ABSTRACT

KIM, JOOYOUN. Investigation on charge deterioration of electrically charged filter media using Electric Force Microscopy. (Under the direction of Dr. Roger L. Barker and Dr. Juan Hinestroza)

Electret filter media is widely used in filtration application as the presence of embedded electrostatic charges allows for better particle capture efficiency with lower pressure drop.

The effect of exposure to organic solvents on filtration performance of electret filter media was investigated using several different organic solvents and electret filter media. The exposure of electret filter media to liquid organic solvents caused a decrease in filtration performance without significant changes in resistance. It is hypothesized that the lowered performance of the electret filter media is due to the changes in electric field caused by the liquid organic solvents or to morphological changes.

Scanning Electron Microscopy (SEM) was used to examine any observable morphological changes in the fibers after exposure to liquid organic solvents. There were no observable changes in morphology of fibers, suggesting the performance deterioration by chemical exposure was not caused by morphological changes in fibers. Electric Force Microscopy (EFM) was used to analyze the electric field of electret filter media prior to and after exposure to organic liquid solvents. Changes in the electric field were detected and quantified. Electric field gradient imaging (EFGI) by phase and frequency detection was shown to be a feasible method for the analysis of charge deterioration in electret filtration media.
Two mathematical models based on electrostatics fundamentals were used to explain the behavior of EFM experimental data. Model I accounted for both a coulombic force and induced polarization phenomena. Model II incorporates a capacitance term. Both models exhibited good quantitative agreement with the experimental data hence the performance deterioration of the electret filter media after chemical immersion was proven to be directly related to changes in the electric field of the sample.
INVESTIGATION ON CHARGE DETERIORATION OF ELECTRICALLY CHARGED FILTER MEDIA USING ELECTRIC FORCE MICROSCOPY

by

JOOYOUN KIM

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

FIBER AND POLYMERS SCIENCE

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APPROVED BY:

Dr. Warren Jasper
Member of Advisory Committee

Dr. Saad Khan
Member of Advisory Committee

Dr. Roger Barker
Co-Chair of Advisory Committee

Dr. Juan Hinestroza
Co-Chair of Advisory Committee
BIOGRAPHY

Jooyoun Kim was born in Gwangju, Korea on May 12, 1973. She received her B.S. and M.S. in Clothing and Textiles in Seoul National University, 1996 and 1999 respectively. She joined the Ph.D. program in Fiber and Polymer Science at North Carolina State University, studying under the guidance of Dr. Roger L. Barker and Dr. Juan Hinestroza.
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CHAPTER 1. INTRODUCTION

Electret filter media is widely used in filtration applications specifically in personal respiratory masks. The presence of embedded electrostatic charges allows for a better particle capture efficiency and lower pressure drops which translates in increased protection and comfort to the user. Electrostatic charge is imposed to polymeric filter media in order to improve their filtration efficiency by adding a electrostatic attraction particle capture mechanism [1-3]. Understanding changes in the performance behavior of electret filter media in scenarios where it can be possibly exposed to organic solvents is of utmost importance as the user may be inadvertently overexposed toxic organic particulates or gaseous matter. Experimental work [4-10] have provided the evidence of performance deterioration in electret filtration media when exposed to organic solvents. However, a systematic analytical understanding of the degradation mechanism is not yet available.

The purpose of this research project is to validate the hypothesis that electrostatic charge degradation plays a major role in the decrease in filtration performance of electret filter media when these materials are exposed to organic chemicals.
This is a highly experimental research and it was carried out in several phases: During phase I, the effect of exposure to organic solvents on filtration performance of electret filter media was investigated. The effect of exposure to the vapor phase as well as the liquid phase of organic solvents on the electret filter media was examined using a custom made experimental setup. During Phase II, Scanning Electron Microscopy (SEM) analysis was carried out to examine any morphological changes in the fibers after exposure to liquid organic solvents. In Phase III, Electric Force Microscopy (EFM) was used to analyze the electric field of electret filter media prior to and after exposure to organic liquid solvents.

The novelty of this research relies on the implementation of scanning probe microscopy techniques (AFM and EFM) to probe the electrostatic field of electret filter media. The expected results of this study may provide a new insight to electret filter media manufacturers and government regulatory agencies on determining the appropriate environments for the safe use of these materials in personal respiratory protection equipment.
CHAPTER 2. REVIEW OF LITERATURE

2.1. Electrically charged filtration media

2.1.1. Filtration media

A fibrous filter consists of loosely packed fibers with preferred orientation across the direction of gas flow. The ratio of the total volume of all the fibers in a filter to the volume of the filter, termed the packing density, is known to be in the range of 1-15%. The low pressure drop across a fibrous filter is the result of the low packing density. Materials used as filter media include glass, polypropylene, polycarbonate, ceramic, and stainless steel, some of which can be used in high temperature filtration [11].

Airborne particles with less than 7 µm in diameter are considered hazardous as they are insoluble in body fluids. Such particles can reach respiratory organs such as lungs and alveoli. Larger particles are of less concern as they usually settle out in the upper respiratory tract, from where normal lung clearance mechanisms remove them. Therefore, personal protection equipment against dust such as respirator masks is aimed at the removal of particles within this size smaller than 7 µm [1, 2].
The capture of relatively large particles (larger than 1 µm) is carried out mainly by an interception mechanism. During interception particles are carried by the streamlines of the air passing through a filter. The particles are captured by direct contact with a fiber as they pass through. The capture efficiency of particles using the interception mechanism is not high [1]. The demand for high-efficiency filters which remove submicron particles from polluted environment has led to the development of electret filters [12]. By imposing electrostatic charge to fibrous filter media, the filtration efficiency can be improved due to the added particle capture mechanism: electrostatic attraction. Electrostatic forces have shown to improve the capture of both charged and neutral particles. A charged fiber will attract oppositely charged particles by Coulombic forces, but it will also capture neutral particles by the action of induced polarization [1-3].

2.1.2. Electret charging

Two charging methods, corona charging and tribo charging, are commonly used to produce electrostatic domains in polymeric fibers. Tribo charging is the process of creating static electrical charges on a material by blending fibers that have different electronegativities. On a macroscopic level, the charge on the materials is low for these types of materials, but they exhibit a balance between positive and negative electric charges [1]. Triboelectric series of textile yarns are provided and shown in Table 2.1.1 [13]. Tribocharged filter media are generally composed of large diameter fibers. The material is generally thick and fluffy compared to fiber glass and has a much lower pressure drop at any given penetration level [14].
Table 2.1.1. Triboelectric series of textile yarns [13].

<table>
<thead>
<tr>
<th>Positive</th>
<th>Modacrylic</th>
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<tbody>
<tr>
<td>Wool</td>
<td>Cotton</td>
</tr>
<tr>
<td>Nylon66</td>
<td>Polyvinyl alcohol</td>
</tr>
<tr>
<td>Nylon6</td>
<td>Cellulose triacetate</td>
</tr>
<tr>
<td>Silk</td>
<td>Acrylic</td>
</tr>
<tr>
<td>Regenerated cellulose</td>
<td>Cellulose diacetate</td>
</tr>
<tr>
<td>Cotton</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>Cellulose triacetate</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Acrylic</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>Cellulose diacetate</td>
<td>Poly(butylenes terephthalate)</td>
</tr>
</tbody>
</table>

The other commonly used charging method is corona charging. During corona charging a static electric charge is induced in the material by placing the sample through an electrostatic field generated by a high voltage device. Electric charges are then placed on a polymer by means of a corona discharge. A point electrode at a high potential emits ions of...
its own sign, and if the material surface is insulating, a charge would develop [1, 15].

The electret charge may consist of surface charge layers (space charges) or polarization. Surface charges comprise layers of trapped positive and negative carriers, often positioned at or near the two surface of the dielectric material. The polarization is usually a frozen-in alignment of dipoles. The electret charges may also consist of carriers displaced within molecular or domain structures throughout the solid, resembling a dipole polarization [12].

Methods for forming space-charge (surface charge) electrets and dipolar electrets differ frequently. The charging of space-charge electrets is mostly achieved by injecting (or depositing) charge carriers by discharges, particle beams, contact electrification, or other techniques through a non-metallized surface [16].

Dipolar electrets are generally polarized by application of an electric field to the material at room temperature or temperatures decreasing from a properly selected higher to a lower value. Dipolar orientation, achieved by corona charging, is caused by the field of the deposited charges [16].

Thermal charging methods of electret charging consist in the application of an electric field to a dielectric at an elevated temperature and subsequent cooling while the field is still applied. In thermal charging, three phenomena can occur: 1) internal polarization with the sign of a heterocharge due to dipole alignment or charge separation within the dielectric, 2) homocharge deposition due to spark discharges in the air gaps, 3) homocharge injection through contacting electrodes. Dipole alignment occurs at elevated temperatures where the molecules or molecular chains are sufficiently mobile. Upon cooling, the aligned dipoles are controlled [16]. However, the heterocharge can be compensated by the homocharge injection caused by the spray discharge, therefore the final homocharge becoming larger if a
dielectric insert is placed in the air gap [16].

The isothermal charge-deposition methods depend on charge transfer due to a discharge in an air gap. In this method, heating is not applied, and heterocharge effects are generally absent. The field is generated by application of a voltage between a point shaped upper electrode placed at a certain distance from one side of the dielectric and a planar back electrode on the other side. Distribution of the deposited charge is generally uniform if the charging is carried to the point of saturation where the potential of sample surface equals the grid potential [16].

2.1.3. Charge retention ability

Tsai et al. [17] investigated charge retention of corona charged meltblown (fiber diameter = 2 µm) and spunbonded nonwovens, corona and tribo charged needle punched felts (fiber diameter = 25 µm), and electrospun nonwoven material, at temperatures from 60 °C to 130°C. They reported that the meltblown samples exhibit better charge retention ability than needle punched felts due to their smaller diameter and less porous structure. These experiments were performed using a custom-built surface potential scanning system. However, these measurements had a coefficient of variation about 50 %, making it difficult to interpret the data [17]. According to this study, charge retention ability was dependent of the electrical properties of material, including conductivity and dielectric constant of the polymers, rather than the charging techniques. The fiber diameter and media structure were also important factors for charge retention [17].

In addition, surface resistivity has been reported to influence the charging efficiency and charge decay rate of electret filtration media [18]. Polymers of higher surface resistivity were found to exhibit improved charging and charge retention abilities [18-20].
For example, it was determined that paper, polyamide and glass fibers, because of their low surface resistivities, did not easily accept charges or hold electrical charges. Polyethylene terephthalate (PET) showed higher charge decay rates than polypropylene (PP). The difference was attributed to the higher moisture content of PET making it more conductive than PP. In addition, PP treated with hydrophilic additives or hydrophilic surfactants exhibited high filtration efficiency but low charge retention ability. This behavior was explained by arguing that PP treated with hydrophilic additives or surfactants could accept charges due to its electrically resistive nature, but the presence of additives or surfactants carried the stored charges away from the PP due to their electrically conductive nature [18].

Mishra [19, 21, 22] investigated factors governing electret stabilities. The most influential factors for stabilities of polyolefin electrets were found to be followings: 1) a high value of resistivity, 2) a high degree of crystallinity, 3) presence of suitable chemical groups acting as trap sites. Molecular chains and groups were considered as sites where the charged particles could be trapped, and it was discussed that the onset of thermally activated motions would tend to dislodge the charges [19].

Arita et al. [23] visualized charge trapping sites in charged PP film using Sudan blue. Their experiments showed that dye particles adhered to the PP surface not randomly but in line along radial directions from the center of a spherulite. This distribution pattern of the adhered dye particles strongly suggested that charge trapping sites exist along a fibrous structure that has radially grown from the center of the spherulite. This explanation is well consistent with the fact that fibrils grow radially from a spherulitic nucleus, branching and creating more fibrils at greater radial distances. This expansion introduces many crystalline defects at the branches, some of which may act as charge trapping sites [23].
Arita et al. [23] assumed that the charges trapped in the amorphous part of the polymer would be affected by the transport of penetrants like organic solvent. Organic solvent molecules act as plasticizer enhancing molecular motions in the amorphous parts in the polymer. As a result, the charge trapping sites in these sections of the polymer would be selectively destroyed. This was validated when dye particles were not shown in peripheral regions of the spherulites after the PP samples were exposed to saturated acetone vapor at room temperature. This work showed that shallow traps preferentially existed in the amorphous regions while the deep traps existed in the crystalline regions at the central parts of the spherulites. Images from Arita et al. are shown in Figure 2.1.1 [23].

![Figure 2.1.1. Visualized image of charged areas for PP before (a), and after (b) acetone vapor exposure [23].](image)

Ikezaki et al. [24] also visualized the lateral charge distribution of spherulitic PP with dye deposited on a transparent indium tin oxide (ITO) electrode. For positive corona charged PP, it was directly seen that charges with lower release energy (TSC peak around 70°C) were trapped in the peripheral and boundary parts while the charges with higher
release energy (TSC peak at higher temperature) were trapped in the central region of the spherulites [24].

### 2.2. Particle capture mechanisms

One of the most important parameters in particle capture is particle size. The main capture mechanisms are shown schematically in the Figure 2.2.1. The filter media is represented by a single fiber and the curved lines represent air streamlines as the aerosol passes through the filter [25].

![Figure 2.2.1. Particle capture mechanisms in air filter media [25].](image)

The primary capture mechanisms of air filtration are diffusion, interception, and inertial impactions. Diffusion is the random Brownian motion of small particles caused from collisions with gas molecules. During diffusion, the particles do not follow the air streams, and their erratic movement causes them to be in contact with the filter fibers. This is the most important mechanism for the smallest particles. Interception is the physical
interference between the particles and the fibers as the particle passes by. If a particle travels with the flow stream and the streamline passes close enough to the fiber so that the particle and the fiber touch, the particle will be captured. Interception is relevant for medium to large sized particles. Inertial impaction results when the particle’s momentum causes it to deviate from the air flow stream and collide with the filter fiber. Inertial impaction depends on the diameter and density of the particle, and it is of relevance during the capture of larger particles [25].

Gravitational settling is generally small compared with other filtration mechanisms, and normally ignored in the modeling, except when aerosol size is extremely large and/or face velocity is unusually slow [5]. Application of electrostatic forces can significantly increase the collection efficiency of a fibrous filter. This was reported to be particularly useful for improving the collection of particles in the size range of 0.15-0.5 \( \mu \)m, which are difficult to capture by other mechanisms [11].
Figure 2.2.2. Particle capture mechanisms: typical fractional penetration curve for filter media [26].

The combined effects of diffusion, interception, and impaction leads to a filter penetration curve similar to what is illustrated in Figure 2.2.2. The exact shape of the curve and the magnitude of the penetration will depend on the filter media characteristics and airflow velocity. The peak in the penetration curve is referred to as the MPPS (Most penetrating particle size). The most penetrating particle size (MPPS) is known to be a function of the charge state of the filter media and particles [27], being typically between 0.1 µm and 0.3 µm for mechanical filters [26]. In terms of particle charge state, MPPS was reported to be in the typical 0.3 µm range for charged particles and close to 0.1 µm for neutral particles. The combination of these two mechanisms leads to an overall filter penetration curve with low penetration at the smallest particle sizes. The curve then
increases until the MPPS is reached and then decreases as particle size increases [27].

During diffusion and electrostatic attraction regimes, which are the dominant filtration mechanisms for the submicrometer sized particles, the face velocity becomes important as it determines the retention time for the aerosol particles and fibers to interact [1, 5, 28-30]. Interception is the only mechanism independent of face velocity, but dependent of particle diameter and density. Inertial impaction increases with increasing face velocity [1, 5, 29, 30].

Chen et al [5] experimentally showed that particles whose diameter is less than 1.7 µm were captured mostly by diffusion or attraction mechanisms. It was noted that the penetration of those particles increased as the face velocity was increased. This study also documented that the penetration of particles larger than 1.7 µm decreased as the face velocity increased, indicating that interception or inertial impaction were the dominant mechanism. The face velocity used for these experiments was 10 cm/sec. This face velocity represents a heavy work rate environment [5].

2.3. Evaluation of filtration performance

In order to ensure wearer protection, “worst case” scenarios have been proposed by NIOSH for testing respirator filter efficiency [31-34]. “Worst case” would be the situation where the filtration media have minimum performance in terms of aerosol penetration. A filter tester was specifically developed for this purpose and the device can be used for testing and approving particulate filters. NIOSH had enforced a new testing and certification standard for particulate respirators which is known as 42 CFR 84 [35].
Under 42 CFR 84, there are nine classes of filters. Three categories for resistance to filter degradation, each with three levels of filter efficiency. The three categories of resistance to degradation are labeled N, R, P depending on the presence or absence of oil particles. N-series filters are not resistant to oil, and are recommended for use against solid aerosols. These filters are tested for certification against a NaCl aerosol. R-series filters are resistant to oil, whereas P-series filters are oil proof. These filters (R and P) are recommended for use in all environments, including those with oil particles (i.e., lubricants and metal working fluids). Within each series of filters, there are three levels of filter efficiency: 95, 99, and 99.97 percent [35].

The 42 CFR 84 standard had led the industry to develop new filter materials such as oil resistant electret filters for lower degradation by oily aerosols. The “worst case” for these filters consist of NaCl aerosols with a count mean diameter (CMD) 0.075 ± 0.020 µm, a geometric standard deviation (GSD) not exceeding 1.86, a liquid polydisperse DOP with a count median diameter (CMD) of 0.185 ± 0.020 µm, and a geometric standard deviation (GSD) not exceeding 1.6 [31-34]. It has been noted, however, that the aerosol particles used during the worst-case criteria were not necessarily indicative of measured efficiencies against “workplace-type” aerosol [7, 31].

In a study led by Janssen, it was reported that some filters seemed much more efficient under plausible workplace conditions than it was under NIOSH test conditions of “worst case” [36]. It was noted that the nature of workplace aerosols should be understood to determine appropriate test conditions for particulate respirator filters, and current filter test criteria of significant aerosol penetrations would not occur in the workplace. The plausible workplace conditions presented was the air flow of 30 lpm, aerosol size of 5 µm mass
median diameter (MMD) with 3 GSD, whereas the “worst case” test particles have approximately 0.3 \( \mu \text{m} \) MMD [36].

The efficiency of a respirator filter medium depends also on some filter characteristics, such as packing density, thickness and fiber diameter. Those material factors together with aerosol loading and flow rate affect the magnitude of the pressure drop of filter. A good respirator filter would have low filter penetration and low pressure drop (low breathing resistance). A respirator filter with very high efficiency and intolerably high resistance would be of no use. Thus it would be useful to consider both the penetration and pressure drop at the same time to evaluate the filter quality. Quality factor (QF) has been usually used as the indicator of filter performance as presented below [28, 37-39].

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

QF: measured in \( 1/\text{mmH}_2\text{O} \)

P: aerosol penetration (% penetration / 100)

\( \Delta p \): pressure drop (mmH\(_2\)O)

2.4. Parameters affecting filtration efficiency of electret filter media

The typical loading behavior of electrically charged filter material is shown in Figure 2.4.1. As particles are loaded in filter media, penetration initially goes up due to reduction in fiber charges by the deposited particles, showing maximum penetration at some point. Then the penetration goes down as mechanical efficiency is added to filter material due to particle caking. Resistance or pressure drop drastically increases as particles form cake as a dendritic structure, indicating the clogging point [40-43]. The clogging point was defined
by Walsh et al. as the mass deposited at which a line extrapolated from the second linear portion of the pressure drop vs. loading curve intersects the mass deposited axis [40]. Filter cake, however, is not easily formed by liquid oil particles as solid particulates such as NaCl do. When oil is used as a testing agent a generally monotonous decrease in the filter efficiency curve is observed [14].

There have been several attempts to explain the initial increase in penetration exhibited by electret filter media. One of them was proposed by Baumgartner and Löffler [44]. They argue that the reduction in efficiency occurred by neutralization of the charges by the deposited particles. However, this theory fails to explain the decrease in filtration efficiency when non-charged particles are used. A second explanation by Brown et al. states that the charge in the fiber is just screened and not neutralized by the deposited aerosol. The magnitude of the screening depends on the covering ability of the aerosol and not on its total mass. A thin complete film of aerosol deposit is likely to be a more effective screen than a few large particles, and a complete film is more likely to be formed if the aerosol is in the form of very small particles [39, 40, 42, 43, 45, 46].

Parameters affecting filtration efficiency of filter media has been extensively studied in terms of particle size, particle charge, charge of filter media, type of particle, environmental effect such as humidity and chemical exposure etc [5, 42, 43, 47].
2.4.1. Particle size effect

Walsh et al [42, 43] studied the effect of particle size on filtration performance of electret filter media. It was determined that smaller particles caused rapid degradation in electrostatic efficiency, reaching maximum penetration and the clogging point quickly. This behavior was explained on the basis of the difference in rate of dendrite formation for different particle sizes, and was later corroborated by a simulation study of Baumgartner et al. [47].
2.4.2. Particle charge effect

Filter efficiency has been documented to be higher for charged particles than for uncharged ones. This behavior is attributed to Coulombic effects enhancing in that way existing capture mechanisms [5, 42, 47, 48]. Ji et al. [48] studied the effect of particle charge on filtration efficiency. NaCl particles were charged by spray electrification. The amount of charge was created by an atomizer and thus the charge was 2-5 times more than that of equilibrium charged particles. Experimental results indicated that at the initial state of NaCl loading, the efficiency of the filter for highly charged particles by spray electrification was higher than that for equilibrium charged particles of all sizes. This higher efficiency suggested that highly charged particles could be more easily captured at initial state of loading in a clean electret filter [48].

The pressure drop of the filter media loaded with equilibrium charged particles increased continuously while that of filter media loaded with highly charged particles by spray electrification rarely increased during the loading [48]. This behavior was later explained by the study of Oh et al [49], which showed that highly charged particles are deposited more uniformly around the fiber surface, and dendrites of particles form slowly in the surface layer, resulting in low flow resistance.

Since the charge of particles would affect the filter efficiency, it would be important to control the charge characteristics of the particles used to test filters. The most severe test would be to use only electrically neutral particles. A more realistic approach is to use a “neutralized” aerosol that has been brought to a state equilibrium charge. The test aerosol is then to be bombarded with high concentrations of equal numbers of both positive and negative ions. When the aerosol reaches equilibrium, most of the individual particles
contain either no charge, or a very low positive or negative charge. Collectively, the entire aerosol has a net zero charge [26]. The certification of air-purifying respirators under the NIOSH respirator standards required that the challenge aerosol particles of NaCl or DOP (dioctyl phthalate) be neutralized to create a worst case challenge aerosol [50].

2.4.3. Particle composition

Ji et al. [48] showed that liquid oil aerosols, DOS (dioctyl sebacate) degraded the filter efficiency more rapidly than NaCl aerosols. This behavior was explained on the basis that the charge on the fiber surface was screened by the DOS wettable films. If liquid particles are wettable, the liquid droplets would spread along fibers and generate thin films covering the fibers, which would rapidly reduce the filter efficiency [46, 48]. Since liquid DOS particles are low viscous and non-volatile, they were considered to be wettable [48]. Deposits of DOS or DOP had been documented to uniformly coat the fiber surface, by wetting and spreading of DOS or DOP on the fiber [7, 9]. Since the DOS or DOP did not form a dendritic structure but rather smoothly coat the fibrous surface, there was no corresponding increase in mechanical collection mechanisms due to clogging of filter pores. This was supported by the fact of no significant increase in filter resistance with the loading [7] and later on by electron micrograph observations [9]. On the other hand, a solid aerosol (NaCl) immediately began to clog the pores of the filter, eventually forming a cake on the filter surface, and greatly increased the resistance as loading occurred [7, 51].

It has also been suggested that the permittivity of particles might affect the capture mechanisms. Walsh et al [42] showed that high permittivity TiO₂ caused more rapid degradation in efficiency than low permittivity stearic acid particles. Permittivity indicates the ability to store energy when placed in an electric field. It was argued that high
permittivity TiO$_2$ would have greater ability to store charge than stearic acid, and that would have caused the electrostatic efficiency to degrade more rapidly by affecting the Coulombic collection mechanism. This result was contrary to the expectation that the TiO$_2$ would be less affecting as they are not as cohesive as the stearic acid particles [42].

2.4.4. Filter charge

Filtration performance has been observed to considerably decrease after exposures to ionizing radiation and high intensity X-rays. While initial studies by Walsh et al. [43] did not quantify the charge level of filter material, they deduced it from penetration measurements instead. This approach has generated controversies in the scientific community as it is very indirect. It was then argued that reduction in fiber charge caused the maximum penetration and clogging point to be reached at lower mass deposits. This explanation implies that filters composed of higher charged fibers would have had better particle holding capacities [43]. This hypothesis has not been validated experimentally as the development of methods aimed at directly measuring fiber charge has been elusive.

2.4.5. Humidity

At first glance, it was considered that humidity might affect the charge decay characteristics of the electret filter media. This was supported by assuming that the charge in the fiber may disappear or be neutralized by the adsorption of water ions on the fiber [52]. However, from humidity experiments conducted by Otani et al. particle penetration remained constant for over a month at relative humidity of 90%. These experiments imply that the electret charge was quite stable in humid air and that charge decay due to surface conduction of dipole charges was negligible [52].
These results may be misleading as an insignificant effect of humidity on electret filter media can be attributed to the nonpolar characteristics of electret filter media used. If the electret filter media were made of polar polymers, discharge would have been caused by moisture, through dipole-dipole interaction of water and the polar functional groups. Protection from humidity can then be obtained if these polar polymers are coated on both sides with nonpolar polymers [22].

2.4.6. Chemical exposure

Several research groups have documented that the electrical enhancement of electret filter media can be reduced by chemical attack or environmental conditions. The filter deterioration by chemical exposure could place considerable restrictions on the applications of charged filters and be a factor limiting its usage.

Work by Moyer et al. and other [4-9] have examined the effect of isopropanol (IPA) immersion on electret filter efficiency revealing that the IPA immersion significantly increased the aerosol penetration without resistance change. Since there was no significant change in resistance, it was assumed that the IPA did not cause significant changes in the mechanical structure of the filter material. However, the IPA exposure caused a significant decrease in the filtration efficiency. This decrease in performance was attributed to charge elimination, but this theory has not been validated [6]. Thus, the increased aerosol penetration or reduced filtration efficiency was interpreted as an indirect measurement of charge removal in the electret filtration media [4-6].

The effect of chemical exposure on filtration efficiency was then more thoroughly studied by Biemann et al [9]. It was found that permanently charged filters showed very slight efficiency deterioration from water immersion. This behavior was attributed to the
neutralization of charges readily accessible on the surface of the filter media. No further
deterioration was shown when the samples were immersed in water containing nitric acid or
NaCl solution [9]. The negligible changes in filter efficiency when the media was
immersed in water may be caused by the hydrophobic nature of polypropylene. When
water solution with surfactant was used to immerse the filter media, moderate deterioration
was shown. This behavior indicated that surface charge could be readily removed on the
filter surface by the action of the surfactant.[9].

Some of these studies have used rather severe exposure levels with intention to
simulate extreme environment to which the filter would be exposed. Biermann’s group
tested filter media that was immersed in alkane solvents such as hexane, heptane and iso-
octane and observed a relatively mild deterioration in efficiency. These results were then
compared to the experiment in which filters were immersed in pure water. The organic
solvents completely wetted the filter surface, causing more reduced performance compared to
pure water. Later on, additional immersion experiments using benzene, toluene, and a
methyl ethyl ketone (MEK) / acetone showed a dramatic decrease in filter performance.
The decrease in performance was of such magnitude that the exposed filters exhibited
efficiencies values equivalent to those of mechanical filters composed of non-charged fibers
of the same diameter. [9].

Biermann’s group also examined the effect of exposure to organic vapors since the
exposure to liquid organic solvent was extreme and unlikely to occur in the workplace.
Electret filter media was exposed saturated MEK / acetone vapors during 24 hrs. The
efficiency at a face velocity of 64 cm/s dropped from 71 % to 49 %. Although the decrease
in filter efficiency was less with organic vapors than with organic liquids, tests demonstrated
that exposure to organics was a major problem with the filters [9]. The problem of filter discharge with exposure to organics could be minimized in respirator applications by placing the permanently charged filter together with a gas adsorber, which is usually manufactured with activated carbon. Organic vapors would then be absorbed in the activated carbon and not reach the filter [9].

2.5. Charge decay mechanism

Biermann et al. [9] suggested possible mechanisms for the decrease in filter efficiency when exposed to organic vapors and solvents. Some of the mechanism proposed as 1) direct neutralization of the fiber charge by charged aerosol or ions, 2) chemical reaction of organic solvents with the charges on the polymer surface, 3) cancellation of the net fiber charge by the close proximity of opposite charges.

Since organic solvents did not have ionic species, the hypothesis of charge neutralization could not hold. Another possible mechanism was that the conductivity of the solvents allowed a conductive path around the filter fiber, thereby effectively short circuiting the positive and negative sides. However, this is not valid because the conductivities of the respective solvents are not high enough to cause this behavior. Therefore, the solvents were able to react chemically with the surface charge, presumably present on the surface as free radicals or ions [9].

Cantaluube et al. [53] also studied the effect of organic vapors on electrets. They suggested that the organic vapor stimulated decay of electrets was not due to the screening of the injected charges by dipoles or by conduction charges when the electret was exposed to solvent. Instead, they suggested the detrapping hypothesis, where the decay was due to the
motion of the charges themselves, which are liberated by the penetration of the solvent. In the initial stage, the charges were thought to be trapped near the surface of the sample. While the solvent penetrate the polymer, the charges are detrapped in the swollen region and driven deeper into the sample by the electric field. In a crystalline polymer such as isotactic PP, the motion in the small chain segments enhanced by the penetration of the solvent would be more likely than that of large parts of the chain. It was speculated that charges trapped close to small segments might be liberated by molecular agitation and that solvent molecules might act as electron scavengers [53].

Kravtsov et al. [54, 55] suggested mechanisms for electret charge formation of polypropylene fibers. His group suggested that during corona discharge, charged particles move to the fiber surface, and these charged particles can cause, in an electric field and under elevated temperature, several phenomena: 1) Trapping of charge carriers by various structural defects of the polymer, impurities, voids, end groups, interfaces of crystalline phase / amorphous phase, 2) Self-trapping of electrons in the polymer bulk, when a high energy electron produces a structural defect and gets trapped in it, 3) Thermal destruction of the polymer, resulting in formation of polar groups and charged fragments of molecules, 4) Formation of ozone or nitrogen oxides in the air gap under the action of an electric field, followed by macromolecules oxidation and polar group formation 5) Breakage of chemical bonds in polymers, when a macromolecule falls apart into charged fragments. These fragments would possess dipole moment and can be responsible for dipole polarization. The formed dipoles would be oriented in the electric field of the corona discharge and then be frozen upon solidification. It was thought that, in an electric field of sufficient intensity
around a corona discharge, many processes can lead to the formation of an electret which shows both dipole and injection polarization [54, 55].

Rychkov et al. [56] suggested two mechanisms to contribute to the time-dependent decay of homocharge (for positively corona charged FEP-Teflon electret) under humid conditions: 1) the deposition of compensation charge from the atmosphere, 2) the internal decay through conduction or drift, perhaps accelerated by invasive humidity.

Under unshielded conditions, the external charge decay due to ion deposition can be very severe. The rapid decay on the unshielded sample is attributed to compensation of the electret charges by atmospheric ions attracted by the electret. Internal charge decay processes in dielectrics are governed by conduction phenomena which depend on carrier mobility, carrier concentration, injection conditions at the electrodes, etc [12].

2.6. Measurement of charge in electret filter media

While several studies have used filtration efficiency measurements as an indirect indication of charge level of electret filter media, very little work has been aimed at obtaining direct measurements [2, 17, 57, 58]. Tsai et al. [17] developed a scanning system to measure surface charge potential; however, their measurement had high coefficient of variation about 50 %, making it difficult to interpret some of the results. Efforts have been made to figure out the charging and charge decay mechanisms of electrically charged filter media, but a definite and reliable technique has not been identified so far. This gap in the understanding of electret behavior may be justified by the difficulty to measure the electric field of a material that shows an almost balanced charged state in macro scale while it would be in high charged state in micro scale.
When the fibrous filter is treated with corona charging, charges are trapped on different structural levels [59]. Charges stored in a polymer can be classified by surface entrapment or volume entrapment [12]. The surface entrapment generally occurs due to the chemical impurities, surface defects, or broken chains, and the volume entrapment occurs at atomic sites on the molecular chain, between groups of atoms in neighboring molecules, in crystallized regions, or at the interface of crystallized and amorphous regions [16]. The energy levels of charges trapped in the filter are different, and the location of the energy level is related to the charge decay [59].

Thermally Stimulated Current Discharge (TSCD) is a useful technique to obtain the profile of charges trapped in electret, and it can characterize the factors that affect charge decay. TSCD accelerates the charge decay rate by the elevation of temperature, and can be used to predict the charge decay rate of the materials. In other words, when the filter is heated, the charges stored in the filter will get sufficient energy for free movement, and the profile of charges trapped (or movement of charges) in fiber is observed by detecting the current as a function of temperature [12, 15, 19]. The several different peaks in the current-temperature represent different release energy levels; i.e., the charges in low release energy will show a peak at low temperature and vice versa.

Huang [59] used TSCD technique and showed that the conductive additives embedded in corona charged electrets accelerated the charge decay rate. Likewise, polymer with higher moisture content had faster charge decay rate. Water molecules decrease the charge release energy (activation energy) for the corona charged electrets. In addition, larger fiber diameters, loft fabric resulted in a higher charge decay rate than smaller fiber diameters of the same basis weight fabric and compact structure fabric [59].
2.7. Electric Force Microscopy (EFM) for qualitative charge measurement

EFM together with AFM (Atomic Force Microscopy) is a family of Scanning Probe Microscopy (SPM), which involves a sharp tip to scan across the sample surface while monitoring the tip-sample interaction to form a high resolution image. EFM provides information of the electric properties of material, using a conductive probe to map the attractive and repulsive forces between the tip and the sample [60].

It has been argued that by applying EFM techniques, the spatial distribution of the charge species responsible for polymer polarization could be observed at the micro and nano levels. It is important to consider that the electrostatic interactions are long-range. This means that the charges buried beneath the sample surface for tens and even a few hundred nanometers can be detectable, but their contribution to the measured potentials will decrease with the square of their distance to the scanning probe [61].

2.7.1. Imaging Process of AFM

AFM consists of scanning a sharp tip on the end of a flexible cantilever across a sample surface. A piezoelectric tube scanner conducts the scanning motion in a raster pattern. Then the tip-sample interaction is monitored by reflecting a laser off the back of the cantilever into a photodiode detector [60].

Commonly used modes of operation in AFM are contact mode and tapping mode (or intermittent contact mode). Contact mode AFM consists of scanning the probe across a sample surface while monitoring the change in cantilever deflection. A feedback loop maintains a constant cantilever deflection by vertically moving the scanner to maintain a constant photodetector difference signal. Tapping mode AFM consists of oscillating the
cantilever at its resonance frequency, lightly tapping on the surface during scanning. A feedback loop maintains constant oscillation amplitude by vertically moving the scanner. While the contact mode can generate images somewhat faster, tapping mode has advantage over the contact mode in that it eliminates the shear forces present in contact mode, and this enables tapping mode to image soft, fragile and adhesive surfaces without damaging them [60, 62].

One of the advantages of AFM over SEM is that AFM can provide three dimensional topography with height information of very high vertical resolution (less than about 0.5 Å usually), whereas the SEM can only image very rough samples due to large depth of field and large lateral scan area. AFM can resolve the 1.4 Å monoatomic silicon steps on the surface while the SEM has difficulty resolving these subtle variations in height on the sample this smooth. However, SEM has advantage over AFM in that SEM can obtain a large area view of the variations in surface structure in several mm scale, whereas the largest scanning area for AFM typically is only 100 µm × 100 µm [60].

AFM can supply compositional information based on physical properties such as stiffness, elasticity, compliance, friction, adhesion, magnetic and electrostatic fields, conductivity etc [60]. One of the most used techniques, phase imaging is performed by monitoring the phase lag between the oscillating drive signal used to drive the cantilever and the oscillating detection signal from the photodiode detector. This signal will indicate differences in material properties including viscoelasticity, adhesion or electric field across the imaged area [60].
2.7.2. Concept of EFM technique

Electric Force Microscopy (EFM) was developed to map electrostatic field gradients, which extend from the sample surface. This technique uses either a magnetic or conductive probe to map the attractive and repulsive forces between the tip and the sample. The long-range electric forces shift the resonance frequency of the oscillating cantilever, which is detected to produce the magnetic image [60].

The EFM technique is based on a two-pass measurement, which allows the imaging of relatively weak but long range electrostatic interactions while minimizing the influence of topography. Measurements are taken in two passes. During the first pass, tip performs a main scan (trace and retrace) by TappingMode™, and it records the surface topographical data. The tip is then raised to the final scan height, and a second interleave scans (trace and retrace) are performed by LiftMode™ while maintaining a constant separation between the tip and local surface topography. During the interleave scan (LiftMode™), the tip is biased with respect to the sample holder, and experiences an electrostatic force at a separation \( z \) from the surface. The Figure 2.7.1 below describes how the two-pass measurement is conducted [63-65].
Figure 2.7.1. Two-pass measurement of EFM LiftMode\textsuperscript{TM}; 1) Cantilever measures surface topography on first scan, 2) Cantilever ascends to lift scan height, 3) Cantilever follows stored surface topography at the lift height above the sample [64].

In this procedure, a conductive AFM tip interacts with the sample through long-range coulombic forces, of which interactions change the oscillation amplitude and phase of the AFM cantilever. These oscillations are detected to create electric field gradient images (EFGI) or surface potential images (SPI) [63, 64, 66].

Electric field gradient imaging (EFGI) is a technique which measures variations in the electric field gradient above a sample. Best candidates for electric field gradient imaging are samples with fairly smooth topography, samples with trapped charge, and/or samples that have large contrasts in the electric force gradient due to material differences or regions at substantially different potentials [64].

In this method, the cantilever is vibrated by a small piezoelectric element near its resonant frequency. The cantilever’s resonant frequency changes in response to any additional force gradient. Attractive forces make the cantilever effectively “softer”
reducing the cantilever resonant frequency. Conversely, repulsive forces make the cantilever effectively “stiffer” increasing the resonant frequency. A comparison of these forces is shown in Figure 2.7.2. Likewise, changes in cantilever resonant frequency due to vertical force gradients can be detected in phase detection, frequency modulation or amplitude detection [64].

Figure 2.7.2. Comparison of attractive and repulsive forces to action of a taught spring attached to the tip [64].

Electric field gradient imaging (EFGI) can be obtained by Phase Detection Mode or Frequency Modulation Mode. Either of the modes generates the signal sensed due to the force gradient from the sample surface [67-71].

2.8. Theory

Progress in AFM and EFM approach were extended to map forces of a different nature, such as attractive van der Waals forces, magnetic forces, and electrostatic forces [72, 73]. This can be achieved by varying the separation between the tip and the surface
EFM can be subdivided into three regimes based on tip-surface separation, which are long range, intermediate, and short range. In the long-range regime where tip-surface separation is greater than 10 to 50 nm, only electrostatic force between tip and the surface is significant. Quantification of surface properties from the force gradient data is difficult, because the exact shape of the tip and even the cantilever must be taken into account, especially for large tip-sample separations [74].

The second operational regime of EFM is characterized by relatively small tip-surface separations (< 10 to 50 nm), but the contribution of electrostatic forces still dominates over that of van der Waals interactions. In this case charge can transfer between the tip and the surface, thus rendering extraction of force and force gradient data from the experimental signal more difficult. However, the tip could be approximated by simple geometrical models such as sphere because the part closest to the surface provides the major contribution to force signal [74].

Lastly, the tip is in contact with the surface. Because van der Waals interactions dominate over electrostatic forces, only contact detection is possible [74].

For a conductive surface with a constant potential, the force between the tip and surface is given by the following Eq. 2.8.1.

\[
F(z) = \frac{1}{2} \frac{dC}{dz} (\Delta U)^2
\]

Eq. 2.8.1.

where \( F(z) \) is the force [N]

\( \Delta U = (V_{\text{tip}} - V_{\text{surf}}) \), the potential difference between the tip and the surface [V]
z is vertical tip-surface separation [m]

\[ C(z) \text{ is a tip-surface capacitance [Farad]} \]

Eq. 2.8.1 implies that the force is a function of the tip and surface geometry through the \( C(z) \) term. The exact functional form of tip-surface capacitance \( C(z) \) is complex and can be obtained by numerical methods, such as finite element analysis. For the typical probe geometry, the total capacitance \( C(z) \) can be conveniently approximated as a sum of the contributions to the tip apex, tip bulk, and cantilever [74].

\[ C(z) = C_a(z) + C_b(z) + C_c(z) \quad \text{Eq. 2.8.2.} \]

where

- \( C(z) \) is the total capacitance
- \( C_a(z) \) is the capacitance contribution to the tip apex
- \( C_b(z) \) is the capacitance contribution to the tip bulk
- \( C_c(z) \) is the capacitance contribution

Approximate models relating tip geometry have been suggested to quantify capacitive force between the tip and the surface [75-79]. Sphere and point charge models represent the \( C_a(z) \) term in Eq. 2.8.2, and can be used for smaller tip-surface separations (\( z \ll \text{radius of curvature of tip apex} \)), in which case the contribution of tip apex dominates. For larger tip-surface separations the contribution from the conical part of the tip \( C_b(z) \) is significant. The cantilever contribution \( C_c(z) \) can usually be modeled by a plate-plate model. Cantilever capacitance can provide non-negligible contribution at large tip-surface separations because
the effective area of the cantilever is much larger than that of the tip. Since the characteristic cantilever-surface separation of about 10 µm is much larger than tip-surface separation (1 to 500 nm), \( C_c(z) \) can usually be approximated as constant [74].

Figure 2.8.1 provides an experimental example of force gradient-bias and force gradient-distance dependency for the sample (conductive material) determined by EFM [68]. The relationship between the force gradient and bias voltage is well described by a parabola as shown in Figure 2.8.1 (a). The parabolic or quadratic dependence is known to indicate induced charge interactions [74].

The relationship between the force gradient and tip-sample separation was studied by Kalinin et al [74]. In Figure 2.8.1 (b), the force gradient dependence on distance was linearized in the log-log coordinates. The slope of the curve was -1.5, and it was determined that a slope for a plane-sphere model (slope was -2) and that for a plane-cone model (slope was -1).

Figure 2.8.1. Electrostatic force gradient showing height and voltage dependence [68].
Advantages of the frequency detection can be shown on materials with built-in non-uniform charge distribution, such as charged grain boundaries in ceramics [69, 74]. Figure 2.8.2 shows the EFM images of a grain boundary in an Nb-doped SrTiO$_3$ bicrystal at positive (left) and negative (right) tip biases. For positive tip bias, the grain boundary appears as a protrusion corresponding to a positive frequency shift, i.e., repulsion between the tip and GB charges. For negative tip bias, GB contrast is dark, i.e., the force is attractive. This observation implies that the charge on GB is positive.

![Figure 2.8.2. EFM force gradient images at tip bias $V_{\text{tip}} = 5\text{V}$ (Left), and $V_{\text{tip}} = -5\text{V}$ (Right) [69].](image)

Considerations affecting EFM response include the adsorption, tip oxidation and water layer formation. These cannot be ruled out as all the measurements were carried out under ambient conditions [80]. Besides, tip parameters tend to change with time in ambient conditions [65]. The high quality factor, $Q$ of the probe may result in a considerable phase shift with a small frequency shift. Employing a softer tip whose $Q/2k$ value is large can
produce large phase signal, thus making it more sensitive to small voltages [65].

As it has been shown in previous studies, the performance of electret filtration media can be deteriorated when it is exposed to organic solvents. In many studies, performance deterioration of electret filter media has been naturally considered to come from charge deterioration of electret filter media without showing evidence or measurement. This gap in the understanding of electret behavior may be justified by the difficulty to measure the electric field of a material that shows an almost balanced charged state in macro scale while it would be in high charged state in micro scale.

Efforts have been made to figure out the charging and charge decay mechanisms of electrically charged filter media, but a definite and reliable technique has not been identified so far. In this study, Scanning Probe Microscopy technique (AFM and EFM) will be implemented to probe the electrostatic field of electret filter media. This approach will be used to validate the hypothesis that electrostatic charge degradation plays a major role in the decrease in filtration performance of electret filter media when these materials are exposed to organic chemicals.
CHAPTER 3. EFFECT OF SOLVENT EXPOSURE ON THE PERFORMANCE OF ELECTRICALLY CHARGED FILTRATION MEDIA

3.1. Introduction

It is well established that electret filter media exhibit improved performance due to the use of the Columbic attraction phenomena as an additional capture mechanism. In addition, there is significant experimental data implying that the filtration performance of electret filter media dramatically decreases when exposed to liquid organic chemicals [4-10]. Several research groups have suggested that the reduced filtration performance can be attributed to charge deterioration of the electret filter media. However, only indirect measurements of charge deterioration via filtration performance experiments appear to support this theory as not direct measurement of charge on a fiber has been achieved so far.

This study was motivated to provide a new insight of this degradation phenomenon. For this purpose, filtration media as well as organic chemicals which can be easily found in a
working environment were deliberately selected. The filter media was exposed to both liquid and gas phases and filtration performance was evaluated prior to and post exposure.

3.2. Experimental

Materials

The electret materials were chosen from commercially available filter media used in particulate respirators, and rated by NIOSH as R, P and N. Two different electret filter media samples and one type of mechanical filter media were used in this study. According to the manufacturer, the electret filter media, E1 and E5, were composed of melt-spun polypropylene nonwoven mats charged by corona treatment. The mechanical filter media consisted of a nonwoven mat of glass fibers without electrostatic charge. Technical specifications for these materials were shown in Table 3.1. All filter media were tested as received from the manufacturers.

Under 42 CFR 84, there are three categories of resistance to filter degradation, which are labeled N, R or P. N-series filters are not resistant to oil, and are recommended for use against solid aerosols. These filters are tested for certification against a NaCl aerosol. R-series filters are resistant to oil, whereas P-series filters are oil proof. These filters (R and P) are recommended for use in all environments, including those with oil particles. Within each series of filters, there are three levels of filter efficiency, that is, 95, 99, 99.97 percent. The selection of filter efficiency is dependent on the amount of acceptable filter leakage [7, 35].

ACS grade organic solvents such as isopropanol (IPA), acetone (ACE), toluene (TOL), hexane (HEX) and dioctyl phthalate (DOP) were obtained from Sigma-Aldrich and used as received. Commercial grade nitrogen gas (Machine and Welding Supply Company, Dunn,
NC) was used as a carrier gas for vapor exposure tests.

A CertiTest 8130 automated filter tester (TSI Incorporated, St. Paul, MN) equipped with oil and salt aerosol generators, was used to determine the performance (percentage of penetration) and resistance (pressure drop in mm of H$_2$O) of the filter media. During this work, DOP was used as the oil aerosol generator to produce particles with a count median diameter of 0.20 $\mu$m and a geometric standard deviation of less than 1.6.

**Filtration test**

A CertiTest 8130 automated filter tester (TSI Incorporated, St. Paul, MN), which is equipped with oil and salt aerosol generators, was used to determine the performance (percentage of penetration) and resistance (pressure drop in mm of H$_2$O) of the filter media. In this work, DOP was used in the oil aerosol generator to produce particles with a count median diameter of 0.20 $\mu$m and a geometric standard deviation of less than 1.6.

Filter media testing was performed in accordance with 42CFR84 which establishes performance criteria for all negative pressure particulate air-purifying respirators and pre-filters [50]. Filter media was tested as flat samples, exposing an area of 6 inches in diameter to the test agent. The aerosol traveled from the generator to the filter holder and down through the filter media. The % penetration of the aerosol through the filter media, and the resistance (pressure drop across the filter media in mm H$_2$O) were time stamped and stored. For baseline tests, five filtration tests were carried out and averaged. For exposure tests, three tests were carried out and averaged.

**Chemical exposure experiments**

The effect of chemical exposure to the filter media was investigated in liquid and vapor phase of organic solvents. For liquid exposure, the filter media was immersed in liquid
organic solvents for 2 min, then the solvent was dripped, and the filter media was dried under a hood.

During vapor exposure tests, the custom-built experimental setup shown in Figure 3.1 was used. Nitrogen was bubbled through a vessel containing the challenging liquid organic solvent in order to generate a saturated vapor. The concentration of solvent in the saturated vapor stream was determined using the molecular thermodynamic NRTL (non-random two liquids) calculation routine. The concentration of solvent in the saturated vapor stream was determined to be 60759 ppm, and the concentration was varied by diluting with N₂ gas. The concentration of the gas reaching the exposure chamber was then controlled by using N₂ gas in continuous dilution stages. The concentration of the vapor was confirmed by gas chromatography analysis. A gas chromatograph (GC-17A Shimadzu Instruments, Columbia MD) equipped with a 30 m capillary column, 0.53 mm ID (Stabilwax® crossbond®, carbowax® -PEG) and a flame ionization detector was used to determine the concentration of the solvents in the gas entering and leaving the exposure apparatus.

Gas flow through the saturator was controlled at 1000 cm³min⁻¹ using a flow-meter. The stream of saturated vapor was connected to the exposure chamber using Tygon tubing. The sample material was loaded in the middle of the vessel using a glass ring, and the chemical vapor was run through the material in upward direction. After 8 hrs of exposure, the sample was taken out and stored in a plastic bag before filtration test.

3.3. Results and discussion

Filtration performance with chemical exposure

The baseline performance of the filter media used in this project is shown in Figure 3.2.
The percentage of penetration is shown as a function of time of DOP loading in Figure 3.2 (a). While the E1 and mechanical filter media samples exhibited negligible changes in penetration as a function of time, E5 exhibited an increase in penetration as a function of time. This behavior may be explained on the differences on weight basis between the two samples. As shown in Table 3.1, the basis weight of E5 (80 g/m²) is smaller than that of E1 (112 g/m²). As expected, electret filter media samples, E1 and E5, exhibited lower resistance than the mechanical filter. The resistance of the filter media shown in Figure 3.2 (b) showed that the electret filter media E1 and E5 exhibited lower resistance than the mechanical filter media as expected.

After performing baseline experiments, the filter media was then exposed to four different organic solvents (isopropanol, acetone, toluene, and hexane) by immersing the samples in the solvents during 2 min. After immersion, the exposed filter media was tested for filtration efficiency and resistance. Figure 3.3 shows the filter performance of E1 filter media after it was exposed to the liquid chemicals. The penetration for immersed filter media considerably increased compared to the baseline penetration. The decrease in performance was larger for toluene and isopropanol than for acetone and hexane. As shown in Figure 3.4, E5 filter media showed a similar trend as E1 filter media. As expected, the mechanical filter media (M) was not affected by exposure to liquid chemicals as shown in Figure 3.5.

These experimental results were consistent with the study by Lehtimäki [6], in which it was reported that exposure to IPA caused a significant decrease in the removal efficiency of filtration media. Lehtimaki [6] also concluded that the immersion procedure did not alter the mechanical structure of the filter material as there were no significant changes in the flow
resistance behavior. While it was mentioned that the decrease in removal efficiency of electret filter media after exposure IPA was due to charge elimination, there was not experimental data to corroborate this statement [6]. It is suggested that the charge deterioration was caused by the rapid sorption of organic solvent onto the polypropylene fibers.

Due to the dramatic changes in performance, the effect of isopropanol in the performance of electret filter media was further investigated. In these new experiments, filter media was exposed to isopropanol vapors during 8 hrs at concentrations corresponding to 90 % saturation (54683 ppm), and TLV (threshold limit value 200 ppm for IPA, ACGIH source). Figure 3.6 indicates that exposure to vapor IPA had no significant effect on the filtration performance of these samples.

Experimental data have shown that the filtration efficiency of electret filter media is affected by exposure to organic solvents in the liquid phase, not the vapor phase. This can occur by direct liquid immersion, an aerosol-spray contact, or the condensing of vapor onto the filter media. It was observed that exposure to organic vapors, having concentrations sufficiently below the dew point, have negligible affect on the filter efficiency. One of the possible explanations is that the interaction of polypropylene with the organic solvent may allow the long polymer chains to rotate into a more relaxed state, thus disrupting the electric field as the dipole moments assume a more random orientation. A second explanation is that the presence of a thin liquid layer may act as a conductor and “wash away” the charges.

3.4. Conclusions

The effect of chemical exposure to electret filter media on filtration performance was
investigated. The exposure of electret filter media to several organic solvents in liquid phase caused decrease in filtration performance without significant changes in resistance (pressure drop). However, organic solvents in vapor phase did not significantly change the filtration performance of the electret filter media.

Unlike the electret filter media, the performance of mechanical filter media was not affected by the exposure to organic solvents used in the experiment.
Table 3.1. Filter Media Specifications.

<table>
<thead>
<tr>
<th>Test Code</th>
<th>Basis Weight (g/m²)</th>
<th>Thickness (mm)</th>
<th>Fiber</th>
<th>Charge</th>
<th>Fiber Diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>112</td>
<td>0.99</td>
<td>Meltblown Polypropylene</td>
<td>Corona</td>
<td>1.7 - 6</td>
</tr>
<tr>
<td>E5</td>
<td>80</td>
<td>0.76</td>
<td>Meltblown Polypropylene</td>
<td>Corona</td>
<td>1.8 – 6.5</td>
</tr>
<tr>
<td>Mech</td>
<td>78</td>
<td>0.40</td>
<td>Micro Glass No Charge</td>
<td>No Charge</td>
<td>0.5 – 9.0</td>
</tr>
</tbody>
</table>
Figure 3.1. Experimental Setup for Chemical vapor exposure test [10]
Figure 3.2. Baseline performance of filter media.
(a) % Penetration (b) Resistance change (mmH₂O).
Figure 3.3. Performance test for E1 filter media after exposure to liquid chemicals. (a) % Penetration. (b) Resistance (mmH2O).
Figure 3.4. Performance test for E5 filter media after exposure to liquid chemicals. (a) % Penetration. (b) Resistance (mmH2O).
Figure 3.5. Performance test of a mechanical filter after immersion in liquid chemicals. (a) % Penetration. (b) Resistance (mmH₂O).
Figure 3.6. Performance test for E1 under several exposure conditions. 
(a) % Penetration. (b) Resistance (mmH2O).
CHAPTER 4. MORPHOLOGICAL ANALYSIS OF
ELECTRET FILTRATION MEDIA USING SEM (SCANNING
ELECTRON MICROSCOPY)

4.1. Introduction

The filtration performance tests of the electret filtration media after exposure to liquid chemicals indicated a reduction in removal efficiency (increase in penetration) while changes were not noted in their filtration resistance (pressure drop). Based on these experimental results, it was initially speculated that this behavior may stem not from morphological changes to the filtration media, but from deterioration of electrets charge. It was argued that if there was any interaction between solvent and the polymer such as swelling or thinning (erosion) of the fiber, these interactions might have been reflected in the resistance behavior.

In order to obtain direct evidence that no morphological changes were caused to the fiber as a result of immersion in the liquid organic solvents a SEM study was undertaken. Isopropanol was selected as a challenge agent for this experiment, as it exhibited one of the most significant deteriorations in filtration performance. The goals of this study were to
investigate 1) whether there was any observable morphological changes, such as swelling or cracking after exposure to liquid isopropanol, and 2) whether there was any observable changes in the fiber caused by DOP aerosol loading after exposure to isopropanol.

4.2. Experimental

SEM analysis was performed on the electret media which were 1) untreated, 2) DOP loaded on untreated sample, 3) immersed in isopropanol (IPA) (Aldrich, ACS grade) for 2 min, 4) DOP loaded on immersed sample.

Samples were mounted as a nonwoven fabric piece and fixed on the stub using carbon tape. Samples were coated with Au/Pd. Experiment was performed using a Hitachi S-3200N Environmental SEM, using the Everhart-Thorney detector. An accelerating voltage of 5 kV was applied during the analysis. A working distance of 23±1 mm was used for the optimum depth of field and resolution. Images were taken with various magnifications from ×30 to ×3000. Fiber diameters were measured using software Image J.

4.3. Results and Discussion

Corona charged filtration media E1 and E5 were examined. The morphological changes or lack thereof in E1 fibers after exposure to liquid IPA could be examined comparing SEM images in Figure 4.1 (a) and 4.2 (a). SEM image on the left is in lower magnification than that on the right. The diameters of E1 fibers were determined to be in the range, 1.5 µm to 8 µm. When compared with the fibers after IPA immersion from Figure 4.2 (a), there were not observed changes in diameter, suggesting there was no significant erosion or swelling involved. In addition, evidence of either cracks or fiber damage was not
noted. These SEM results are consistent with other microscopic studies [5, 9], which showed no discernable difference in the morphology of electret filter media after exposure to IPA.

The indication of no swelling or damage after exposure to liquid chemicals is in agreement with the resistance results from the filtration tests. If significant swelling or dissolution of fibers may have happened, it would be expected that the resistance of the filtration media may differ from the baseline resistance. From the filtration test, the resistance was unchanged after the samples were exposed to liquid IPA or vaporous IPA. This is in agreement with previous studies where no morphological changes were assumed from the results showing no changes in flow resistance [6].

Moreover, there was no observable effect of IPA exposure on DOP loading behavior as indicated by comparison of figures 4.1 (b) and 4.2 (b). No significant difference is again observed between these two images; neither changes in diameter nor evidence of solvent induced cracks were observed.

Likewise, morphological changes in E5 after immersion into IPA were not observed (Figures 4.3 (a) and 4.4 (a), 4.3 (b) and 4.4(b)). Fiber diameters ranged from 1.3 µm to 7.5 µm, when randomly selected fibers were measured using Image J software.

These SEM pictures confirm the initial assumption that no morphological changes were induced by immersing the fibers into IPA and that the changes in filtration performance may be originated by degradation of the electrostatic charge of the filter media. However, although indirect experimental data appear to support this hypothesis, a direct experimental method is required to validate this theory.
4.4. Conclusions

SEM analysis was performed on electret filtration media to observe morphological changes after chemical exposure. There were no observable changes in morphology of fibers, suggesting the performance deterioration by chemical exposure was not caused by morphological changes in fibers.
Figure 4.1. E1 fibers.

(a) unexposed E1. (b) unexposed E1 after loaded with DOP aerosol.
Figure 4.2. E1 fibers after immersion in IPA for 2 min.

(a) IPA immersed E1. (b) IPA immersed E1 after loaded with DOP aerosol.
Figure 4.3. E5 fibers.

(a) unexposed E5. (b) unexposed E5 after loaded with DOP aerosol.
Figure 4.4. E5 fibers after immersion in IPA for 2 min.

(a) IPA immersed E5. (b) IPA immersed E5 after loaded with DOP aerosol.
CHAPTER 5. ATOMIC FORCE MICROSCOPY (AFM) OF AN INDIVIDUAL FIBER FROM ELECTRET FILTRATION MEDIA

5.1. Introduction

While SEM images and filtration performance data confirm the initial assumption that no morphological changes were induced by immersing the fibers into IPA, these experimental techniques do not provide direct and definite evidence that changes in filtration performance may be originated by degradation of the electrostatic charge of the filter media.

In order to completely validate this hypothesis, it is necessary to develop a method able to visualize the electric field of the electret filter media. EFM uses a conductive probe to map the attractive and repulsive forces between the probe and the sample. However, EFM can not be easily implemented to probe fibrous materials as it is usually applied to films or samples with a smooth topography.

As a preliminary step to implement EFM as a technique to probe the electric field in fibrous materials, AFM (Atomic Force Microscopy) experiments were performed as part of a feasibility study due to the familiarity between the two techniques. EFM and AFM are
family of Scanning Probe Microscopy (SPM), which involves a sharp tip to scan across the sample surface while monitoring the tip-sample interaction to form a high resolution image. AFM is used to investigate the surface topography of the material, usually for films or smooth materials.

Since AFM technique is mostly used for films or smooth materials, it was critical to develop the appropriate sample preparation method. It was expected that an AFM scanning procedure could be developed and optimized to probe the surface of individual fibers, and this knowledge and expertise could easily transferred to the EFM experiments.

After optimizing the sample preparation, preliminary EFM experiments were carried out. EFM images of E1 fiber and E1 fiber previously immersed in IPA were compared using Phase Detection Mode.

5.2. Experimental

AFM experiments were performed on a Dimension 3000 AFM (Nanoscope III, Veeco), with silicon cantilevers (NSC 15/50, μmasch). In order to image the surface of the fiber, the TappingMode™ was used, which involves tapping on the surface to map the topography of the material.

The most challenging step was sample preparation and mounting. Several mounting methods were attempted to fix the fibers onto a glass slide. The first method used a gel-type glue (Super glue, commercially available) as shown in Figure 5.1 (a). However, the fibers were easily wet and wicked, so this method was abandoned. The second method included the use of double sided tape. As shown in Figure 5.1 (b), two strips of tape were attached to the glass substrate and several fibers were carefully laid over the two tape strips. Due to the
small diameters of the fiber compared to the thickness of the tape, the fiber was not firmly fixed, and the AFM tip was unable to be engaged. The third procedure also used double sided tape (Figure 5.1 (c)), but this time fibers were laid on a piece of tape which was attached to a glass slide. Fibers were taken from filtration media, and were gently pressed onto the sticky tape. Excess fibers were removed or gently pressed onto the sticky tape using a tweezer. This method proved to be the most appropriate.

After optimizing the sample preparation method, preliminary EFM experiments were performed on a Dimension 3000 AFM (Nanoscope III, Veeco), connected to an Extender Electronics Module, with electric force microscopy cantilevers (antimony doped and Pt/Ir coated silicon tip, SCM-PIT, Veeco). Detailed specification of the cantilever is shown in Table 5.1.

A bias voltage of 10 V was applied to the tip by connecting an analog signal using Extender Electronics Module. In order to image the electric field of the fiber, LiftMode™ was used with a lift height of 75 nm from the surface of the fiber. Phase Detection Mode was used to image the electric field gradient of the fiber. Phase detection reflects the phase lag between the drive and the cantilever response. Gradients in the electric force cause a shift $\Delta F_0$ in the resonance frequency. Resonance shifts also give rise to phase shifts $\Delta \phi$ used to generate an image of the electric force gradients [81].

Preliminary tests were performed to examine the difference in phase response from E1 and E1-IPA. Effort was made to minimize the external tension or strain on the fiber, which can be induced while pulling out the fiber from the nonwoven web, and also while mounting a fiber on a sticky tape. 5 μm of scans for E1 and E1-IPA were collected using Phase Detection Mode.
5.3. Results and discussion

Two and three dimensional surface topography images of individual fibers taken from electret filtration media were obtained using AFM. An example of AFM images from E5 fibers are presented in the Figures 5.2. However, due to relatively larger height of the fibers compared to that of flat and smooth films, tip artifacts could occur. Thus, the topographic information obtained from these fibers might have to be interpreted in the most conservative way.

The phase angle of the oscillation can be altered by external forces that the tip may experience from the material’s surface. The phase shift in an EFM image, which is obtained when the EFM tip feels the electric field from the material surface, is represented as the contrast of the EFM image. In other words, the contrast of the EFM image is attributed to electric field of the sample surface.

Figure 5.3 shows AFM and EFM images of unexposed E1 fibers. The contrast of the EFM image in terms of phase angle can be numerically shown from the sectional EFM image as shown in Figure 5.3 (b). The phase angle difference from the base to the top of the E1 fiber surface was measured as 35°.

AFM and EFM images of E1 fiber exposed to IPA are shown in Figure 5.4. From the sectional EFM image, the phase angle difference between the E1-IPA and the substrate was measured around 10°. This is considerably lower than the phase angle difference for the untreated fiber. These preliminary results were encouraging as it opened the possibility of using EFM for qualitative analysis of charge deterioration in electret filtration media.

It is the purpose of this study to further develop this method in order to provide direct
visualization of the electric field intensity of electret filter media before and after exposure to liquid organic chemicals.

5.4. Conclusions

AFM images of individual fibers from the filter media were successfully taken using TappingMode™. Each individual fiber was isolated and mounted on the double sided sticky tape used as the substrate.

After optimizing sample preparation and AFM conditions, preliminary EFM experiments were carried out for E1 fibers, adopting Phase Detection Mode. When EFM phase response from E1 and E1-IPA were examined, the phase angle difference for E1-IPA was reduced considerably compared to E1 untreated fiber. The smaller phase angle difference for E1-IPA seems to imply lowered charge level after exposure to liquid IPA.
Table 5.1. Cantilever specifications for EFM experiments: antimony doped and Pt/Ir coated silicon tip.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>2.5-3.5 µm</td>
</tr>
<tr>
<td>Mean Width</td>
<td>22.5-32.5 µm</td>
</tr>
<tr>
<td>Length</td>
<td>220-230 µm</td>
</tr>
<tr>
<td>Spring Constant</td>
<td>1.2-5.5 N/m</td>
</tr>
<tr>
<td>Resonance Frequency</td>
<td>60-90 kHz</td>
</tr>
</tbody>
</table>
Figure 5.1. AFM sample preparations for fibers: (a) using gel-type glue, (b) fiber crossing over the tape, (c) mounting fibers on the tape.
Figure 5.2. AFM images of an E5 fiber (scan size of 8 µm): (a) Left topography, Right phase, (b) Topography only, (c) 3D image of topography, (d) sectional image of topography.
Figure 5.3. Phase Detection Mode EFM images for E1: (a) Left topography, Right phase image, (b) Sectional image of EFM phase image.

Phase difference between fiber and substrate: $35^\circ$
Figure 5.4. Phase Detection Mode EFM images for E1 immersed in IPA: (a) Left topography, Right phase image, (b) Sectional image of EFM phase image.
Chapter 6. Electric Force Microscopy Investigation on an Electret Fiber Using Phase Detection Mode

6.1. Introduction

Based on SEM analysis and filtration tests described in the previous chapters, the filtration performance of the electret filter media samples dramatically decrease when exposed to liquid organic solvents while morphological changes of fibers were not observed. It was hypothesized that this decrease in performance might be caused by charge deterioration induced by the exposure to the liquid organic solvent. In order to obtain direct evidence of the intensity of the surface charge in the electret filter media samples before and after chemical exposure, a set of EFM experiments was implemented.

Electric Force Microscopy (EFM) is a family of Scanning Probe Microscopy (SPM), which involves a sharp tip that scans across the sample surface while monitoring the tip-sample interaction. EFM can provide local information of the electric properties of material, using conductive probes to map the attractive and repulsive forces between the tip and the sample. EFM techniques have been mainly used to analyze conductive planar substrates
having small charge densities. The application of EFM technique to fibrous materials is a serious challenge due to the rough surface and the high curvature ratio of the fiber as electrical fields may be highly influenced by the topography of the samples.

The EFM technique used in this study was based on a two-pass LiftMode™ measurement, which allows the imaging of relatively weak but long range electrostatic interactions while minimizing the influence of topography. Measurements are taken in two passes. During the first pass, topographical data is taken in TappingMode™ using one trace and one retrace. The tip is then raised to the final scan height, and a second trace and retrace are performed while maintaining a constant separation between the tip and the local surface topography. The conductive tip is expected to interact with the sample and experience a range of electrostatic forces (coulombic, polarization, etc) influencing in that way the oscillation phase of the vibrating cantilever. The changes in phase angle are detected and processed to generate an electric field gradient image [81].

The preliminary AFM/EFM imaging work described in the previous chapter facilitated the development of optimized EFM probing procedures. EFM Phase Detection data was used to investigate the relationship between phase angle and the tip bias voltage as well as the tip-sample separation. The phase response of the E1 and E1 treated with IPA (E1-IPA) samples as a function of bias voltage and tip-sample separation were compared and a plausible interpretation of the experimental data was developed on the basis of coulombic and polarization effects.

6.2. Theory

EFM applications can be subdivided into three regimes, based on tip-surface separation,
including long range, intermediate, and short range. In the long-range regime where the tip-surface separation is greater than 10 to 50 nm, electrostatic forces between tip and the surface are significant. Accurate quantification of surface properties from the force gradient data is complicated, because the exact shape of the tip and the cantilever must be taken into account [74].

The second operational regime of EFM is characterized by relatively small tip-surface separations where the tip-surface separation is less than 10 to 50 nm. In this regime the contribution of electrostatic forces still dominates over that of van der Waals interactions. In this regime it is possible that charge transfer between the tip and the surface coupled with the electromechanical response of the surface may contribute to the detected force signal [74].

In the short separation regime, the tip is in contact with the surface and van der Waals interactions dominate over electrostatic forces [74]. Thus, a lift height of 75 nm was chosen for this experimental work in order to mainly detect the long-range electrostatic forces.

During EFM operation, the tip-surface interaction depends both on the electric and geometric properties of the tip, and those of the sample. Quantification of the electrostatic tip-surface interaction is known to be significantly complex for dielectric materials as induced polarization image charges as well as surface/volume trapped charges may influence the total force experience by the tip [74].

From fundamental relationship for driven, damped harmonic oscillations, the phase shift was described as follows [82, 83].

$$\Delta \Phi = -\frac{Q}{k} \frac{dF}{dz}$$  \hspace{1cm} \text{Eq. 6.1.}
where $\Delta\Phi$ is phase shift

$Q$ is the quality factor of the tip [unitless], $Q = \frac{\omega_0}{\Delta\omega}$, where $\omega_0$ is the resonance frequency [Hz] and $\Delta\omega$ the full bandwidth at $\omega_0$, at 0.707 of the maximum amplitude

$k$ is the spring constant of the tip [N/m]

$z$ is the distance between the tip and the sample [m]

$F$ is the force [N]

The force between the biased tip and a charged dielectric sample can be explained as a contribution of two phenomena; the coulombic force (attraction or repulsion between the biased tip and the sample) and the induced polarization force due to the biased tip (attraction between the biased tip and the sample).

If one-dimensional system is considered, the electric field $E$ generated by the biased tip in $z$ direction can be described as following.

$$E = \frac{\Delta U}{z} = \frac{V_{tip} - V_0}{z}$$  \hspace{1cm} \text{Eq. 6.2.}

where $E$ is the electric field at the sample surface

$\Delta U$ is the potential difference between the biased tip and the surface [V]

$z$ is the lift height or tip-sample separation [m]

$V_{tip}$ is the tip bias [V]

$V_0$ is the bias offset due to the sample charge [V]
Via fundamental electrostatic definitions, the force due to the presence of charge on the surface of the sample can be described as:

\[ F_1 = q_f E \]  

\[ F_1 = q_f \frac{(V_{tip} - V_0)}{z} \]  

where \( F_1 \) is the force due to the presence of charge on the surface of the sample surface [N], \( q_f \) is the fiber charge [C], and \( E \) is the electric field in z direction [N/C or V/m].

Most dielectric materials become polarized when they are placed in an external electric field, and the polarization is proportional to the electric field [84, 85]. Polypropylene exhibits induced polarization in the presence of an electric field. The induced polarization is proportional to the tip bias voltage.

The force \( F_2 \) due to the induced polarization by the biased tip, in z direction, can be described as following.

\[ F_2 = P \frac{dE}{dz} \]  

\[ P = \alpha E \]  

\[ F_2 = \alpha E \frac{dE}{dz} \]
\[ F_2 = \alpha \left( \frac{V_{tip}}{z} \right) \frac{d}{dz} \left( \frac{V_{tip}}{z} \right) \]

\[ F_2 = -\alpha V_{tip}^2 \frac{1}{z^3} \]  

Eq. 6.7.

where  \( F_2 \) is the force due to induced polarization [N]

\( P \) is the induced dipole moment by the electric field [C·m]

\( \alpha \) is the electric polarizability [C²m/N]

\( V_{tip} \) is the tip bias voltage [V]

Combining Equation 6.7 and 6.4 we obtain,

\[ F = F_1 + F_2 \]

\[ F = qf \left( \frac{V_{tip} - V_0}{z} \right) - \alpha V_{tip}^2 \frac{1}{z^3} \]  

Eq. 6.8.

Hence the force gradient is

\[ \frac{dF}{dz} = -qf \left( \frac{V_{tip} - V_0}{z^2} \right) + 3\alpha V_{tip}^2 \frac{1}{z^4} \]  

Eq. 6.9.

Incorporating Eq 6.9 into Eq 6.1 yields

\[ \Delta \Phi = -\frac{Q}{k} \left( -qf \left( \frac{V_{tip} - V_0}{z^2} \right) + 3\alpha V_{tip}^2 \frac{1}{z^4} \right) + \text{constant} \]  

Eq. 6.10.

In order to simplify the acquisition of experimental data, a phase angle of 0 degrees was set when the bias voltage applied to the tip was 0 V. In this way all other measurements
were easily related to the 0 V baseline. Due to this artificial offset, a constant is included in Eq 6.10 without losing the generality of the expression.

Constant is the offset to 0 degrees when $V_{tip} = 0$ V. The value of constant can be determined by solving Equation 6.10.

$$\text{constant} = \frac{QV_0q_f}{kz^2}$$

The expression for phase angle becomes

$$\Delta \Phi = -\frac{Q}{k} \left( -\frac{q_fV_{tip}}{z^2} + \frac{3\alpha V_{tip}^2}{z^4} \right)$$

This equation can also be expressed as a function of $V_{tip}$ as follows.

$$\Delta \Phi = C_1V_{tip} + C_2V_{tip}^2$$ \hspace{1cm} \text{Eq. 6.11.} \hspace{1cm} \text{[Model I]}$$

where \( C_1 = \frac{Q}{kz^2} q_f \) \hspace{1cm} \text{[V$^{-1}$ or C/Nm]} \hspace{1cm} \text{Eq. 6.12.}$$

$$C_2 = \frac{Q}{k} \frac{3\alpha}{z^4} \hspace{1cm} \text{[V$^{-2}$]} \hspace{1cm} \text{Eq. 6.13.}$$

In Eq. 6.11 $C_1$ and $C_2$ can be defined as functions of the surface charge and the electric polarizability (or electric susceptibility) of the sample providing that the tip-sample distance is maintained constant. Equation 6.11 will be called Model I.

Another theoretical approach including a capacitance term can be considered to explain the experimental data. This model, Model II, is based on a previously developed model used in the study of conductive and semi-conductive specimens [65, 74, 86]. Force as a function of capacitance in z direction can be defined as follows.
\[ F(z) = \frac{1}{2} \frac{dC}{dz} (\Delta U)^2 \]

\[ \frac{dF(z)}{dz} = \frac{1}{2} \frac{d^2C}{dz^2} (\Delta U)^2 \]

Eq. 6.14.

Substituting Eq 6.14 into Eq 6.1 yields

\[ \Delta \Phi = -\frac{Q}{2k} \frac{d^2C}{dz^2} (\Delta U)^2 \]

Eq. 6.15.

where \( C \) is the capacitance between the tip and the sample [Farad]

\( \Delta U \) is the potential difference between the tip and the sample [V]

Equation 6.15 indicates that the force experienced by the tip is a function of the tip and surface geometry through the capacitance, \( C(z) \) term. It can be easily shown that \( C(z) \) and consequently \( F(z) \) are rapidly decaying functions of tip-surface separation, thus a measurable signal can only be obtained at relatively small tip-surface separations. The exact functional form of tip-surface capacitance \( C(z) \) is complex even for flat surfaces and can be obtained only by numerical methods, such as finite element analysis. For a typical AFM probe geometry, the total capacitance \( C(z) \) can be conveniently approximated as a sum of the contributions from the tip apex, tip bulk, and cantilever as follows [74].

\[ C(z) = C_a(z) + C_b(z) + C_c(z) \]

Eq. 6.16.

where \( C(z) \) is the total capacitance

\( C_a(z) \) is the capacitance contribution to the tip apex
$C_b(z)$ is the capacitance contribution to the tip bulk

$C_c(z)$ is the capacitance contribution to the cantilever with its geometry

Several geometrical approximations have been suggested in order to quantify the capacitance between the tip and the surface. Sphere and point charge models can be used for smaller tip-surface separations, i.e., where the tip-sample separation is much smaller than the radius of curvature of tip apex; in that case the contribution of the tip apex dominates. For larger tip-surface separations the contribution from the conical part of the tip $C_b(z)$ becomes significant, and cone model [59, 87-89] can be considered. The cantilever contribution $C_c(z)$ may provide a non-negligible contribution at large tip-surface separation because the area of the cantilever is much larger than that of the tip; $C_c(z)$ can usually be modeled by a plate-plate model. Since the characteristic cantilever-surface separation of about 10 $\mu$m is much larger than tip-surface separation (1 to 500 nm), $C_c(z)$ is usually approximated to be a constant [68].

At first glance Eq. 6.15 (Model II) becomes complex due to the non-linear form of the capacitance and its expected second derivative. However, the model can be simplified if the tip-sample separation, $z$ is maintained constant. At a constant tip-sample separation,

$$\frac{Q}{2k} \frac{d^2C}{dz^2}$$

becomes another constant, and $\Delta \Phi$ will be only function of $\Delta U$.

As in Model I, a constant is required in Equation 6.15 to compensate for the arbitrary setting of a 0 phase angle for experiments carried out at 0 V.
\[ \Delta \Phi = -\frac{Q}{2k} \frac{d^2C}{dz^2} (V_{tip} - V_0)^2 + \text{constant} \]

\[ \Delta \Phi = C_3 (V_{tip} - V_0)^2 + C_4 \quad \text{Eq. 6.17.} \]  
[Model II]

where \( C_3 \) is \( -\frac{Q}{2k} \frac{d^2C}{dz^2} \) \([V^2]\]

\( C_4 \) can be obtained from Equation 6.17,

\[ C_4 = \frac{QV_0^2}{2k} \frac{d^2C}{dz^2} \quad \text{[unitless]} \]

The value of \( Q/2k \) may be assumed to be constant as the same tip was used during all the experiments. \( C_3 \) will depend on the second derivative of capacitance in terms of tip-sample separation. Due to the specific experimental conditions \( C_3 \) can also be considered as a constant. \( V_0 \) is related to the initial voltage in the electret sample.

Model I (Equation 6.11) and Model II (Equation 6.17) will be used to fit the phase data collected from the EFM experiments. The charge on the electret fiber will be roughly determined using \( C_i \) in Eq. 6.12.

6.3. Experimental

Specimens were prepared by attaching double sided tape (Scotch\textsuperscript{®} Permanent Double Sided Tape 137DM-2, 3M, St. Paul, MN) to a microscope glass slide (Fisherbrand\textsuperscript{®}, Fisher Scientific, Pittsburgh, PA). Fibers were then pulled out from electret filter media, laid on the double sided tape, and gently pressed onto the tape using a tweezer.

EFM experiments were performed on a Dimension 3000 AFM (Nanoscope III, Veeco...
Instruments, Santa Barbara, CA), connected to an Extender Electronics Module. Conductive cantilevers coated with Pt/Ir were used (SCM-PIT, Veeco Instruments, Santa Barbara, CA).

To image the electric field of the fiber, LiftMode™ was used with various values of lift height from the surface of the specimen (50-1000 nm). A bias voltage was applied to the tip of the cantilever using the analog 2 signal from the NanoScope III controller.

Phase Detection Mode was used to image the electric field of the fiber. Phase detection reflects the phase lag between the drive and the cantilever response. Gradients in the electric force cause a shift $\Delta \omega_{0}$ in the resonance frequency, and this resonance shift causes a rise in the phase shifts $\Delta \phi$, which is used to generate an image of the electric force gradients [81].

Linescans were carried out perpendicular to the main axis of the fiber in order to observe the effect of changes in bias voltage and lift height, while eliminating potential variations coming from different regions of the sample.

6.4. Results and Discussion

6.4.1. Constant tip-sample separation/variable applied bias voltage

Linescan images of the E1 samples as a function of bias voltage (-10 to 10V) at a constant lift height of 75 nm are shown in Figures 6.1, 6.3, and 6.5. Section (a) of the figures simultaneously shows the topographical (left) and the electric field gradient (right) images. The contrast in the EFM image (right) is generated by the phase shift $\Delta \phi$, in response to electric field gradient that the probe senses from the specimen.
The cantilever is vibrated near its resonant frequency by a small piezoelectric element. The cantilever’s resonant frequency changes in response to any additional force gradient that it may encounter. Attractive forces reduce the cantilever resonant frequency. Conversely, repulsive forces increase the resonant frequency. Changes in cantilever resonant frequency due to the presence of a force gradient are then detected by monitoring changes in the phase angle [81]. During these experiments, the bright contrast in EFM image represents the repulsive force between the cantilever and the specimen, and the dark contrast represents the attractive force.

As shown in the images, the contrast in the EFM image is a function of the bias voltage while the AFM image is not affected by it. It is expected that the minimum response from the cantilever will occur when the bias voltage is 0 V and as the bias voltage increases, the contrast in the EFM image is expected to increase.

Section (b) in Figures 6.1, 6.3, and 6.5 shows a cross sectional EFM image of sample E1 when different bias voltages are applied. In Figure 6.1 (b) and 6.3 (b), the fiber appears as a protrusion (bright) corresponding to a positive phase shift when positive tip biases are used. This shows the repulsion between the tip and E1 fiber. When negative tip biases are used, the contrast of E1 image is dark, indicating attraction between the tip and the sample. It can also be observed that the application of negative voltages to the tip caused a movement in the phase shift to negative values (attractive force). The application of a positive bias voltage caused a phase shift into positive territory (repulsive force). These results indicate that the specimens in Figures 6.1 and 6.3 are positively charged. However in Figure 6.5, the EFM contrast of E1 fiber in response to the applied tip bias is opposite the behavior exhibited in Figures 6.1 and 6.3. The fiber in Figure 6.5 appears to be negatively charged.
The values of phase shifts as a function of bias voltage are shown in Table 6.1 through 6.3. As mentioned previously, the phase shift at 0 V was set to 0 °, and the phase shifts at other bias voltages were compared to that at 0 V. The data in Tables 6.1 through 6.3 are plotted in Figures 6.2, 6.4, and 6.6 respectively.

From Figures 6.2 and 6.4, the phase shift values obtained when a positive bias was used (repulsive regime) appear to increase with voltages up to 6 V. A decrease in the repulsive response is noted at 10 V. The decrease in the repulsive response at the highest voltage may be attributed to the presence of opposite charges caused by induced polarization.

Due to the initial positive charge in the fiber, induced polarization phenomena will increase the attractive force experienced by the tip when negative voltages are used. This induced polarization force will decrease the amount of the repulsive force when positive voltages are used.

The phase shifts in Figure 6.6 show an opposite behavior to those in Figures 6.2 and 6.4. The phase shifts at negative biases appear to increase up to -3 V, then decrease at -6 V and -10 V. In this case, the fiber is negatively charged, and the repulsive response is compensated with induced polarization at negative tip biases. When positive tip biases are used, the attractive force will increase due to the induced polarization.

Model I and Model II were used to fit the experimental data by minimizing the square of the error between the experimental and the predicted values. As mentioned previously, Model I considers both the fiber charge effect and the induced polarization effect while Model II is based on capacitance relationship which relates to the sample charge via the bias offset.

The EFM response as a function of applied bias voltage using the “Scope Mode” is
shown in Figure 6.7. “Scope Mode” provides better sectional information than the “Image Mode” as changes in the sectional shape as a function of applied voltage can be easily observed. The sample shown in Figure 6.7 is positively charged, and a distended region appears at positive bias voltages while an indented region appears at negative bias voltages.

The EFM phase shift response as a function of applied bias voltage for an E1 sample after immersion in IPA is shown in Figure 6.8. The phase shift behavior of E1 exposed to IPA sample is significantly different than that of the E1 as received.

The E1-IPA sample experiences a negative phase shift when either a positive or a negative bias voltage is applied to the tip. That is to say: the tip only senses an attractive force that may be due to the induced polarization effect. It is speculated that the charge of the electret fiber was reduced significantly after exposure to the organic solvent, to the extent that the sample behaves as non-charged insulator.

Phase shift as a function of biased voltage are summarized in Table 6.4, and plotted in Figure 6.9. The experimental data was fitted to both Model I and Model II. The force gradient-bias dependence is well described by a parabola indicating the presence of induced charge interactions [74].

The best fit values for constants in Model I and Model II are summarized in Table 6. The constants for specimens E1 and E1-IPA are highlighted for comparison. All the constants are presented in two significant figures.
Table 6. Best fit values for Model I and Model II.

<table>
<thead>
<tr>
<th>Model I</th>
<th>C1 (V⁻¹ or C/Nm)</th>
<th>C2 (V⁻²)</th>
<th>q₁ (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>0.013</td>
<td>-0.0013</td>
<td>3.0×10⁻¹⁹ ~ 2.1×10⁻¹⁸</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>-0.0014</td>
<td>4.7×10⁻¹⁹ ~ 3.2×10⁻¹⁸</td>
</tr>
<tr>
<td></td>
<td>-0.0059</td>
<td>-0.0011</td>
<td>-1.4×10⁻¹⁹ ~ -9.4×10⁻¹⁹</td>
</tr>
<tr>
<td>E1-IPA</td>
<td>0.00034</td>
<td>-0.00070</td>
<td>7.9×10⁻²¹ ~ 5.4×10⁻²⁰</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model II</th>
<th>C3 (V⁻²)</th>
<th>V₀ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>-0.0013</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>-0.0014</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>-0.0011</td>
<td>-2.7</td>
</tr>
<tr>
<td>E1-IPA</td>
<td>-0.00070</td>
<td>0.25</td>
</tr>
</tbody>
</table>

In Model I, C₁ is proportional to the charge in the fiber, and C₂ describes the degree of induced polarization. From Table 6 above, the value of C₁ for the E1-IPA sample is two orders of magnitude smaller than the value for the E1 sample. This is in agreement with the initial hypothesis that the exposure to IPA will degrade the electrical field of the electret filter media.

Theoretically, the value of the charge q₁ in the sample can be obtained using Model I.
The spring constant $k$ and quality factor of the tip are very sensitive to the environment, variations in tip geometry, tip wear, and impurities preventing the calculation of an absolute charge value. According to the tip manufacturer, the values for $k$ lie between 1 N/m to 5 N/m. The quality factor $Q$ was directly using the Nanoscope III controller, and it was found to be $209 \pm 32$.

From Model II, the bias offset $V_0$ can be estimated. Bias offset is the voltage that makes the potential difference between the biased tip and sample surface to be zero. For uncharged samples, bias offset is expected to be negligible. For a charged sample, the bias offset is expected to be proportional to the value of the charge. The values of $V_0$ for the E1 samples were larger compared to that of the E1-IPA.

Model II appears to be more robust than model I as the uncertainties coming from the calculation can be reduced. Model I however can discriminate between the coulombic effect and the induced polarization effect. Although both models fit the experimental data, due to the complexities of the tip and sample’s geometry neither model can provide an exact value of the localized charge inside the fiber.

### 6.4.2. Constant applied bias voltage/variable tip-sample separation

The evolution of phase shift as a function of tip-sample separation for E1 can be observed in Figures 6.11, 6.13, and 6.15. A constant bias voltage of -10 V was used as it provided the best image contrast. Lift heights of 50 nm, 75 nm, 100 nm, 200 nm, 500 nm

$$q_f = \frac{k \varepsilon^2 C_1}{Q} \quad [\text{unit in C}]$$
and 1 µm were used in this study. As the tip-sample separation decreased, the contrast in the EFM image was improved revealing an increase in the phase shift. The phase shift at 1 µm lift height was set as 0 degrees, and the phase shifts at other lift heights were compared to this value. The changes in phase shifts as a function of lift heights at -10 V are summarized in Tables 6.5 through 6.7, and plotted in Figures 6.12, 6.14, and 6.16.

According to Eq. 6.10, both $z^{-2}$ and $z^{-4}$ are related to phase response (coulombic and polarization effects). Best fit of Model I to the experimental data is shown in Figures 6.12, 6.14 and 6.16. The model shows an agreement with the experimental data for tip-sample separations only up to around 100 nm. The fact that the experimental values at large tip-sample separation does not appear to follow the proposed trend may be an indication of the lateral contribution caused by the adjacent charges.

In Model II (Eq. 6.15), the phase shift is dependent of the second derivative of tip-surface capacitance, $d^2C/dz^2$. In order to determine the distribution of charges or polarizability, the capacitive interactions between the tip and the surface should be fully characterized. Since the EFM probe is in an irregular pyramid with a small rounded apex, there is no simple analytical solution. Some published works approximated the capacitance behavior of the tip with a cone geometry [59, 79, 87-89].

At small tip-surface separations ($z$ is smaller than tip apex radius) where the spherical tip apex provides the major contribution to the force. Therefore the bias and distance dependence of the force can be described by sphere or point charge models [88, 89].

At large tip-sample separations ($R < z < L$, where $R$ is the radius of the tip curvature, $L$ is the cone height of the tip), a cone model approximations is known to provide the best description. The cone model predicts a logarithmic dependence of the force (or capacitance
gradient) on tip-sample separation of the numerically calculated form [59, 78, 87-89]. The second derivative of the capacitance (or force gradient) will depend on 1/z, which is the derivative form of the ln z.

Figures 6.12 (b), 6.14 (b) and 6.16 (b) illustrate the exponential decrease in phase shift as a function of tip-sample separation. When a log-log plot was used, the slope of the curves was determined to be around -1, which agrees with that of a cone model.

6.5. Conclusions

EFM phase shift measurements were performed on individual electret fibers. Changes in phase shift as a function of tip bias voltage indicate the feasibility of using EFM as a qualitative method to probe charge deterioration in electret filtration media.

The E1 samples exhibited attractive or repulsive interactions depending on the sign of applied tip bias voltage. On the other hand, E1-IPA sample exhibited only attractive response for either positive or negative applied bias voltages. This behavior is probably due to the dominant contribution of the induced polarization effect. From the dissimilar behavior of E1 and E1-IPA, it is suggested that the electric field of the E1 fiber was decreased after exposure to liquid IPA.

Two models were used to interpret the experimental data. Model I includes the coulombic term and induced polarization term. The values of constants used in Model I to account for the coulombic term were considerably smaller for the E1-IPA sample than for E1 specimen.

Model II includes the bias offset which is indirectly related to the fiber charge. The bias offset $V_0$ was found to be higher for the E1 sample than for the E1-IPA specimen. Both
models fit the experimental data and corroborate the hypothesis that the electric field in the fiber decreases when the sample is exposed to the liquid IPA.

The relationship of phase shift as a function of tip-sample separation was also studied. Model I fits the experimental data at smaller tip-sample separation, but fails to do so at larger distances. This behavior is expected as at larger distances, the tip experiences lateral contribution from adjacent charges. The log-log plot of phase shifts vs. $z$ shows a slope close to -1 which agrees with a cone model for the capacitive force gradient between the tip and the sample.
(a) Topography and electric field gradient images for the E1 sample as a function of applied bias voltage. Tip-sample separation was 75 nm. Left: topographic image via TappingMode (AFM), Right: electric field gradient image via LiftMode (EFM).

(b) Phase shift section image of the E1 sample as a function of applied bias voltage. Figure 6.1. Linescan images for the E1 fiber as a function of applied bias voltage (Sample 1 for E1).
Table 6.1. Phase shift values for the E1 sample as a function of applied bias voltage (phase angle was set at 0 degrees when the applied bias voltage was 0 V); Separation between tip and sample was constant at 75 nm (Sample 1 for E1).

<table>
<thead>
<tr>
<th>Applied Bias Voltage (V)</th>
<th>Phase shift (Degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>1.9</td>
</tr>
<tr>
<td>3</td>
<td>1.9</td>
</tr>
<tr>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>-3</td>
<td>-2.6</td>
</tr>
<tr>
<td>-6</td>
<td>-7.1</td>
</tr>
<tr>
<td>-10</td>
<td>-15.1</td>
</tr>
</tbody>
</table>
Figure 6.2. Phase shifts vs. applied bias voltage for E1 sample at a tip-sample separation of 75 nm (Sample 1 for E1).
(a) Topography and electric field gradient images for the E1 sample as a function of applied bias voltage. Tip-sample separation was 75 nm. Left: topographic image via TappingMode (AFM), Right: electric field gradient image via LiftMode (EFM).

(b) Phase shift section image of the E1 sample as a function of applied bias voltage. Figure 6.3. Linescan images for the E1 fiber as a function of applied bias voltage (Sample 2 for E1).
Table 6.2. Phase shift values for the E1 sample as a function of applied bias voltage (phase angle was set at 0 degrees when the applied bias voltage was 0 V); Separation between tip and sample was constant at 75 nm (Sample 2 for E1).

<table>
<thead>
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<th>Applied Bias Voltage (V)</th>
<th>Phase shift (Degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.4</td>
</tr>
<tr>
<td>6</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>2.7</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-3</td>
<td>-4.1</td>
</tr>
<tr>
<td>-6</td>
<td>-10.1</td>
</tr>
<tr>
<td>-10</td>
<td>-20.1</td>
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Figure 6.4. Phase shifts vs. applied bias voltage for E1 sample at a tip-sample separation of 75 nm (Sample 2 for E1).
(a) Topography and electric field gradient images for the E1 sample as a function of applied bias voltage. Tip-sample separation was 75 nm. Left: topographic image via TappingMode (AFM), Right: electric field gradient image via LiftMode (EFM).

(b) Phase shift section image of the E1 sample as a function of applied bias voltage. Figure 6.5. Linescan images for the E1 fiber as a function of applied bias voltage (Sample 3 for E1).
Table 6.3. Phase shift values for the E1 sample as a function of applied bias voltage (phase angle was set at 0 degrees when the applied bias voltage was 0 V); Separation between tip and sample was constant at 75 nm (Sample 3 for E1).

<table>
<thead>
<tr>
<th>Applied Bias Voltage (V)</th>
<th>Phase shift (Degrees)</th>
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<tr>
<td>6</td>
<td>-4.2</td>
</tr>
<tr>
<td>3</td>
<td>-1.5</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-3</td>
<td>0.5</td>
</tr>
<tr>
<td>-6</td>
<td>-0.2</td>
</tr>
<tr>
<td>-10</td>
<td>-2.7</td>
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Figure 6.6. Phase shifts vs. applied bias voltage for E1 sample at a tip-sample separation of 75 nm (Sample 3 for E1).
Figure 6.7. Linescan scope images of E1 fiber with various bias voltage application (at Lift height 75 nm): Sample 4 for E1.
(a) Topography and electric field gradient images for the E1 sample after IPA immersion as a function of applied bias voltage. Tip-sample separation was 75 nm. Left: topographic image via TappingMode (AFM), Right: electric field gradient image via LiftMode (EFM).

(b) Phase shift section image of the E1 sample after IPA immersion as a function of applied bias voltage.

Figure 6.8. Linescan images for the E1 fiber after IPA immersion as a function of applied bias voltage (Sample 1 for E1-IPA).
Table 6.4. Phase shift values for the E1 sample after IPA immersion as a function of applied bias voltage (phase angle was set at 0 degrees when the applied bias voltage was 0 V); Separation between tip and sample was constant at 75 nm (Sample 1 for E1-IPA).

<table>
<thead>
<tr>
<th>Bias Voltage (V)</th>
<th>Phase shift (Degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-3.6</td>
</tr>
<tr>
<td>6</td>
<td>-1.4</td>
</tr>
<tr>
<td>3</td>
<td>-0.3</td>
</tr>
<tr>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>-3</td>
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</tr>
<tr>
<td>-6</td>
<td>-1.5</td>
</tr>
<tr>
<td>-10</td>
<td>-4.0</td>
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Figure 6.9. Phase shifts vs. applied bias voltage for E1 sample after IPA immersion at a tip-sample separation of 75 nm (Sample 1 for E1-IPA).
Figure 6.10. Linescan scope images of E1 fiber after IPA immersion with various bias voltage application (at Lift height 75 nm): Sample 2 for E1-IPA.
Figure 6.11. Linescan images of E1 fiber with various lift height application (at bias voltage of -10 V): Sample 5 for E1.
Table 6.5. Phase shift above E1 with voltage changes (phase at 1 µm was set as 0°); Bias voltage was -10 V. Phase shift at 1000 nm lift height was set as 0 degrees (Sample 5 for E1).

<table>
<thead>
<tr>
<th>Lift Height (nm)</th>
<th>Phase shift (Degree)</th>
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</thead>
<tbody>
<tr>
<td>50</td>
<td>-11.7</td>
</tr>
<tr>
<td>75</td>
<td>-7.9</td>
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<tr>
<td>100</td>
<td>-6.0</td>
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<tr>
<td>200</td>
<td>-3.4</td>
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<tr>
<td>500</td>
<td>-1.5</td>
</tr>
<tr>
<td>1000</td>
<td>0</td>
</tr>
</tbody>
</table>
(a) Phase shift above E1 with lift height changes (phase at 1 µm was set as 0° and phase shifts at other lift heights were compared to that at 1 µm).

(b) Log-Log plot for phase shift above E1 with lift height changes (phase at 1 µm was set as 0° and phase shifts at other lift heights were compared to that at 1 µm).

Figure 6.12. Plot for phase shifts with lift height changes for E1 fiber (at bias voltage of -10 V): Sample 5 for E1.
Figure 6.13. Linescan images of E1 fiber with various lift height application (at bias voltage of -10 V): Sample 6 for E1.
Table 6.6. Phase shift above E1 with voltage changes (phase at 1 µm was set as 0˚); Bias voltage was -10 V. Phase shift at 1000 nm lift height was set as 0 degrees (Sample 6 for E1).

<table>
<thead>
<tr>
<th>Lift Height (nm)</th>
<th>Phase shift (Degree)</th>
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<tbody>
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<td>75</td>
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<tr>
<td>100</td>
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<tr>
<td>200</td>
<td>-6.1</td>
</tr>
<tr>
<td>500</td>
<td>-2.0</td>
</tr>
<tr>
<td>1000</td>
<td>0</td>
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</table>
(a) Phase shift above E1 with lift height changes (phase at 1 µm was set as 0° and phase shifts at other lift heights were compared to that at 1 µm).

(b) Log-Log plot for phase shift above E1 with lift height changes (phase at 1 µm was set as 0° and phase shifts at other lift heights were compared to that at 1 µm).

Figure 6.14. Plot for phase shifts with lift height changes for E1 fiber (at bias voltage of -10 V): Sample 6 for E1.
Figure 6.15. Linescan images of E1 fiber with various lift height application (at bias voltage of -10 V): Sample 7 for E1..
Table 6.7. Phase shift above E1 with voltage changes (phase at 1 µm was set as 0°); Bias voltage was -10 V. Phase shift at 1000 nm lift height was set as 0 degrees (Sample 7 for E1).

<table>
<thead>
<tr>
<th>Lift Height (nm)</th>
<th>Phase shift (Degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
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</tr>
<tr>
<td>75</td>
<td>-9.0</td>
</tr>
<tr>
<td>100</td>
<td>-7.2</td>
</tr>
<tr>
<td>200</td>
<td>-3.8</td>
</tr>
<tr>
<td>500</td>
<td>-1.3</td>
</tr>
<tr>
<td>1000</td>
<td>0</td>
</tr>
</tbody>
</table>
(a) Phase shift above E1 with lift height changes (phase at 1 µm was set as 0° and phase shifts at other lift heights were compared to that at 1 µm).

(b) Log-Log plot for phase shift above E1 with lift height changes (phase at 1 µm was set as 0° and phase shifts at other lift heights were compared to that at 1 µm).

Figure 6.16. Plot for phase shifts with lift height changes for E1 fiber (at bias voltage of -10 V): Sample 7 for E1.
Chapter 7. Electric Force Microscopy Investigation on an Electret Fiber Using Frequency Modulation Mode

7.1. Introduction

In the previous chapter, EFM-Phase Detection Mode was used in order to examine the hypothesis that charge deterioration of the electret media caused the deterioration in filtration performance when the media was exposed to liquid chemicals. In addition to Phase Detection Mode, Frequency Modulation Mode can also be used for Electric Field Gradient Imaging (EFGI).

In Frequency Modulation Mode, a gradient in the electric force causes a shift $\Delta F_0$ in the resonance frequency. This resonance shift is used to generate an image of the electric force gradients in the sample [81]. The relationship of the frequency shift vs. bias voltage as well as the frequency shift vs. lift height will be discussed using the models proposed in the previous chapter.

7.2. Theory

From fundamental relationship for driven, damped harmonic oscillations the frequency
shift was described as follows [65]

\[
\Delta \omega = -\frac{\omega_0}{2k} \frac{dF}{dz}
\]

Eq. 7.1.

where

- \(\Delta \omega\) is frequency shift [Hz]
- \(\omega_0\) is the resonance frequency [Hz]
- \(k\) is the spring constant of the tip [N/m]
- \(z\) is the distance between the tip and the sample [m]
- \(F\) is the force [N]

In Chapter 6, the force between the biased tip and a charged dielectric sample was explained as a contribution of two phenomena; the coulombic force (attraction or repulsion between the biased tip and the sample) and the induced polarization due to the biased tip (attraction between the biased tip and the sample) as follows.

\[
F = q_f \left( \frac{V_{tip} - V_0}{z} \right) - \alpha V_{tip}^2 \frac{1}{z^3}
\]

Eq. 7.2.

\[
\frac{dF}{dz} = -q_f \left( \frac{V_{tip} - V_0}{z^2} \right) + 3\alpha V_{tip}^2 \frac{1}{z^4}
\]

Eq. 7.3.

Incorporating Eq. 7.3 into Eq 7.1 yields

\[
\Delta \omega = -\frac{\omega_0}{2k} \left[ -q_f \left( \frac{V_{tip} - V_0}{z^2} \right) + 3\alpha V_{tip}^2 \frac{1}{z^4} \right] + \text{constant}
\]

Eq. 7.4.
In order to simplify the acquisition of experimental data, a frequency shift of 0 Hz was set when the bias voltage applied to the tip was 0 V. In this way all other measurements were easily related to the 0 V baseline. Due to this artificial offset, a constant is included in Eq 7.4 without losing the generality of the expression.

Constant is the offset to 0 Hz when $V_{\text{tip}} = 0$ V. The value of constant can be determined by solving Equation 7.4.

$$\text{constant} = \frac{\omega_0 q_f V_0}{2kz^2}$$

The expression for frequency shift then becomes

$$\Delta \omega = -\frac{\omega_0}{2k} \left[ -\frac{q_f}{z^2} V_{\text{tip}} + \frac{3\alpha}{z^4} V_{\text{tip}}^2 \right]$$

The frequency shift can also be expressed as a function of $V_{\text{tip}}$ as follows

$$\Delta \omega = C_1 V_{\text{tip}} + C_2 V_{\text{tip}}^2 \quad \text{Eq. 7.5.}$$

[Model I]

where

$$C_1 = \frac{\omega_0 q_f}{2kz^2} \quad [\text{Hz C/Nm or Hz/V}] \quad \text{Eq. 7.6.}$$

$$C_2 = -\frac{3\alpha \omega_0}{2kz^4} \quad [\text{Hz/V}^{-2}] \quad \text{Eq. 7.7.}$$

In Eq. 7.5 $C_1$ and $C_2$ can be defined as functions of the surface charge and the electric polarizability (or electric susceptibility) of the sample providing that the tip-sample separation is maintained constant. Equation 7.5 will be called Model I.

A second theoretical model including capacitance term can also be considered to
explain the experimental data. This model, Model II, is based on the study of conductive and semi-conductive specimens [65, 74, 86]. Force gradient as a function of capacitance in the $z$ direction was defined by Eq. 6.14 [65].

Substituting Eq. 6.14 into Eq. 7.8 yields

$$
\Delta \omega = -\frac{\omega_0}{4k} \frac{d^2C}{dz^2} (\Delta U)^2
$$

Eq. 7.8.

where $C$ is the capacitance between the tip and the sample [Farad]

$\Delta U$ is the potential difference between the tip and the sample [V]

Eq. 7.8 can be simplified if the tip-sample separation, $z$, is maintained constant. At a constant tip-sample separation, $-\frac{\omega_0}{4k} \frac{d^2C}{dz^2}$ becomes another constant, and $\Delta \omega$ will be a function of $\Delta U$.

As in Model I, a constant is required in Equation 7.8 to compensate for the arbitrary setting of a 0 Hz for experiments carried out at 0 V.

$$
\Delta \omega = -\frac{\omega_0}{4k} \frac{d^2C}{dz^2} (V_{tip} - V_0)^2 + \text{constant}
$$

$$
\Delta \omega = C_3(V_{tip} - V_0)^2 + C_4
$$

Eq. 7.9.

[Model II]

where $C_3$ is $-\frac{\omega_0}{4k} \frac{d^2C}{dz^2} $ [Hz/V$^2$]

$$
C_4 = \frac{\omega_0 V_0^2}{4k} \frac{d^2C}{dz^2} $ [Hz]
The value of $k$ or $\omega_0$ can be assumed to be constant as the same tip was used during all the experiments. $C_3$ will depend on the second derivative of capacitance as a function of tip-sample separation. Due to the specific experimental conditions, $C_3$ can also be considered as a constant. $V_0$ is related to the initial voltage in the electret sample.

Model I (Equation 7.5) and Model II (Equation 7.9) will be used to fit the frequency shifts collected from the EFM experiment. The charge on the electret fiber can be roughly determined by the value of $C_1$.

7.3. Experimental

Specimens for EFM were prepared by attaching double sided tape (Scotch® Permanent Double Sided Tape 137DM-2, 3M, St. Paul, MN) to a microscope glass slide (Fisherbrand®, Fisher Scientific, Pittsburgh, PA). Fibers were then pulled out from electret filter media, laid on the double sided tape, and gently pressed onto the tape using a tweezer.

EFM experiments were performed on a Dimension 3000 AFM (Nanoscope III, Veeco Instruments, Santa Barbara, CA), connected to an Extender Electronics Module. Conductive cantilevers coated with Pt/Ir were used (SCM-PIT, Veeco Instruments, Santa Barbara, CA).

To image the electric field of the fiber, LiftMode™ was used with various values of lift height from the surface of the specimen (50-1000 nm). A bias voltage was applied to the tip of the cantilever using the analog 2 signal from the NanoScope III controller. Frequency Modulation Mode was used to image the electric field gradient imaging of the fiber.

Linescans were carried out perpendicular to the main axis of the fiber in order to
observe the effect of changes in bias voltage and lift height, while eliminating potential variations caused by the topography of the sample.

**7.4. Results and discussion**

**7.4.1. Constant tip-sample separation/variable applied bias voltage**

Linescan images of the E1 samples as a function of bias voltage (-10 to 10V) at a constant lift height of 75 nm are shown in Figures 7.1, 7.3, 7.5, and 7.7. These sections of the figures simultaneously show the topographical (left) and the electric field gradient (right) images. The contrast in the EFM image (right) is generated by the frequency shift $\Delta \omega$, in response to the force gradient that the probe senses from the specimen. During these experiments, the bright contrast in the EFM image represents the repulsive force, and the dark contrast represents the attractive force between the cantilever and the specimen.

As shown in Figures 7.1, 7.3, 7.5 and 7.7, the contrast in the EFM image is a function of the bias voltage while the AFM image is not affected by it. It is expected that the minimum response from the cantilever will occur when the bias voltage is 0 V and as the bias voltage increases, the contrast in the EFM image is expected to increase.

Section (b) of Figures 7.1, 7.3, 7.5 and 7.7 shows a cross sectional EFM image of sample E1 when different bias voltages are applied. In Figure 7.1 (b) and 7.3 (b), the fiber appears as a protrusion (bright) corresponding to a positive frequency shift when a positive tip bias voltage is applied. This shows repulsion between the tip and E1 specimen. When negative tip biases are used, the contrast of the image is dark, indicating attraction between the tip and the sample. It can also be observed that the application of negative voltage to the tip caused a movement in the frequency shift to negative values (attractive force).
application of a positive bias voltage caused a frequency shift into positive territory (repulsive force). These results indicate that the specimens in Figures 7.1 and 7.3 are indeed positively charged. However in Figures 7.5 and 7.7, the EFM contrast of E1 fiber in response to the applied tip bias exhibit an opposite behavior. The fibers in Figures 7.5 and 7.7 appear to be negatively charged.

The values of frequency shift as a function of bias voltage are shown in Tables 7.1 through 7.4. As mentioned previously, the frequency shift at 0 V was set to 0 Hz, so the frequency shifts at other biases were compared to that at 0 V. The data in Tables 7.1 through 7.4 are plotted in Figures 7.2, 7.4, 7.6, and 7.8.

Figures 7.2 and 7.4 illustrate that the frequency shift values obtained when a positive bias voltages were applied (repulsive regime) appear to increase up to 6 V. A decrease in the repulsive response is noted at 10 V. The decrease in the repulsive response at the highest voltage may be attributed to the presence of opposite charges caused by induced polarization.

Due to the initial positive charge in the fiber, induced polarization phenomena will increase the attractive force experienced by the tip when negative voltages are used. This induced polarization force will decrease the amount of repulsive force when positive voltages are used.

Figures 7.6 and 7.8 show opposite behavior to those described by Figures 7.2 and 7.4. The frequency shifts at negative biases appear to increase and then decrease afterwards. In this case, the fiber is negatively charged, and the repulsive response is compensated with induced polarization at negative tip biases. When positive tip biases are used, the attractive force will increase due to the induced polarization.
Model I and Model II were used to fit the experimental data by minimizing the square of the error between the experimental and the predicted values. As mentioned previously, Model I considers both the fiber charge effect and the induced polarization effect while Model II is based on capacitance relationship which relates to the sample charge via the bias offset. Both models exhibit good agreement with the experimental data.

The EFM response as a function of applied bias voltage using the “Scope Mode” is shown in Figure 7.9. “Scope Mode” provides better sectional information as changes in the sectional shape as a function of applied voltage can be easily observed. The sample shown in Figure 7.9 is positively charged. Distended region appears at positive bias voltages while an indented region appears at negative bias voltages.

The EFM frequency shift response as a function of applied bias voltage for an E1 sample after immersion in IPA is shown in Figure 7.10. The frequency shift behavior of E1 exposed to IPA sample is significantly different than that of the E1 as received.

The E1-IPA sample experiences a negative frequency shift when either a positive or a negative bias voltage is applied to the tip. That is to say: the tip only senses an attractive force that may be caused by the induced polarization. It is speculated that the charge of the electret fiber was reduced significantly after exposure to the organic solvent, to the extent that the sample behaves as non-charged insulator.

Values for frequency shift as a function of biased voltage are summarized in Table 7.5, and plotted in Figure 7.11. The experimental data was found to fit to both Model I and Model II. The force gradient vs. bias voltage dependence is well described by a parabola indicating the presence of induced charge interactions [74].

The best fit values for the constants in Model I and Model II are summarized in Table 7.
The constants for E1 and E1-IPA are highlighted for comparison. All the constants are presented in two significant figures.

Table 7. Best fit values for Model I and Model II.

<table>
<thead>
<tr>
<th></th>
<th>Model I</th>
<th></th>
<th>Model II</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_1$ (Hz/V)</td>
<td>$C_2$ (Hz/V$^2$)</td>
<td>$q_f$ (C)</td>
<td>$V_0$ (V)</td>
</tr>
<tr>
<td>E1</td>
<td>2.5</td>
<td>-0.19</td>
<td>$4.5 \times 10^{-19} \sim 2.3 \times 10^{-18}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>-0.19</td>
<td>$2.5 \times 10^{-19} \sim 1.3 \times 10^{-18}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1.1</td>
<td>-0.20</td>
<td>$-2.0 \times 10^{-19} \sim -1.0 \times 10^{-18}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-3.0</td>
<td>-0.19</td>
<td>$-5.4 \times 10^{-19} \sim -2.8 \times 10^{-18}$</td>
<td></td>
</tr>
<tr>
<td>E1-IPA</td>
<td>0.025</td>
<td>-0.11</td>
<td>$4.5 \times 10^{-21} \sim 2.3 \times 10^{-20}$</td>
<td></td>
</tr>
<tr>
<td>E1</td>
<td>-0.19</td>
<td></td>
<td></td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>-0.19</td>
<td></td>
<td></td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>-0.20</td>
<td></td>
<td></td>
<td>-2.8</td>
</tr>
<tr>
<td></td>
<td>-0.19</td>
<td></td>
<td></td>
<td>-8.2</td>
</tr>
<tr>
<td>E1-IPA</td>
<td>-0.11</td>
<td></td>
<td></td>
<td>0.12</td>
</tr>
</tbody>
</table>

In Model I, $C_1$ is proportional to the charge in the fiber, and $C_2$ describes the degree of induced polarization. From Table 7, the value of $C_1$ for the E1-IPA sample is much smaller
than the value for the E1 sample. This is in agreement with the initial hypothesis that the
exposure to IPA will degrade the electric field of the electret filter media.

Theoretically, the value of the charge \( q_f \) in the sample can be obtained using Model I.

\[
q_f = \frac{2k^2C_1}{\omega_0} \quad [\text{unit in C}]
\]

Eq. 7.10.

According to the tip manufacturer, the values for \( k \) lie between 1 N/m to 5 N/m. \( \omega_0 \) of
the tip was measured to be 62 ± 2 kHz.

From Model II, the value of bias offset \( V_0 \) can be estimated. Bias offset is the voltage
that makes the potential difference between the biased tip and sample surface to be zero.
For uncharged samples, bias offset is expected to be negligible. For a charged sample, the
bias offset is expected to be proportional to the value of the charge. The values of \( V_0 \) for the
E1 samples are larger than that of the E1-IPA.

Model II appears to be more robust than model I as the uncertainties from calculation
can be reduced. Model I however can discriminate between the coulombic effect and the
induced polarization effect. Although both models fit the experimental data, due to the
complexities of the tip and sample’s geometry neither model can provide an exact value of
the localized charge inside the fiber.

Analysis of frequency response has advantage over that of phase response in that the
models do not include the quality factor \( Q \) of the probe.
7.4.2. Constant applied bias voltage/variable tip-sample separation

The evolution of frequency shift as a function of tip-sample separation can be observed in Figures 7.13, 7.15, and 7.17. A constant voltage of -10 V was used as it provided the best image contrast. Lift heights of 50 nm, 75 nm, 100 nm, 200 nm, 500 nm and 1 µm were used in this study. As the tip-sample separation decreased, the contrast in the EFM image was improved revealing an increase in the frequency shift. The frequency shifts at 1 µm lift height was set as 0 Hz, and the frequency shifts at other lift heights were compared to this value. The changes in frequency shifts as a function of lift heights at -10 V are summarized in Tables 7.6 through 7.8, and plotted in Figures 7.14, 7.16 and 7.18.

According to Eq. 7.4, both $z^{-2}$ and $z^{-4}$ are related to frequency shifts (coulombic and polarization effects). Best fit of Model I to the experimental data is shown in Figures 7.14, 7.16 and 7.18. The model shows an agreement with the experimental data for tip-sample separations only up to around 100 nm. The fact that the experimental values at large tip-sample separation does not appear to follow the proposed trend may be an indication of the lateral contribution caused by the adjacent charges.

In Model II, the frequency shift is dependent of the second derivative of tip-surface capacitance, $d^2C/dz^2$. Characterization of the capacitive interactions between the tip and the surface is shown in Chapter 6, adopting cone model for the tip geometry.

Figures 7.14 (b), 7.16 (b) and 7.18 (b) illustrate the exponential decrease in frequency shift as a function of tip-sample separation. When a log-log plot was used, the slopes of the curves were determined to be around -1, which agrees with that of a cone model indicating $1/z$ dependence of force gradient.
7.5. Conclusions

Individual electret fibers were characterized via EFM frequency measurements. Changes in frequency shift as a function of tip bias voltage indicate the feasibility of using EFM as a qualitative method to probe charge deterioration in electret filtration media.

The E1 samples exhibited attractive or repulsive responses depending on the sign of applied tip bias voltage. On the other hand, the E1-IPA sample exhibited only attractive response for either positive or negative applied bias voltages. This behavior is probably due to the dominant contribution of the induced polarization effect. From the dissimilar behavior of E1 and E1-IPA, it is suggested that the electric field of the E1 fiber was reduced after exposure to liquid IPA.

Two models were used to interpret the experimental data. Model I includes the coulombic term and induced polarization term. The values of constants used in Model I to account for the coulombic term were considerably smaller for the E1-IPA sample than for E1 specimen.

Model II includes the bias offset which is indirectly related to the fiber charge. The bias offset $V_0$ was found to be higher for the E1 sample than for the E1-IPA specimen. Both models fit the experimental data and corroborate the hypothesis that the electric field in the fiber decreases when the sample is exposed to the liquid IPA.

The relationship of frequency shift as a function of tip-sample separation was also studied. Model I fits the experimental data at smaller tip-sample separation, but fails to do so at larger distances. This behavior is expected as at larger distances, the tip experiences lateral contribution from adjacent charges. The log-log plot of frequency shifts vs. $z$ shows the slopes close to -1 in agreement with a cone model for the capacitive force gradient.
between the tip and the sample.
(a) Topography and electric field gradient images for the E1 sample as a function of applied bias voltage. Tip-sample separation was 75 nm. Left: topographic image via TappingMode (AFM), Right: electric field gradient image via LiftMode (EFM).

(b) Frequency shift section image of the E1 sample as a function of applied bias voltage. Figure 7.1. Linescan images for the E1 fiber as a function of applied bias voltage (Sample 8 for E1).
Table 7.1. Frequency shift values for the E1 sample as a function of applied bias voltage (Frequency was set at 0 Hz when the applied bias voltage was 0 V); Separation between tip and sample was constant at 75 nm (Sample 8 for E1).

<table>
<thead>
<tr>
<th>Applied Bias Voltage (V)</th>
<th>Frequency shift (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6.0</td>
</tr>
<tr>
<td>6</td>
<td>8.3</td>
</tr>
<tr>
<td>3</td>
<td>5.8</td>
</tr>
<tr>
<td>0</td>
<td>0.</td>
</tr>
<tr>
<td>-3</td>
<td>-9.2</td>
</tr>
<tr>
<td>-6</td>
<td>-21.9</td>
</tr>
<tr>
<td>-10</td>
<td>-43.7</td>
</tr>
</tbody>
</table>
Figure 7.2. Frequency shifts vs. applied bias voltage for E1 sample at a tip-sample separation of 75 nm (Sample 8 for E1).
(a) Topography and electric field gradient images for the E1 sample as a function of applied bias voltage. Tip-sample separation was 75 nm. Left: topographic image via TappingMode (AFM), Right: electric field gradient image via LiftMode (EFM).

(b) Frequency shift section image of the E1 sample as a function of applied bias voltage.

Figure 7.3. Linescan images for the E1 fiber as a function of applied bias voltage (Sample 9 for E1).
Table 7.2. Frequency shift values for the E1 sample as a function of applied bias voltage (Frequency was set at 0 Hz when the applied bias voltage was 0 V); Separation between tip and sample was constant at 75 nm (Sample 9 for E1).

<table>
<thead>
<tr>
<th>Applied Bias Voltage (V)</th>
<th>Frequency shift (Hz)</th>
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<tbody>
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<td>10</td>
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<tr>
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<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-3</td>
<td>-5.8</td>
</tr>
<tr>
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</tr>
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</table>
Figure 7.4. Frequency shifts vs. applied bias voltage for E1 sample at a tip-sample separation of 75 nm (Sample 9 for E1).
(a) Topography and electric field gradient images for the E1 sample as a function of applied bias voltage. Tip-sample separation was 75 nm. Left: topographic image via TappingMode (AFM), Right: electric field gradient image via LiftMode (EFM).

(b) Frequency shift section image of the E1 sample as a function of applied bias voltage. Figure 7.5. Linescan images for the E1 fiber as a function of applied bias voltage (Sample 10 for E1).
Table 7.3. Frequency shift values for the E1 sample as a function of applied bias voltage (Frequency was set at 0 Hz when the applied bias voltage was 0 V); Separation between tip and sample was constant at 75 nm (Sample 10 for E1).

<table>
<thead>
<tr>
<th>Applied Bias Voltage (V)</th>
<th>Frequency shift (Hz)</th>
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</tr>
<tr>
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<td>-8.5</td>
</tr>
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Figure 7.6. Frequency shifts vs. applied bias voltage for E1 sample at a tip-sample separation of 75 nm (Sample 10 for E1).
(a) Topography and electric field gradient images for the E1 sample as a function of applied bias voltage. Tip-sample separation was 75 nm. Left: topographic image via TappingMode (AFM), Right: electric field gradient image via LiftMode (EFM).

(b) Frequency shift section image of the E1 sample as a function of applied bias voltage.
Figure 7.7. Linescan images for the E1 fiber as a function of applied bias voltage (Sample 11 for E1).
Table 7.4. Frequency shift values for the E1 sample as a function of applied bias voltage (Frequency was set at 0 Hz when the applied bias voltage was 0 V); Separation between tip and sample was constant at 75 nm (Sample 11 for E1).

<table>
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<th>Applied Bias Voltage (V)</th>
<th>Frequency shift (Hz)</th>
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<tr>
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<td>11.9</td>
</tr>
<tr>
<td>-10</td>
<td>11.5</td>
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</table>
Figure 7.8. Frequency shifts vs. applied bias voltage for E1 sample at a tip-sample separation of 75 nm (Sample 11 for E1).
Figure 7.9. Linescan scope images of E1 fiber with various bias voltage application (at Lift height 75 nm): Sample 12 for E1.
(a) Topography and electric field gradient images for the E1 sample after IPA immersion as a function of applied bias voltage. Tip-sample separation was 75 nm. Left: topographic image via TappingMode (AFM), Right: electric field gradient image via LiftMode (EFM).

(b) Frequency shift section image of the E1 sample after IPA immersion as a function of applied bias voltage.

Figure 7.10. Linescan images for the E1 fiber after IPA immersion as a function of applied bias voltage (Sample 3 for E1-IPA).
Table 7.5. Frequency shift values for the E1 sample after IPA immersion as a function of applied bias voltage (Frequency was set at 0 Hz when the applied bias voltage was 0 V); Separation between tip and sample was constant at 75 nm (Sample 3 for E1-IPA).

<table>
<thead>
<tr>
<th>Applied Bias Voltage (V)</th>
<th>Frequency shift (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.0</td>
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<td>-6</td>
<td>-4.4</td>
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<tr>
<td>-10</td>
<td>-11.1</td>
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Figure 7.11. Frequency shifts vs. applied bias voltage for E1 sample after IPA immersion at a tip-sample separation of 75 nm (Sample 3 for E1-IPA).
Figure 7.12. Linescan scope images of E1 fiber after IPA immersion with various bias voltage application (at Lift height 75 nm): Sample 4 for E1-IPA.
Figure 7.13. Linescan images of E1 fiber with various lift height application (at bias voltage of -10 V): Sample 13 for E1.
Table 7.6. Frequency shift above E1 with voltage changes (frequency at 1 µm was set as 0 Hz); Bias voltage was -10 V. Frequency shift at 1000 nm lift height was set as 0 Hz (Sample 13 for E1).

<table>
<thead>
<tr>
<th>Lift Height (nm)</th>
<th>Frequency shift (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
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<tr>
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<td>-40.7</td>
</tr>
<tr>
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<td>-33.8</td>
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<tr>
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<td>-19.4</td>
</tr>
<tr>
<td>500</td>
<td>-6.3</td>
</tr>
<tr>
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<td>0</td>
</tr>
</tbody>
</table>
(a) Frequency shift above E1 with lift height changes (frequency at 1 \( \mu \text{m} \) was set as 0 Hz and frequency shifts at other lift heights were compared to that at 1 \( \mu \text{m} \)).

(b) Log-Log plot for frequency shift above E1 with lift height changes (frequency at 1 \( \mu \text{m} \) was set as 0 Hz and frequency shifts at other lift heights were compared to that at 1 \( \mu \text{m} \)).

Figure 7.14. Plot for frequency shifts with lift height changes for E1 fiber (at bias voltage of -10 V): Sample 13 for E1.
Figure 7.15. Linescan images of E1 fiber with various lift height application (at bias voltage of -10 V): Sample 14 for E1.
Table 7.7. Frequency shift above E1 with voltage changes (frequency at 1 µm was set as 0 Hz); Bias voltage was -10 V. Frequency shift at 1000 nm lift height was set as 0 Hz (Sample 14 for E1).

<table>
<thead>
<tr>
<th>Lift Height (nm)</th>
<th>Frequency shift (Hz)</th>
</tr>
</thead>
<tbody>
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<tr>
<td>75</td>
<td>-10.1</td>
</tr>
<tr>
<td>100</td>
<td>-8.1</td>
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<tr>
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<td>-3.9</td>
</tr>
<tr>
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<td>-0.9</td>
</tr>
<tr>
<td>1000</td>
<td>0</td>
</tr>
</tbody>
</table>
(a) Frequency shift above E1 with lift height changes (frequency at 1 µm was set as 0 Hz and frequency shifts at other lift heights were compared to that at 1 µm).

(b) Log-Log plot for frequency shift above E1 with lift height changes (frequency at 1 µm was set as 0 Hz and frequency shifts at other lift heights were compared to that at 1 µm).

Figure 7.16. Plot for frequency shifts with lift height changes for E1 fiber (at bias voltage of -10 V): Sample 14 for E1.
Figure 7.17. Linescan images of E1 fiber with various lift height application (at bias voltage of -10 V): Sample 15 for E1.
Table 7.8. Frequency shift above E1 with voltage changes (frequency at 1 µm was set as 0 Hz); Bias voltage was -10 V. Frequency shift at 1000 nm lift height was set as 0 Hz (Sample 15 for E1).

<table>
<thead>
<tr>
<th>Lift Height (nm)</th>
<th>Frequency shift (Hz)</th>
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</thead>
<tbody>
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<tr>
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<td>-27.6</td>
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</table>
(a) Frequency shift above E1 with lift height changes (frequency at 1 μm was set as 0 Hz and frequency shifts at other lift heights were compared to that at 1 μm).

(b) Log-Log plot for frequency shift above E1 with lift height changes (frequency at 1 μm was set as 0 Hz and frequency shifts at other lift heights were compared to that at 1 μm).

Figure 7.18. Plot for frequency shifts with lift height changes for E1 fiber (at bias voltage of -10 V): Sample 15 for E1.
CHAPTER 8. FUTURE WORK AND SUGGESTIONS

For future study, it is suggested that electret film rather than electret fiber may be used to pursue more fundamental EFM analysis. This will reduce analytical complications coming from 3D geometry of the electret fibers. Electret films with smooth surfaces may be obtained with several materials including PP (polypropylene), PE (polyethylene), and PTFE (polytetrafluoroethylene) using solution casting, spin coating or self-assembled nanolayers. If a model surface is used, the charge deterioration may be correlated to the material properties.

In-situ EFM experiments in the presence of organic vapors is suggested. EFM experiments may be performed in a sealed environment containing organic vapors with predetermined concentration, and the EFM response or the charge deterioration may be monitored as a function of time. This can be achieved by using a liquid-gas cell currently available at Veeco, Inc.

The EFM tip is worn out with use hence the tip geometry changes as a function of time influencing the EFM response. If a tip with high aspect ratio is used, the problems related to tip wear may be reduced. Tips with high aspect ratio can be obtained at Team Nanotech in Germany.

This work has shown that filter performance can decrease if filter media comes into
contact with liquid organic solvents or liquid aerosols. A possible scenario, where the respirator filter media could be in contact with liquid solvents, would be the painting industry, where solvents are sprayed or brushed on surfaces. It is possible that airborne solvents could be pulled into the filter media while the inhaling action occurs through the air purifying respirators. A study simulating the inhaling action of chemical aerosol might be needed for better understanding of “real” situation in working environment. A field study including working environment conditions may help relating fundamental data to practical applications.

Electret filter media generally shows high performance before exposure to liquid chemicals. There are a few considerations for reducing the effect of liquid chemical on the filtration performance. One would be lowering the surface energy of the material, to keep the filter media from wetting. Coating with a fluorinated chemical or producing electret media using fluorinated material could be considered.

Electret filter media made of small fiber, nano-fibers for example, would be another consideration. It was shown by Huang [59] that the smaller the fiber, the lower the charge decay rate by heat treatment. There would be another chance to investigate the filtration performance of electret filter media made from nano-fibers, which can be produced by electrospinning.
References


[35] "NIOSH Guide to the Selection and Use of Particulate Respirators Certified Under 42


X. Liang, J. Liu, L. Han, H. Tang, and S.-Y. Xu, "Electric force microscopy study of


