the distance between spinneret and collector (tip-target distance), and the feeding rate of the polymer solution ,the humidity and temperature of the surroundings [14-17].

The effect of concentration on PAN nanofiber morphology is still being investigated. Generally as the concentration increases the fiber diameter increases and bead formation decreases [18-21].

PAN polymer [Mw 150,000] was gently supplied from AKSA Acrylic. The solvent used was dimethylformamide (DMF) purchased from Sigma. To conduct the experiment a solution was prepared by dissolving PAN polymer in DMF. The solution was arranged by stirring magnetically for one hour at a temperature of 90 °C.

The high voltage power supply used in the experiment can provide voltages between 0 to 50 kV. However, the tests were done at 35 kV and 0.7 mm jet diameters. The other parameters as such flow rate, the distance between capillary and the collector, voltage were selected as 0.5 ml/hour, 100 mm, 35 kV respectively. The fibers were collected on the aluminum foil in the form of non-woven fabric. The temperature and humidity were kept constant as 25 ºC and 30 %.

To examine the effect of concentration on electrospinning of PAN nanofibers, the concentration values were gradually increased from 6 wt.% to 16 wt.% with 2 wt.% intervals.

The morphological appearance of the electrospun PAN fiber mats and that of the individual fibers was investigated by a JEOL JSM-6390LV scanning electron microscope (SEM), operating at an acceleration voltage of 10 kV. The diameters of nanofibers were measured using Image-Pro Plus 6.0. 50 measurements were performed and average diameter of the nanofibers was calculated.
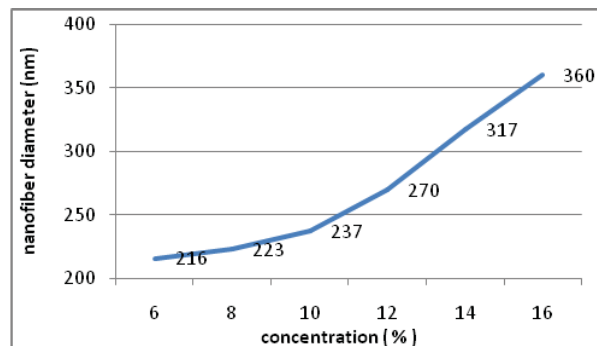

Figure 1. Relationship between nanofiber diameter and concentration (tip-collector distance is 10 cm voltage 35 kV)

The experimental results show that when the concentration increases the fiber diameter increases (Figure 1). At low concentrations bead formation and diameter variation are seen. When concentration increases the bead formation decreases. At 6 wt.% and 8 wt.% concentrations the beads are clearly seen but after 10 wt.% the bead formation decreases. Also as the concentration increases the diameter variation decreases.

*Corresponding author: 0Tozkoc@gantep.edu.tr

[1] M. E. Adomavičiūtė, R. Milašius, R.Levinskas, Materials Sci. 13, 2, (2007).
[2] L. Y. Yeo, J. R. Friend, 1, 177–209 (2006).
[3] J. A. Matthews, et al. Biomacromolecules 3, 232-238, (2002).
[4] H. Fong, I. Chun, D.H. Reneker, Polymer 40 4585–4592 (1999).
[5] P.K. Baumgarten, J. Colloid Interf Sci. 36, 71 (1971).
[6] A. Frenot, I. S. Chronakis, Curr Opin Colloid Interf Sci. 8, 64–75 (2003).
[7] D.H. Reneker, I. Chun, Nanotechnology 7, 216 (1996).
[8] W.E.Teo , S Ramakrishna Nanotechnology 17, R89–R106 (2006).
[9] J.Tao, S.Shivkumar, Mater Lett 61, 2325–2328 (2007).
[10] Y.S. Kang, H.Y. Kim, Y.J. Ryu, D.R. Lee, S.J. Park, Polymer-Korea 26, 360 (2002).
[11] S.F. Fennessey and R.J. Farris, Polymer 45, 4217 (2004).
[12] T. Lin, et al., J. of Mat. Sci.& Tech. 21, 9 (2005).
[13] R. Samatham and K.J. Kim, Polymer Eng. and Sci. 46, 954 (2006).
[14] J. M. Deitzel, et al., Polymer 42, 261-272 (2001).
[15] X. Zong, et al., Polymer 43, 4403 (2002).
[16] C.J. Buchko, et al., Polymer 40, 7397 (1999).
[17] S.L. Zhao, et al., Appl. Polym. Sci. 91, 242 (2004).
[18] T. Wang, S. Kumar, J Appl Poly Sci. 102, 1023-1029 (2006).
[19] R. Jalili, M. Morshed, and S. A.Hosseini Ravandi, Iranian Polymer J. 14, 1074-1081 (2005).
[20] J.H. He, Y.Q. Wan, and J.Y. Yu, Fiber Polym 9, 140-142 (2008).
[21] J. Sutasinpromprae, et al., Polym Int 55, 825–833 (2006).

Functional Nanofibers and Their Potential Application Areas

Aslı Çelebioğlu[1], Fatma Kayacı[1], Ali Ekrem Deniz[1] and <u>Tamer Uyar</u>[1]*

[1]UNAM-Institute of Materials Science & Nanotechnology, Bilkent University, Ankara, 06800, Turkey

Abstract- Nanofibers/nanowebs from many different kinds of polymers have been produced by electrospinning technique. These functional nanofibers/nanowebs are expected to be used in variety of application areas including nanofiltration, functional textiles, biomedical and energy.

Electrospinning is the most versatile and cost-effective technique to produce nanofibers from a wide range of materials such as natural/synthetic polymers, sol-gels, ceramics, metal oxides and composites. In this technique nanofibers are produced by applying a very high voltage (10-60 kV) to a polymer solution or a polymer melt. Polymer/solvent types and electrospinning process parameters such as; applied voltage, feed rate, tip-to-collector distance determine the ultimate structure of electrospun fibers. Electrospun nanofibers and their nanowebs have unique properties such as very large surface area, nano porous structure and design flexibility for specific functionalization, etc. Due to these properties, electrospun nanofibers/nanowebs show superiority to conventional textile materials which make them more attractive for many applications such as filtration, biomedical, textile and energy, etc [1-5].

In our work, we have produced functional electropun nanofibers/nanowebs from many different kinds of natural/synthetic polymers and metal oxides and we investigated their potential applications in filtration, biomedical, packaging and energy.

In our studies, we produced nanowebs from polymers such as; polyamide (PA), polyethylene terephthalate (PET), polyacrylonitrile (PAN) and polyvinylidene fluoride (PVDF) which are resistant to most chemicals and they have high mechanical strength which make them suitable for filtration materials.
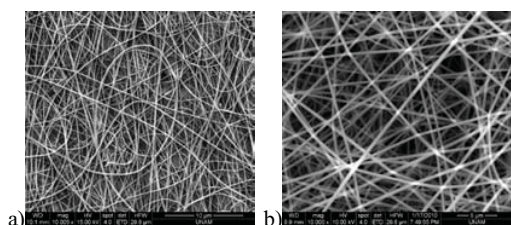

Figure 1. a) SEM image of PA nanofibers b) PAN nanofibers

Tissue engineering, wound healing and drug delivery are the potential application areas for nanofibers/nanowebs in biomedical field [2,4-5]. In order to obtain required functions from these structures; the polymeric nanofibers should be biocompatible and/or biodegradable. In our studies; we produced nanofibers/nanowebs from polymers such as; poly(vinyl alcohol) (PVA), poly(caprolactone) (PCL), poly(ethylene oxide) (PEO), cellulose acetate (CA), chitosan and polyvinylprolidone (PVP) which are known for their biofunctionality and can be used for scaffolds, wound dressing, drug delivery, antibacterial textile applications, etc.
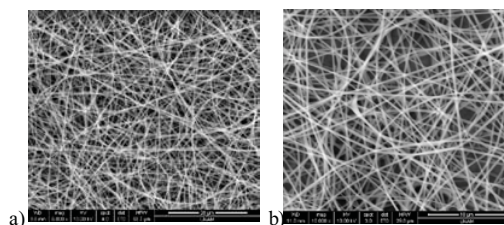

Figure 2. a) SEM image of PEO nanofibers b) PVA nanofibers

Electrospun metal oxide nanofibers (TiO$_2$, SiO$_2$, ZnO, etc) are very important in the applications solar cells and sensors, etc. due to their high surface area, high porosity and their nanostructure feature. In our research, we produced TiO$_2$, SiO$_2$ and ZnO nanofibers by electorspinning technique and we are investigating their use in solar cells, catalysis, sensors, etc.
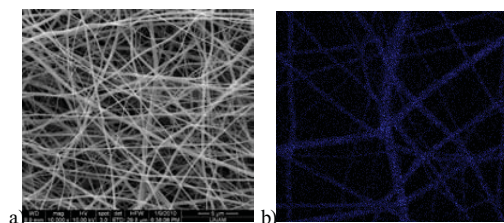

Figure 3. a) SEM image of TiO$_2$ nanofibers b) EDX image of TiO$_2$ nanofibers

* Corresponding author:
0Tuyar@unam.bilkent.edu.tr

[1]Reneker, D.H. and A.L. Yarin, Electrospinning jets and polymer nanofibers. Polymer, 2008. 49(10): p. 2387-2425.

[2]Li, D. and Y. Xia, Electrospinning of nanofibers: reinventing the wheel? Advanced Materials, 2004. 16(14): p. 1151-1170.

[3]Huang, Z.-M., et al., A review on polymer nanofibers by electrospinning and their applications in nanocomposites. Composites Science and Technology, 2003. 63(15): p. 2223-2253.

[4]Greiner, A. and J. Wendorff, Electrospinning: a fascinating method for the preparation of ultrathin fibers. Angewandte Chemie-International Edition, 2007. 46(30): p. 5670-5703.

[5]Ramakrishna, S., et al., Electrospun nanofibers: solving global issues. Materials Today, 2006. 9(3): p. 40-50.

Electricity Generation by Photovoltaic Textile Structures

Ayşe Bedeloğlu[1]*, Ali Demir[2] and Yalcin Bozkurt[1]

[1] *Dokuz Eylül University, Textile Engineering Department, Tinaztepe Yerleskesi, 35160, Izmir, Turkey*
[2] *Istanbul Technical University, School of Textile Technologies and Design, Istanbul, Turkey*

Abstract- Recently, organic materials based solar cells among the other solar cells attract scientific and economic interest thanks to their unique properties. In our study, photovoltaic textile structures were developed using organic solar cell materials. Light absorbing nano-materials were deposited as photoactive layer on thin and flexible textile structures. While light was passing through a semi-transparent cathode based on thin Lif/Al metal layers, electricity was generated. Photoelectrical characteristics were measured and evaluated. This device design can be applied for smart textiles after further optimization studies.

In last years, concerns about increase in quantity of carbon dioxide (CO_2) in the atmosphere and effects of global warming problem triggered researchers and governments to search, develop and use alternative renewable energy production technologies. Among the renewable energy production technologies, photovoltaic technology, which converts sun light into electricity, is environmental friendly. When solar cells having both low cost and high power conversion efficiency are developed, inexpensive electricity production can be achieved. Therefore, organic solar cells which can fulfill these desires can be promising structures to generate electricity, in the future [1-2].

Figure 1. Installation of silicon based solar cells onto a roof

Organic solar cells have some advantages including transparency, flexibility, cost effective, lightness, chrominance, etc. Organic solar cells can be also prepared in low temperature by easier production methods. Suitability and integrability of organic solar cells onto thin and flexible surfaces [3] are interesting features for new applications fields and large scale industrial productions. However, the efficiency of organic solar cells is too low to be industrialized. According to latest report on confirmed solar cell efficiencies, while silicon (crystalline) based solar cells have ca.25.0% efficiency, organic polymer based solar cells have only ca.5.15% [4].

Different devices were developed [5] using Poly(3,4-ethylenedioxythiophene: poly(styrene sulfonic acid) (PEDOT:PSS) as hole conducting material and polymer based nano-materials (i.e. Poly(3-hexylthiophene-2,5-diyl): [6,6]-Phenyl C_{61} butyric acid methyl ester, P3HT:PCBM) which can be applied easily using solution based processes as active layer. Nano-composite organic solar cell materials were coated onto thin textile substrates to obtain photovoltaic effect. In contrast to common organic solar cells on glass substrates, semi-transparent electrode was developed with thin layers of lithium fluoride (LiF) and aluminum (Al) metals as cathode of the device and rough polypropylene (PP) tapes and fibers, non-transparent and non-conductive, were used as substrate of the devices.
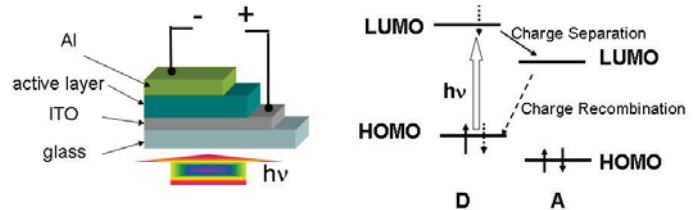

Figure 2. Schematic description for working principle of a conventional organic solar cell structure [6]
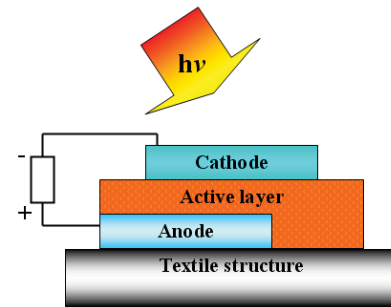

Figure 3. Simple demonstration of a photovoltaic textile structure

Devices were characterized in the dark and under sun light (100 mW/cm^2) simulated using a solar simulator under AM 1.5 conditions. Photoelectrical parameters including short-circuit current (I_{sc}) and power conversion efficiency (η) of the photovoltaic textile using polymer based solar cell materials was improved significantly. Such a photovoltaic structure may be a candidate for wearable low-cost photovoltaics after further optimization studies.

* Corresponding author: ayse.celik@deu.edu.tr

[1] Brabec, C.J., Dyakonov, V., Parisi, J., and Sariciftci, N.S., Organic Photovoltaics Concepts and Realization, first ed., Springer, New York, 2003.
[2] Tang, C.W., Two-layer organic photovoltaic cell. Applied Physics Letters, 48, 183, 1986
[3] Krebs F.C., Biancardo M., Jensen B.W., Spanggard H., and Alstrup J., Strategies for incorporation of polymer photovoltaics into garments and textiles, Solar Energy Materials & Solar Cells, 90, 1058–1067, 2006.
[4] Green, M.A., Emery, K., Hishikawa Y., and Warta, W., Solar cell efficiency tables (version 35), Progress in Photovoltaics: Research and Applications, 18:144–150, 2010.
[5] (Celik) Bedeloglu A. Development of fibres with photovoltaic effects. PhD thesis, University of Dokuz Eylul, Department of Textile Engineering; 2009.
[6] http://staff.science.nus.edu.sg

Electrostatic Self-Assembly Dyeing of Cotton Fabrics

Şule S. Uğur[1*], Merih Sarıışık[2]

[1]*Department of Textile Engineering, Süleyman Demirel University, Isparta 32260, Turkey*
[2]*Department of Textile Engineering, Dokuz Eylül University, İzmir 35160, Turkey*

Abstract— We report a new approach about dyeing of cotton fabrics with electrostatic self-assembly method. Cotton fabrics were pre-treated with 2,3-epoxypropyltrimethylammonuium chloride and cationic charges produced on the fabric surfaces. For cotton fabric dyeing, reactive and acid dyes were used. Oppositely charged anionic reactive/acid dyes and cationic poly(diallyldimethylammonium chloride) (PDDA) were alternately deposited on the surface of cationized cotton fabrics. 10 multilayer films of dye/PDDA were deposited on the cotton fabric surfaces by using padder. The buildup of the multilayer films has been discussed on the level of color strength (K/S) achieved. Cotton fabrics dyed with the same dyes by exhaust method and the both dyed samples were compared. Dyed samples color fastness to washing, rubbing and light were determined.

Starting in early 1990s, after Decher's group rediscovered Electrostatic Self Assembly (ESA) or Layer-by-Layer Deposition (LbL) processing, the interest to fabricate multilayer thin films from oppositely charged polyelectrolytes is increased in various fields of science. LbL process is based on the alternating adsorption of charged cationic and anionic species such as charged molecules, nanoparticles, dyes, proteins and other supramolecular species [1,2]. Generally, polyelectrolyte self-assemblies of different textile fibers and structures were studied and these studies investigated only the possibility of using LbL method for textile materials [3,6]. In our previous studies, we investigated the possibility of nanoparticle film deposition on cotton fabrics with LbL deposition and we showed that LbL process could be used to obtain functional textiles with antimicrobial, UV-protective, self-cleaning and flame retardancy properties [7-8].

In this study, we examine the possibility of cotton fabrics dyeing by using electrostatic self-assembly method and proved that dye/polyelectrolyte based multilayer films can be created using the LbL process.

Mercerized and bleached woven cotton fabrics were used as substrate for the LbL process. Cationization process was used to generate cationic sites on the surface of cotton fibers [9]. Cationic cotton fabric was prepared by using 2,3-epoxypropyl trimethylammonium chloride (EP3MAC). As EP3MAC reacts with the hydroxyl groups of cellulose, cationic charges on the surface of the sample were created. EP3MAC solution was pad applied to the cotton specimens at 100 % wet pick-up and fabric samples were kept for 24 h at ambient conditions (20 °C and % 65 RH) in Ziploc bags. Cationized cotton fabrics were dried in a commercial dryer at 60 °C.

Reactive and acid dyes (Remazol BrBlue R spec, Remazol Brilliant Red 3BS gran, Telon Red M-3B 80%, Telon Turquoise M-5G 85%) were used for dyeing process and purchased from DyStar. The concentration of dye solution was adjusted to 2 wt %. Poly(diallyldimethylammonium chloride) (PDDA), Mw 100.000-200.000 were purchased from Aldrich and used as received. Aqueous solution of the polyelectrolyte was prepared at concentrations of 3 mMl^{-1} with using deionized water. For reactive or acid dye/PDDA multilayer films deposition process, the positively charged cotton fabrics were immersed into the following solutions alternately; (a) the anionic dye solution, (b) the deionized water, (c) the cationic PDDA solution, (d) the deionized water. We deposited 10 dye/PDDA multilayer films on the cotton fibers by using laboratory type padding machine. Multilayer films deposited on cotton fabrics were cured at 150 °C for 3 min. Cotton fabrics were dyed with exhaust method with the same dye concentration, too.

Minolta 3600d spectrophotometer was used to obtain the K/S values of the dyed samples with LbL and commercial dyeing processes. Washing fastness of the dyed cotton fabrics were tested according to TS EN ISO 20105-C01 with laboratory type washing machine Gyrowash. Rubbing fastness was tested according to TS EN ISO 105-X12:1993 using Crockmeter. Light fastness was tested according to TS 1008 EN ISO 105 B02 using Atlas Xenotest ALPHA light fastness apparatus. Dyed fabrics with LbL process showed 4/5, 3/4, 4 and 4/5 staining washing fastness values for Reactive Red, Reactive Blue, Acid Red and Acid Blue dyes, respectively. Same fabrics wet rubbing fastness values are obtained as 4, 3, 3 and 3 for the same sort order of dyes.

In summary, we showed that dyeing process of cotton fabrics with reactive and acid dyes can be generated via electrostatic self assembly without using any chemical compound in dye bath solution within a short time period.

*Corresponding author: sule@mmf.sdu.edu.tr

[1] G. Decher, 1997. Fuzzy Nanoassemblies: Toward layered polymeric multicomposites, Science 277, 1232-1237.

[2] P. Bertrand, A. Jonas, A. Laschewsky, R. Legras, 2000. Ultrathin polymer coatings by complexation of polyelectrolytes at interfaces: suitable materials, structure and properties, Macromol. Rapid Commun. 21, 319-348.

[3] K. Hyde, M.Rusa, J. Hinestroza, 2005. Layer-by-layer deposition of polyelectrolyte nanolayers on natural fibres: cotton Nanotechnology 16, 422-428.

[4] S. T., Dubas, L., Limsavarn, C., Iamsamai,, P. Potiyaraj, 2006. Assembly of polyelectrolyte multilayers on nylon fibers, Journal of Applied Polymer Science 101, 3286-3290.

[5] R., Jantas, S., Polowinski, 2007. Modifying of polyester fabric surface with polyelectrolyte nanolayers using the layer-by-layer deposition technique, Fibres&Textiles in Eastern Europe, 15, No.2(61), 97-99.

[6] S., Polowinski, 2007. Deposition of polymer complex layers onto nonwoven textiles, Journal of Applied Polymer Science, 103, 1700-1705.

[7] Ş. S., Uğur, M., Sarıışık, A. H., Aktaş, 2009. Layer-by-layer deposition of anatase TiO$_2$ nanoparticles on cotton fabrics, 5th Nanoscience and Nanotechnology Conference, 412.

[8] Ş. S., Uğur, M., Sarıışık, A. H., Aktaş. 4th International Technical Textile Congress (2010).

[9] P. J. Hauser, A.H. Tabba, 2001. Improving the environmental and economic aspects of cotton dyeing using a cationised cotton, Coloration Technology, 117, 282-288.

Investigation of Seaweed Polysaccharides As An Elicitor of Plant Defence Mechanism

Fatima Bi[1]*, Seema Iqbal[1], Amanat Ali[1], Muhammad Arman[1] and Mahmood-ul-Hassan[1]

[1]PCSIR Laboratories Complex, Karachi, Pakistan

Abstract- High molecular weight crude polysaccharides obtained from various algal plants were evaluated as an elicitor of disease resistance responses in chickpea tissues in terms of induced browning and production of induced secondary metabolites. The field trials of these elicitor preparations against chickpea and maize plants showed significant increases in the average plant height, number of leaves, flowers and fruits per plant.

The idea of biochemical basis of defence mechanism conferring disease resistance in plants is now under active investigation [1, 2]. Natural or synthetic molecules which are able to elicit induced resistance in plants against diseases are grouped together and known as Elicitors, they are biotic, abiotic and endogenous in nature [3]. Biotic elicitors are obtained from pathogenic microbial cell wall or cell cultures and include polysaccharides, glycoproteins and fatty acids [4]. These molecules induce hypersensitive responses in plants, widely studied are induced browning and phytoalexin production [5, 6]. It is previously reported that in most cases elicitor activity was associated with the polysaccharide fractions of various preparations [7]. Seaweeds are generally comprised of 40-69% of carbohydrates. The major interest of this study is to exploit these polysaccharides as an inducer of hypersensitive responses. Generally elicitors are effective in very small quantities, only micrograms of elicitor are required for protecting the plants from diseases that results in good quality crops.

In the present study ten algal plants viz: *Hypnea musciformis, Botryocladia leptopoda, Acanthophora delili and Dictoyta haukiana of* Red algae, *Sargassum tererumium, lyengaria stellata and Padina tetrastromatica of* brown algae and *Codium elongatum, Caulerpa texiflora and Ulva lactulus* of green algae were collected from coastal area of Karachi. Water, moisture and ash contents of fresh seaweeds were found as 85-90%, 6-12% and 6-38% respectively. Air dried materials were extracted with water, dilute alkali and acid, High Molecular Weight Crude Elicitor Preparations 'HMWCEP' were obtained by ethanol precipitation and lyophilisation of these extracts. Chemical composition of HMWCEP isolated from seaweed extraction revealed that total sugar (12-76%) and sulphate contents were high in most of the plants. Uronic acids were found in negligible amounts with one or two exceptions.

Elicitor activity of seaweed polysaccharides was determined and established first time in this research work, activity was determined by using elicitor preparations of the tested plants at a concentration of 100 µg glu eq/ml in chickpea tissues. On the basis of preliminary screening, the potentially active elicitor preparation of *H.musciformis* was selected for dose response and time course studies in terms of production of induced secondary metabolites. Results showed that 100 µg elicitor dose and 24 hour incubation time were the optimum conditions to induce metabolites at maximum level in the treated tissues of chickpea.

Field trials of the this elicitor preparation were designed and conducted to examine the effect of elicitor against chickpea and maize plants grown in the field of PCSIR Laboratories Complex Karachi. This was four months study and plants growth was regularly monitored during this period. Elicitor treated plants of both crops responded well to the applied elicitor. Promising results were obtained such as increases in the average plant height, number of leaves, branches, flowers and fruits per plant, as shown in the figure.

Figure 1. (A) Elicitor treated chickpea plants, (B) control chickpea plants.

It is concluded from the present study that treated tissues of chickpea responded differentially to the various polysaccharide preparations of algae and produced a positive and definite resistance response in terms of induced browning and phytoalexin production. A very small quantity of active elicitor preparation applied in the field can improve the yield and quality of crops.

*Corresponding author: 0Tfatima_bi220@hotmail.com

[1] Bailey, J. A., 1982. *Active Defence Mechanism in Plants,* New York, *R. K. S.* Wood, ed Plenum press.

[2] Bi, F. et al. 2008. Induction of secondary metabolites in chickpea, pea, carrot and potato tissues in response to elicitor of *Hypnea musciformis. Indian J. plant Physiol.* 13:101-106

[3] Keen, N.T., Zaki, A., Sims, J.J. 1972 Pathogen-produced elicitor of a chemical defence mechanism in soy beans monogenically resistant to *phytophthora megasperma* var sojae. *Phytochemistry,* 22: 2729-2733.

[4] Rao, R.S., Sarada R., Ravishankar G.A.. 1996. Phycocyanin, a new elicitor for capsacin and anthocyanin accumulation in plant cell cultures. *Appl. Microbiol. Biotechnol.* 46: 619-621.

[5] Castoria, A.R., Maria F.M., Anna T.A., Marisa. C.F., 1995. Interrelationship between browning and phytoalexins accumulation elicited by arachidonic acid. *J.Plant Physiol.* 145, 209-214.

[6] Liu C.J et al. 2006. Structural basis for dual functionality of isoflavonoid o- methyl transferases in the evolution of plant defence responses,*The Plant Cell.* 18, 3656-3669.

[7] Kessman,H., Daniel S., Barz, W., 1988. Elicitation of pterocarpon phytoalexins in cell suspension cultures of different chickpea (*Cicer arietinum* L.) cultivars by an elicitor from the fungus *Ascochyta rabiei, Z Naturforsch C: Bio Sci.* 43, 529-535.