ABSTRACT

YUKSEK, ILKAY OZSEV. Hybrid Woven Nonwoven Composite for Protection. (Under the direction of Dr. Behnam Pourdeyhimi.)

There have been many studies on improving protection performance of military uniforms with various systems. Different levels of protection can be obtained for various applications. However, the main threshold in military systems is keeping comfort and protection level in a balance. The systems with highest protective level require heavy weight activated carbon layer or impermeable coatings which increase the heat stress and reduce comfort. Current efforts on military clothing are to optimize barrier properties without sacrificing comfort.

The purpose of this study is to improve the chemical-biological protection performance of current military combat fabric (NYCO) with use of low basis weight functional composite nanofibers. PA6 is chosen as the main polymer due to compatibility with NYCO (50% Nylon – 50% Cotton) fabric. The effects of electrospinning parameters on PA6 nanofiber structure, filtration and air permeability of nanofiber web are investigated. For functionalization of PA6 nanofibers, various metal oxides (Al₂O₃, TiO₂, ZnO and Fe₂O₃) with different forms, particle sizes and concentrations are used. The effects of particle concentration and additives on distribution of nanoparticles in nanofibers are studied. Photocatalytic activities of functional composite nanofibers against acid orange dye and effect of particle size, concentration and type are addressed.
This study provides a contribution to the current literature on low fiber diameter nanofiber formation, in situ electrospun composite nanoparticle/nanofiber formation with uniform dispersion and no aggregation, and optimizing the composite fiber properties for improved photocatalytic activity.
Hybrid Woven Nonwoven Composite for Protection

by
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DEDICATION

To my beloved family

My mother İlknur,

My father Vahip,

My brother Özgün Mert.

For their lifelong support and encouragement
BIOGRAPHY

Ilkay Ozsev Yuksel was born on May 30, 1985 in Bursa, Turkey. After graduating from Sukru Sankaya Anatolian High School in 2002, she attended Uludag University and received her Bachelor of Science and Master of Science degrees in Textile Engineering in 2006 and 2008 respectively. Upon graduation, she began pursuing her PhD in Fiber and Polymer Science Program at North Carolina State University. During her PhD, she received a Graduate Certificate in Nonwovens Science and Technology and Technology Entrepreneurship and Commercialization Certificate. After graduation, she will be returning to Turkey to work in academia.
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CHAPTER 1: INTRODUCTION

Since ancient times, chemical and biological warfare agents have been used for homicide. However, mass destruction with these warfare agents started in World War I. Since then, with the technological advancements, production, detection and protection from chemical and biological warfare agents become more of an issue (Szinicz, 2005).

The first protective systems developed against warfare agents were resin and solution based systems which were applied by spraying or pouring the resin on contaminated surfaces. In terms of clothing, studies focus on charcoal based systems with an activated carbon layer to absorb and hold the warfare agents. However, decontamination and disposal of the activated carbon is problematic as carbon only holds the warfare agents by absorption, and there is a need for decontamination afterwards. In addition to decontamination and disposal problems, heavy weight (4-5 kg) and lack of comfort due to weight are the major drawbacks of activated carbon based systems. However, they are still in use in various countries including US. For improved protection, impermeable membranes have been developed in 1960s. Despite the fact that they do not let any chemical or biological warfare agent to pass through, there is no moisture transmission for reduction of heat stress. Thus, impermeable protective clothing systems require an additional moisture transmission unit, and are mostly used for short term exposure.
The latest commercial technology in protective clothing systems is the Joint Service Lightweight Integrated Suit Technology (JSLIST) that has been developed in 1990’s by US Army. JSLIST is made of activated carbon layer with a 50% nylon 50% cotton NyCO outer shell and water repellent finish. The system is protective against chemical-biological warfare agents at least for 24 hours in contaminated areas (Truong and Wilusz, 2005).

Current studies in protective clothing design focus on reduction of weight, improving moisture transport with enhanced protection, flexibility, etc. for eliminating heavy and toxic activated carbon layer and classical butyl rubber uniforms that require an extra breathing apparatus (Sundarrajan et al, 2007).

Nanofibers with their high surface area, small pore size and effectiveness in capturing small particles such as viruses and bacteria, are promising as barrier materials for protection. To perform as a protective material, nanofibers need to have detoxification properties. However, they do not have any active functional groups along the polymer chain which makes them insufficient for detoxification (Wilusz, 2008).

Metal oxide nanoparticles recently take interest in decomposition of chemical warfare agents and antibacterial activity against biological warfare due to their reactive edge groups, high surface area, and surface hydroxyl groups. However, current studies on nanoparticle systems focus on using the particle itself or electrospraying nanoparticles on the top of the electrospun nanofibers or charcoal based fabrics (Sundarrajan and Ramakrishna, 2007)
(Vitchuli et al., 2011). In order to use nanoparticles in commercial applications, they need to be attached to a high surface area medium.

This study aims to improve the protective performance of the military woven fabric NyCO (50% Nylon – 50% Cotton) by depositing nanofiber/nanoparticle composite web.

The main objectives of this research are:

- To increase the filtration properties of woven fabric with depositing Polyamide 6 (PA6) nanofibers
- Enhance the chemical-biological protection performance of the nanofiber mat by functionalization with Al₂O₃, TiO₂, Fe₂O₃, ZnO nanoparticles
- Investigate the morphology of nanofiber-nanoparticle composites
- Analyze the antibacterial and photocatalytic activities of nanofiber-nanoparticle composites with the effect of nanoparticle type and particle size on these properties

To achieve these goals, following tasks has been completed:

1) Improving the filtration properties of woven fabric by deposition of nanofibers: The base woven fabric was chosen as NyCO which is the most used military fabric. PA6 polymer was chosen due to compatibility with NyCO. PA6 nanofibers were electrospun with Elmarco Nanospider™ NS lab nozzle-less electrospinning system. Polymer concentration (9-20%) and fabric speed (0.1-0.3 m/min) were
altered and nanofibers with different fiber diameter and basis weights were obtained. To achieve high filtration efficiency with low pressure drop, effect of nanofiber structure on filtration properties, and air permeability of woven/nanofiber composite fabric were analyzed.

2) Enhancing the chemical-biological protection performance of the composite by loading nanoparticles to PA6 nanofiber web: Effect of Al$_2$O$_3$, TiO$_2$, ZnO, Fe$_2$O$_3$ nanoparticles, nanoparticle size and concentration, and NaCl addition on nanofiber/nanoparticle composite structure were studied. Composite fiber morphology with viscosity and conductivity measurements was assessed.

3) Evaluation of photocatalytic activity of metal oxide nanoparticle/PA6 nanofiber web: Effect of metal oxide nanoparticle type, size, and concentration on discoloration of acid orange dye were evaluated.

The organization of the dissertation is as follows.

- Chapter 1 will describe the problems in current protection mechanisms and proposed approach to overcome these problems.
- Chapter 2 of this research briefly describes protective clothing, protection mechanisms and current state if art technologies in personal protection.
• Chapter 3 focuses on improving filtration efficiencies of current military fabric (NyCO) by incorporating PA6 nanofibers mats. Controlled deposition of PA6 nanofibers onto woven fabric is achieved by changing polymer concentration and fabric speed.

• PA6 nanofiber/metal oxide nanoparticle formation is analyzed in Chapter 4. Optimization of electrospinning conditions, controlling dispersion of nanoparticles with addition of additives and effect of nanoparticles and additives on electrospinning solution properties are investigated.

• The evaluation of PA6 nanofiber/metal oxide nanoparticle composites are discussed in Chapter 5. Photocatalytic activity measurement setup and effect of metal oxide type, amount and distribution on photocatalytic activities of composite nanofibers are analyzed.

• In Chapter 6, overall conclusions and recommended future works are given.
REFERENCES


CHAPTER 2: LITERATURE REVIEW

2.1. PROTECTIVE CLOTHING

Improvements in technology and growing health concerns lead to advancements in personal protection. Both military and environmental protection in work areas became major concerns. As a result, protective clothing is now a significant field of study in technical textiles (Zhou et al, 2005) (Raheel, 1994).

Protective clothing is defined as “garments or other fabric related items designed to protect the wearer from harsh environmental effects that may result in injuries or death” (Adanur, 1995). Protective clothing systems not only protect wearer, but also protect other people from potential hazards that might arise from the contaminated person. There is not a single type of protective clothing that can provide protection against all kinds of warfare. A combination of different protection mechanisms is often required when various types of hazards are present. Enhanced protection for various hazards usually adds some restrictions to the wearer such as loss of comfort, high heat stress, less mobility, etc. Thus, adequate level of protection should be determined for each specific application (Bajaj and Sengupta, 1992).
Protective clothing can be categorized based on the type of hazards against which the clothing is designed. These hazards are:

- Chemical-biological
- Nuclear
- Thermal
- Mechanical etc.

As mentioned, the requirements from proper protective clothing depend on the application. The main requirements for advanced military clothing, which is the main subject of this study, are:

- Good mechanical properties, durability in different environmental conditions, high barrier properties
- Liquid repellency, protection from wind, snow and insects
- Comfort related properties such as low weight, air permeability, moisture transmission, low heat stress
- Application related properties like chemical-biological protection, nuclear and radiation protection, ballistic protection… etc (Adanur, 1995).

As these requirements need incorporation of different materials, it is impossible to fulfill all of them. As an example, the best barrier materials are impermeable and have comfort problems. Likewise, ballistic materials are heavy in weight. To have the proper protection,
the conditions must be totally determined, and proper requirements need to be selected (Adanur, 1995).

2.2. CHEMICAL – BIOLOGICAL PROTECTIVE CLOTHING

2.2.1. Chemical warfare agents, effects and degradation mechanisms

Chemical warfare is “the use of toxic chemical substances utilized to kill, injure or incapacitate an enemy in warfare and associated military operations” (Ellison, 2000). Various chemicals have been used to poison individuals throughout the history; however, the mass production of chemical warfare agents began with the 19th century (Chauhan, 2008) (Ellison, 2000).

Chemical warfare agents are classified into five groups depending on their target organ and impact: Nerve (organophosphorus) agents, blister agents, choking agents, blood agents (asphyxiants) and behavioral altering agents (Chauhan, 2008) (Ellison, 2000).

Nerve (organophosphorus) agents are the most dangerous and the deadliest of all chemical warfare agents. The two main groups of nerve agents are V series agents (VX, VE, VG) which are alkylphosphonothiolates, and G series agents (GB -sarin, GA-tabun, GD-soman) that are methylyphosphonofluoridate esters. V represents venomous and G represents Germany as NATO codes.
Nerve agents are produced similarly with insecticides. At standard conditions nerve agents are in liquid form and have high volatility. They mainly attack to the nervous system by disrupting the acetylcholinesterase enzyme (Rameseshan et al., 2006), (Malosse, 2008) (Ellison, 2000) (Trapp, 1985).

When inhaled, the symptoms begin in a few minutes; however, in case of liquid exposure, it takes 30 minutes to 2 hours for the symptoms to be recognized. Main symptoms include miosis, bronchospasm, hypoxia, and eventually death. Decontamination of the agents, disposing the contaminated surfaces, and decontamination of the skin with either water or sodium hypochlorite is needed for treatment of nerve agents (Hurst, 1997).

Blister agents (vesticants) cause severe blistering of eyes, lungs and skin by destroying the tissue. They are mostly used to incapacitate people and impair the health care system of the enemy by increasing the number of patients. Mustard agents (sulfur mustard, nitrogen mustard) and lewisite are the main types of blistering agents (Blackand, 2009). Mustard agents are named according to the types of the central atom of chemical structure (sulfur or nitrogen). They contain 2 or more 2-chloroethly side chains (Trapp, 1985). Sulfur mustards are in liquid form in cold environments with vaporizing temperature of 25°C, and decomposition temperature of 217.5°C. The sulfur mustard gasses distort the epithelial surfaces and cellular death begins in 2-12 hours. Nitrogen mustards have similar effects with sulfur mustards. However, depending on the exposure concentration, symptoms tend to
Lewisites were first developed in 1920s, but not used in WWII due to lack of effectiveness compared to other chemical warfare agents. It is still categorized as a chemical warfare agent but not currently in use. With a melting point of -18\textdegree{}C, and decomposition temperature of 190\textdegree{}C, lewisites are in liquid form at most environments. As a blistering agent, the effects are similar to sulfur and nitrogen mustards (Ellison, 2000).

Chlorine, chloropicrin, phosgene are commonly used and most dangerous forms of choking agents. These agents are stored in liquid form and turn into gas form in the atmosphere. As inhalation is the main route of exposure for choking agents, respiratory system, especially lungs are the target organs. Chocking agents can also cause throat and chest problems, and headache when inhaled. The side effects depend on the dosage and concentration (Ellison, 2000) (Blackand, 2009).

Blood agents get absorbed in the blood and disrupt the oxygen transfer mechanism between blood and cells. They are highly volatile compounds and become effective by ingestion or inhalation. They can cause deaths if high concentration of these agents is absorbed (Ellison, 2000).

Behavioral altering (incapacitating) agents are mostly used to reduce the performance of the enemy rather than killing them. These agents are also deadly when high dosage is applied at certain conditions, however; the common usage is to prevent the enemy from work, and overload the healthcare system. They are usually categorized as psychobehavioural chemical
incapacitating agents such as ketamine, fentanyl, glycolate anticholinergics etc (Kinbgsbury, 1990) (Ellison, 2000).

The degradation methods of chemical warfare agents are; physical degradation, enzymatic degradation, chemical degradation and photo-catalytic degradation. Physical degradation is the removal of chemical warfare agents without active decontamination, whereas; enzymatic, chemical and photo-catalytic degradation techniques reduce the toxicity of the agents (Dumas, 1990) (Boone, 2007).

Physical decontamination is either by encapsulating or discarding the agents. Depending on the contaminated surface and type of the chemical warfare agent, chemical warfare agents are removed from the contaminated area (Boone, 2007). Evaporation and weathering also reduces chemical warfare agent over time (McGuire et al., 1993) (Boone, 2007). Microbial degradation is one of the cheap and efficient physical degradation systems for soil systems and liquid cultures. Although nerve agents can be easily decontaminated with some bacteria and fungi, soil sample handling is an important restriction (D'Agostino et al., 1992) (Rameseshan et al., 2006).

Enzymatic degradation is a simple, environmental friendly and fast method, but high cost, change in the enzyme stability and small production scale are some of its limitations. Biological warfare agents can also be destructed by this method. Different enzymes may be required for different chemical warfare agents (Dumas, 1990).
Chemical degradation is a cheap and an efficient method which is widely used in personal protection. Chemicals with hydroxyl groups, oximes, nucleophiles, and enzymes such as organophosphorus hydrolase (OPH) and organophosphorus acid anhydrolize (OPAA) are reported to hydrolyze nerve agents by breaking the phosphorus bond (Hill et al., 2003) (Singh, 2006). Cyclodextrins function the same way with enzymes, but reacts faster than activated carbon. β-cyclodextrin has been combined with o-iodosobenzoic acid (IBA) and found to hydrolyze nerve agents (Rameseshan et al., 2006). Metal oxide nanoparticles such as MgO, CaO, TiO$_2$, ZnO, Al$_2$O$_3$ are also found to be effective against nerve agents. They are reported to break the phosphorus bond of the organophosphorus agents. Surface area and the reactivity of metal oxides are the main factors that influence effectiveness of detoxification (Koper et al., 1992) (Carnes et al., 2002) (Medine et al., 2004).

Photocatalytic degradation occurs by application of ultrasound on photocatalysts and generation of electron-hole pairs to react with chemical warfare agents. Metal oxide nanoparticles especially TiO$_2$ is known to have phototcatalytic properties, and has been studied recently (Martyanov and Klabunde, 2003) (Kozlov et al., 2003) (Vorontsov et al., 2009).
2.2.2. Biological warfare agents, effects and degradation mechanisms

Biological warfare agents are bacteria and toxins in aerosol form and airborne spread viruses. As most of the biological warfare agents are in aerosol form, their particle size is one of the most important factors that need to be considered. Most bacteria are between 0.3-35\(\mu\)m, and viruses are 0.005-0.3\(\mu\)m in size. However, viruses are carried by large particles so their effective particle size is 0.3 \(\mu\)m or larger (Lala et al., 2007).

Anthrax and brucellosis are the most common diseases caused from biological warfare agents. They are both transferred in aerosol form. Bacillus anthracis bacteria cause anthrax disease with symptoms such as fever, cough, and respiratory problems. The particle size of bacillus anthracis bacteria is between 0.5–5.0 \(\mu\)m, and the symptoms appear in 2-3 days after exposure (Pile et al., 1998). Brucellosis is a disease that is transmitted from animal products. The bacteria brucella is a rod shaped gram negative bacteria with a size of 0.5-2 \(\mu\)m and it takes 6-60 days for the symptoms such as headache, fatigue, sweat to appear (Rubinstein and Levi, 2002).

Yellow fever and encephalitis are the commonest viral diseases that are transmitted by air. Yellow fever has an incubation period of 2-6 days, and the main symptoms include diarrhea, fever, pain and vomiting are. Encephalitis causes brain damage with loss of muscular coordination after 5-15 days which is the incubation period (Ellison, 2000).
Toxins are man-made poisonous substances derived from living organisms. The type and dosage of the toxin determines their severity and symptoms (Demers, 2001) (Hawley and Eitzen, 2001) (Miller, 2002).

Textiles for protection from biological warfare agents have two main functions: protection from bacteria, fungi, etc, and protecting the textile from breakdown of materials by microbial action (Belkin, 1999, 2002).

Chemical disinfection by solutions such as halogens and alcohols, and physical decontamination methods are used for biological warfare agent decomposition. Chemical disinfectants are not always preferred as they are corrosive, toxic, and hard to dispose ecological ways. On the other hand, physical decontamination method has high energy consumption (Koper, 2003).

The most common way for decontamination of biological warfare agents is using silver compounds as antibacterial agents. Silver ion (Ag⁺) binds the sulfur, nitrogen and oxygen containing groups and damages the virus or bacteria cells. The antibacterial activity depends on the effective surface area, so the particle size is important (Morrison, 2002) (Morones et al., 2005) (Melaiye et al., 2005) (Lala et al., 2007).

In addition to silver particles, composites with metal oxide nanoparticles such as TiO₂, ZnO, MgO, Al₂O₃ are used for antibacterial properties (Stoimenov et al, 2002). MgO was reported to destroy the cell wall by attacking the peptide linkages whereas TiO₂ is known to kill the
bacteria by formation of free radicals and reactive oxidative species (Choi et al., 2006). The antibacterial properties of these nanoparticles are reported to depend on the particle size (Stoimenov et al., 2002).

2.3. CHEMICAL-BIOLOGICAL PROTECTION SYSTEMS

2.3.1. Solution based systems

Traditional chemical biological protection methods focus on decontamination of warfare agents, and equipment used for decontamination are considered to be replaced after each use. Solution based systems include Supertropical bleach, Decontamination Solution Number 2 (DS2) and XE555. Supertropical bleach is one of the first decontamination methods which are used to neutralize nerve and blistering agents since 1950s. It is composed of 93% calcium hypochlorite and 7% sodium hydroxide and applied against nerve, blistering and biological agents. It is sprayed onto contaminated surfaces and then washed with water. However, Supertropical bleach is not used in clothing due to high corrosiveness to fabrics and metals (Modec, 2003) (Epstein et al., 1956).

DS2 is composed of 2% NaOH, 28% 2-methoxyethanol, and 70% diethylenetriamine and effective against nerve and mustard agents, but not decompose biological agents. It is quite toxic and corrosive to plastics and leather. In order to prevent any corrosion, DS2 is sprayed and kept on the sample on 30 minutes, and rinse with water. DS2 is expensive and dispose

XE-555 is a carbon like black powder with strong acid and base ion exchange resins that is used as a skin decontaminant. The drawbacks of XE-555 are high cost and limited usage on the skin (Hurst, 1997) (Wagner and Batram, 1999).

2.3.2. Chemical-biological protective clothing

The level of protection required is the main factor that defines the protective clothing type needed. To fulfill the protection requirements in battle field, chemical-biological protective military uniforms consist protective clothing system with battle dress overgarment, hoods, boots, outer protection, respiratory system, cooling system, protective mask, helmets,…,etc. There are four main protective materials that are used for these applications. They are permeable, impermeable, semipermeable and selectively permeable systems (Wilusz and Truong).

Permeable systems contain activated carbon layer to absorb the warfare agents and a repellent outer layer. The advantage of this system is permeability. However, as carbon holds the warfare agents rather than destroying them, disposal after contamination is a major drawback (Wilusz et al, 1997).
Impermeable butyl rubber uniforms are the traditional protective clothing systems which have excellent protection properties provided by impermeability. They contain a charcoal layer for absorption. High heat stress is the major problem for butyl rubber uniforms, so they require a separate heat reduction unit. They are not preferred because of the heavy weight, lack of moisture transport and comfort (Wilusz et al, 1997).
Semipermeable membranes are similar to permeable membranes in terms of protection mechanism. Either porous or solution diffusion membranes which does not allow penetration of liquid chemicals and aerosol form of chemical-biological warfare are used as semi-permeable membranes. The system improves the comfort by moisture transport. For protection against toxic vapors, they also require an activated carbon layer, which restricts the use of impermeable systems (Wilusz et al, 1997).

Figure 2.2. Impermeable systems (Wilusz et al, 1997).
Selectively permeable systems are nonporous structures that are highly protective without a need for activated carbon layer. Moisture vapor transmission is achieved by solution diffusion process. They provide protections against chemical and biological agents as well as toxic vapors (Wilusz et al, 1997).

Figure 2.3. Selectively permeable systems (Wilusz et al, 1997).

JSLIST (Joint Service Lightweight Integrated Suits Technology) is the current military system since 1997. It contains activated carbon layer and NyCO (50% Nylon-50% Cotton) outer shell with a water repellent finish. Activated carbon layer with a surface area between 500-1500 m$^2$/g is required for absorption. The system is protective at least 24 hours in
contaminated areas, and can be worn more than 45 days without any contamination. They can be laundered 6 times (RIMPEL, 2008) (Military specification MIL-S-43926, Suit, Chemical protective, 1991).

Figure 2.4. JSLIST protective clothing (RIMPEL, 2008) (Wilusz et al, 1997).

As mentioned earlier, one of the main objectives of current protective clothing studies is to reduce the weight and heat stress of the garment by eliminating activated carbon layer. Ideal
Chemical-biological protective clothing should be effective against chemical and biological warfare agents in an environmentally friendly and non-toxic and non-aggressive way. Current protective clothing systems are not capable of fulfilling these needs (Tiron, 2003).

Current efforts about chemical-biological protective clothing focus on incorporating smart textiles such as self detoxifying and self cleaning membranes. These membranes decompose chemical and biological warfare agents and do not require activated carbon layer as an absorbent. With eliminating carbon based component, lightweight, high comfort protective clothing can be designed. However, self detoxifying membranes have not been commercialized for protection applications yet. Selectively permeable membranes are also of interest as they are permeable to water vapor, but impermeable to hazardous organic chemicals (Schreuder-Gibson, 2002, 2003).

![Self-detoxifying systems](image)

**Figure 2.5.** Self-detoxifying systems (Wilusz et al, 1997).
2.4. NANOFIBERS AND NANOPARTICLES FOR CHEMICAL-BIOLOGICAL PROTECTION

2.4.1. Electrospun nanofibers for chemical-biological protection

Electrospinning is a simple, single step method to produce fibers between 100-1000nm in diameter. This fiber fineness means high specific surface area which leads the use of electrospun nanofibers widespread in various applications (Ramakrishna, 2005). The Elmarco Nanospider™ electrospinning setup used in this study is shown in Figure 2.6.

Figure 2.6. Elmarco Nanospider™ electrospinning system

(a) polymer solution, (b) solution bath, (c) rotating electrode, (d) ground electrode,
(e) support layer
In electrospinning process, a droplet forms at a nozzle/needle which is electrically charged. When this charging with high voltage exceeds the surface tension of the liquid; a polymer jet is ejected from the cone. The jet experiences bending instabilities and whipping motion thus move towards the collector. During this motion, solvent evaporates and nanofibers are attached to the collector (Yarin et al, 2001)

In addition to controlling fiber diameter, uniform bead-free nanofiber formation is also critical. Nanofiber diameter, uniformity and structure are controlled by solution parameters, electrospinning conditions, or environmental factors. The main parameters of electrospun nanofiber formation are:

- **Solution parameters**
  - Type of the polymer: The chemical nature of the polymer is the main factor in electrospinning. Each polymer has unique properties and electrospinning variables must be selected depending on the polymer type and properties (Ramakhrishna, 2005).
  - Molecular weight of the polymer: The molecular weight of the polymer is the length of the polymer chain. Thus, higher molecular weight results as higher solution viscosity and produce fine fibers (Buchko et al, 1999).
  - Polymer concentration: Increase in polymer concentration leads to increase in viscosity and resistance to jet stretching. Thus, the fiber diameter increases. When the viscosity is too low, there is not enough chain entanglements for electrospinning (Fong et al, 1999) (Shenoy et al, 2005). The polymer dries at the tip of the needle when the viscosity
is too high, and electrospinning is impossible (Zhong et al, 2002). Polymer concentration is also related to bead formation. Spherical beads are observed in low viscosities, whereas spindle like beads are common in higher viscosities (Fong et al, 1999) (Mit-uppatham et al, 2004).

- Conductivity: In case of high conductivity, the stretching of the solution increases, and smooth fibers are formed. Beads are formed in insufficient stretching, thus, smooth fibers are obtained. Salts such as NaCl can be added to electrospinning solutions to increase conductivity (Ramakrishna, 2005).

- Solvents: Dielectric constant, conductivity and dipole movement of solvent(s) affect the nanofiber web. High dielectric and conductivity reduces the fiber diameter (Son et al, 2004) (Jarusuwannapoom et al, 2005).

- Surface tension: Surface tension and viscosity are reported to be the two parameters that control spinnability of the polymer with various conditions. For the jet formation, surface tension must be overcome by the electrical repulsion. (Diertzel et al, 2001).

- Electrospinning conditions
  
  - Electrospinning voltage: When voltage increases, the electric field and cumbic forces, thus jet stretching increases and fine fibers are formed (Buchka et al, 1999).
○ Feed rate: When feed rate increases, amount of polymer solution ejected from the needle increases, and fiber diameter increases (Zong et al, 2002) (Jalili et al, 2005).

○ Tip-to-collector distance: Electrospinning distance indicates the space for solvent evaporation. When the distance is too low, there is not enough space for solvent evaporation and fibers are stuck together. Increase in tip-to collector distance has the same effect with increasing the voltage, so fiber diameter reduces (Jalili et al, 2005) (Ramakhrisna, 2005).

○ Type of the collector: The geometry and the conductivity of the material the collector is made is important. More fibers are deposited on collectors with high conductivity such as aluminum foil (Liu et al, 2002). Rotating drum type electrodes are being used to have tubular structures (Ramakhrishna, 2005).

- Environmental conditions: Environmental conditions such as temperature, humidity and pH affect the fiber morphology depending on the polymer and solvents. For polyurethane fibers higher temperature is reported to decrease the viscosity and increase the evaporation rate of the solvent during spinning which lowered the fiber diameter (Demir et al, 2002). Humidity was studied by Casper et al, and reported to increase solvent evaporation, thus lower fiber diameter was observed for polystyrene nanofibers (Casper et al, 2004). Formation of pores with increased humidity in polystyrene nanofibers was observed by Megelski et al (Megelski et al, 2002).
Electrospun nanofibers are gaining importance as barrier materials in protection applications with their low fiber diameter, basis weight, high surface area, air permeability and porosity. However, they lack mechanical properties and durability. To overcome these disadvantages, nanofibers are being formed on a substrate. In the composite web, nanofibers give the functionality and the substrate enhances the mechanical properties.

The published research about nanofiber mats for protective applications focus on the filtration and moisture vapor transmission studies (Graham et al, 2003) (Vitchuli et al, 2010). High filtration efficiency of electrospun nanofibers prevents the diffusion of chemical and biological warfare agents as those agents are mostly delivered as aerosols which are the suspended solid and liquid particles in air.

There are four main filtration mechanisms: Brownian diffusion, interception, impaction and gravitational settling. Diffusion occurs when the particle size is small compared to fiber size. Because of the Brownian motion of the particle, it is captured by the fiber. Interception is most effective when “the distance from the center of mass of the particle to the fiber surface is equal or less than the radius of the particle” (Lastow and Podgorski, 1998) Impaction is defined as “a particle, because of its inertia, is unable to adjust quickly enough to the abruptly changing streamlines near the fiber and crosses those streamlines to hit the fiber”. In gravitational settling, the particle is captured by the gravitational force (Hinds, 1999) (Wang, 2008).
The combined efficiencies for particle sizes causes a V shape total filter efficiency curve, in which the lowest efficiency point is called Most Penetrating Particle Size (MPPS). MPPS shows the particle size in which none of the filtration mechanisms is dominant and is

**Figure 2.7.** Filtration mechanisms (NIOSH, 2003)
between 0.1-0.3 µm for neural filters (Wang, 2008). Figure 2.8 shows the total efficiency curve for filter media with 2 µm fiber diameter, 5% SVF (solid volume fraction), 1mm thickness and tested with 10 cm/s face velocity with multiple sized particles (Hinds, 1999).

Figure 2.8. Collection efficiency curve for filter media (Hinds, 1999)
Nanofiber webs are reported to be high efficient with small fiber diameter and the efficiency was found to increase with decreasing fiber diameter. Most penetrating particle size also decreased with fiber diameter (Maze et al, 2007)

According to the single fiber theory, filtration efficiency is defined as:

\[
E = 1 - \exp\left(-\frac{4\alpha t}{\pi d_f (1-\alpha)}\right)
\]

Equation 2.1.

Where, E: filtration efficiency

\(\alpha\): solidity

\(\eta\): total single fiber efficiency

\(t\): thickness of the filter media

\(d_f\): fiber diameter \hspace{1cm} (Brown,1993)

It is clear from the equation that, filtration efficiency increases with the decrease in fiber size. Fibers with small fiber diameter also reduce the MPPS which means an increase in efficiency (Brown, 1993) (Hinds, 1998).

Pressure drop can be also described by,

\[
\Delta P = f(\alpha) \frac{n t u}{a^2 f}
\]

Equation 2.2.
Where; \( \Delta P \): Pressure drop

\( \eta \): single fiber efficiency

\( U \): Face velocity

\( f(\alpha) \): parameter related to solidity (Hinds, 1999)

To define \( f(\alpha) \), different models use different equations. As an example; for Kuwabara cell model \( f(\alpha) \) is defined by Hinds as:

\[
f(\alpha) = 16 \frac{\alpha}{Ku}
\]  

Equation 2.3.

Where;

\[
Ku = - \left( \ln \frac{\alpha}{2} \right) - \left( \frac{\alpha}{4} \right) + \alpha - \left( \frac{\alpha^2}{4} \right) \quad (Hinds, 1999)
\]  

Equation 2.4.

Both filtration efficiency and pressure drop increases with solidity. To have a good filter material, the filtration efficiency should be kept high with pressure drop being low. The ratio of efficiency to pressure drop is called “Quality factor” and is a measure of how good the filter is. Thus, filters with high quality factors should be preferred.

The Quality factor is defined as:

\[
QF = - \frac{\ln \left( \frac{1}{P} \right)}{\Delta P}
\]  

Equation 2.5.

Where, \( P \): Penetration = \( 1 - E \)  

Equation 2.6.
Nanofibers, with their high surface area, are used as barrier materials for a wide range of applications. Recently, nanofibers are functionalized with catalysts to obtain a functional detoxifying membrane. In that case, polymer becomes the high surface area carrier for uniformly dispersed catalyst. Active functional groups should be added either during electrospinning, or after production of nanofibers as a coating. In terms of coating, nanoparticles have been electrosprayed onto electrospun nanofiber webs, and found to be effective against warfare agent stimulants (Sundarajjan et al, 2007) (Vitchuli et al, 2011). The addition of metal oxides during electrospinning, and their effect on detoxification of warfare agents have not been studied.

2.4.2. Metal oxide nanoparticles for chemical-biological protection

To obtain self-detoxifying protective media, metal oxide nanoparticles are highly preferred with their reactive side groups, high surface area and surface hydroxyl groups. These nanoparticles improve the detoxification and antibacterial activity of the structure they are used with.

Powder form metal oxides are used alone or as an attachment to a surface for functionality. Metal oxide nanoparticles such as Al₂O₃, ZnO, MgO and TiO₂ have been reported to decompose nerve and mustard agents. The phosphorus linkage of nerve and mustard agents is catalytically broken, and conversion of agents to non-toxic side products occurs. Different
metal oxides are also effective in blend form. \( \text{Al}_2\text{O}_3 \), \( \text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3\text{-CuO} \) nanoparticles are also reported to be effective against sulphur mustard. Mixed nanocrystals such as \( \text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3\text{-CuO} \) are found to be more effective than single \( \text{Al}_2\text{O}_3 \) sample (Prasad et al, 2010). \( \text{Al}_2\text{O}_3 \), \( \text{MgO} \) and \( \text{Al}_2\text{O}_3\text{/MgO} \) mixed metal oxides are also reported to decompose 2-chloroethylethyl sulfide (2-CEES) successfully in 200 minutes. \( \text{Al}_2\text{O}_3 \) was found to be more effective than \( \text{MgO} \). It is proposed that the hydrolization occurred with conversion of chloride by –OH groups on the surface (Martin et al, 2005). \( \text{MgO} \) nanoparticles and their halogen treated forms (\( \text{MgO}/\text{Cl}_2 \) and \( \text{MgO}/\text{Br}_2 \) powders), are reported to be effective against gram positive and gram negative bacteria as well as spores (Stoimenov et al, 2002).


Metal oxide nanoparticles are good candidates for absorption and decomposition of chemical
warfare agents as they are non-toxic and effective. However, they cannot be used alone; and require a medium to be attached. Approaches such as combination of these particles with high surface area mediums are getting common nowadays.

Recent interest in chemical-biological protective systems focused on making inorganic nanofibers. Use of ceramic nanofibers increases the filtration properties; however, ceramic nanofibers do not have functional groups that induce detoxification of chemical warfare agents. There is a need for reactive surface edge groups even with ceramic nanofibers. The detoxification properties of zinc titanate nanofibers (contains 20-60% TiO\textsubscript{2}) has been studied by Rameseshan et al. (2007) and found that composite nanofibers can detoxify up to 70-90% of paraoxon (nerve agent stimulant), and 60-70% of CEES (mustard agent stimulant) (Rameseshan et al, 2007). As mentioned in the study, the functional part is not zinc titanate nanofibers. The increased filtration efficiency is obtained by zinc titanate nanofibers, whereas, the detoxification properties are enhanced with TiO\textsubscript{2} nanoparticles. Ceramic nanofibers are hard to produce and only acts as a filter media, thus use of polymer nanofibers is an easier procedure for detoxification. Metal oxide nanoparticles are also produced as a part of nanofiber composites with polymeric nanofibers. In that case, electrospun nanofibers act as the medium for nanoparticles. In addition, they become a barrier for airborne particles with their high filtration efficiency. Based on current literature, there are very few studies of electrospun
nanofiber/nanoparticle functional composite structures for protective applications. In situ electrospinning of aerogel prepared 5% MgO nanoparticles with PSU polymer was tested against paraoxon (a nerve agent stimulant), and found to be twice as effective as charcoal (Sundarajjan et al., 2007).

ZnO nanoparticles are also electrospayed on electrospun Nylon 6 nanofibers for chemical and biological protection. The composite fabric had a detoxification efficiency of 95% against paraoxon, and 99.99% antibacterial against gram positive bacteria (B. cereus) and gram negative bacteria (E. coli) (Vitchuli et al., 2011).
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CHAPTER 3: FILTRATION AND AIR PERMEABILITY PROPERTIES OF PA6 NANOFIBER/ WOVEN FABRIC COMPOSITES

Abstract

PA6 nanofiber webs with different fiber diameter and basis weights were produced onto NYCO (50% Nylon – 50% Cotton) woven fabric with electrospinning. By changing the processing conditions, nanofibers as small as 41 nm were obtained. Reduction of fiber diameter was achieved by decreasing the polymer concentration in the electrospinning solution, and basis weight was controlled by changing the fabric speed. Filtration and air permeability properties of these composite webs were evaluated, and increase in filtration efficiency and air permeability with decrease in fiber diameter was observed.

3.1. INTRODUCTION

Nanofibers are of interest in many applications due to their high surface area and small pore size. Electrospinning is a widely preferred method to produce nanofibers that is being used tissue engineering, drug delivery, medical textiles, batteries…etc. (Doshi et al., 1995) (Huang et al, 2003).
Recently, electrospun nanofibers are being used in filtration applications as a part of a composite along with a nonwoven or woven fabric. In the composite system, nanofibers provide high filtration efficiency, and woven or nanofiber layer provides strength and durability (Dotti et al, 2007).

The most important parameters for perfect protective clothing are high filtration efficiency for protection, and sufficient air permeability for comfort. Lightweight, low thickness protective clothing can be formed by electrospun nanofiber webs with enhanced protection (Vitculi et al., 2011). Nanofibers are commonly used in filtration applications with their high efficiency caused by high surface area. It was reported that the filtration efficiency increases and most penetrating particle size decreases with reduction in fiber diameter (Hinds,1999) (Maze et al, 2007). Nanofiber diameter can be controlled by changing electrospinning parameters such as solution parameters (polymer concentration, solvents…etc.) and electrospinning parameters (voltage, tip-collector distance, feed rate…etc.). In addition to nanofiber diameter, basis weight and thickness of the nanofiber mat are significant factors to have high efficiency filters. This relationship as defined by Hinds is,

\[ E = 1 - \exp \left( -\frac{4\alpha l t}{\pi df (1-\alpha)} \right) \]  

Equation 3.1.
Where, $E$: filtration efficiency

$\alpha$: solidity

$\eta$: total single fiber efficiency

$t$: thickness of the filter media

$df$: fiber diameter \hspace{1cm} (Hinds, 1999)

This chapter focuses on the electrospun fiber morphology and its impact on filtration properties and air permeability. Nanofiber webs were produced with 9-20% PA6 polymer concentrations and 0.1-0.3 m/min fabric speeds. Fabric speed is the most effective factor to control basis weight and nanofiber diameter was managed by changing the polymer concentration. The aerosol filtration properties and air permeability were analyzed.

3.2. EXPERIMENTS

3.2.1. Electrospinning of PA6 nanofibers

Nylon 6 was provided by BASF (Ultramid B27 02 Nylon 6, 34MFI) and used as the base polymer without further purifications. Nylon 6 pellets was dissolved in the mixtures of 70% Acetic acid and 30% Formic acid by weight continuously stirring at 80°C for 8 hours. In order to examine the effect of solution concentration on fiber diameter, solutions containing
9-20% PA6 by weight were prepared. Solutions were electrospun with Elmarco Nanospider™ NS LAB continuous electrospinning system with 70 kV voltage and 14 cm electrode-to-collector distance onto 50% Nylon 50% Cotton (NyCO) military fabrics. Fabric speeds ranging between 0.1m/min – 0.3m/min were used.

**Figure 3.1.** Continuous electrospinning system (a) polymer solution, (b) solution bath, (c) rotating high voltage electrode, (d) ground electrode, (e) supporting frame, and (f) support layer.
In Elmarco’s Nanospider™ electrospinning process, rotating electrode is located inside the polymer solution in the liquid form. Very little amount of polymer solution is subjected to high electrical voltage. The rotation speed of the electrode can be controlled during the process. In this study, the electrode speed was kept constant to 5 rpm.

3.2.2. Fiber diameter measurements

Electrospun Nylon 6 nanofiber webs were examined with a JEOL 6400 is a Cold Field Emission Scanning Electron microscope with 5 kV accelerated voltage. The samples were coated with Au/Pd to reduce charging. About 20 SEM images were taken for each sample and the diameters of all fiber in these images were measured (total around 100 fibers) with Image J software. Average fiber diameters as well as fiber diameter distributions are reported for each sample.

3.2.3. Basis weight

The basis weights of the samples were measured with Mettler AT201 balance, and 5 replicates were used.
3.2.4. Determining filtration properties of composite fabrics

The filtration performance of the nanofiber/woven fabric composites were measured with TSI CERITEST 3160 automated filter tester.

![TSI 3160 Automated filter tester](image)

**Figure 3.2.** TSI 3160 Automated filter tester (TSI Manual, 2003)

The nanofiber/woven fabric composites were tested with DOP aerosols with particle sizes between 0.02-0.3 µm with 5.33 cm/s face velocity 32 l/min air flow rate. The default sample holder with 100 cm² area was used for filtration testing. The samples were conditioned at 20°C and 65% relative humidity for 24 hours.
3.2.5. Air permeability measurements

Air permeability of the nanofiber/woven fabric composites was measured with TEXTEST FX3300. The testing pressure was 125 Pa, and a 5 cm² round test area was used. The samples were conditioned at 20°C and 65% relative humidity for 24 hours before the test.

3.3. RESULTS AND DISCUSSION

3.3.1. Nanofiber web characteristics and nanofiber diameter

The average fiber diameter of PA6 nanofibers were reduced down to 41 nm by changing the polymer concentration from 9% to 19% during electrospinning. The average nanofiber diameters are shown in Figure 3.3.
Figure 3.3. Change in the fiber diameter with the polymer concentration in the electrospinning solution

As can be seen from Figure 3.3., the increase in the polymer concentration leads to increase in average fiber diameter. The standard deviations are less than 30% of average fiber diameter. The average fiber diameters are between 41-350 nm and, smooth and uniform fiber formation is observed even in 47 nm fiber web, which is a huge improvement in terms of decreasing the fiber diameter. PA6 nanofibers with average fiber diameters as low as
73 nm has been reported previously (Yeom et al, 2010).

The change in fiber diameter with polymer concentration is due to the viscosity of the electrospinning solution. Increased polymer concentration increases the viscosity and lowers the surface tension. Thus, course fibers are formed. (Zhang et al, 2005) (Dietzel et al, 1999) (Dietzel et al, 2001)

Nanofiber web with 9% polymer concentration has the lowest average fiber diameter at all, however the mat contains significant amount of beaded fibers. Beaded fibers are usually formed when the polymer chains are less entangled, viscosity and/or surface tension is low and net charge density is high (Jaeger et al, 1996) (Jaeger et al, 1998) (Fong et al, 1999) (Yarin, 1993). The increase in the viscosity results with larger fiber and bigger beads. The higher the viscosity, the more spindle-like beads are formed. High net charge density lowers the fiber diameter of the mat, thus, lowers the bead formation and bead size (Fong et al, 1999) (Magarvey et al, 1962). SEM images and fiber diameter distribution graphs of the samples are given in Figure 3.4.
Figure 3.4. SEM images and fiber diameter distributions for electrospun nanofiber webs with 9-19% polymer concentration
a) SEM image and fiber diameter distribution graph for 9% PA6 polymer concentration

b) SEM image and fiber diameter distribution graph for 10% PA6 polymer concentration

c) SEM image and fiber diameter distribution graph for 11% PA6 polymer concentration
d) SEM image and fiber diameter distribution graph for 12% PA6 polymer concentration

e) SEM image and fiber diameter distribution graph for 13% PA6 polymer concentration

f) SEM image and fiber diameter distribution graph for 14% PA6 polymer concentration
g) SEM image and fiber diameter distribution graph for 15% PA6 polymer concentration

h) SEM image and fiber diameter distribution graph for 16% PA6 polymer concentration

h) SEM image and fiber diameter distribution graph for 17% PA6 polymer concentration
i) SEM image and fiber diameter distribution graph for 18% PA6 polymer concentration

j) SEM image and fiber diameter distribution graph for 19% PA6 polymer concentration
After increasing the polymer concentration from 9% to 10%, PA6 nanofibers with smooth fine fibers are formed. Nevertheless, when the polymer concentration exceeds 17%, the solution becomes too viscous to electrospin. In this case, small spider net like structures or in other words filament like structures are formed.

![SEM images of nanofiber webs with spider net like structures](image)

**Figure 3.5.** SEM images of nanofiber webs with spider net like structures

Fabric speed is the other parameter changed during electrospinning. Decrease in fabric speed causes more contact time between fabric surface with and the electrode. There is more fiber deposited on the fabric surface, thus, basis weight increases. This relationship is shown in
Figure 3.6. As shown in figure, nanofiber basis weight for all polymer concentrations is less than 0.5 g/m².

Figure 3.6. Effect of fabric speed on basis weight
3.3.2. Filtration properties of PA6 nanofiber/NYCO woven composite webs

3.3.2.1. Filtration efficiency and pressure drop

Filtration efficiencies and pressure drops of nanofiber/woven fabric composites at 5.33 cm/s face velocity and 0.3 µm particle size are shown in Figure 3.6. As shown in the graph, the NyCO woven fabric, which is the control sample, has an efficiency of 32%, and a pressure drop of 428 Pa. With the addition of nanoparticles below 0.1 gsm, the filtration efficiencies of the composite fabrics increased up to 60 – 99.97% and the pressure drop values for that efficiency is between 472-800 Pa. More than 75% of the composite samples achieved efficiency greater than 95%. It is obvious that the smaller the fiber diameter, the higher the filtration efficiency. This is because of the increase in surface area with reduction fiber diameter. However, the filtration efficiency is not the only parameter that is considered for protection. Pressure drop needs to be kept as low as possible in addition to high filtration efficiency and air permeability for comfort. Otherwise, coatings that are 100% efficient with no air permeability would be considered as the perfect material. There is a region that nanofibers with 47 nm, 53 nm and 100 nm average fiber diameter webs that are produced with 10-11-12% PA6 polymer concentration, have more than 95% efficiency with less than 550 Pa pressure drop. So, by adding less than 0.2 g/m² of nanofibers onto NyCO fabric, there is a tremendous increase in filtration efficiency from 32% to more than 95%. The woven/nanofiber composites that fall into this region might be a potential candidate for use in
protective clothing material (Jamriska, 2009) (Hutten, 2007). Effects of polymer concentration and basis weight on filtration efficiency with different particles sizes are further discussed in the following section.

**Figure 3.7.** Filtration efficiency and pressure drop values of composite fabrics
3.3.2.2. DOP aerosol fractional penetration

Figure 3.8 shows the change in the filtration efficiencies of the composite fabrics with 0.1 to 0.3 m/min electrospinning fabric speed for the particle sizes between 0.01 – 0.4µm at 5.33 cm/s face velocity. The composite fabric electrospun with 0.3 m/min fabric speed has the lowest nanofiber basis weight and 0.1 m/min has the heaviest nanofiber web as shown previously on Figure 3.6. For all fabrics, penetration increased with increasing particle size to 0.09 µm. This is the highest penetration value which is called “Maximum Penetrating Particle Size” (MPPS), which none of the filtration mechanisms are dominant. For particles smaller than MPPS diffusion is the dominant mechanism whereas the particles that are greater than MPPS in size are captured by impaction (Maze et al, 2007). For all composite fabrics with different nanofiber diameters, penetrations are lower with decreasing fabric speed which corresponds to increased basis weight. Hence, increasing basis weight decreases penetration. When the fabrics with different nanofiber diameters are compared, it can be seen that reducing nanofiber diameter leads to decrease in penetration.
**Figure 3.8.** Fractional penetration for PA6 nanofiber / NyCO woven fabric composites
a) Penetration vs. particle size for 47 nm nanofiber web/woven fabric composites

b) Penetration vs. particle size for 53 nm nanofiber web/woven fabric composites
c) Penetration vs. particle size for 100 nm nanofiber web/woven fabric composites

d) Penetration vs. particle size for 116 nm nanofiber web/woven fabric composites
e) Penetration vs. particle size for 226 nm nanofiber web/woven fabric composites
3.3.2.3. Quality factor

Quality factor is a measure of overall performance of the filter media that is calculated with penetration and pressure drop. Optimum protection is achieved by low penetration and pressure drop which results as high quality factor. (Quality factor is calculated based on penetration measured with 5.33 cm/s face velocity and 0.3 μm particle size) (Hinds, 1999)

\[
QF = -\ln(1/P) / \Delta P \ (1/kPa)
\]

Equation 3.2.

Where, QF: Quality factor

P: Penetration (-)

\(\Delta P\) : Pressure drop (Hinds, 1999)
As can be seen from the Figure 3.9, when webs with same nanofiber diameters are compared, increase in basis weight increases the quality factor. This is because of the efficiency increase with higher basis weight. Even though filtration efficiency of 10% polymer concentration (47 nm nanofiber) / woven fabric composites is high, the webs do not provide the best quality factor due to the high pressure drops that reduces the overall performance of the webs.
3.3.3. Air permeability

As mentioned earlier, barrier materials that have the highest filtration efficiency are impermeable membranes. However, they have zero comfort which makes them inconvenient to use. To increase protection, penetration should be kept low while air permeability is still high (Ellison, 2000). This is one of the major challenges in current protection systems. As can be seen from the Figure 3.10, increased fabric speed results as decreased air permeability. However, composites produced with 0.25-0.3 m/min fabric speeds have air perm abilities that are comparable with non-treated woven fabric. Therefore, improved filtration efficiency can be obtained without a significant decrease in air permeability.

![Figure 3.10. Air permeability of composite fabrics with different fabric speed and nanofiber diameter](image)

Figure 3.10. Air permeability of composite fabrics with different fabric speed and nanofiber diameter
3.4. CONCLUSIONS

PA6 nanofibers with 9-19% polymer concentrations are electrospun onto 50/50 NyCO woven fabrics. Bead-free smooth nanofibers as small as 47 nm are obtained by changing electrospinning conditions. The effects of the nanofiber web characteristics on the composite web properties are evaluated and it is observed that at least 200% increase in filtration efficiency can be achieved with only 20% increase in pressure drop. It is also found that the filtration efficiency increases with decreasing the fiber diameter and basis weight. With addition of 0.5 g/m² of nanofibers, there is a significant improvement in filtration properties and filtration efficiency increases from 32% to more than 95% for all composite fabrics. In order to compare the performance of different composites, aerosol particle size is a significant factor. Penetration increases up to particle sizes that corresponds to MPPS, and begin to decrease after that. In order to select the potential candidate for protection, the target material must be addressed, so that the effect of testing variables can be eliminated.
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CHAPTER 4: FORMATION OF FUNCTIONAL NANOPARTICLE NANOFIBER COMPOSITES

Abstract

PA6 nanofiber/metal oxide nanoparticle composites are produced with single step in situ electrospinning to functionalize PA6 nanofibers to obtain self detoxifying protective properties. Al₂O₃, TiO₂, ZnO and Fe₂O₃ nanoparticles with different particle size and forms are selected as the metal oxides due to their decomposition properties. Up to 30% nanoparticle addition inside the nanofiber layer was achieved without increasing the nanofiber diameter, and effect of NaCl addition is observed to improve nanoparticle dispersion significantly.

4.1. INTRODUCTION

Nanofibers have been used for protective applications as filter media due to their low fiber diameter, increased surface area and porosity. However, protection systems require decomposition properties in addition to filtration. As nanofibers do not have any active
functional groups along the polymer chain, they cannot be used for detoxification or decomposition of hazards. As a result, nanofiber mat, itself is not sufficient for chemical-biological protection (Ramaseshan et al, 2007).

Metal oxide nanoparticles recently take an interest in decomposition of chemical warfare agents and antibacterial applications due to their reactive edge groups, high surface area, and surface hydroxyl groups (Carnes et al, 2002) (Medine et al, 2004) (Li et al, 1992). However, current studies on nanoparticle systems focus on using only the metal oxide nanoparticle, or coating the nanofiber layer with nanoparticles. This is not feasible in terms of clothing, as nanofibers require a high surface area medium for commercial use. Nanofibers with their high surface area are a good candidate for nanoparticle loading in protective applications. In addition, with their low fiber diameter, incorporation of nanofibers enhances filtration properties, and porous structure improves breathability (Sundarrajjan and Ramakhrishna, 2013).

Incorporation of metal oxide nanoparticles to nanofiber mats is a promising approach for both chemical warfare agent detoxification and antibacterial activity (Ramaseshan R., 2006). In order to obtain desired properties, the nanoparticle concentration and distribution are main parameters (Stoimenov, 2002) (Schreuder-Gibson, 2002) (Schreuder-Gibson H., 2003).

This chapter focuses on producing metal oxide nanoparticle/nanofiber composites with uniform dispersion and high loadings. Maximum amount of nanoparticle loading uniformly
in the nanofiber layer without sacrificing particle diameter is the main objective.

4.2. EXPERIMENTS

4.2.1. Materials

The 11% PA6 polymer solution and its preparation method are previously described in Chapter 4. BASF Ultramid B27 Nylon 6 pellets with 70% Acetic acid and 30% Formic acid were continuously stirred at 80°C for 8 hours. The metal oxide nanoparticle characteristics are shown in Table 4.1.

Table 4.1. Metal oxide nanoparticle characteristics

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Particle Size</th>
<th>Form of the Particle</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>20 nm</td>
<td>dispersed in caprolactam, water and additive</td>
<td>Nanophase</td>
</tr>
<tr>
<td></td>
<td>40 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>150 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 nm</td>
<td>powder</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>15 nm</td>
<td>powder</td>
<td>Nanomaterials Inc</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>30 nm</td>
<td>powder</td>
<td>Nanophase</td>
</tr>
<tr>
<td>ZnO</td>
<td>20 nm</td>
<td>powder</td>
<td>Nanophase</td>
</tr>
</tbody>
</table>
4.2.2. In situ electrospinning of metal oxide nanoparticle / PA6 nanofiber composites

The 11% PA6 polymer solution was chosen for electrospinning due to low fiber diameter, high filtration efficiency and high quality factor compared to other composites produced in Chapter 4. All forms of nanoparticles were added to the polymer solution with 10%, 20% and 30% of polymer. Nanoparticles in caprolactam solution were added as dispersion form by calculating the amount of nanoparticle in the dispersion. The powder form nanoparticles were directly added to PA6 solution. All samples were stirred 30 minutes before electrospinning, and samples were continuously stirred during electrospinning.

Instead of the nozzle-less electrode, the vertical round electrode was used. The electrospinning conditions are kept same as PA6 spinning. 70 kV voltage and 14 cm electrospinning distance were chosen.

Required NaCl salt was added to PA6 polymer/metal oxide nanoparticle solution at the same time with nanoparticles and stirring time was again set to 30 minutes for all solutions. NaCl addition is 0-5-10% of polymer for Al₂O₃ samples, whereas, 0-10% of polymer for TiO₂, Fe₂O₃, ZnO samples.
4.2.3. Fiber diameter measurements

The SEM imaging was acquired with The JEOL 6400 is a Cold Field Emission Scanning Electron microscope with 5 kV accelerated voltage. The charging of the mat is prevented by coating the samples with Au/Pd. Image J software was used to measure nanofiber diameter and 100 measurements per sample were performed.

4.2.4. Nanoparticle dispersion analysis with Transmission Electron Microscopy

In order to analyze the dispersion of nanoparticles in nanofibers, JEOL 2000 FX TEM was used for imaging. The samples were stuck onto copper grids with superglue/acetone mixture.

4.2.5. Viscosity and conductivity measurements

Viscosities of nanofiber/nanoparticle electrospinning solutions were measured with AR 2000 cone and plate rheometer. 4 cm steel plate was used as the geometry for measurements. 3 replicates were performed for each solution.

Conductivities of the nanofiber/nanoparticle solutions were measured with Oaklon PC650 conductivity probe. Five replicates were measured for each sample.
4.2.6. Characterization of nanoparticles with energy dispersed spectroscopy (EDS)

TEM analysis is only helpful to see the dispersion of the particles. However, some samples contain NaCl particles that might be within the nanofiber structure. To decide if the particles observed are NaCl or the metal oxide nanoparticle composite mat, Energy dispersed spectroscopy (EDS) characterization was performed. The Variable Pressure Scanning Electron Microscope (VPSEM) with 5 kV accelerated voltage and backscattering was used for spectra.

4.3. RESULTS AND DISCUSSION

4.3.1. Effect of nanoparticle addition on nanofiber web formation and fiber morphology

SEM and TEM observations reveal that nanoparticle additions on PA6 nanofiber web do not affect fiber diameter and morphology significantly. Average fiber diameters of the composite fibers are between 50-60 nm even for 10-30% addition of 20 nm Al₂O₃ nanoparticles. Fiber diameters from a similar study with PSU nanofibers and MgO nanoparticles (35%) are found to be between 400-550 nm (Sundarajjan et al, 2007). Figure 4.1 demonstrate effects of 20 nm Al₂O₃ nanoparticle concentrations on fiber morphology and fiber diameter distribution. Figure 4.2 shows the average fiber diameter with addition of 20 nm Al₂O₃ nanoparticles.
Figure 4.1. 20 nm Al₂O₃ nanoparticle/PA6 nanofiber composite fibers and fiber diameter distributions
As shown in Figures 4.1 and 4.2., nanofiber diameter slightly changes with the addition of nanoparticles. The addition of nanoparticles increase the viscosity of the electrospinning solution, so higher fiber diameter is expected. Unlikely, the fiber diameters are still low, so fiber diameter advantage was remained. The effect of nanoparticle addition on electrospinning solution viscosity and conductivity is shown in Figures 4.3. and 4.4.
As shown in Figure 4.3, the viscosities of electrospinning solutions increased with addition of nanoparticles. However, the viscosities of samples with 0 and 10% of Al₂O₃ and 20 – 30% Al₂O₃ are almost same, and all four viscosities are almost same for high shear rates.
As seen on Figure 4.4., conductivities additions of nanoparticles increase the conductivity. Fiber diameters tend to decrease with increasing conductivity. As viscosity increases fiber diameter, the combined effects of viscosity and conductivity may be the reason for small fiber diameter after nanoparticle addition. In addition to 20 nm Al₂O₃ nanoparticle/nanofiber composite samples, other samples with different metal oxides show slightly change in nanofiber diameter with nanoparticle addition. This trend for other metal oxide nanoparticle/nanofiber composites is shown in Figure 4.5.
a) Effect of nanoparticle addition on Al₂O₃ nanoparticle/ PA6 nanofiber composite fibers

b) Effect of nanoparticle addition on TiO₂, ZnO, Fe₂O₃ nanoparticle/ PA6 nanofiber composite fibers

**Figure 4.5.** Change in composite fiber diameter with increase in nanoparticle loading
In general, the composite nanofiber diameters are still below 70 nm, which means that the high surface area advantage of nanofiber web is still remained.

Even though nanoparticles are observed in nanofiber web, aggregation and lack of uniform distribution of nanoparticles were major problems. The TEM images are shown in Figure 4.6.
Figure 4.6. TEM images of 20 nm Al₂O₃ nanoparticle / PA6 nanofiber composite fibers

a) 10% Al₂O₃  
b) 20% Al₂O₃  
c) 30% Al₂O₃
4.3.2. Effect of NaCl addition on nanofiber web formation and fiber morphology

As mentioned, the main problem in composite fibers is lack of uniform dispersion and aggregation of nanoparticles. In general, for all types of nanoparticles studied, there is a significant improvement in nanoparticle dispersion, and reduction on the number and size of the clusters with the increase in NaCl concentration from 5-10%. In addition, the nanoparticle dispersion at the nanofiber mat is very low without NaCl salt. 10% addition of NaCl is found to be optimum for uniform dispersion. Also, no nanoparticle aggregates is found on 10% NaCl added samples. This is the reason why 5% of NaCl addition was not used for TiO₂, ZnO and Fe₂O₃ added composite fibers. Figure 4.7 shows the change in nanoparticle dispersion with addition of NaCl salt for 20 nm Al₂O₃ nanoparticles incorporated PA6 nanofiber web.
Figure 4.7. Change in nanoparticle dispersion with NaCl for 20 nm Al₂O₃ nanoparticles dispersed in solution (30% Al₂O₃ addition)
Addition of NaCl is mentioned to reduce the fiber diameter and beads by increasing the net charge density and electrical conductivity, and decreasing the viscosity (Liu et al, 2012) (Fong et al, 1999) (Xhang et al, 2005) (Zong et al, 2002). In the case of nanofiber/nanocomposite webs, the nanofiber mats produced had almost no beads, whereas a little increase in fiber diameter was observed with the addition of NaCl which might be due to the addition of high amounts of nanoparticles.

To see the effect of NaCl addition on nanofiber diameter, SEM images, nanofiber diameters and distributions for 11% PA6, 11% PA6 with 5% NaCl and 11% PA6 with 10% NaCl samples are given in Figure 4.8. All samples are produced with same electrospinning conditions. In other words, only the electrospinning solutions have been changed among the samples.
Figure 4.8. SEM images and fiber diameter distributions of 11% PA6, 11% PA6 5% NaCl and 11% PA6 10% NaCl nanofiber webs
As mentioned earlier, Al₂O₃ nanoparticles are used in two different forms. The dispersed solution form of particles have average particle diameters of 20nm, 40nm and 150nm, and the powder form particle has 30nm average particle diameter. For TiO₂, ZnO and Fe₂O₃ incorporated fibers; only 10% NaCl was added to the solutions as the most uniform dispersion without aggregation is obtained with 10% NaCl addition. Figure 4.10 and 4.11. show the change in fiber diameter with addition of nanoparticles and 0-10% NaCl salt.
Figure 4.10. Fiber diameter results for 11% PA6 and Al₂O₃ solution with NaCl
a) Change in fiber diameter with NaCl concentration and 10-30% 20 nm Al₂O₃ nanoparticles

b) Change in fiber diameter with NaCl concentration and 10-30% 40 nm Al₂O₃ nanoparticles
c ) Change in fiber diameter with NaCl concentration and 10-30% 150 nm Al₂O₃ nanoparticles

d ) Change in fiber diameter with NaCl concentration and 10-30% 30 nm Al₂O₃ nanoparticles in powder form
Figure 4.11. Fiber diameter results for 11% PA6 and TiO$_2$, ZnO and Fe$_2$O$_3$ solutions with NaCl
a) Change in fiber diameter with NaCl concentration and 10-30% TiO$_2$ nanoparticles

b) Change in fiber diameter with NaCl concentration and 10-30% ZnO nanoparticles
c) Change in fiber diameter with NaCl concentration for 10-30% Fe$_2$O$_3$ nanoparticles
The results from nanoparticle loaded samples show a similar trend compared to the control sample and samples without NaCl. The fiber diameter of composite fibers slightly changes with addition of NaCl. This might be because of the increase in viscosity and conductivity of samples with increasing NaCl as shown in Figures 4.12 and 4.13 respectively.

Figure 4.12. Effect of NaCl addition on electrospinning solution viscosity
When the effects of NaCl and nanoparticles are compared, NaCl addition is found to be more effective on both viscosity and conductivity than Al\textsubscript{2}O\textsubscript{3} nanoparticles. Increase in conductivity with NaCl is expected. In current literature, as mentioned, NaCl is reported to increase conductivity and reduce the viscosity (Fong et al, 1999). Unlikely, viscosity increases with the addition of NaCl.
4.3.3. Energy dispersed spectroscopy (EDS) analysis of composite nanofibers

TEM images reveal that there were particles are formed through the composite nanofiber mat, but, to confirm the nanoparticle and NaCl existence in the composite fibers, EDS analysis of the mats are performed with Scanning Electron Microscope. Figure 4.14. shows an example EDS result for each nanoparticle type. Detailed results are given in Appendix section.
**Figure 4.14.** Energy dispersed spectroscopy graphs for each nanoparticle type
a) EDS graph of 11% PA6 nanofiber with 30% Al₂O₃ nanoparticle and 10% NaCl

b) EDS graph of 11% PA6 nanofiber with 30% TiO₂ nanoparticle and 10% NaCl
c) EDS graph of 11% PA6 nanofiber with 30% ZnO nanoparticle and 10% NaCl

d) EDS graph of 11% PA6 nanofiber with 30% Fe$_2$O$_3$ nanoparticle and 10% NaCl
For all nanoparticle/nanofiber composite fibers, the metal and oxygen atoms are recognizable. Also, the fibers contain some of Na\textsuperscript{+} and Cl\textsuperscript{−} ions due to the addition of NaCl. The carbon atoms came from the background and gold and palladiums are the coatings on the nanofiber surface. This EDS images are proof of the nanoparticle formation inside the nanofibers.

4.4. CONCLUSIONS

To form a chemical-biological protective layer, functional nanocomposites are produced with PA6 nanofiber and Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, ZnO metal oxide nanoparticles by single step electrospinning. In the literature up to 10% of nanoparticles is added to nanofibers, however in this study nanofiber loadings up to 30% are achieved with all particle types. Nanoparticle dispersion is controlled with addition of NaCl, and uniform dispersed nanofibers are obtained with 10% NaCl addition to the solutions. It is found that the nanoparticle addition increases nanofiber diameter by increasing the viscosity. However, nanofiber diameters are still lower than 100 nm. In the literature, electrospun nanofibers are over 100 nm without any functional groups, so obtaining a functional composite web below 80 nm average fiber diameter is a significant improvement. In addition, increased filtration and protection performance gained by Nylon 6 nanofibers is still remained with this small fiber diameter.
REFERENCES


CHAPTER 5: EVALUATION OF FUNCTIONAL PROPERTIES OF NANOFIBER/NANOPARTICLE COMPOSITES

Abstract

To investigate the photocatalytic detoxification of Acid orange dye with metal oxide nanoparticle/PA6 nanofiber composites, samples were exposed to 350 nm UVa light for 24 hours. Discoloration of acid orange dye with nanofiber/nanoparticle composites have been analyzed with UV spectra. It is observed that use of ZnO and TiO$_2$ improves the photocatalytic reaction whereas, Fe$_2$O$_3$ and Al$_2$O$_3$ are found to be less effective against acid orange dye for particle sizes over 30 nm. However, decreasing the particle size of Al$_2$O$_3$ improves the photocatalytic activity, so particle size must be controlled to optimize photocatalytic properties.

5.1. INTRODUCTION

Use of metal oxides for detoxification is a recent development in protective applications. Powder form of metal oxide nanoparticles are commonly used for detoxification of warfare
agents, discoloration of dyes, antibacterial activity..etc. because of their high adsorption capability per unit surface and high amount of reactive groups on the surface. Along with the chemical structure, particle size affects the photocatalytic activity. Photochemical reactions occur on the surface of the particle, so increasing the surface area increases the photocatalytic properties (Linsebigler et al, 1995) (Burda et al, 2005). Thus, diminishing particle size and controlling the shape of the nanoparticles are major concerns (Niederberger and Garnweitner, 2006). The crystal structure of the nanoparticle is also a major parameter for surface reactivity. As an example, anatase form of TiO$_2$ showed better photocatalytic activity then rutile phase (Linsebigler et al, 1995) (Augustynski, 1993).

Up to date, functional properties such as decomposition of dyes, chemical warfare agent detoxification, self-cleaning properties, and antibacterial activity of metal oxide nanoparticles have been addressed by various researchers (Sundarrajjan and Ramakhrishna, 2013). However, as metal oxide nanoparticles cannot be used alone for clothing, there is a need for high surface area medium to hold those particles. Current efforts on detoxifying materials are on incorporating metal oxide nanoparticles on nanofibers. Single step electrospinning, which is done by mixing metal oxide with polymer solution reported to be ineffective because metal oxide nanoparticle surface was covered by polymer (Sundarrajjan and Ramakhrishna, 2013). Thus, electrospraying nanoparticles on the top of the nanofibers at a time or one by one are being studied. As the nanoparticles are on the top of the nanofibers, electrospraying
technique is found to be effective against nerve and mustard agent stimulants (Sundarraian, 2007) (Vitchuli N, 2011).

Various forms and compositions of metal oxide nanoparticles have also been reported to have photocatalytic activities against different dyes. Particles such as TiO₂, ZnO, MgO, Fe₂O₃, Al₂O₃ are reported to decompose dyes with different rates depending on their particle size and crystal structure. Especially TiO₂ is mostly used in many studies to add self-cleaning nature to the systems (Sundarrajjan and Ramakhrishna, 2013).

This chapter addresses decomposition of acid orange dyes by TiO₂, ZnO, Fe₂O₃, Al₂O₃ nanoparticle/PA6 nanofiber composites. The effect of metal oxide type, particle size and distribution of particles on nanofiber web is addressed.

5.2. EXPERIMENTS

5.2.1. Materials

Metal oxide nanoparticle and PA6 solution preparation, and electrospinning procedure of the composite webs are described in Chapter 4. in detail. TiO₂, ZnO, Fe₂O₃, Al₂O₃ nanoparticles were mixed with 11% PA6 by weight electrospinning solution (70% acetic acid – 30% formic acid as solvents). Metal oxide nanoparticles were added between 10-30% of PA6 by weight. To control distribution of the nanoparticles, up to 10% NaCl was also added to the
solution. Electrospinning was performed with constant conditions of 70 kV and 15 inches electrode to collector distance.

5.2.2. Photocatalytic activity measurements

For the decomposition test, 400 mg/L of Tiglon Acid Orange dye solution was used. 20 mg nanofiber composite sample was added to 20 ml of dye solution and composite nanofibers were exposed to UVa (350 nm wavelength) for 24 hours. Luzchem photoreactor with 4.2 mW/cm² light intensity is used for UVa exposure. After UVa exposure, nanofibers are filtered out and UV spectra of the remained solution are measured. For the comparison, UV spectra of acid orange dye that was used in the study was analyzed. Figure 5.1. shows the chemical structure of acid dye and Figure 5.2. shows the UV curve and chemical structure of the acid orange dye.

![Chemical structure of acid orange dye](image)

**Figure 5.1.** Chemical structure of acid orange dye (M Stylidi et al, 2004)
As can be seen from the Figure 5.2., there are three identical peaks for the acid orange dye. The first one is benzene ring (228 nm), the second one is naphthalene ring (310 nm), and the
third one is azo linkage (485 nm). The main discoloration reaction occurs on azo linkage. The chemical reaction for decomposition is described by M. Stylidi et al. previously (M Stylidi et al, 2004).

The rate of discoloration is calculated by:

\[
\text{Discoloration rate (\%)} = \frac{(A_0 - A_1)}{A_0} \times 100
\]

Where, \(A_0\): Absorbance at 485 nm of acid orange dye solution
\(A_1\): Absorbance of remained dye solution after UV exposure with functional composite nanofibers

5.3. RESULTS AND DISCUSSION

5.3.1. Effect of nanoparticle type on photocatalytic activity of nanofiber/nanoparticle composites

To compare effect of each nanoparticle, samples with same amount of metal oxide nanoparticle (30% of PA6 by weight) and uniform dispersion (10% NaCl) were prepared. The images of the remained dye solution after UVa exposure is shown in Figure 5.3.
Acid orange dye solution

After UVa exposure with PA6

After UVa exposure with TiO₂

After UVa exposure with ZnO

After UVa exposure with Al₂O₃

After UVa exposure with Fe₂O₃

**Figure 5.3.** Dye solutions before and after UVa exposure with composite nanofibers
For Al₂O₃ samples, only the composite with 20 nm Al₂O₃ nanoparticle loading is added in the images and Figure 5.4. as that composite provides highest reactive surface. The discoloration reaction is clearly visible in the images. There is high discoloration by functional composite fibers with TiO₂ and ZnO whereas, Al₂O₃ and Fe₂O₃ incorporated nanofibers are not as effective as others. To see the changes in absorbance, UV spectra of each solution is analyzed. The UV spectra obtained from the samples are shown in Figure 5.4.

![Figure 5.4. Effect of metal oxide type on discoloration of acid orange dye](image-url)
PA6 sample absorbs some dye which caused reduction in the peaks. TiO$_2$ and ZnO incorporated nanofibers had almost no absorbance for all three peaks which proved a complete discoloration of acid orange dye. This discoloration reaction was in agreement with previous study by M.Stylidi et al for pure nanoparticles (M Stylidi et al, 2004). However, Fe$_2$O$_3$ and Al$_2$O$_3$ samples has little change compared to PA6. This means that Fe$_2$O$_3$, Al$_2$O$_3$ did not have photocatalytic properties as good as TiO$_2$ and ZnO against acid orange dye.

5.3.2. Effect of nanoparticle concentration on photocatalytic activity of nanofiber/nanoparticle composites

As seen in the previous section, high loading of nanoparticles (30% of polymer) proves the decomposition of acid orange dye with nanofiber/nanoparticle composites. To see discoloration depending on the particle concentration, 10-20-30% (of polymer) metal oxide loaded samples has been compared. For uniform dispersion 10% NaCl was added to all samples. The UV spectra of TiO$_2$ loaded samples are given in Figure 5.4. Other metal oxide nanoparticle/PA6 nanofiber composites have the same trends and their UV spectra are given in Appendix C.
Figure 5.5. Effect of metal oxide concentration on discoloration of acid orange dye

As can be seen from Figure 5.5., increasing the amount of TiO$_2$, increases the discoloration reaction. This is in agreement with the fact that discoloration increases with surface area. As there are more nanoparticles in samples with 30% TiO$_2$, total surface area is higher, the number of reactive groups is higher, and there is more bonding between dye molecule and metal oxide nanoparticle. This is in agreement with study of Zlamal et al (Zlámal et al, 2009).
5.3.3. Effect of nanoparticle dispersion on photocatalytic activity of nanofiber/nanoparticle composites

As mentioned in Chapter 4., addition of 10% NaCl reduces aggregation and clustering, and improves uniform dispersion of nanoparticles. Samples with and without NaCl had been compared to analyze the effect of dispersion of nanoparticles. Both samples contain 30% TiO₂ by weight (of polymer) and UV spectra are shown on Figure 5.6. UV spectra’s for other metal oxides are shown in Appendix C.

![UV spectra](image)

**Figure 5.6.** Effect of nanoparticle dispersion on discoloration of acid orange dye
Uniformly dispersed particles has improved photocatalytic activity compared to samples without NaCl. Electrospinning metal oxide powders with polymers were reported to have no surface for photocatalytic applications previously by Sundarajjan et al, however, in this system with 30% addition of TiO₂ even without NaCl, the system has high photocatalytic properties against acid orange dye (Sundarrajjan and Ramakhrishna, 2013). This relationship can be seen from Figure 5.7.

**Figure 5.7.** Effect of metal oxide and NaCl concentrations on discoloration rate of acid orange dye
From Figure 5.7., it is obvious that discoloration increased with higher metal oxide and NaCl content. Unlike the literature, as an advantage, there is still high discoloration rate (around 85%) even with only adding the nanoparticle in the solution.

5.3.4. Effect of nanoparticle size on photocatalytic activity of nanofiber/nanoparticle composites

To see the effect of particle size on photocatalytic activity, Al₂O₃ with various particle sizes incorporated samples are compared in Figure 5.8.
It is obvious from Figure 5.8. that lower particle size lead to high discoloration. This is because of the high surface area, and more reactive groups on the total surface. This result is in agreement with previous study by Dodd et al and Zlamal et al. for nanoparticle powders (Dodd et al, 2006) (Zlámal et al, 2009). When the discoloration rates are compared as in Figure 5.9., it is obvious that higher discoloration occurs with reduction of nanoparticle diameters. As mentioned earlier, there are more reactive edge groups on the high surface area.
provided by low nanoparticle size. The discoloration rates for all nanoparticle sizes for 30% metal oxide and 10% NaCl is given in Figure 5.8. Even though particle size is larger, ZnO has the same discoloration rate with TiO$_2$.

**Figure 5.9.** Effect of particle size on discoloration rate of acid orange dye
5.4. CONCLUSIONS

Photocatalytic activity of nanofiber/metal oxide nanoparticle composites with different metal oxide concentrations, metal oxide types, particle sizes and dispersions are compared to analyze the effect of chemical structure and particle size. It is found that photocatalytic activity increases with decreasing particle size, increasing the particle concentration and changing the particle structure. This is expected as all of them is related to increased amount of reactive groups in high surface area. Particle dispersion is not as effective as other parameters. There is slightly improvement in photocatalytic activity for high particle concentrations. Hence, the parameters that are controlling the reaction are found to be; surface area and chemical structure of the surface rather than dispersion.
REFERENCES


CHAPTER 6: OVERALL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1. OVERALL CONCLUSIONS

This research focuses on improving current protective systems with functional nanofiber/metal oxide nanoparticle composites. PA6 nanofiber/metal oxide nanoparticle composite fibers are produced with in-situ electrospinning system for protective applications. Main conclusions include:

- Polymer concentration in the electrospinning process increases the viscosity, thus the fiber diameter. PA6 nanofiber diameters can be reduced down to 41 nm by changing the electrospinning conditions.
- Nanofiber basis weight can be controlled with fabric speed. Increase in fabric speed reduces the basis weight of nanofibers.
- Due to their high surface area, nanofibers have high filtration efficiency. The lower the nanofiber diameter, the higher the filtration efficiency is. Even though the filtration efficiency is high for small fibers, the quality factor can be low because of their high pressure drop. Optimization of filtration efficiency and pressure drop is significant to choose the proper barrier material.
• Air permeability defines the comfort for barrier properties. It is observed that fabric speed thus basis weight is more effective than fiber diameter in permeability. Low basis weight samples are highly permeable for all nanofiber webs.

• Composite nanofibers with up to 30% metal oxide nanoparticles were obtained. Uniform metal oxide nanoparticle distribution without aggregatation is observed with addition of NaCl salt in electrospinning solution for different metal oxide nanoparticles. The increase in NaCl concentration results as better dispersion of nanoparticles.

• Even though there is high amount of nanoparticles in nanofiber web, the average fiber diameter did not increase significantly. Depending on the nanoparticle concentration, webs with 45-95 nm average fiber diameters are observed.

• Addition of nanoparticles and NaCl increases the viscosity and conductivity of the solutions as expected. NaCl addition is found to be more effective on both viscosity and conductivity compared to nanoparticle addition.

• All nanoparticle/nanofiber composites are found to be effective against acid orange dye after 24 hour UVa exposure. TiO$_2$ and ZnO have better photocatalytic properties than Al$_2$O$_3$ and Fe$_2$O$_3$. Photocatalytic activity is found to be depended on chemical structure of the particle, particle concentration and particle size. Increase in nanoparticle concentration and decrease in particle size leads to high surface area and more reactive edge groups, so there is more photocatalytic activity.
6.2. RECOMMENDATIONS FOR FUTURE WORK

- Composite nanofiber/woven fabric adhesion can be studied for product development
- Studies for improving durability can be carried out
- Addition of nanoparticles may change barrier properties as well as comfort properties. Study of these properties can be carried out for the final composite structure.
- Fundamental study polymer/nanoparticle interface for uniform nanoparticle dispersion can be carried out to analyze effect of additives on the structure
- This study focuses on the use of in situ electrospinned nanofiber/nanoparticle composites for protective application. These fibers can be implemented to other applications such as tissue engineering, sensors…
APPENDIX A : SEM and TEM images and fiber diameter distribution graphs of nanofiber/nanoparticle composite fibers

SEM images and fiber diameter distribution graphs

- 20 nm Al₂O₃ (dispersed in solution) incorporated samples
  - 11% PA6 10% Al₂O₃ NO NaCl
  - 11% PA6 10% Al₂O₃ 5% NaCl
- 11% PA6 10% Al₂O₃ 10% NaCl

- 11% PA6 20% Al₂O₃ NO NaCl

- 11% PA6 20% Al₂O₃ 5% NaCl
- 11% PA6 20% Al₂O₃ 10% NaCl

- 11% PA6 30% Al₂O₃ NO NaCl

- 11% PA6 30% Al₂O₃ 5% NaCl
- 11% PA6 30% Al₂O₃ 10% NaCl

- 40 nm Al₂O₃ (dispersed in solution) incorporated samples
  - 11% PA6 10% Al₂O₃ NO NaCl
  - 11% PA6 10% Al₂O₃ 5% NaCl
- 11% PA6 10% Al₂O₃ 10% NaCl

- 11% PA6 20% Al₂O₃ NO NaCl

- 11% PA6 20% Al₂O₃ 5% NaCl
- 11% PA6 20% Al₂O₃ 10% NaCl

- 11% PA6 30% Al₂O₃ NO NaCl

- 11% PA6 30% Al₂O₃ 5% NaCl
- 11% PA6 30% Al₂O₃ 10% NaCl

- 150 nm Al₂O₃ (dispersed in solution) incorporated samples
  - 11% PA6 10% Al₂O₃ NO NaCl
  - 11% PA6 10% Al₂O₃ 5% NaCl
- 11% PA6 10% Al₂O₃ 10% NaCl

- 11% PA6 20% Al₂O₃ NO NaCl

- 11% PA6 20% Al₂O₃ 5% NaCl
- 11% PA6 20% Al₂O₃ 10% NaCl

- 11% PA6 30% Al₂O₃ NO NaCl

- 11% PA6 30% Al₂O₃ 5% NaCl
- 11% PA6 30% Al₂O₃ 10% NaCl

- 30 nm Al₂O₃ (powder) incorporated samples
  - 11% PA6 10% Al₂O₃ NO NaCl
  - 11% PA6 10% Al₂O₃ 5% NaCl
- 11% PA6 10% Al₂O₃ 10% NaCl

- 11% PA6 20% Al₂O₃ NO NaCl

- 11% PA6 20% Al₂O₃ 5% NaCl
- 11% PA6 20% Al₂O₃ 10% NaCl

![Image of sample 1]

- 11% PA6 30% Al₂O₃ NO NaCl

![Image of sample 2]

- 11% PA6 30% Al₂O₃ 5% NaCl

![Image of sample 3]
- 11% PA6 30% Al<sub>2</sub>O<sub>3</sub> 10% NaCl

- TiO<sub>2</sub> incorporated samples
  - 11% PA6 10% TiO<sub>2</sub> NO NaCl
  - 11% PA6 10% TiO<sub>2</sub> 10% NaCl
- 11% PA6 20% TiO₂ NO NaCl

- 11% PA6 20% TiO₂ 10% NaCl

- 11% PA6 30% TiO₂ NO NaCl
- 11% PA6 30% TiO₂ 10% NaCl

- ZnO incorporated samples
  - 11% PA6 10% ZnO NO NaCl
  - 11% PA6 10% ZnO 10% NaCl
- 11% PA6 20% ZnO NO NaCl

- 11% PA6 20% ZnO 10% NaCl

- 11% PA6 30% ZnO NO NaCl
- 11% PA6 30% ZnO 10% NaCl

- Fe$_2$O$_3$ incorporated samples
  - 11% PA6 10% Fe$_2$O$_3$ NO NaCl
  - 11% PA6 10% Fe$_2$O$_3$ 10% NaCl
- 11% PA6 20% Fe$_2$O$_3$ NO NaCl

- 11% PA6 20% Fe$_2$O$_3$ 10% NaCl

- 11% PA6 30% Fe$_2$O$_3$ NO NaCl
- 11% PA6 30% Fe₂O₃ 10% NaCl
TEM images

- Al$_2$O$_3$ incorporated samples
  - 11% PA6 10% Al$_2$O$_3$ NO NaCl
    - 20 nm
    - 40 nm
    - 150 nm
    - 30 nm powder

- 11% PA6 10% Al$_2$O$_3$ 5% NaCl
  - 20 nm
  - 40 nm
  - 150 nm
  - 30 nm powder
11% PA6 10% Al₂O₃ 10% NaCl

20 nm      40 nm      150 nm      30 nm powder

○ 11% PA6 20% Al₂O₃ NO NaCl

20 nm      40 nm      150 nm      30 nm powder

○ 11% PA6 20% Al₂O₃ 10% NaCl

20 nm      40 nm      30 nm powder
- 11% PA6 30% Al₂O₃ NO NaCl

20 nm                              40 nm                              150 nm                              30 nm powder

- 11% PA6 30% Al₂O₃ 5% NaCl

20 nm                              40 nm                              150 nm                              30 nm powder

- 11% PA6 30% Al₂O₃ 10% NaCl

20 nm                              40 nm                              150 nm                              30 nm powder
• Other metal oxides incorporated samples

  o 11% PA6 10% metal oxide  NO NaCl

    TiO₂                                      ZnO

  o 11% PA6 10% metal oxide  10% NaCl

    TiO₂                                      ZnO                                      Fe₂O₃
- 11% PA6 20% metal oxide 10% NaCl
  
  TiO₂  ZnO  Fe₂O₃

- 1% PA6 30% metal oxide NO NaCl
  
  TiO₂  ZnO

- 11% PA6 30% metal oxide 10% NaCl
  
  TiO₂  ZnO  Fe₂O₃
APPENDIX B : EDS results

- 11% PA6 30% NaCl

- 11% PA6 10% NaCl 30% 20 nm Al₂O₃ (dispersed in solution)
○ 11% PA6 10% NaCl 30% 40 nm Al₂O₃ (dispersed in solution)

○ 11% PA6 10% NaCl 30% 150 nm Al₂O₃ (dispersed in solution)
- 11% PA6 10% NaCl 30% 30 nm Al₂O₃ (powder)

![X-ray spectrum of Al₂O₃ sample](image1)

- 11% PA6 10% NaCl 30% TiO₂

![X-ray spectrum of TiO₂ sample](image2)
- 11% PA6 10% NaCl 30% ZnO

- 11% PA6 10% NaCl 30% Fe₂O₃
APPENDIX C : Photocatalytic activity results

Effect of ZnO concentration on discoloration of acid orange dye
Effect of ZnO distribution on discoloration of acid orange dye

![Graph showing absorbance over wavelength for different samples: Acid orange dye, 10% NaCl & 30% ZnO, NO NaCl & 30% ZnO.](image)