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Preparation of Nanocomposite Based on Poly Amide with Nanosilver Prepared by Novel Reducing Agents.

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ABSTRACT

Enter to nano region causes the advent of new properties that leads to expansion of its application in different industries that nano composite by virtue of its diverse application has much more importance. As the most of polymeric compounds are the good environment for duplication of microbes and also produced nano fiber because of increase in its special surface have more sensitive to microbes. Therefore, in this research, we used the insitu production of nanosilver on the polymeric nylon context through the reduction process and production of nano fiber from nanocomposite by electro spinning. In this article for the first time, we represented the novel reducing agent as sodium bisulfite and sodium thiosulfate for synthesizing of nanosilver on polymeric nylon 6. Properties of the obtained nanocomposites according to different reducing such as antimicrobial properties, the degree of yellowness and whiteness, the nanoparticle size and morphology properties were compared. The results are showed significant differences in antimicrobial testing against Gram-positive bacteria staphylococcus aureusas and gram-negative bacteria Escherichia coli.

Keywords: Antimicrobial, Nanofiber, Nanocomposite, Nanosilver, in situ synthesize.

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INTRODUCTION

According to special nylon use in industry, domestic and army product and increase in its consume in developed countries, scientists launch individual research on this subject[1-2].Increase fibers softness caused the development of nylon application and its new properties in textile That leads to increase in use of nylon[3].One of the most used nylon is produced by caprolactam that reductive reagents such as amides salt.is used for the polymerization of that[4].Enter to nanotechnology and nanostructure area leads to individual properties and it needs special material for use in nanocomposite, chemical reaction for drug design, storage of energy and thousands other application and it is the part of modern and dynamic technology[5].One of the used nanostructure is nanoparticles that their properties are depend on geometrical structure, particle size, stability of atoms and synthetic procedures. Inorganic nanostructures such as titanium dioxide, silver, gold and their composite are used in antibacterial processes or carried to the surface by cyclodextrin, micro or nanocapsules and nanodendrimers[6].Silver is capable to destroy around 650 microorganisms in low concentration and also is nontoxic that their properties increased by its higher concentration per surface unit[7].Use of nanosilver/nano titanium dioxide composite, because of silver high potential and close to titanium dioxide in biological material is increased and in this case silver is synthesized on the surface of titanium dioxide[8].In this case, exited electrons are transfer between silver and titanium dioxide and leads to exchange of microscopic analytical peaks[9].There are several procedures for the synthesis of silver nano particles that are vapor phase synthesis, gamma beam, electrochemical method, reductive procedure and tolene[10].All in all, silver nanoparticles can be synthesized by reduction of its metallic salt in the presence of stabilized material such as polymers or surfactants[11-18].In this study, we used the reductive material based on sulfur and for its impact factor, anti-bacterial effect and stability , the synthetic process carried out by one-pot procedure and through producing of nano fiber by electro spinning method, the softness of produced composite was increased and also the achieved properties were checked.

MATERIAL AND METHOD

The used material such as formic acid and sodium thiosulfate by trade mark of Ajax purchased from Australia and acetic acid, sodium borohydride, sodium bisulfate and silver nitrate were purchased from Germany by trade mark of Merck and granule nylon 6 by trade mark of delamid was purchased from china. For determination of color changes between samples, the refractive spectrophotometer (Color–Eye 7000) was used. FT-IR bruker tensor 27 was used for determining of chemical structure, functional groups and the effect of synthetic process on functional groups of samples.For monitoring of fiber surface, SEM (Philips XL30) was used and the gold cover was used for preparation of samples during 60 seconds. For producing of nano fiber, the KATO TECH Co,LTD produced in Japan was used. For determination of material content, the elemental analysis EDAX (Samx England)was used. The absorption spectrophotometer UV-VIS, Cary 100 Bio, England was used for determination of absorption wave length in prepared sample solutions and the atomic absorption Graphite Method, PG990, England (AAS) was used for determining of element content in samples.

Experimental

In this method for preparation of solvent in spinning by electro spinning procedure, synthesis of nano silver and nylon 6 solvent simultaneously carried out in one-pot condition and also for this synthesis, the unusual reductive on the base of sulfur was used that this information are summarized in table 1.

For preparation of standard solvent A, nylon granule was heated in 90 ^{0}C for 20 min with formic acid and for preparation of other solvent for electro spinning, silver nitrate, nylon granule and reductive agent were poured in beaker coincide and then acetic acid and formic acid was added with different ratio to this beaker and put into the warm bath in 90 ^{0}C for 20 min to produce the homogenous solvent and prepared for spinning.After preparation of sample, their solvent were spun with following condition by electro spinning machine and after preparation of fiber, the complementary tests on samples were done to examine the created properties that represented in follow.

For electro spinning of samples solution was used 15 Kv, syringe pump speed 0.201 mm/min and 10 cm distance between syringe and collector. This condition was continued until obtained a nano fiber web of samples on collector.

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Table 1: Prepare condition of samples

Materials & condition	amounts					
Nylon6(%)	13	13	13	13	13	13
AgNO3(ppm)	0	2000	2000	2000	2000	2000
NaBH4(%)	0	0	0	0.01	0	0.01
Na2S2O3(%)	0	0	0.01	0	0	0
NaHSO3(%)	0	0	0	0	0.01	0
CH3COOH(%)	0	50	60	75	25	75
HCOOH(%)	100	50	40	25	75	25
Temperature(0 C)	90	90	90	90	90	90
Time(min)	20	20	20	20	20	20
Sample Code	A	B	C	D	E	F

RESULTS AND DISCUSSION

Antimicrobial test

For this test, gram positive bacteria, Staphylococcus aurous and gram negative bacteria, Escherichia Coli were examined. This examination was done by AATCC 100-1993 method. In this procedure, 1 ml of cultured bacteria with concentration of 105 cfu/ml was transferred to examine tube and then placed in incubator for controlling of its moisture and temperature and after 24 hr it diluted and 1ml of this solvent was added to plate contain 25 ml of sterile Notrite agar and after homogenizing, this sample was placed in incubator for 18-24 hrs in 37 ^{0}C. after the completion of this process, counting of bacteria number was done. Bacteria reduction rate was calculated by equilibrium 1, and obtained result produced after 5 times examination that shows the growth percentages of bacteria.

$$R(\%) = \frac{A-B}{A} \times 100 \quad (1)$$

Where A is the number of bacterial colony on the not functioned sample, B is the number of bacterial colony in functioned sample and R is the rate of reduction.

Gram Positive bacteria easily passed through the cells wall by virtue of its cytoplasm membrane that contains mono wall glycogenic peptide antibacterial component and destroy the microbe cell. Therefore gram positive bacteria such as Staphylococcus aurous are more sensitive toward antimicrobial compound whereas gram negative bacteria such as Escherichia coli are more resistant toward antimicrobial drug. For this reason antimicrobial compound such as nano silver shows less effect of the duplication reduction of gram negative bacteria. Table 2, illustrates that the type of reductive agent and the amount of synthesized nano silver has profound impact on the antibacterial effect. As it has been shown, samples F and C have more reduction in the volume of produced colonies that proved the strong reductive agent such as sodium thiosulfate generated the more antimicrobial effect for nano fibers.

Table 2: Antimicrobial activity of samples

Sample code	*Escherichia coil (R%)*	*Staphylococcus aureus (R%)*
A	52	73
B	46	61
C	30	42
D	45	59
E	38	52
F	37	48

(R%) : percent Reduction of colony.

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Evaluation of nano silver synthesis

Absorption wave length of nano silver colloidal solvent by hydrazine reductive is 418 nm that is raised to 520 nm by addition of striate acid. Multi branched amine group functioned as a reductive agent and caused the reduction in absorption wave length to 408 nm. Sodium borhydrate caused that the absorption wave length placed in the range between 390 to 535 nm[4]. Therefore, the condition of reduction process is effective in the synthesis of nano silver and absorption wave length of their solvent because reduction condition was affected to nano silver size therefore, absorption pick were shown shifted. For evaluation of the nano silver synthesis by different reductive agents, at first, the absorption wave length of reductive agents and silver nitrate are separately obtained by use of spectrophotometer that were shown in figure 1.For assurance of reduction of silver by reductive agents and synthesis of nano silver, solvent of them were prepared that in the case of silver synthesis and reductive reaction, the absorption wave length should be closed to nano silver absorption region that obtained results were illustrated in fig. 1.

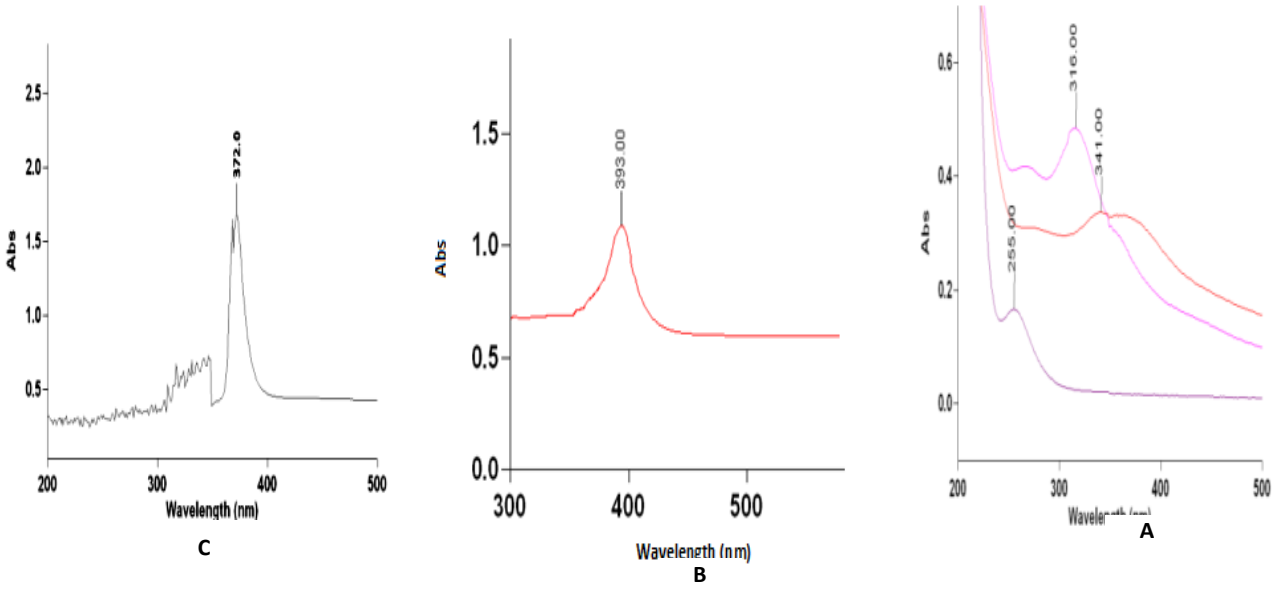

Figure 1: A (absorption of sodium thiosulfate (316nm), sodium bisulfite(341 nm) and silver nitrate(255nm) solution), B (absorption diagram aqueous solution of silver nitrate 0.05% and 1.5% sodium bisulfite), C(absorption diagram polymer solution sample E).

It shows in fig.1(A-C) that the changing in absorption wave length of samples by reductive solvent and silver nitrate is the reason for synthesizing of nano silver in both aqua solution in fig.1 B and polymeric solution contain thiosulfate in fig.1 C.

Measurement of color difference and color capability of samples

Table 3: Results of color difference and color capability of samples

Cod sample	Color Capability(K/S)	Color Difference(ΔE)
A	0.36	1.43
B	0.31	1.53
C	0.41	3.29
D	0.25	4.29
E	0.47	0.74
F	0.34	3.25

For measuring of color difference in sample, refractive spectrophotometer Color–Eye7000 was used and its results were collected in table 3 for optimized samples. Interaction between reducing agents such as sodium bisulfate causes the cleavage and reduction between crossings on nylon macromolecules bonds and

changes of structural system that these changes causes the obvious difference between sample A and other samples so that by refractive spectrophotometer, color differential and color strength can be measured and their results are collected in Table 3. And also for measuring of color differential between samples, CIE LAB standard system was used.

Infrared results obtained by FT-IR

The samples A-D infrared spectra are summarized in Table 4 and Fig. 2 and analyzed their functional groups and structure of molecules. Absorption peak in 3710-3770 cm^{-1} proved the presence of water and OH groups in samples. Evaluation of peptide groups (NHCO) in nylon have been done by their amide group. Absorption peaks between 1640-1700 cm^{-1} are related to stretch bond of CO in amidic groups [13]. Absorption peak between 1510-1530 cm^{-1} is the changed peak of C-N-H and it shows the stretch bond of C-N and bending bond of N-H.

Evaluation of Fig.2, A-D show that samples are affected by experimental condition, synthesis of nano silver and reducing agents of functional groups and this phenomenon can affect the coating condition of texture. Therefore the positions of active peaks have been shown in Table 4. By these data can be proved that, sample B has the most effective than others and used acids have the reductive effect in this sample and affected the functional groups. Beside of that, other reducing agents such as sodium thiosulphate and bisulfate can be effective in this reaction and can shift side group picks in polymers chain of Nylon 6.

Table 4: FTIR position of peaks sample

Sample	Position (cm^{-1})	group	Reference range(cm^{-1})
A	1634	-CO	1600-1700
	1536	C–N–H	1500-1600
B	1640	CO	1500-1600
	1544	C-N-H	1500-1600
C	1638	CO	1500-1600
	1544	C-N-H	1500-1600
D	1631	-CO	1500-1600
	1535	C-N-H	1500-1600

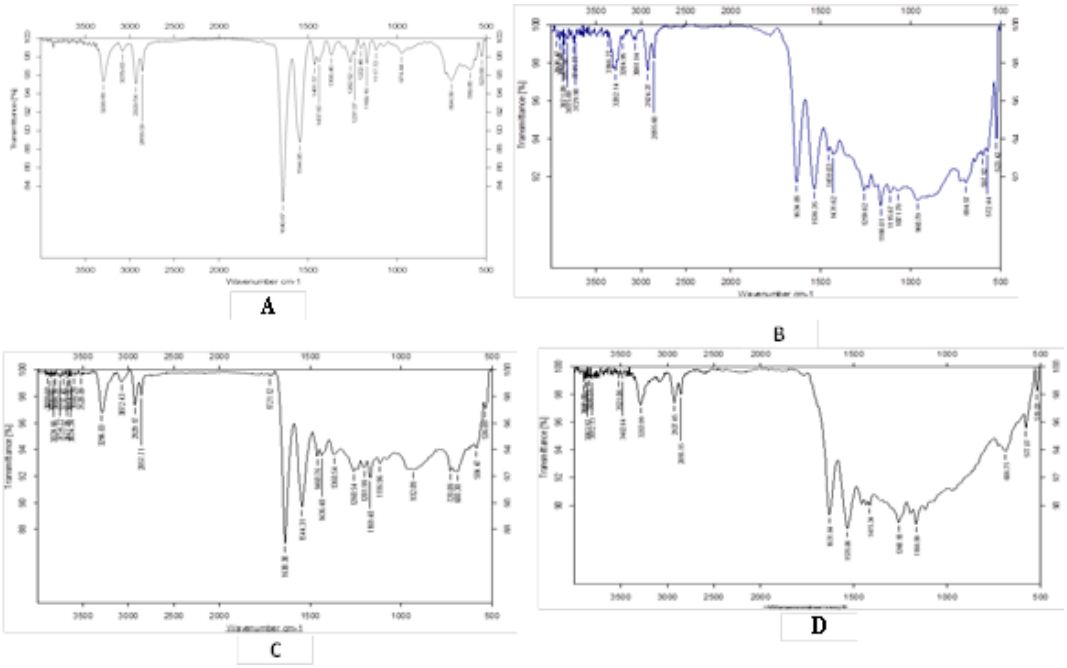

Figure 2: FTIR of Samples

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Determination of Yellowness and Whiteness degree of samples

For determination of yellowness degree of sample, the refractive spectrophotometer is used by standard procedure of ASTM D 1925 and for determination of Whiteness degree of samples, standard CIS Canz 82 was used. These results are summarized in Table 5.According to the results of yellowness and whiteness of samples in Table 6-2 characterized that the condition for yellowness and whitish of samples were using the stronger reducing agents because of their effect of synthesis process, the size of particle and amount of that and sodium bor hydride is privileged when non coincide process is used but in coincide process that polymerization and synthesis of nanosilver took place at the same time, it acceptable to use weaker acids and this means that samples D and F are more useful.

Table 5: Results of Yellowness and Whiteness degree of samples

Sample	Yellowness	Whiteness
A	3.37	71.02
B	1.63	75.76
C	5.97	63.12
D	1.38	80.62
E	11.82	40.32
F	2.83	71.85

Evaluation of surface morphology using SEM & EDAX

The SEM images were shown in fig. 3.Using stronger reductive was caused decreased size of nano silver and nano particles, also concentration changes, kind of reducing agent and type of used solvent can affected on the size and shape of silver nano particles. Also, fig. 3 are show, the amount of synthesis nano silver on surface of nan fiber was decreased by reductive strength reducing agent. Also, due to comparison of SEM in situ samples show that in in situ samples synthesized nano silver was increased.

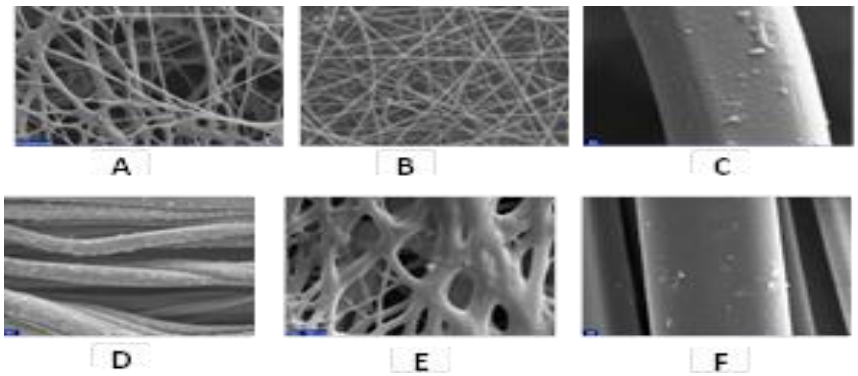
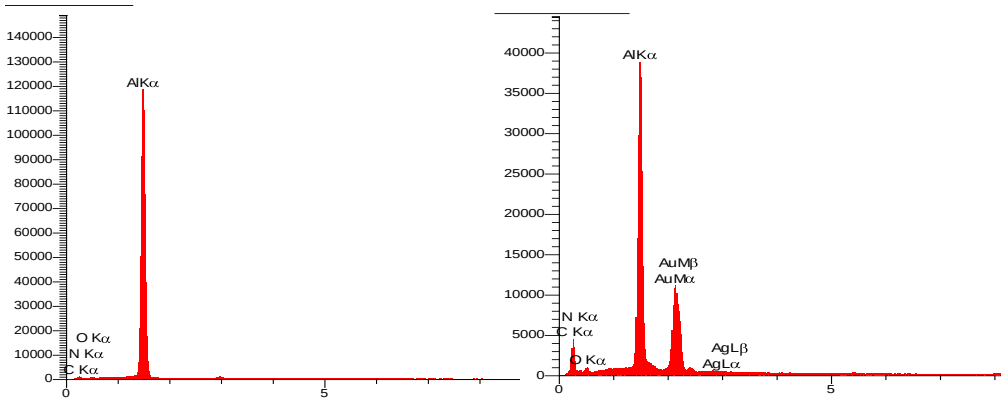


Figure 3: SEM image samples

Figure 4: EDX for A&C samples



A C

Table 6: EDX test results

Sample Code	A	B	C	D	E	F
Ag(%Wt) (%Wt)	0	0.12	0.23	0.11	0.15	0.18

CONCLUSION

Antibacterial results show that if the antibacterial view is considered by virtue of more synthesized nano silver in the process of non in situ is produced therefore this procedure is more acceptable and also increase of reductive agents can enhance this property (sample F).Also UV absorption peaks proved the synthesis of nano silver by reduction using sodium thiosulfate and sodium bisulfate that is not general reducing agent for nano silver.The color differences results also prove that the reduction process and type of reducing agent can have a profound impact on the visual characterization and color of samples that also show the non in situ procedure have the better affect.

Due to the results of samples in situ methods was affected to amount synthesize nanosilver and with this method was could nanosilver of synthesize in bulk nanofiber therefore, may be permanence nanosilver for after wet treatment product of this nanomaterials. The results of anti-bacterial properties of samples were proved increasing of after treatment of products.

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