

Enhanced De-inking and Recyclability of Laser Printed Paper  
by Plasma-Assisted Fiber Coating

A Thesis  
Presented to  
The Academic Faculty

By  
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In Partial Fulfillment  
of the Requirements for the Degree  
Master of Science in the  
Paper Science & Engineering  
from  
School of Chemical & Biomolecular Engineering

Georgia Institute of Technology  
May 2006

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Date Approved: January 9, 2006

## **ACKNOWLEDGEMENTS**

I would like to express my sincere appreciation to my faculty advisors, Dr. Dennis Hess and Dr. Timothy Patterson for their support and guidance throughout my graduate career at Georgia Institute of Technology, also allowing me to work on a project that merged the paper industry with the semiconductor industry.

I also would like to thank my family and friends for their support, especially Raymond W. Chafin II for his endless support and encouragement.

Lastly I would like to thank my fellow group members, Prabhakar Tamarasi and Ashiwini Sinha for their help and support.

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## SUMMARY

Office waste paper is one of the fastest growing segments of the recycled fiber industry. Toner particles are rigid, insoluble and difficult to disperse and detach from fibers. Therefore papers made from recycled office waste having high toner content will contain noticeable ink particles. This work will consider an alternative way of efficient de-inking using plasma polymers which will not affect the fibers chemically or mechanically. The focus is development and characterization of plasma-deposited films to serve as a barrier film for the adhesion of ink toner to the paper fibers and thereby enhance ink lift off from the fibers. The plasma treated paper is coated with fluorocarbon (PFE) and polyethylene glycol (PEG) films, with constant thickness of PFE and varying the thickness of PEG by 1500Å, from 1500Å to 4500Å, for the three cases studied (PFE>PEG, PFE=PEG, PFE<PEG). Handsheets were made using virgin fibers to eliminate effects of fillers. Once the sheets were coated and printing performed, they were re-pulped and both the slurry and the de-inking surfactant were placed in a flotation cell. Handsheets were made from the collected foam and stock and were scanned for particle count. The results indicated higher ink loss for the cases with increased thickness of polymer films. A handsheet with a 7500Å film (PFE = 3000Å and PEG = 4500Å) showed 61% ink removal compared to 38% for handsheets with no film deposited. There was also less material loss for the cases with higher polymer film thickness.



## **CHAPTER 1**

### **INTRODUCTION**

Office waste paper is one of the fastest growing segments of the recycled fiber industry. However, the toners used in xerographic and laser printers present a special removal challenge. They consist of thermoplastic polymers of styrene and butadiene, acrylic or polyester along with carbon black or other pigments [3] and are attached to the surface of the paper where they fuse to the fibers.

Toner particles are rigid, insoluble and difficult to disperse and detach from fibers. Therefore papers made from recycled office waste having high toner content will contain noticeable ink particles often referred to as specs. Their presence even in small quantities in the raw material results in a loss of de-inking efficiency and lower de-inked pulp brightness [4-6]. Recycled office waste with more than 15% toner content commands a lower price, and is recycled into less valuable paper materials [7].

Before examining the effectiveness of de-inking laser and xerographic printed wastes, it is essential first to understand the printing process involved and the toners (inks) used in the printed paper produced by such methods. In both laser and xerographic processes the printer forms images by placing dots of toner or 'ink' on a regular matrix which is then fused to leave a permanent image. Toner systems work by the adherence of charged toner particles onto an oppositely charged image area [8, 9]. In the basic dry xerographic printing technique imaging is done on an electrostatically charged metal drum [10]. Exposure to light causes the drum to discharge. Ink powder, which ranges from 8 to 15

microns in diameter (toner and carrier) cascades over the imaged surface, and adheres to the unexposed (dark) area. Paper then contacts the drum and picks up the ink (by static charge). The paper is conveyed to a heater zone where toner is thermally fused at approximately 100°C [11, 12].

The principle of a laser imaging system is similar to dry xerographic printing with two exceptions; a) imaging is done with a computer directed laser that ‘prints’ on a plastic film, b) ink is fixed much more rapidly, using a combination of heat and pressure.

The pigments in both these inks are carbon black mixed with thermoplastic resin binders (styrene-acrylate copolymer) that will set (crosslink) at 100°C during the fusing stage of the copying/printing process [13, 14]. The factors likely to affect the de-inkability are similar in both the laser and xerographic processes.

### **1.1 Present de-inking practice for laser and xerographic printing waste**

The two most common techniques for removing ink particles from laser and xerographic printing wastes are washing and flotation de-inking. The chemistry involved in the two processes is based on different principles. Washing systems attempt to reduce the size of the ink particles, thus facilitating their removal with the filtrate [11]. Conversely, a flotation system aims to keep the size of the ink particles large so that effective surface collection can be achieved using specific chemical systems. Both of these processes normally operate at high pH (10 to 11) [15, 16] with the use of conventional alkaline de-inking agent such as sodium hydroxide, sodium carbonate, sodium silicate and hydrogen peroxide [12]. In this environment the paper structure collapses rapidly and releases the ink particles into suspension. A dispersant is added to stabilize the colloidal suspension

of ink particles in washing processes. The dispersant is replaced with collector soap in flotation de-inking.

### **1.2 Problems in current de-inking technology**

The laser and xerographic inks are thermoplastics which are copolymers of styrene and acrylate designed to be non-tacky at room temperature but to melt at temperatures of 70 to 120°C [17]. During the fusing stage of the printing/copying process at high temperatures (~100°C), these thermoplastic resin binders set to form the printed film by cross-linking.

These heavy cross linked, strongly bound systems will be fragmented to micron size only by strong mechanical forces, which in turn lead to fiber degradation. Conventional chemical treatment is not effective in reducing particle size further; particles are seen as dirt in the finished product [12].

Due to their small size and hydrophilic nature, these ink particles are not attracted to the dispersed air bubbles. Therefore, they are poorly collected by air bubbles during flotation [5]. Although xerographic and laser toner inks are difficult to remove, a combination of chemicals (fatty acid soaps, fatty acids, fatty acid dispersions, liquid chemicals) and multiple stage de-inking and dispersion (repeating the de-inking and in some cases dispersion) processes can produce pulp suitable for printing and writing paper. Promising processes are wash/flotation, two stage flotation and agglomeration and densification with subsequent removal by screening and cleaning. These processes for de-inking laser and xerographic waste require specific chemicals (surfactants), depending

on the process. However, it is well established that the conventional flotation process is ineffective at removing toner inks [4-6, 18]. The proposed plasma enhanced de-inking process requires no chemicals to de-ink these waste papers and the ink is easily removed.

### **1.3 Recycling Overview**

Mixed office waste is an available and inexpensive source of high quality bleached chemical fiber [19]. As a result, the industry is responding by adding more de-inking and bleaching chemicals and energy intensive process to meet target brightness and cleanness.

The paper recovery rate reached an all-time high of 50.3 percent in 2003. A survey in 2002 showed that 18% of household waste is mixed office waste, Figure 1.1. The paper industry has set an aggressive goal to recover 55 percent of all paper consumed in the U.S. by 2012 [20].

Recycling waste paper has important environmental implications both positive and negative. In addition to conserving valuable fiber, the need for new landfill sites is decreased. Unfortunately, other environmental problems are often created when conventional technologies are used to reprocess paper printed with advanced technology inks and printing techniques. Recycling generates large quantities of sludge and effluents high in oxygen-demanding material [21].

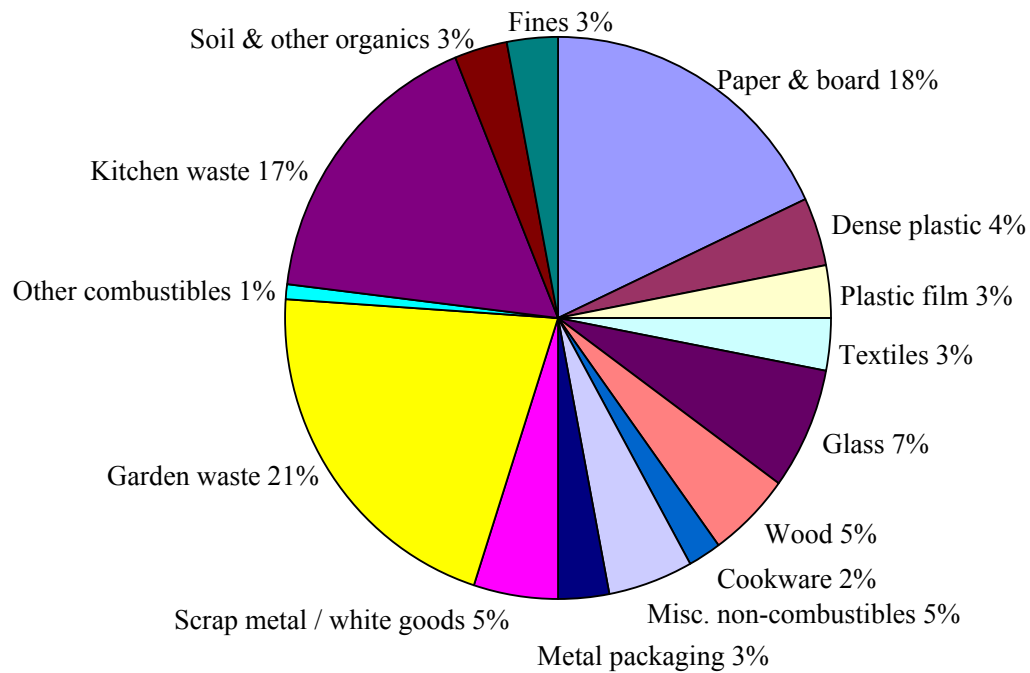


Figure 1.1: Analysis of household waste[1].

There is a need to consider alternative ways of efficient de-inking that do not affect the fibers chemically or mechanically. The plasma treated paper, coated with fluorocarbon (PFE) and polyethelyene glycol (PEG) films offer advantages over non-treated paper. The PFE and PEG have hydrophobic and hydrophilic characteristics, respectively, that inhibit the ink from wrapping around the fiber and also assist ink lift off during flotation. As a result of the above needs and driving forces, the investigation of plasma treated paper for recycling offers an alternative and perhaps more efficient and effective approach to de-inking. This work focuses on the development and characterization of plasma-deposited films to serve as a barrier film to the adhesion of ink toner to the paper fibers and to enhance ink lift off from the fibers.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Plasma**

Every material has an interface that contacts another material, and the properties at the surface and interface are different from the bulk material. In this thesis, plasma treatments are used to modify the surface of substrates. The surface modification generates a functional substrate by controlling surface properties. Surface modification is limited to the surface of the substrate, as the name implies, therefore the modified layers are at the surface and are not characteristics of the bulk material [22]. There are several advantages of plasma modification: (1) a dry and solventless process, (2) environmentally friendly and easy to handle, (3) a versatile technique where a large variety of chemically active species (ions and/or radicals) can be created to attach specific functional groups to the surface. The latter allows the formation of thin (nanometer thick) surface layers that do not affect the bulk properties of the substrate [23]. Applications of plasma polymerization include materials for improved hydrophobicity, printability, biocompatibility, adhesion and corrosion protection [24-27]. Specifically, hydrophobicity and printability are important for the surface modification of paper and paper products.

Plasma polymerization refers to the formation of polymeric materials through the use of a partially ionized gas, termed a plasma or glow discharge. Glow discharges are generated by transfer of power through an electric field to electrons, Figure 2.1, where transfer depends in part on the frequency of the field activating the glow discharge [28]. A glow

discharge can result from the application of either DC or RF power. For a DC glow discharge, the mechanism to sustain the plasma involves the bombardment of the cathode with positive ions, resulting in the generation of secondary electrons [22]. The secondary electrons in turn are accelerated away from the cathode until they have gained enough energy to ionize a molecule (atom) by inelastic collision. The most efficient means of carrying out plasma polymerization involves the use of a radio frequency (RF) glow discharge at reduced pressure; thus the term glow discharge polymerization has been used [28].

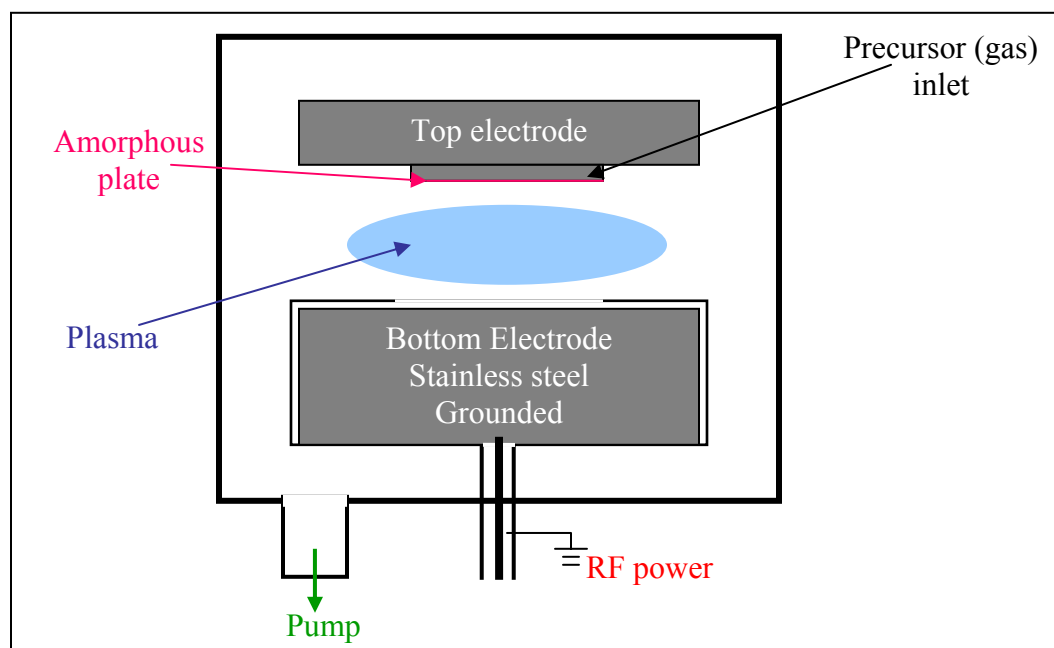


Figure 2.1: Schematic of top and bottom electrode with the glow discharge in between the two electrodes.

Activation of organic vapors in a radio frequency gas plasma (glow discharge) leads to partial ionization of the vapor phase; subsequent reactions involving various ions and radical species and transport of reactants to the surface of substrates in contact with the plasma, yield polymeric deposits. Plasma polymer coatings typically have an excellent

uniformity of thickness and adhesion to substrates [29]. The plasma polymer coatings are extremely versatile because they modify the surface properties of solids to tailor bulk properties [30]. Chemical reactions that occur under plasma conditions are generally very complex and therefore are nonspecific in nature [31].

Plasma polymerization involves reactions between plasma species. In terms of free-radical mechanism : “plasma-induced polymerization” and “plasma-state polymerization” are the two types of reactions that may be proposed [32] . The first one is the conventional free-radical induced polymerization of molecules containing unsaturated carbon-carbon bonds but initiated by plasma-generated radicals. This mode of polymerization is important only for condensed phases including monomers adsorbed onto surfaces at low temperatures [33]. The reaction can occur at the highest temperature (the ceiling temperature), at which the thermodynamic free energy is zero ( $\Delta G = \Delta H - T \Delta S$ ) and the enthalpy contribution is equal to the entropy contribution ( $\Delta H = - T \Delta S$ ). It is experimentally observed that  $\Delta S$  increases with decreasing pressure; it is for this reason that the conventional free-radical induced vinyl polymerization is considered unlikely at the low pressures present in glow discharges. The primary process leading to plasma polymerization, depends on the presence, in a plasma, of electrons and other species energetic enough to break any bond [33].

A plasma can serve as an initiator to cause plasma surface modification and plasma polymerization or adsorption. The interaction of surfaces with plasma plays an important role in the process [28]. Plasmas and the substrate can have two types of interactions.



First, a conventional polymer film substrate can be modified (e.g., cross-linked or covered with polar oxygen- or nitrogen-containing functional groups) by exposure to a non-polymerizing plasma (e.g., Ar, N<sub>2</sub>, or O<sub>2</sub>). Thus, a conventional polymer surface in contact with a polymerizing plasma will be modified to some extent before being covered by a plasma polymer coating, and such modification results in the formation of chemical bonds between the conventional polymer and plasma polymer (adherent coating). The plasma polymer is a vertically growing surface that results in the formation of a highly coherent cross-linked surface film [34-36]. The second type of interaction occurs when the adsorbed species react by active fragmentation due to the plasma (the rupture of one C – H bond is considered fragmentation). This leads to reaction with species in the plasma phase or with sites in the cross-linked plasma polymer film.

In plasma polymerization, the chemical structure of the monomer(s) is sufficiently altered that no repeat unit is recognizable in the structure of the product. Indeed, fragmentation of the monomer is the reason for the lack of structural regularity. Hence, the generally accepted terms “monomer”, describes the feed gas, and “polymer” the resultant film, which are misleading since there is no repetition of a repeat unit along a polymer chain. The degree of fragmentation and cross-linking can be controlled by variation in plasma process parameters. In addition, variation in the plasma polymer structure extends to the bulk physical properties. Although usually investigated in the form of thin cross-linked films, plasma polymers may be obtained as oils, powders, and soluble films with proper manipulation of process parameters [28].

Different monomers are used to create polymer films depending on the chemical and physical properties desired in the final film. By tailoring polymer film composition it is possible to vary the film permeability, chemical reactivity, electrical conductivity, etc.

The classes of monomers most commonly encountered are:

- (1) Hydrocarbons,
- (2) Hydrocarbons containing polar groups,
- (3) Fluorocarbons,
- (4) Silicon containing monomers, and
- (5) Metal containing monomers.

Historically, polymers formed under plasma conditions were considered undesirable insoluble deposits that only generated difficulty in cleaning the plasma apparatus. This undesirable deposit, however, has extremely important characteristics that are useful in modern technology of coatings; that is, coatings display are (1) excellent adhesion to substrate materials and (2) strong resistance to most chemicals.

To appreciate the uniqueness of plasma polymerization, it is useful to compare the steps necessary to obtain a good coating by a conventional coating process and by plasma polymerization. If one wants to coat a certain substrate with a conventional polymer, at least several steps are required: (1) Polymerization of monomer to form a polymer or intermediate polymer to be further processed in a succeeding step, (2) Preparation of coating solution, (3) Cleaning and /or conditioning of the substrate surface by application of primer or coupling agent, (4) Application of the coating, (5) Drying of the coating, and

(6) Curing of the coating. The features of plasma polymers include a more random structure than conventional polymers, extensive cross-linking, covalent bonding to substrates, and ease of control of thickness in the range of nm to  $\mu\text{m}$ . Plasma polymers do not consist of repeat units built from reactive monomers; instead they contain an assemblage of various molecular structures and thus a range of chemical functionalities.

A cold plasma is a non-equilibrium plasma with a zero net charge, i.e. the number of electrons is equal to the number of positive ions [37]. Typically when a gas is subjected to plasma process, it forms a highly cross-linked polymer that is completely different from conventional monomer. These thin films formed by plasma polymerization have minimal defects, and this makes plasma polymerization valuable [33]. Plasma is neutral and the resulting surface treatment is typically used to obtain specific surface properties while retaining the bulk properties of the material. This type of plasma is generated when a low-pressure gas at a specific temperature is subjected to an electric discharge, i.e. a radio frequency or a microwave field [38]. Among these polymer films are the fluoropolymer films which have unique properties such as good thermal stability, chemical resistance, low dielectric constant, a low coefficient of friction, low surface energy, and high impact strength [39]. The study of fluorocarbon discharges has received a lot of attention because of their dual functionality as; (a) plasmas which are suitable to promote etching of a variety of substrates utilized in microelectronic technologies and (b) plasmas allowing deposition of plasma polymerized fluorinated monomer (PPFM) films [30, 33]. The PPFM coating are widely utilized because of their good adhesion to many organic and inorganic substrates [30], the presence of low intermolecular forces, which

results in a relatively inert surface with extremely low free energy [33], biocompatibility, and low friction coefficient, the chemical composition.

## **2.2 De-inking**

Paper waste is the single largest component of solid waste and therefore has a negative impact on the environment. As a result, recycling of waste paper is of growing importance as a source of fiber for the paper industry. For this reason the paper industry has investigated methods to remove ink from paper without damaging or losing fibers. One of the most important requirements in paper recycling is the effective separation of valuable pulp fiber from substances that are added during utilization, i.e. inks [40]. The toner particles of xerographic papers, which includes photocopiers and laser printers, are difficult to remove using conventional de-inking methods [17, 41]. The difficulties encountered in the flotation of xerographic inks are partly due to their different chemical compositions as compared to traditional oil-based inks. The strong adherence of the polymeric toner particles to the fiber surface results in reduced efficiency of recycling. Therefore, recycle mills increase the use of mechanical devices to break down the fibers and to help removal of ink particles by flotation or washing. These mechanical forces are energy demanding, which results in increased costs. Also, these devices cut the fibers and shorten the length and consequently decrease the freeness and the strength of the paper formed from the fibers [12, 42]. Hence it would be highly beneficial to find an effective way to promote the release of toners from office waste paper.

De-inking is the most efficient process for removing finer ink particles,  $\sim <20\ \mu\text{m}$ , and specifically flotation de-inking is more effective for larger particles,  $20 - 300\ \mu\text{m}$ . Traditionally, the de-inking process is performed in two steps; (1) washing, (2) flotation[43].

The flotation process is highly preferred due to the higher efficiency of separation. In the past decade the amount of printed waste paper has increased. Also newer inks, such as xerographic and laser printer toner, have entered the market which has caused difficulties in the flotation process. In addition, the ink particles are too small and hydrophilic which means that they will not attach to the collectors, i.e. surfactants [40, 43]. The xerographic toner contains 5-10% carbon black, which is added as pigment, and 85-90% polystyrene-polyacrylate copolymer. In some cases iron oxide is added as a magnetic carrier. During the printing process the toner particles fuse and stick to the paper surface [40].

In the de-inking process, the first step is re-pulping of collected waste. During re-pulping the ink is removed from the fiber surface which reduces particles to a most favorable size for downstream removal. This is achieved through the forces imposed on the fiber by the action of the rotor. Ink detachment is proportional to the fiber-rotor contact area. The amount of ink removed from the fibers depends on the strength of ink attachment to the fiber surface and the magnitude of forces applied. It also depends on ink particle size and ink surface chemistry. Thus the amount of ink removed is enhanced by high shear conditions, chemical action, moderate temperatures in the range from  $55$  to  $70^\circ\text{C}$  and high pH (8-11) which will help fiber swelling [17, 44-46].

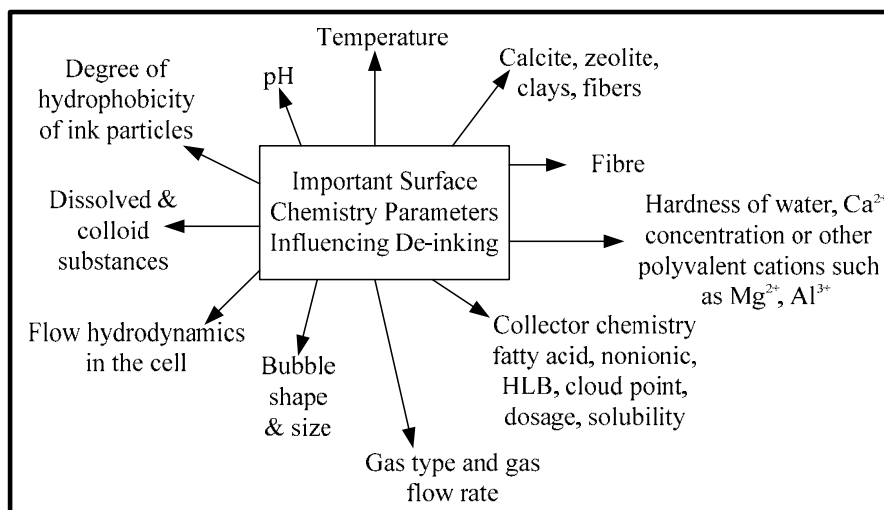


Figure 2.2: Important parameters, which influence the performance of de-inking flotation [47].

Chemicals such as collectors, frothers, pH regulators, and dispersants, and are required in the flotation, typically these are added during the pulping stage to ensure good mixing [47]. Figure 2.2 above gives a list of important parameters that influence the performance of de-inking flotation. In our studies de-ionized water was used to which therefore eliminated accounting for water hardness. Handsheets were made from bleached fiber, which ensured no additives such as calcites, zeolites, and clays. The pH was adjusted to 9 since a fatty acid substrate was used, which created a basic solution and allowed the surfactant to stabilize the ink particles. The Wemco flotation cell was connected to compressed air and other gases were investigated. The flow of compressed air was adjusted to the lowest flow at 300 rpm. The PFE film deposited also allowed for neglecting the degree of hydrophobicity of the ink particles. The main focus of this research was removal of ink particles and other variables were not investigated in detail.

The second step is the flotation step. The role of the flotation cell is to remove the ink that has been released from the fiber during re-pulping. Flotation is a physical-chemical process of separating ink particles from the pulp slurry via the differences in wettability of the two components. The flotation process has been described as a multistage process consisting of a sequence of micro-processes. These sequences include the approach of an air bubble to a particle, and the interception of the particle by the bubble, Figure 2.3. Flotation separates ink particles from pulp slurry via the differences in wettability of the two components, whether the surface is hydrophilic or hydrophobic.

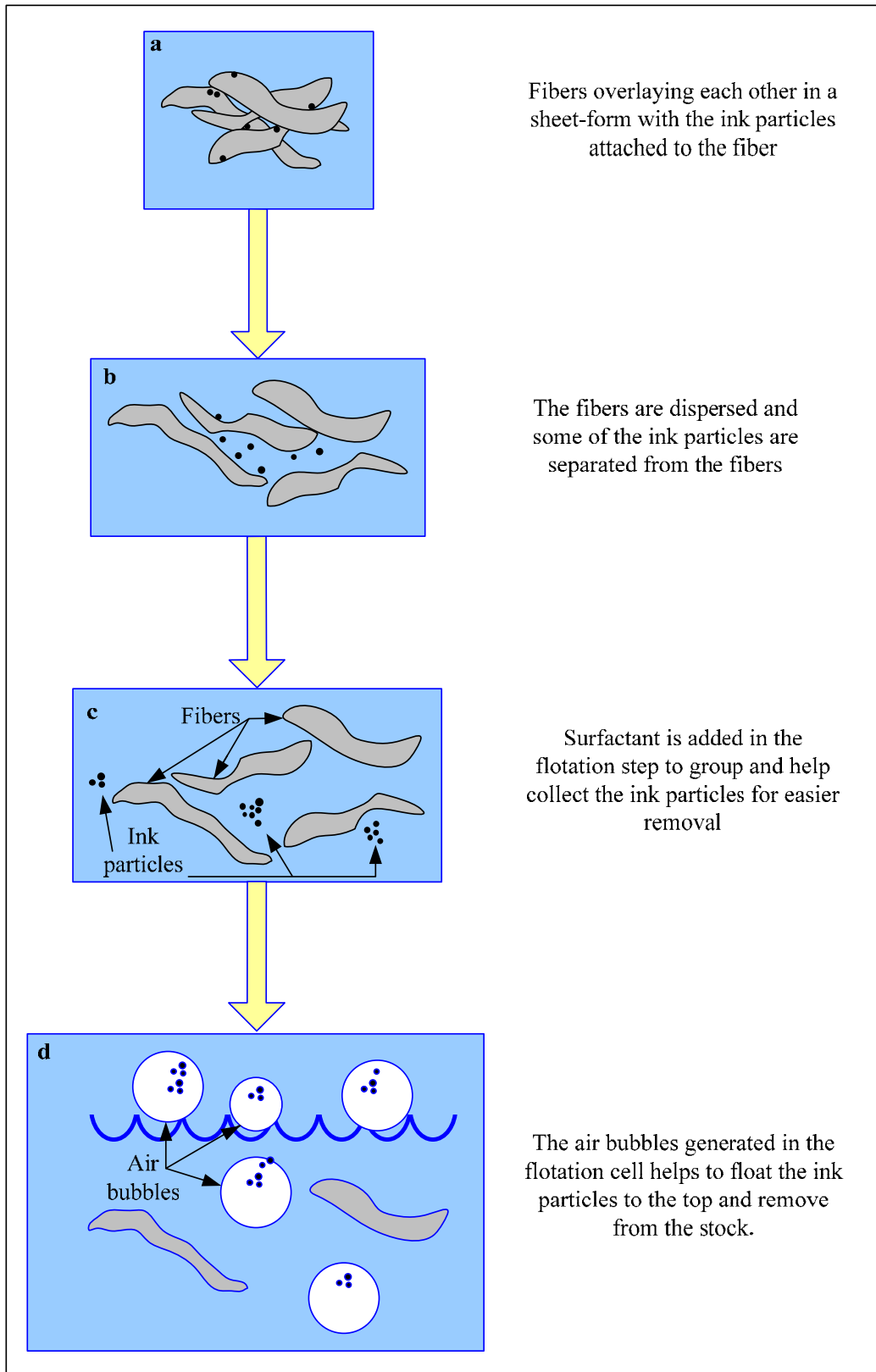


Figure 2.3: Review of the steps in de-inking [48].



A large contact angle is necessary for a particle to attach to a bubble, causing them to rise to the surface of the cell where they are removed as a dirt-laden layer of froth. The contact angle is defined by the Young equation [49]:

$$\cos \theta = \frac{(\sigma_{sv} - \sigma_{sl})}{\sigma_{lv}}$$

where;  $\theta$  = equilibrium contact angle

$\sigma_{sv}$  = solid-vapor interfacial energy

$\sigma_{sl}$  = solid-liquid interfacial energy

$\sigma_{vl}$  = liquid surface tension

High surface energy materials are treated with collectors in order to be removed by flotation. Collectors are used to selectively adsorb onto the solid and lower the surface energy thereby producing a finite contact angle and bubble attachment. Xerography toners have relatively low surface energies, 28-38 dynes/cm, which will have a finite contact angle with aqueous solutions provided that the liquid surface tension is kept relatively high; therefore no surface-energy lowering collectors should be used during flotation de-inking [12]. Surface tension is an inverse function of temperature; therefore one means of promoting high surface tension is to keep the de-inking liquor temperature low.

The flotation process can be influenced by the variation of physical and chemical factors. Physical variables include the particle size and particle density, the size of the air bubbles, the consistency and temperature of the slurry or suspension, as well as the

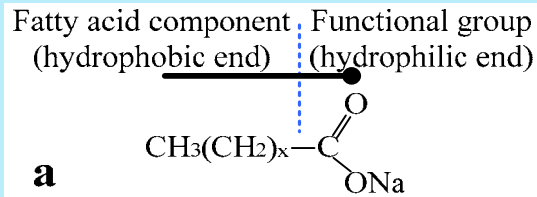
velocity and flow conditions in the flotation cell. Chemical variables are the quality of the water (e.g., water hardness), the pH value of the suspension or slurry, and the addition of flotation agents, such as frothers and collectors.

In addition to the conventional flotation method, flake flotation is used in the paper industry to remove impurities. In flake flotation, chemicals are added to the liquid/solid solution, which will deposit on the solid particles to activate formation of flakes. Once the flakes are formed air bubbles are introduced and the flotation process occurs. This process is not a selective flotation process, therefore all solid particles are removed by the flakes. The removal of ink particles by a flotation process is similar to flake flotation. In this case only the ink particles should be eliminated and not all solids. Therefore in this process the froth is considered the waste product (containing ink particles).

In de-inking flotation processes, the process is controlled so that the flakes only carry the ink particles and some filler to the surface, while the fibers are not discharged. There are two ways to achieve this: (1) by addition of specialty chemicals for flake formation or (2) by the presence of a certain amount of turbulence in the flotation cell. In the latter case both too strong or too weak turbulence levels should be avoided, because there would then be a risk of ink particles being removed from the air bubbles or distributing fiber flotation.

As mentioned previously flotation agents include frothers and collectors. The best known agents are soaps, the alkali salts of fatty acids, with a long chain of molecules containing a hydrophobic (fatty acid) group at one end and a hydrophilic (functional) group at the other (Figure 2.4a). Oleic and other fatty acids can also be added to the

slurry in the pulper where they foam in the alkaline suspension. Synthetic products such as surfactants, preferably the nonionic type are also used. Surfactants such as ethoxylated fatty acids, alkyl benzol sulfonates, and alkyl phenol-polyglycolether are usually added in small quantities to improve the flotation process. These surfactants reduce surface tension which leads to the formation of froth at the water-air boundary. As a result, the enveloped ink particles appear hydrophilic on the outside and detach more easily from the fiber (Figure 2.4c). To deposit the dispersed ink particles (Figure 2.4d) on air bubbles (Figure 2.4b), the hydrophilic ends of the soap molecules must react with the hardening chemicals of the water (e.g.  $\text{Ca}^{++}$ ) so that they act as collectors (Figure 2.4e). If fibers are present at too high a fiber consistency, they will decelerate the rise of the air bubbles carrying ink particles (Figure 2.4f). Moreover, the increased frictional resistance of the stock suspension may loosen the ink particles from the air bubbles and prevent discharge with the froth.



- a. Alkali salts of fatty acids
- b. Air bubbles stabilized by frother
- c. Ink particles detaching from fibers
- d. Dispersed ink particles
- e. Ink Particles whose surface-active substance (soap) has reacted with hardening constituents and which can now deposit on air bubbles
- f. Foam laden with ink particles

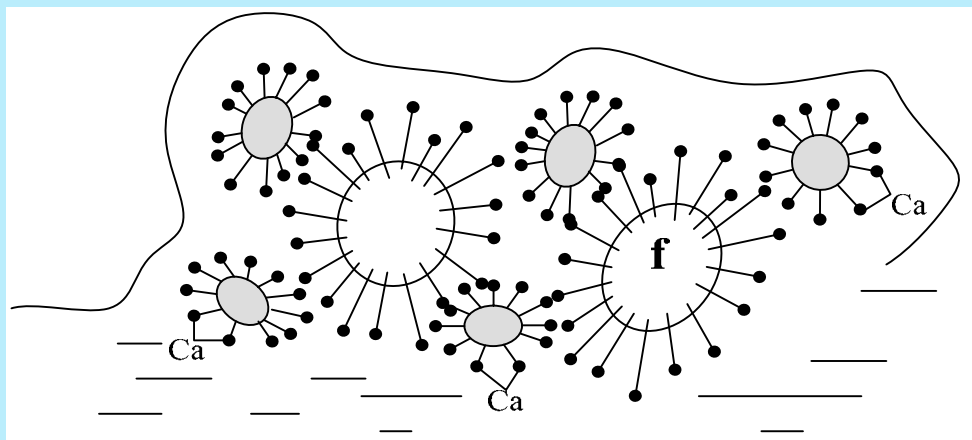
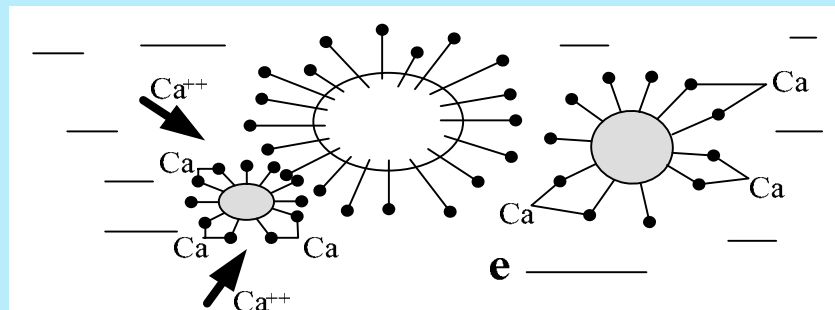
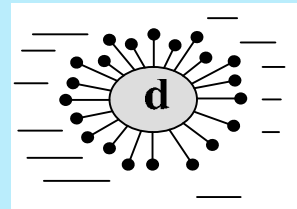
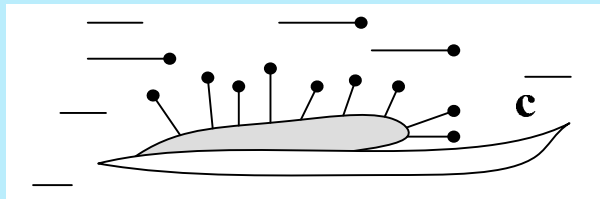
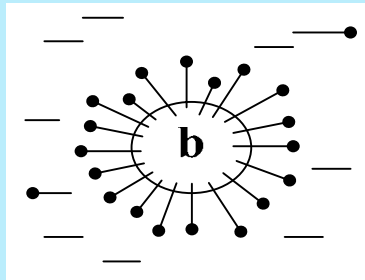


Figure 2.4: Flotation process; ink removal from fiber and floating air bubbles [31]

The technique of flotation depends on the flotation machines used [49]. A distinction is made between agitator cells, compressed-air cells, sub-aeration units, and vacuum flotation machines. Most common are agitator cells. These are primarily used in the flotation de-inking of secondary fibers. The basic arrangement of the flotation machines, vertical or horizontal, also plays a decisive role. Also whether or not accepts (clean fibers) and rejects (ink particles, fibers and foam) are collected from the same end or different ends has an affect.

The flotation cells common in ore and coal dressing were initially taken over unchanged for flotation de-inking. The Denver cell, sub-aeration type, was the first flotation cell applied to the regeneration of printed secondary fibers in the United States after World War II.

The Voith flotation cell, developed especially for printing ink flotation, is shown in Figure 2.5 [49]. It is also an agitator cell with a square cross section. The cell is fitted with a vertical shaft that extends from above to the center of the tank, with an impeller seated at the bottom end of the shaft. The impeller has radially arranged blades surrounded by a stationary, concentrically arranged dispersing ring. The ring is connected to the bottom of the cell and sealed at the top against the interior of the tank. The impeller draws the gray stock from underneath and forces it from a spiral inlet toward the vertical shaft; the spiral case ensures uniform distribution of the stock over the impeller, which is highly essential to flotation. At the same time, air is drawn in at the center. The air and the gray stock blended with the flotation agent are mixed by the impeller. Subsequently, the suspension is pressed outward through the perforations or special stator elements in the cylinder.

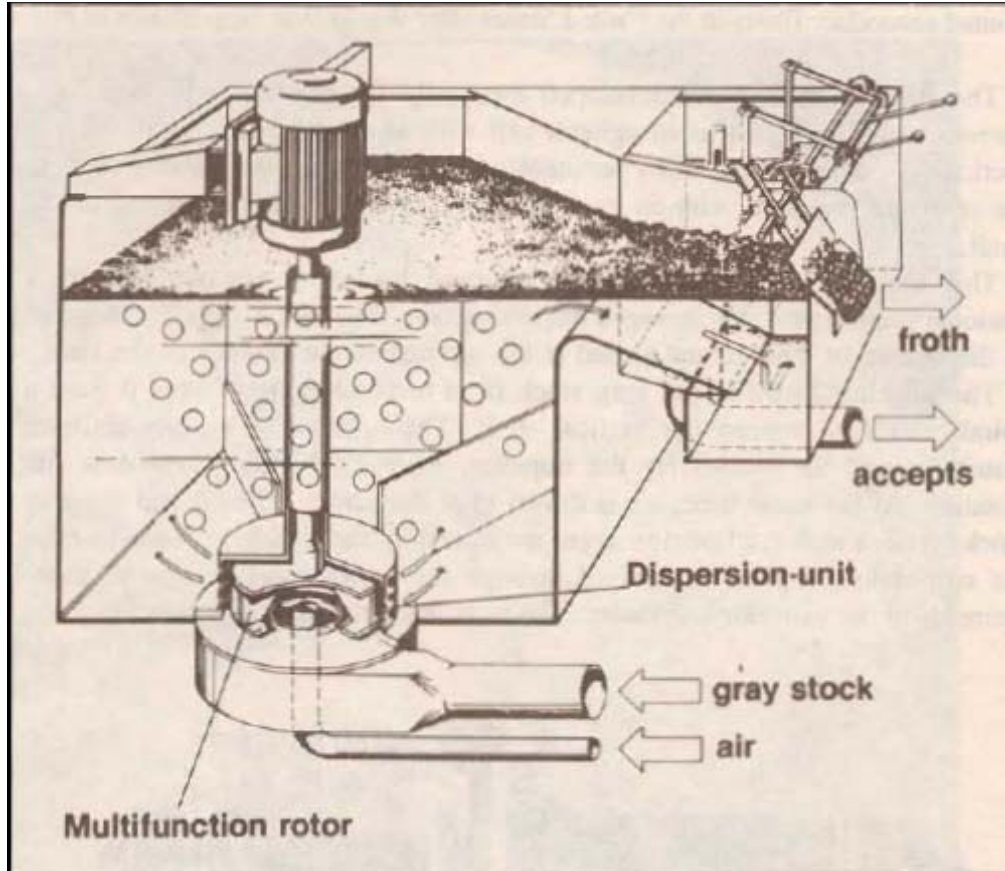


Figure 2.5: Voith flotation cell [49].

The turbulence produced by the suspension when forced through the perforations/stator elements provides the necessary fine dispersion of air in the liquid and a uniform distribution of the stock to be floated throughout the cross section of the cell bottom. Only a uniform dispersion can ensure that each ink particle is actually brought in contact with an air bubble. The froth accumulating on the surface is collected by paddles, while accepts (clean fibers) are directed through a siphon down to the next cell.

## CHAPTER 3

### METHODOLOGY

This chapter presents a detailed description of the plasma reactor and flotation cell along with experimental procedures used to deposit both fluorocarbon and polyethelyene glycol films. The deposited films were evaluated for their chemical composition and bonding structure using x-ray photoelectron spectroscopy (XPS) while the thickness and refractive index were measured using an ellipsometer. As shown in table 3.1 to prepare three cases for comparision required 200 hours of deposition time. This deposition time afforded one data point per case and therefore it was impractical to repeat experiments at this time.

Table 3.1: Amount of fiber, sheets and number of runs and hours for each case.

Case A Case B Case C	10 g of fiber needed for each case	Average weight of each sheet ~1.2g (30sheets/1 .2g)	One sheets per plasma run (one PEG + one PFE = 2 plasma runs per sample) Only one sample at a time	43 hours per sample (50 samples * 3hrs)
<b>3 Cases</b>	<b>30 g of fiber</b>	<b>25 sheets</b>	<b>50 plasma runs</b>	<b>200 hours</b>

#### 3.1 Substrate - Handsheets

To reduce the variables in comparing re-pulping and flotation results, handsheets were made using bleached softwood fiber. The pulp was refined using a valley beater for 35 minutes. The consistency and Canadian freeness of the pulp were measured following TAPPI methods T240 and T227, respectively. The handsheets were made using TAPPI Method T218, with the exception that the sheets were dried on the steam drum. This

exception was made to speed up the handsheet making process since the drying conditions had no effect on the printing or de-inking.

### **3.2 Plasma Reactor**

A parallel plate radio frequency (RF) plasma reactor was used to deposit films from polyethylene glycol (PEG) and pentafluoroethane (PFE) precursors. Top and bottom electrodes of the reactor were both stainless steel disks 15.24 cm in diameter, and were electrically isolated from other parts of the reactor. The distance between the electrodes was fixed at 2.54 cm and 1.02 cm for PEG and PFE films respectively. The distance for the PFE deposition was determined based on the lowest possible distance between the two electrode, and was a physical limitation of the reactor. For the PEG depositions the distance was decided based on the opening from which the vaporized PEG entered the reactor. RF power at 13.56 MHz was generated using an ENI Power Systems HF-300 RF generator and was coupled to the top electrode through a Heathkit SA-2060A antenna tuner. The RF power during deposition was held constant at  $100 \pm 10$  W for both PEG and PFE depositions. The bottom electrode was electrically grounded and heated with Omegalux CIR 2015 cartridge heater and the temperature was measured using a type K thermocouple fitted into the bottom electrode. The temperature of the bottom electrode was controlled using a Syskon RKC temperature controller and was set at 110°C for all of the experiments. All substrates, paper and silicon wafer chips, were placed on the grounded electrode. The top electrode was a porous plate that allowed introduction of various gases including oxygen, argon, nitrogen and the monomer PFE (DuPont HFC 125) into the plasma region. Teflon flowmeters were used to control the flow rates of



each gas. The flow rates of PFE and Argon were 20 SCCM and 75 SCCM respectively. The PEG was introduced into the reactor (figure 3.1), from a side port in the reactor. The flow rate of the vapor was not monitored. The argon flow was kept at 50 SCCM through the top electrode for PEG deposition. The pressure inside the reactor was monitored with a Kurt J. Lesker vacuum gauge with a range of 1 mTorr to 1500 Torr. The typical base pressure in the chamber was  $6 \pm 2$  mTorr and the operating pressure was maintained at 1 Torr for all experiments. The reactor was evacuated with an Alcatel 2063 C rotary vacuum pump through the bottom port.

The precursors investigated for this study were pentafluoroethane ( $C_2F_5H$ ) and Polyethylene glycol ( $COH-[C_2O]_n-COH$ ). In the case of PEG the liquid precursor was heated to  $140^\circ C$  and vaporized. The vapors were then transported through a heated tube ( $\sim 110^\circ C$ ) assembly to the side of the reactor. Argon (Air Products, 99.99% purity) was used as the carrier gas for each monomer.

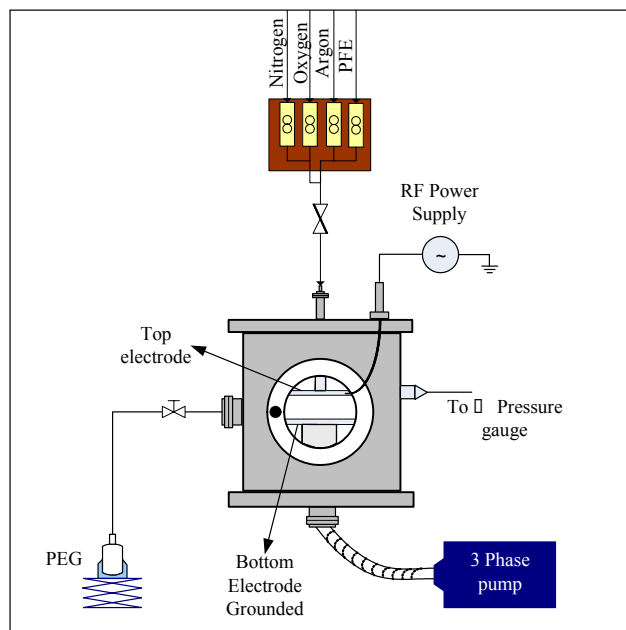


Figure 3.1: Plasma Reactor Set-up

The plasma system was checked every 15-20 runs for leaks and oxygen plasma cleaned at 1 torr to remove deposits from the walls and the bottom electrode.

The detailed system operating procedure for deposition of fluorocarbon films is as follows:

1. Close the throttle valve and bring the chamber pressure to atmospheric pressure by filling it with nitrogen gas.
2. Open the sample loading port and place the substrate (paper and/or silicon) on the bottom electrode.
3. Close the loading port and slowly open the throttle valve to the pump to evacuate the chamber.
4. Allow the reactor to reach the base pressure. Typically 4 – 8 mtorr.
5. Turn on the heater for the bottom electrode and allow it to heat to 110°C and stabilize at that temperature.

6. Open the argon flow valve and allow flow through the reactor before opening the precursor flow valve.
7. Adjust the throttle valve to achieve 1 torr pressure inside the chamber.
8. Once the pressure is at 1 torr turn on the RF power to the top electrode.
9. Adjust the variable capacitors and inductors on the matching network to achieve minimum reflected RF power.
10. After running the system for the desired period of time turn off the RF power and the gas flow to the reactor.
11. Turn off the bottom electron heater and open the throttle valve to allow for the excess gases to exit the system.
12. Wait for about 30 minutes before closing the throttle valve and backfilling the system with nitrogen.
13. Once the system is at atmospheric pressure, open the sample loading port and remove the sample.
14. Slowly open the throttle valve and allow the system to reach base pressure.

The system is operated similarly for the polyethylene glycol with the exception that the precursor (PEG) enters the system from a side port and it is heated to 130°C before it enters the reactor. This high temperature was to create a vapor pressure, which would then allow the gas to flow from the vessel into the reactor, and to prevent quick liquefaction of PEG vapors.

### **3.2.1 X-ray Photoelectron Spectroscopy (XPS)**

XPS was used to determine the relative composition and chemical bonding structure of the films. The XPS spectra were collected with a PHI<sup>TM</sup> (Eden Prairie, MN) model 1600 spectrometer using a Al K<sub>α</sub> x-rays generated at a power of 350 W. A 180° hemispherical analyzer and a multi-channel detector provided high sensitivity and high-energy

resolution. Chamber pressure was typically below  $5 \times 10^{-9}$  Torr during analysis. An electron pass energy of 11.75 eV was used to analyze the regions of interest in each sample, specifically  $C_{1s}$ ,  $F_{1s}$ ,  $O_{1s}$ ,  $N_{1s}$ , and  $Si_{2p}$  photoelectrons were analyzed. The binding energy shifts were corrected for surface charging by aligning the highest binding energy  $C_{1s}$  peak to 293.2 eV. Finally, curve fitting was performed on each spectral region assuming all peaks to be perfectly Gaussian and to have the same full width half maximum (FWHM) [50].

### **3.2.2 Ellipsometry – Thickness Measurements**

Fluorocarbon films were deposited on paper and cellulose. Since it is difficult to measure film thicknesses on paper, a piece of silicon wafer was included along with the paper samples to enable film thickness measurements using ellipsometry. The thickness of the film deposited on the fibers of the surface of the paper was assumed to be the same as the silicon wafer [50]. Paper and cellulose are strongly polar due to hydroxyl groups, acetal, and ether linkages (C-O-C) in their structures. The surface of paper consists of hydroxyl (-OH) groups therefore rendering it hydrophilic in nature. Silicon substrates, upon exposure to oxygen or air, oxidize to form silicon dioxide ( $SiO_2$ ). In the presence of moisture, the native oxide formed in the presence of water vapor has hydroxyl functionalities on the surface, making the surface of silicon hydrophilic. Therefore, while the silicon and paper substrates are materially different, their surfaces are similar in chemical functionality, and so plasma deposition rates on silicon wafers can be considered comparable to those on paper or cellulose.

### 3.3 Experimental Plan

Based on preliminary studies, three different structures were investigated, as indicated in Table 3.1. The thickness of PFE remained the same for all of the three structures while the thickness of PEG varied by 1500Å, starting at 1500Å.

Table 3.2: Experimental variation in film thickness, PEG deposited directly on the surface of paper and PFE on top of PEG.

Case	PEG Thickness	PFE Thickness
A $\rightarrow$ PEG < PFE	$\sim 1500 \text{ \AA}$	$\sim 3000 \text{ \AA}$
B $\rightarrow$ PEG = PFE	$\sim 3000 \text{ \AA}$	
C $\rightarrow$ PEG > PFE	$\sim 4500 \text{ \AA}$	

#### 3.3.1 Plasma Reactor – Film Deposition

The reactor body and the lines out of the reactor to the pump were wrapped with heating tape and the temperature of the heating tapes set at 110 °C. The PEG ( $\text{C}_{10}\text{H}_{22}\text{O}_5$ ) was poured into a glass vial and was heated by a heating mantel.

##### *Placing the Sample in the Reactor*

The first step was to turn on the heater on the bottom electrode. The reactor pressure was increased to  $7.20 \times 10^2$  torr. The paper sample and small silicon wafer chip for thickness measurement purposes were placed on the bottom electrode. The throttle valve was opened very slowly to bring down the pressure inside the reactor to base pressure.

##### *PEG Deposition*

The vial containing the liquid PEG was heated to 140°C, and the Ar at 50 SCCM was introduced into the system along with vaporized PEG. The throttle valve was then slowly

closed to bring the pressure inside the reactor to 1 torr. Once the pressure inside the reactor was stable, the plasma was turned on and the film was deposited for the appropriate time to generate the film thicknesses listed in Table 3.1. The deposition times and the average film thickness are given for each case in Table 3.2. Since not two samples had the same thickness of film the average difference was evaluated to be  $\pm 50 \text{ \AA}$  for each case.

Table 3.3: Deposition time and film thickness associated with each case.

Case	Deposition Time	Film Thickness
A	11 min 30 sec	1500 $\text{\AA} \pm 50 \text{ \AA}$
B	23 min 54 sec	3000 $\text{\AA} \pm 50 \text{ \AA}$
C	37 min 12 sec	4500 $\text{\AA} \pm 50 \text{ \AA}$

### *PFE Deposition*

In the case of PFE the reactor was not wrapped with heating tape, because the PFE precursor enters the reactor as a gas and the inside temperature of the reactor does not have an affect on its deposition. After the sample was placed on the bottom electrode and the reactor reached its base pressure, the precursor (PFE) and Argon were flowed into the reactor at 20 SCCM and 75 SCCM respectively. The throttle valve was then slowly closed so that the pressure inside the reactor reached 1 torr. After the pressure stabilized the plasma was turned on and the film deposited for ~30 minutes.

### **3.3.2 Reactor Maintenance – Oxygen cleaning**

In order to avoid polymer build up in the reactor, the reactor was oxygen plasma cleaned after every 3 runs of PFE and after every ~ 1.5 hours of PEG run for 15 minutes and 40

minutes respectively. Once the sample was removed from the reactor, and reactor reached the base pressure, oxygen was introduced into the reactor at 488 sccm and the plasma was powered at 100 W.

### **3.4 Re-pulping of Paper - Disintegrator**

The paper feedstock for our experiments consisted of the handsheets made as described previously. The sheets were printed on by printing consistently, 4 circles of 1 inch in diameter, using an HP Laser Printer (4200) operating at a standard speed of 11 pages per minute. The sheets were adhered to a 8.5 inch by 11 inch sheet using laser printer label. They were soaked for 30 minutes in a heated water bath at 50°C. They were then pulped in a hydropulper (Beloit Jones Barracuda, Model # 3100-08), at 1% fiber consistency until all the fibers were dispersed. The pH was kept constant at 9 by the addition of 0.1M of NaOH. The temperature in the hydropulper was maintained at 45-50°C. After dispersing the paper, the pulp slurry was diluted to a consistency of 0.33% (10g of fiber in 3L of water), figure 3.2.

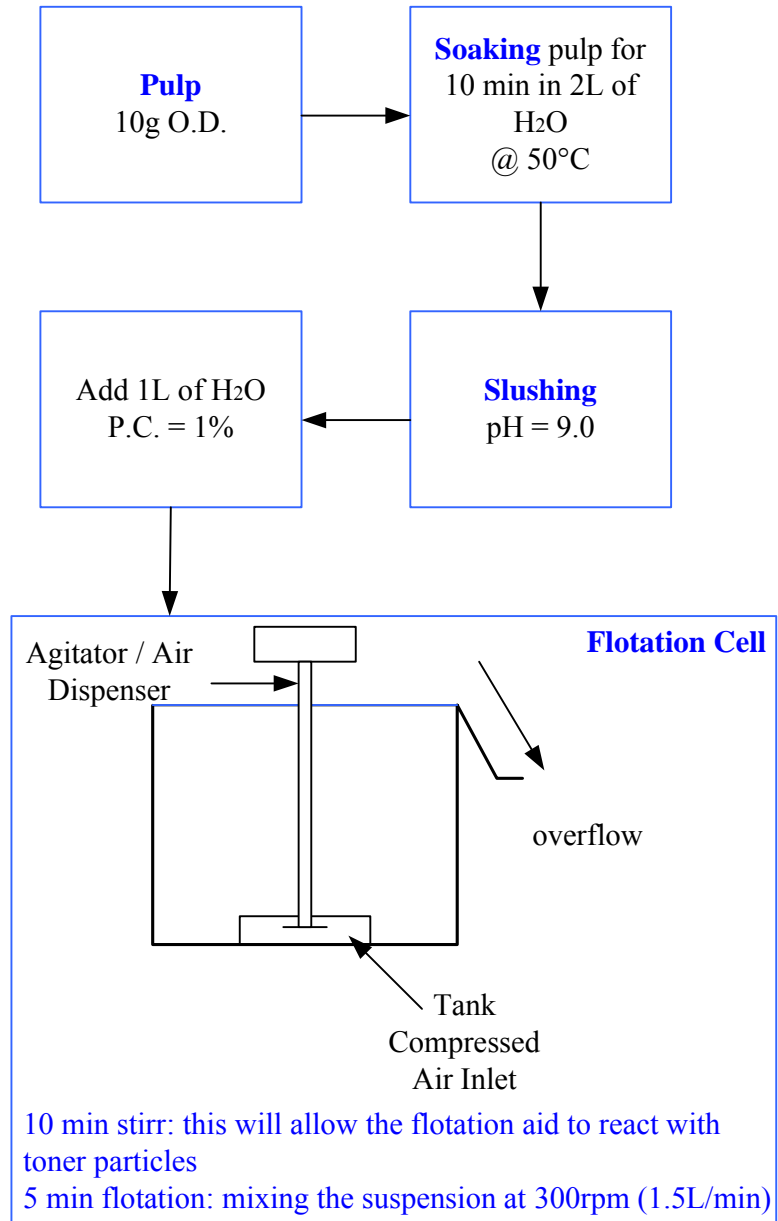


Figure 3.2: Re-pulping and Flotation Process.

### 3.5 Flotation Cell

De-inking experiments were conducted in a Wemco laboratory-scale flotation cell (Sacramento, CA), in the batch mode. The total amount of de-inking chemical (flotation



aid DI-700A), supplied by Kao Specialties Americas (High point, North Carolina), that was added to the slurry per experiment was 2% by weight based on the mass of fiber [51], which in this case was approximately 0.2g of DI-700A. Once the disintegrated fiber and the de-inking chemical were added to the flotation cell the mixture was stirred for 10 minutes to allow the flotation aid to react with toner particles. The flotation was carried out for 5 minutes by activating an air inlet at the rate of 300 rpm (1.5L/min) located at the bottom of the stirring shaft. The froth was then collected by hand using a small beaker from the top of the flotation cell; this was done carefully to ensure not to scrape too deeply into the froth; Figure 3.2 shows the schematic of the flotation cell. After 5 minutes of flotation, the flow of air into the cell was stopped, and the remaining slurry in the cell was collected. In order to determine the efficiency of de-inking and percent fiber retained, handsheets were formed. The sheets were made from both the froth and the slurry by following the TAPPI Method T218 using a 290 mesh accepts wire, although repulping was not performed. The percent fiber retained for each case was calculated using the equation;

$$\% \text{ Fiber retained} = \frac{\text{Weight of fiber in stock}}{\text{Total weight of fiber}} * 100$$

which the weight of fiber in stock is the weight of the clean fiber collected at the end of flotation and the total weight of fiber is the sum of fiber collected from foam and from the clean fiber. The percent ink loss was then calculated using the following equations;

$$\% \text{ ink loss} = \frac{\% \text{ ink on surface of foam sheet}}{\% \text{ ink on original sheet}} * 100$$

The percent ink on surface of foam sheet corresponds to percent covered surface area of the foam divided into the percent surface area covered with ink before de-inking. In

order to consider the percent material loss after de-inking it is important to consider that samples contained 5% moisture since they were stored in room conditions.

## **CHAPTER 4**

### **RESULTS & ANALYSIS**

This chapter presents the results of fluorocarbon and PEG film deposition and the effect of the two films on de-inking. Some of the initial experiments in this work were conducted at the same thickness of the films and the pH of the slurry was not taken into account. Deposition rates of both films and properties of PFE are discussed in this chapter. For fluorocarbon film characterization, x-ray photoelectron spectroscopy and infrared spectroscopy were used to understand the film composition and chemical bonding of the deposited film. Film thicknesses for both PFE and PEG were measured using spectroscopic ellipsometry.

#### **4.1 Initial Results**

Initially both PFE and PEG were deposited on the substrate at approximately at 700 Å/min and 150 Å/min respectively. For the initial experiment spray adhesives were used to attach the sample to a printer paper in order to print on the sample. Five cases were studied as exploratory experiments to find out: a) the effect of adhesive during re-pulping and b) the effectiveness of single layer film versus dual layer films, the results from these experiments were not intended to be defended, Table 4.1.

Table 4.1: Initial cases studied to determine an experimental plan

Case	Type
1	Blank
2	Blank with adhesive
3	PFE & PEG
4	PFE with adhesive
5	PFE

In order to determine the effect of spray adhesive on disintegration of paper fiber a blank run with and without the spray adhesive was performed. The results indicated a longer disintegration time for a blank sample with adhesive (3449 rpm) than without (1501 rpm). In order to avoid fiber shortening during re-pulping the samples were attached to the paper with laser printer safe tape (Avery clear mailing labels 1/2" and 1 3/4"). The tapes came off the samples with out damaging the sheets.

Handsheets were made from the stock and foam for each of the five cases mentioned, table 4.1 and are presented in figure 4.1. Based on the handsheets made, it was clear that the thin films deposited have an effect on separating the ink particles. For the case of samples 1 and 2, a very thin sheet was formed from the foam, and for samples 3, 4, and 5, the ink particles and the fibers are attached to the blotting paper (a piece of heavy stock paper that is used to squeeze the last bit of water out of the handsheet). This shows that in the case of thin film deposited samples, there is less fiber loss and more particle removal. Also comparing the sheets from the stock and the foam, it is clear that there are more ink particles in the sheets made from foam than in those made from the bottom stock. In the case of sample 3 there are more ink particles removed than in samples 4

and 5. This may be due to the fact that the PEG underlying the PFE acts as a sponge once it comes in contact with water, and therefore helps the floatation to remove ink particles. The preliminary studies showed that the deposited thin film may help the recycling of laser printed-paper. To continue with the study, analysis techniques were looked at to determine the concentration of ink particles and the concentration of fiber in the foam. To avoid having to account for the filler in the original paper, handsheets were made from bleached softwood virgin fibers.

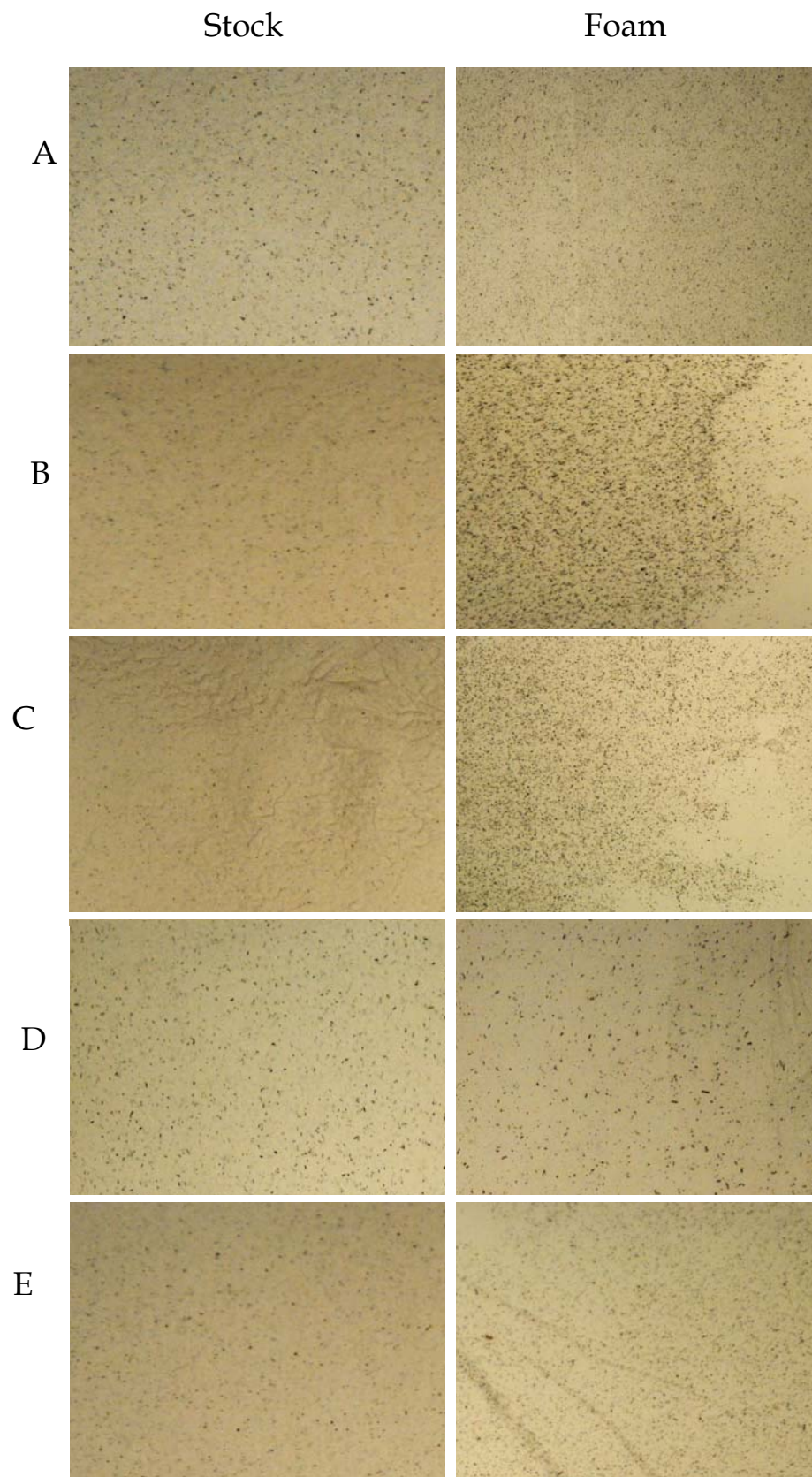


Figure 4.1: Images of the handsheets from the exploratory experiments of stock and foam sheets.

## **4.2 Results and Analysis**

Once the initial de-inking experiments showed favorable results, it was decided to deposit PEG on paper first and then deposit PFE on top of that. As explained in Chapter 3, three different PEG thicknesses were deposited. After the PEG experiments were performed, the reactor was cleaned by opening all the lines to the reactor to remove the liquid PEG that was collected inside the tubes and the reactor. The tubes were cleaned in a KOH bath and were heated using heating tapes to ensure complete removal of the PEG residues. Once the reactor was completely cleaned, PFE experiments were carried out. Initially the deposition rate for PFE and PEG were approximately at 700 Å/min and 150 Å/min respectively. The clean reactor needed to be conditioned, since the clean walls attract the ions and result in some deposition on the reactor walls. Therefore the deposition rate of the PFE filmed ranged from 100 to 180 Å/min, which meant that after every run the deposition time was adjusted to achieve the desired deposition rate. The deposition rate change by 80 Å/min because gradually the walls had some residual film on them and therefore did not attract the ions and hence more film was deposited on the substrate.

## **4.3 XPS Results on Fluorocarbon Films**

XPS studies were performed on fluorocarbon films deposited on silicon. This was done to ensure that the PFE films deposited after the PEG runs and cleaning of the reactor are the same as the previous films used for the initial experiments. Survey scans of fluorocarbon films deposited on silicon indicates the presence of fluorine, carbon and a small amount of oxygen, which is consistent with PFE composition. A high-resolution scan was performed to gather bonding information of PFE. Since oxygen content in

fluorocarbon films were low, the C1s spectrum was deconvoluted into five Gaussian peaks corresponding to[52]  $\text{CF}_3$  (293 eV),  $\text{CF}_2$  (290.9 eV),  $\text{CF}$  (288.5 eV),  $\text{C-CF}_x$  (286.5 eV), and  $\text{C-C}$  or  $\text{C-H}$  (284.9 eV) with chi-squared value of 1.209 (Figure 4.1). These assigned binding energies are within the range of published literature values, Table 4.2.

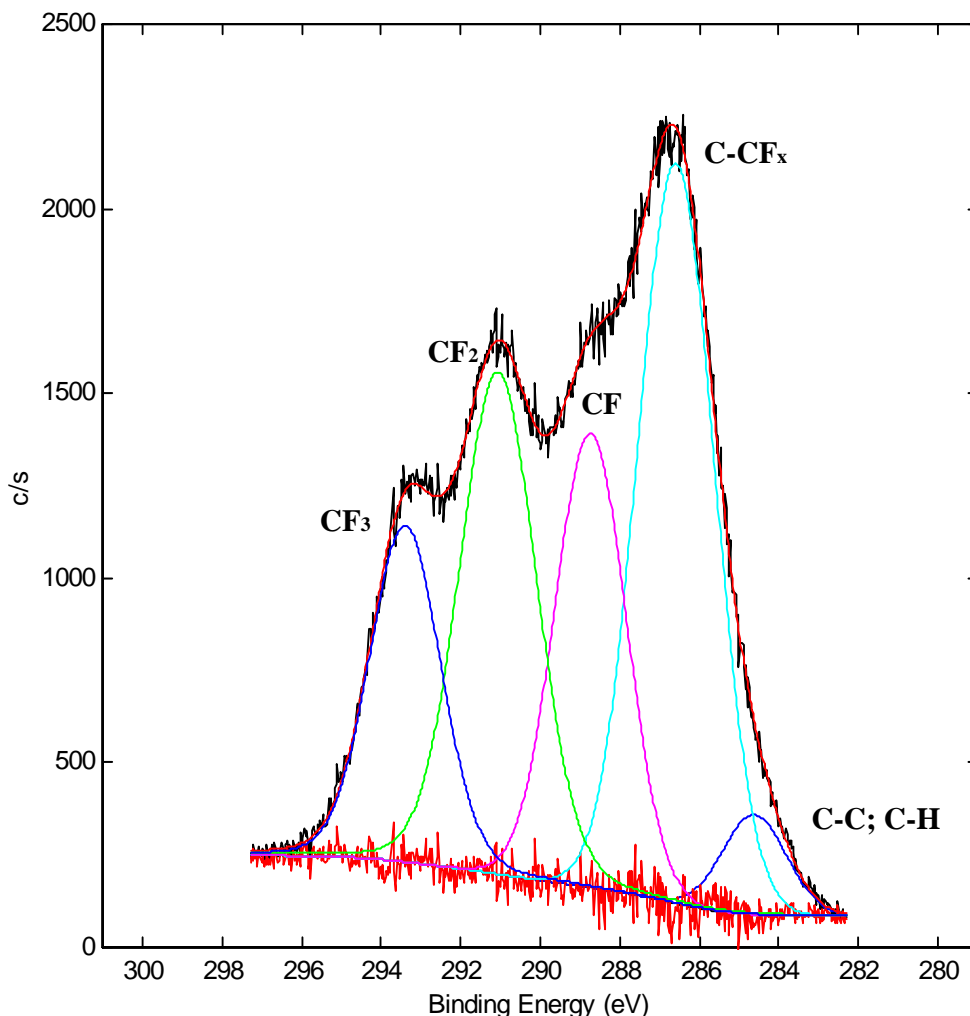


Figure 4.2: High resolution C1s spectrum of fluorocarbon film deposited on cellulose surface [Deposition conditions: RF = 100 W, P = 1 Torr, T = 110°C, PFE flowrate = 20 sccm, Ar flowrate = 75 sccm]



Table 4.2: Published literature values for binding energies [2].

Peak/Group	Binding Energy range, eV
CF <sub>3</sub>	292.6 – 295
CF <sub>2</sub>	290.3 – 293
CF	288 – 290
C-CF <sub>x</sub>	285.5 – 287.2
C-C    C-H	283.5 - 286

#### 4.4 De-inking Results

As mentioned previously in Section 3.5, handsheets were made from the foam and the slurry. Images of ink particles attached to the fibers (using a Mitutoya microscope at 20x) were taken (Figure 4.2) for each case, which indicate less attachment of the ink to the fibers with the presence of plasma deposited films. The images were selected at random only to show what is expected to see for each case.

The handsheets were sent to the University of Massachusetts at Lowell to be scanned for particle size analysis using Oppomax speck check unit with 250 gray scale sensitivity and minimum accuracy of 0.007 square millimeter and max of 32,768 particle counts. This machine scans the surface of samples and measures the percent light and percent dark area. The fiber loss for each case was calculated using the weight of the sample with the deposited films and printed ink (Table 4.3) and the weight of the fibers collected from the stock and the foam (Table 4.4).

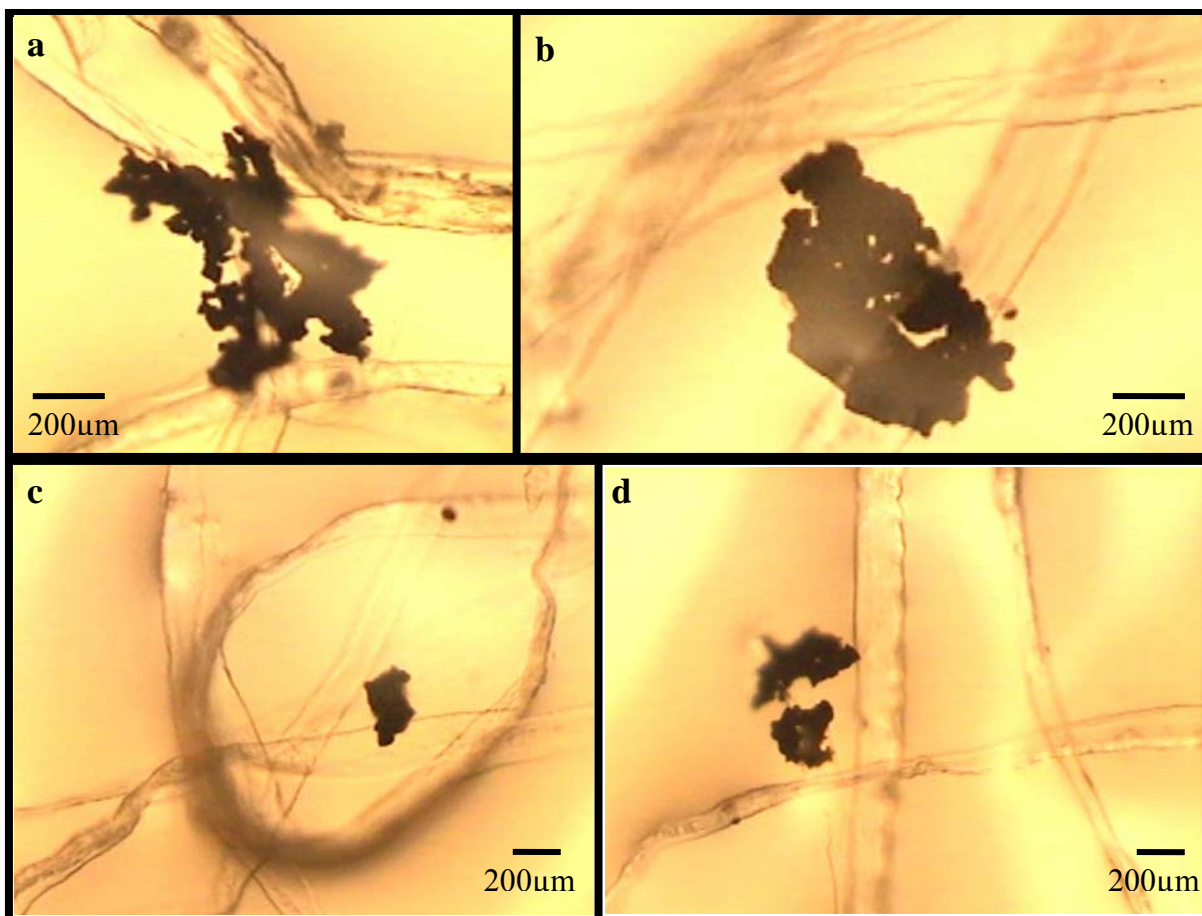


Figure 4.3: Images of ink particles at 20 X a) Control Sample: (no film deposited) ink particle is attached to multiple fiber stands holding them together, b) case A (PFE>PEG) the ink particle is wrapped strand. c) case B (PFE=PEG) d) case C (PFE<PEG) the ink particle is barely attached to the fiber. (the scale bars are approximates)

Table 4.3: Sample weight for each case (including the weight of the films and ink).

Case	Handsheet weight (g)	Handsheet + deposited films + ink (g)
Control (no film)	9.597	9.980
A	9.906	10.908
B	9.934	10.675
C	10.120	10.775

Table 4.4: Total weight of fibers collected after de-inking.

Case			Total Weight (g)
Control	Foam	6.254 g	9.82
	Stock	3.566 g	
A	Foam	7.589 g	9.012
	Stock	1.423 g	
B	Foam	8.941 g	10.351
	Stock	1.410 g	
C	Foam	8.509 g	10.191
	Stock	1.682 g	

The percent loss of material after de-inking is calculated using the equation below and the calculated values are presented in table 4.5;

$$\%Loss = \frac{\text{weight(g) of material before deinking} - \text{weight (g) of material after deinking}}{\text{weight (g) of material before deinking}} * 100$$

Table 4.5: Percent ink and material loss calculated for each case.

Case	Thickness of dual layer Å	% material loss
Control (no film)	0	1.6
A (PFE > PEG)	4500	3.14
B (PFE = PEG)	6000	3.0
C (PFE < PEG)	7500	5.42

The calculated material loss shows an increase for the samples with deposited film. For the case of control sample there are only fiber and the ink particles and the cases A, B and C not only there are ink particles on the surface but also PFE and PEG which together the thickness of the films are 4500, 6000 and 7500Å, respectively. The thicker the film the more weight it would contribute to the sample and therefore the higher the percent material loss. It is possible the PFE and PEG films were lifted off the fibers completely and exited the system along with the ink particles and some fibers, or some could still be attached to the fibers remained as stock and became part of the new sheets made. Looking at Table 4.5, it is apparent the ratio of fibers collected from the stock and foam for cases B and C are higher than the case A and control case.

The percent-retained fiber for each case was also calculated from weight of fiber in stock divided by the total weight of fiber, the results are shown in table 4.6.

$$\% \text{ Fiber retained} = \frac{\text{Weight of fiber in stock}}{\text{Total weight of fiber}} * 100$$

The ink loss for each case is also calculated and reported in Table 4.6. As mentioned previously, four-1 inch diameter circles were printed on each sheet, which means ~11% of each sheet is covered with ink (the handsheets have a surface area of 730 cm squared and the total surface of sheets covered in ink, 81 cm square). Therefore the % ink loss for each case was calculated as follows;

$$\% \text{ ink loss} = \frac{\% \text{ ink on surface of foam sheet}}{\% \text{ ink on original sheet}} * 100$$

Table 4.6: Percent ink present on the surface after de-inking and calculated %ink loss after de-inking

% ink on surface	Stock	Foam	Total →	% ink loss
Control	2.53	4.28	6.82	38.61
A	3.30	3.78	7.08	34.02
B	4.51	5.84	10.35	52.57
C	3.76	6.78	10.54	61.02

For the control case and case A the total percent of ink collected after de-inking is lower than what originally entered the system. This is due to the fact that the slurry for these cases re-pulped longer than case B and C. Because the ink was wrapped around the fiber and holding it together, a longer de-pulp time was required. The longer de-pulping results in smaller ink particles which would easily pass through the wire in the handsheet mold and leave the slurry.

The results show an improvement in ink removal for the samples with a deposited coating. Case C, PFE<PEG, indicates the most amount of ink loss. This could be the result of the fact that the PEG acts as a sponge. Once the paper is soaked in the water the PEG swells up and lifts the PFE coating, which acts as a barrier for the ink so that it cannot effectively wrap around the fiber, and the ink lifts off the surface of the paper easier.

## **CHAPTER 5**

### **CONCLUSIONS**

The results described in this thesis indicate that an enhanced ink removal process may be possible. The increase in material loss is due to the films deposited on the paper as explained by de-inking experiments. In films with higher thickness PEG films, it was shown that a large amount of fiber was retained in the stock sheets. This indicates that the deposited films protect the underlying fiber and allow removal of ink particles from the printed surface. The amount of ink removed based on the area deposited also increased for the cases of higher deposition thickness of PEG. The fluorocarbon and hydrogel films described in this research provide an excellent barrier for the ink and prevent it from wrapping around the fibers.

Although more work needs to be done, based on the results described above it is reasonable to conclude that dual layer films help the de-inking of laser printed paper with less fiber loss and more ink removal, relative to paper with no barrier films.

## **CHAPTER 6**

### **RECOMMENDATIONS & FUTURE WORK**

Although this work illustrates that these films provide aid in ink removal, additional work is needed to study the effect of the PFG film alone without the PFE film. Also it is important to find the least amount of film thickness needed for to achieve efficient de-inking, considering the cost of polymer film deposition. In addition, further ink removal may be possible by repeating the flotation step.

Based on a study in 1997 five million ton of copier paper was consumed in United States, out of which only two million ton was recycled to less valuable paper and not back to its original quality [53]. This is a big economical issue for the paper industry. In considering the recycling of laser printed-paper using plasma coatings, it is important to consider the costs of the films in use. It would be economically more feasible if a cheaper polymer that has similar characteristics to PFE is used, simply because the PFE gas is very costly.

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