Preparation of Blended Nanocomposite Nanofiber Materials for Air Purification

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Abstract. In this study, two types of nanofibers, blended nanofibers of Polyamide 6/Chitosan and blended nanofibers of Polyamide 6/Chitosan/Nano-silver particles, were prepared in order to develop air filters suitable for use in medical applications such as hospital care, smoke lounges, and general surgery applications. UV-absorption spectrophotometer, Atomic Force Microscopy, Porosity SEM, and Wettability tests were used to characterise the material properties, solutions, and membranes. The results showed that the porosity ranged from 39.263% to 49.33%, with most membranes showing hydrophobic behaviours. The average pore size ranged from 112.36 nm to 92.36 nm, allowing the air filters in this research to remove all bacteria, most tobacco smoke, droplet nuclei and most general smoke.

1. Introduction
Nanofiber materials have unique properties such as flexibility, good stiffness, and tensile strength in contrast with other materials due to their large surface area to volume ratios; this makes them appropriate in many applications, including sound absorption materials, protective clothing, electrical and optical applications, tissue engineering, wound dressing, drug delivery, and filtration [1].

Electrospinning is the most interest current technique because of simple, efficient, useful, low-cost versatility in terms of spinning a large range of polymer nanofibers for a range of feasible applications such as electronic devices, nano composites, and membranes [1,2]. Polymer nanofibers can be prepared by electrospinning processes through accelerating a charged polymer jet in an electric field. The output nanofibers have diameters ranging from 10 nm to 10 μm [1,2,3 and 4]. Polyamide 6 (PA6) is a synthetic polymer with good mechanical properties that is biodegradable and biocompatible, with good resistance to humidity. PA6 nanofibers are easy to produce and can be dissolved in formic acid or formic acid/acetic acid solvents, which are non-toxic, making PA6 a good candidate for preparing filtration membranes [5,6].

Chitosan has excellent chemical and biological characters that make it suitable for use in a wide range of manufacturing and medical applications. Chitosan is a potential polysaccharide due to its free amino groups that contribute polycationic substances which give it the ability to chemically bind with negatively charged fats, lipids, cholesterol, metal ions, proteins, and macromolecules. Anti-bacterial filters are widely used in several fields to avoid bacterial infections [7].

In 2011, Danielle [8] prepared two types of anti-microbial and bio fouling resistant nano fibres with silver nanoparticles for water filtration, using PVA and PAN nanofibers with nanosilver particles, comparing these with respect to morphology, silver nanoparticle content, physical distribution of silver nanoparticles, and levels of silver leaching from the fibres in water, which could imply toxicity. The most important comparison was of anti-microbial efficacy. Scattering electron images revealed that silver nanoparticles in the PVA nano fibres were more evenly dispersed than in the PAN nano fibres, but that the PAN nano fibres had higher silver nanoparticle content. This was confirmed by energy dispersive X-ray (EDX) analysis. Both PVA and PAN nano fibres containing silver nanoparticles showed excellent anti-microbial activity, and neither type of nano fibre leaked nanosilver into the water. In 2013, Carla et al. [9] produced PVA/CS with PVA/EPS blends of nanofibers by using the electrospinning method. The diameters obtained were 50 nm and 130 nm, with no beads creation and smooth morphology. PVA/EPS membranes gave good tensile mechanical properties compared to PVA
and PVA/CS, and PVA/EPS membranes also resisted degeneration at temperatures between 10 to 50 °C more effectively.

In 2013, Mohammad, et al. [10] manufactured air masks from chitosan, which showed greater metal pollutant (Cd, Pb, Sb) absorption compared with the usual air masks, by using the electrospinning method. By varying conditions, the SEM-measured diameters of nanofiber were shown to be 100 and 500 nm, at 1.7%, 1 ml/min 15 kV and 13 cm conditions. The EDAX test suggested that chitosan nanofiber masks allowed additional metal pollutants to be captured compared with the normal air mask.

The aim of this research is to produce air filters suitable for use in medical applications.

2. Materials and Methods
Polyamide 6 (C6H11NO)n powder with molecular weight 80 to 100 g/mol, and Chitosan (C6H11NO4)n as shells with ≥ 75% degree of deacetylation, from India, were provided for blending with polyamide 6. Silver Nano-particles (Ag 99.99%, metal basis, 20 nm to 40.3 nm) obtained from Sigma-Aldrich Chemistry, USA, as an antibacterial material. Formic Acid at about 85% (CH2O2) with 101 Tb and 1.57 cP viscosity was used to dissolve the polymer materials.

2.1 Preparation of (Polyamide 6/chitosan) solution: Two concentrations were prepared by dissolving (PA6/CS) in formic acid at a ratio 95/5 wt.% and 90/10 wt.%, heated at 90 °C with continuous stirring for 4 hours and then cooled to room temperature.

2.2 Preparation of (Polyamide 6 + chitosan + Nano Silver) solution: Two concentrations were prepared by dissolving the ingredients in formic acid at ratios (95/10) + 0.02 Ag and (90/10) + 0.02 Ag. All concentrations were placed on a magnetic stirrer for 6 hours and dispersed using an ultrasonic device to obtain homogenous solutions prior to the electrospinning process.

3. Electrospinning process:
In this study, a Nano-azma direct system was used, consisting of a direct high voltage power supply (DC-HV at 0 kV to 50 kV), a syringe pump with a flow rate of 0.1 to 10 ml/hr, and a stainless steel metallic collector used as a rotating cylinder of 8 cm in diameter and 13 cm in length. A syringe containing the polymer solution was located in a syringe pump to create an invariable flow of fluid through the needle. The negative electrode of the HV was connected to the earthed metallic collector, while the needle was connected to the positive electrode of the HV.

The conditions used in the electrospinning process for all samples were 45 kV voltage, 1 ml/hr flow rate, 15 cm distance between the needle and collector, and 8 hours duration.

4. Results and Discussion
4.1 UV Test Result:
Waves in the UV spectrum break the outer membranes of bacteria, moulds, and viruses due to their short wavelength. Light attacks the DNA of these microorganisms and destroys them, while catalytic molecules that destroy carbon-based contaminants that UV light alone cannot take care of can also be added [11]. The results from the PA6 UV test, as seen in Figure (1), demonstrate that the absorption in the UV region has a very low value (0.7), while Figure (2) shows the PA6/CS UV test, which demonstrates higher values than the visible region (1.7). This has very high absorbance because there are lots of molecules to interact with the light due to the grain size of the material increasing as the chitosan content increases. This is according to the Beer–Lambert law which defines the linear relationship between absorbance and concentration of an absorbing species [12].

With the presence of nanosilver, as shown in Figure (3) for the UV test for PA6/CS/Ag-NPs, the absorption increased to 2.5 because the nanosilver particles absorbed more light, leading to increased absorption.
Table (1) represents the values of UV light absorption for PA6, the PA6/CS blend, and the PA6/CS/Ag nanoparticle nanocomposite.

| Solution                  | values of UV light absorption |
|---------------------------|-------------------------------|
| PA6                       | 0.7                           |
| PA6/CS blend              | 1.7                           |
| PA6/CS/Ag nanoparticles   | 2.5                           |

4.2 Porosity Test Result:
Porosity was tested using ImagJ software. Table (2) shows the result of porosity tests for the samples.

| Sample Number | Polymer        | Concentration (wt.%) | Pore Size (nm) | Porosity (%) |
|---------------|----------------|----------------------|----------------|--------------|
| 1             | PA6/CS         | (95/5)               | 112.36         | 39.263       |
| 2             | PA6/CS         | (90/10)              | 92.36          | 49.33        |
| 3             | PA6/CS/Ag-NPs  | (95/5)/0.02          | 108.14         | 47.878       |
| 4             | PA6/CS/Ag-NPs  | (90/10)/0.02         | 101.93         | 46.475       |

For polymer blend nanofibers without added nanosilver particles, the porosity increased from 39.263% to 49.33% due to the increase in chitosan content from 5 to 10%, which led to an increase in the viscosity of the solution as a result of the high viscosity of the chitosan. Higher viscosity at constant values of applied voltage and spinning distance lead to higher porosity [13]. This also the cause of the fibre diameter increasing from 93 nm to 97 nm, which led to a decrease in the pore size from 112.36 nm to 92.36 nm. As fibre diameter plays a major role in forming the pore structure and porosity of the medium, according to filtration theories, the porosity can be inferred from fibre diameter [13]. At high viscosity values, there is some difficulty in the ejection of jets of polymer solution, which results in larger fibre diameters; moreover, the desirable morphology is converted to a defective structure with the increase in chitosan content in the blend solution [14], as seen in Figures (4) and (5).
When nanosilver particles are added to the polymer blend solution, this leads to improvements in the morphology and fibre spinnability and improved uniformity, as well as good porosity percentages of 47.878% and 46.475%, as shown in Figures (6) and (7). The increase in fibre diameter to 109 nm and 107 nm leads to pore sizes of 108.14 nm and 101.93 nm. This increase might be due to the fact that during the electrospinning process, the Ag-NPs unite or agglomerate in the syringe tip and may suddenly drop down with nanofiber ejections, leading to an increase in fibre diameter [15].

Porosity is one of the most important parameters in filter design and filter performance. Adequate porosity is thus an important candidate for high performance filters. Porosity should be adequate to avoid pressure drop. Filter porosity is thus a static parameter that gives necessary information about the initial state of a filter tissue.

4.3 Antibacterial Properties:
The anti-bacterial properties of the membranes are determined by pore size, which should be smaller than bacteria size as shown in Table (2). As the range of bacteria size is 0.3 to 1.0 µm per ASHRAE Standard 52.1 and 52.2 and [16,17], smaller pores lead to asphyxiation of the bacteria and prevent them from passing through the membranes. Further, Nanosilver is a strongly antibacterial material [18].

4.4 Wettability Test Results:
The wettability of a surface can be determined by measuring the contact angle of a liquid drop over the solid surface, defined as the angle formed between the solid surface and the tangent drawn at the liquid drop [19]. The surface contact angles of the nanofiber membranes are shown in Table 3 below.
It is obvious from Table (3) that surface roughness influences the contact angle of the samples. The Wenzel equation predicts that the hydrophilicity and hydrophobicity of a surface depends on the nature of the corresponding surface. For a hydrophilic surface, with any increase in surface roughness, hydrophilicity also increases. Conversely, for a hydrophobic surface, surface hydrophobicity increases with increasing surface roughness [19]. As chitosan has functional groups of NH$_2$ in its structure, this causes the surface of the samples to follow Wenzel's hydrophilic surface theory [20], whereby the highest surface roughness gives the lowest contact angle and vice versa.

Filters with low values of solidity (α) can tolerate large quantities of dust loading without clogging. However, in some cases, where liquid droplets act as aerosols, both the filtration efficiency and pressure drop will decrease over time. The liquid droplets which are deposited on the fibres wet the fibres, resulting in them drawing together due to capillary effects. This leads to an increase in pore size [21]. Thus, the wettability test is important when assessing air filters.

### 4.5 SEM Results:

Figure 8 shows the SEM morphology of the nanosilver particles, indicating that the size of Ag particles used in this study ranged from 20 to 40.3 nm.

![Figure 8: SEM Morphology of Ag Particles.](image)

### 5. Conclusion:

The results from these tests show that porosity ranges from 39.263% to 49.33%, and that most membranes display hydrophobic behaviours. The average pore size ranges from 112.36 nm to 92.36 nm, allowing the air filters in this study to remove all bacteria, most tobacco smoke and droplet nuclei, and most general smoke due to the small pore size. Moreover, all samples show good UV light absorption making them useful in louvers that are exposed to sunlight and in window filters.

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