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Investigation of Electrical, Thermal and Structural Properties on Polyacrylonitrile Nano-Fiber

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***Abstract*—**Polymer composite nano-fibers including (1, 3 wt %) silver nano-particles have been produced by electrospinning method. Polyacrylonitrile/N,N-dimethylformamide (PAN/DMF) solution have been prepared and the amount of silver nitrate have been adjusted to PAN weight. Silver nano-particles were obtained from reduction of silver ions into silver nano-particles by chemical reduction by hydrazine hydroxide (N_2H_5OH). The different amount of silver salt was loaded into polymer matrix to obtain polyacrylonitrile composite nano-fiber containing silver nano-particles. The effect of the amount of silver nano-particles on the properties of composite nano-fiber web was investigated. Electrical conductivity, mechanical properties, thermal properties were examined by Microtest LCR Meter 6370 (0.01 mΩ-100 MΩ), Tensile tester, Differential scanning calorimeter DSC (Q10) and SEM respectively. Also antimicrobial efficiency test (ASTM E2149-10) was done against to *Staphylococcus aureus* bacteria. It has been seen that breaking strength, conductivity, antimicrobial effect, enthalpy during cyclization increase by use of silver nano-particles while the diameter of nano-fiber decreases**.**

***Keywords*—**Composite polyacrylonitrile nano-fiber, electrical conductivity, electrospinning, mechanical and thermal properties, silver nano-particles.

I. Introduction

POLYMER composite materials with metal nano-particles have been used in a lot of different areas due to having numerous properties such as having good thermal and mechanical behavior, having high ratio of surface area to volume and good antimicrobial activity [1]. Silver nano-particles which embedded in the polymer matrix represent high electrical conductivity and good antimicrobial efficiency among the metal nano-particles [2].

Polymer composite materials containing silver salts have been drawn attention due to its antibacterial feature especially in usage such as wound dressings, chemical and biological protective materials and medical devices and biotextiles [3], [4]. PAN fibers are one of the most important polymers that have been widely used due to its good thermal, mechanical properties that make it suitable for different applications [5].

When there are different methods of preparing a polymeric matrix containing metal nano-particles [3]. The silver ions that provided from silver salt have been reduced into silver nano-particles in a polymeric matrix by *in situ* reduction methods [6]. Chemical reduction by hydrazine hydroxide, UV- light reduction, Xenon Arc reduction, reduction by heat and DMF are one of the reduction methods [7], [8].

As seen from literatures, studies mostly focused on antibacterial properties and electrical conductivity of silver nitrate ($AgNO_3$) loaded composite nano-fibers. However, in this study we have focused on both mechanical and thermal properties, also antimicrobial efficiency and electrical conductivity of different loaded (1% and 3% silver nitrate loaded) nano-fibers.

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II. Experimental

A. Materials

Polyacrylonitrile (PAN) possessing a molecular weight of 150.000 g/mol have purchased from Sigma Aldrich. *N,N-Dimethylformamide* (DMF) and hydrazine hydroxide (N_2H_5OH) were obtained from Merck. $AgNO_3$ with the purity of 99.9995 % was obtained from Alfa AesarPremion.

B. Solution Preperation & Electrospinnig

Polyacrylonitrile (PAN), *N,N-Dimethylformamide (*DMF), silver nitrate ($AgNO_3$) were used to prepare PAN composite nano-fibers by electrospinning. The weight percentage of $AgNO_3$ in the solution was calculated on the basis of PAN weight.

PAN was dissolved in DMF solvent in 60 °C. The solution was stirred with the magnetic mixer at 400 rpm through 1.5 hours. After mixing, silver nitrate ($AgNO_3$) was added to solution and stirred 1 hour at 400 rpm. The prepared PAN/$AgNO_3$ solutions were used to produce nano-fibers by electrospinning. In the electrospinning system, a high-voltage power supply was used to generate an electric field. The polymer solution including silver nitrate was loaded into a 10 mL syringe and the solution was purged to the needle tip that used as spinneret by the syringe pump. A positive voltage was applied to needle tip and the negative voltage was connected to the collector that covered with aluminum foil. A nonwoven nano-fiber mat was covered on the aluminum foil for collecting the produced nano-fibers. The collecting distance between the needle tip and the collector was 10 cm, the feeding rate of the solution is 1 mL/h under the 15 kV voltages.

C. Reduction

Hydrazine hydroxide (N_2H_5OH) was used for chemical reduction of composite PAN nano-fiber. The reduction of

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nano-fibers was done according to distilled water/hydrazine hydroxide ratio of 20:1. The aqueous solutions of the hydrazine were prepared and nano-fibers were laid into this solution through 30 minutes. After reduction time, nano-fibers were bath with distilled water for two times. The reduced nano-fibers were dried in oven at 40˚C for two hours and then two days at room temperature.

D.Measurements & Characterizations

The mechanical behaviors of samples were measured by tensile tester. Average has been taken from seven and more samples. The crosshead speed was 20 mm/min and the gauge length was 15 mm. The length of nano-fibers was 5cm and the width was 5mm. The nano-fiber thicknesses were measured with digital micrometer. Average of tensile strength has been taken from 10 or more samples. Thermal behavior of prepared silver loaded composite PAN nano-fibers were characterized by differential scanning calorimeter DSC (Q10), (temperature range between 30-400˚C by heating rate of 20˚C/min). Morphological analyses were done by SEM Carl Zeiss EVO MA10. The tests were applied at 5 kV voltages. Electrical conductivity of nano-fibers was measured by Microtest LCR Meter 6370 (0.01 mΩ-100 MΩ) with two probe four wire.

III. Results & Discussions

Table I shows the mechanical properties of PAN/Ag nano-fibers loaded with different $AgNO_3$weight ratios. It can be concluded that the addition of a small quantity of $AgNO_3$ (1%) improved the mechanical properties of PAN nano-fibers while 3 wt % loading decreased the strength of composite nano-fiber. This may be due to an increase of agglomeration tendency of nano-particles with an increase of the amount of nano-particles which worsen the mechanical properties. Breaking elongation of samples with 1% loading decreases because of reducing effect of nano-silver on molecular mobility. However, breaking elongation of samples with 3% loading increases, this may be due to an increase of void (pores) tendency around of agglomerated silver nano-particles which can contribute stretching until some critical point [9].

TABLE I
The Effect of Silver Content on Mechanical Properties

	Tensile Strength (N/mm^2)	Tensile Strain (%)	Modulus (N/mm^2)
Pure PAN nano-fiber	1.56	17.24	12.64
1 wt % $AgNO_3$ loaded PAN/Ag	1.84	9.86	5.34
3 wt % $AgNO_3$ loaded PAN/Ag	1.27	16.22	3.23

The conductivity of composite nano-fibers can be seen in Table II. It can be concluded that the nano composite which have 3 wt % $AgNO_3$ has better conductivity than pure PAN (insulator) and 1% wt $AgNO_3$. Nano composite which has 3% wt $AgNO_3$ is semiconductor material while pure PAN is insulator. Increase in the concentration of the silver nitrate may provide better electrical conductivity due to increasing mobile charge carriers [3], [7].

TABLE II
The Effect of Silver Content on Electrical Conductivity

	Conductivity (S/cm)
1 wt % $AgNO_3$ loaded PAN/Ag nano-fiber	$3.65x10^{-8}$
3 wt % $AgNO_3$ loaded PAN/Ag nano-fiber	$1.36x10^{-7}$

Thermal behavior of reference and silver loaded composite nano-fibers examined by DSC at a heating rate of 20˚C/min under nitrogen atmosphere. It can be concluded from the Table III that silver nano-particles in the composite structure cause an increase in enthalpy due to increased total amount of matter in the polymer composite structure [4]. 3% $AgNO_3$ loaded samples have lower cyclization temperature than pure and 1% $AgNO_3$ loaded nano-fiber. This means that cyclization occurs in less temperature with higher energy at the sample with 3 wt % $AgNO_3$.

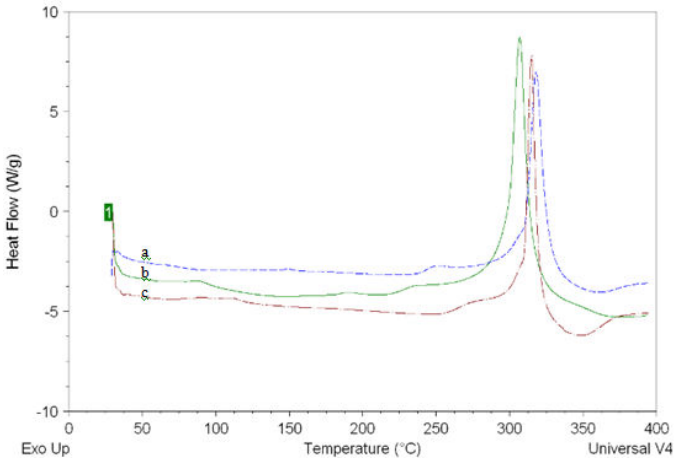
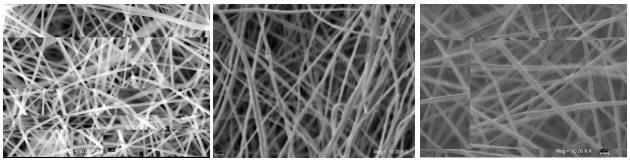


Fig. 1 DSC plots of nano-fibers. a) 1 % $AgNO_3$ loaded PAN/Ag nano-fiber, b) 3% loaded PAN/Ag nano-fiber, c) Pure PAN nano-fiber

TABLE III
Cyclization Temperatures and Enthalpy Values of Nano-Fibers

	T_c (˚C)	ΔH (J/g)
Pure PAN nano-fiber	314.79	483.8
1 wt % $AgNO_3$ loaded PAN/Ag nano-fiber	318.22	473.8
3 wt % $AgNO_3$ loaded PAN/Ag nano-fiber	306.89	691.0



(a) (b) (c)

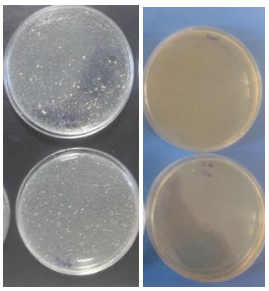
Fig. 2 SEM images of composite nano-fibers. a) Pure PAN, b) 1 % wt loaded $AgNO_3$, c) 3 wt % loaded $AgNO_3$

Table IV represents the diameters of nano-fibers. It can be seen Table IV that addition of silver nitrate into the composite structure causes decrease in diameter of nano-fibers as indicated at literature [2], [3]. It can be explained by the increase in the solution conductivity that causes higher

electrical forces in ejected jet and provides finer nano-fibers [7].

TABLE IV
DIAMETER OF PURE PAN AND $AgNO_3$ LOADED COMPOSITE NANO-FIBERS

	Pure PAN	1% $AgNO_3$	3% $AgNO_3$
Mean Diameter (nm)	389	387	358
Coefficient of Variation %	21	27	16



(a) (b)

Fig. 3 Antimicrobial efficiency test of nanowebs. a) 1 % AgNO3 loaded nano-fiber, b) 3 % AgNO3 loaded nano-fiber

TABLE V
ANTIMICROBIAL EFFICIENCY FOR NANO-FIBERS

Sample Name	Antimicrobial Efficiency (%)
1% $AgNO_3$ loaded PAN nano-fiber	45
3% $AgNO_3$ loaded PAN nano-fiber	99.99

It can be seen that 99. 99% efficiency was obtained from 3% loaded $AgNO_3$ nano-fiber after 24 hours (Table V) against to *Staphylococcus aureus* bacteria. 1% $AgNO_3$ loaded PAN nano-fiber does not have enough antimicrobial efficiency.

IV. CONCLUSION

- The addition of a small quantity of $AgNO_3$ (1%) improved the mechanical properties of PAN nano-fibers while 3 wt % loading decreased the strength of composite nano-fiber. This may be due to an increase of agglomeration tendency of nano-particles with an increase of the amount of nano-particles which worsen the mechanical properties.
- Breaking elongation of samples with 1% loading decreases because of reducing effect of silver nano-particles on molecular mobility.
- Samples with 3% wt $AgNO_3$ has better conductivity than pure PAN (insulator) and 1% wt $AgNO_3$. Nano composite which has 3% wt $AgNO_3$ is semi-conductor material while pure PAN is insulator.
- Silver nano-particles in the composite structure cause an increase in enthalpy. 3% $AgNO_3$ loaded samples has lower cyclization temperature than pure and 1% $AgNO_3$ loaded nano-fiber. This means that cyclization occurs in less temperature with higher energy at the sample with 3% $AgNO_3$ points of the paper, do not replicate the abstract as the conclusion. A conclusion might elaborate on the importance of the work or suggest applications and extensions.
- Addition of silver nitrate into the composite structure causes decrease in diameter of nano-fibers. It can be explained by the increase in the solution conductivity that causes greater electrical forces in ejected jet and provides finer nano-fibers.
- 99. 99% antimicrobial efficiency was obtained for 3% loaded $AgNO_3$nano-fiber after 24 hours (Table II) against to *Staphylococcus aureus* bacteria. 1% $AgNO_3$ loaded PAN nano-fiber does not have enough antimicrobial efficiency.

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