PREPARATION OF HIGHLY REFLECTIVE FILMS BY SUPERCRITICAL INFUSION OF A SILVER ADDITIVE INTO POLY (ETHER ETHER KETONE)

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(ABSTRACT)

There has been a great interest in preparing polymeric reflective surfaces in the last few years. The application of supercritical fluid technology in this area is beginning to receive a great deal of attention. Poly ether ether ketone (PEEK) is well known for its excellent thermal, chemical, mechanical and electrical properties. These properties make it ideal for use in aerospace, electrical, fluid handling and coating industries. Supercritical infusion of a silver–containing additive (1,5-cyclooctadiene- 1,1,1,5,5,5-hexafluoroacetylacetonato)silver(I) into a PEEK film was achieved with moderately high density CO_2 at various temperatures, pressures, and times. During the infusion process: 1) polymer sample was exposed to both supercritical CO_2 and the additive under pressure for a brief time, 2) depressurization of the system caused the CO_2 to rapidly diffuse out of the polymer; while the remaining additive in the polymer desorbed at a much slower rate governed by its diffusivity in the CO_2-free polymer. Following this process the infused film was heated for a short time period to thermally reduce the infused metal and to form a reflective surface. In this research the effect of different additive concentrations, infusion conditions (e.g. temperature, pressure, time), and curing conditions (e.g. air flow rate, temperature, time) on the nature of the PEEK surface will be presented.

This Thesis is dedicated

to my mom, dad, Nikoo

and

Mehdi

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1. Introduction

The unique characteristics of supercritical fluids have been known since 1822[1]. Supercritical fluids have received a great deal of attention in a number of important scientific fields[2-15]. There are several reasons for choosing a supercritical fluid over a conventional solvent[16] such as 1) more favorable mass transport properties[6], and 2) easier adjustment of the chemical potential of the system by changing the pressure and/or temperature[14]. One can therefore access a significant range of physicochemical properties (density, diffusivity, viscosity, dielectric constant, etc.) without passing through a phase boundary, such as changing from gas to liquid. In other words, a supercritical fluid can be considered a continuously adjustable solvent.

A supercritical fluid can be defined as any substance that is above its critical temperature and pressure, such that no distinct liquid or gas phase can exist. Supercritical fluids have high diffusivity and low viscosity compared to their corresponding liquid state, thus allowing rapid mass transport and enhanced matrix penetration. Fluid density which often is a measure of solvating power is related to temperature and pressure. The most common supercritical fluid is CO_2 because of its moderate critical pressure and temperature (P_C = 73 atm, T_C =31°C), inertness, non-toxicity, and wide availability in pure form.

The potential of supercritical fluid (SCF) technology for polymer processing is being realized in areas ranging from extraction and synthesis to the preparation of new composite materials. The range of polymer properties which have been attained over the years has been continually extended. Polymers today are used for everything from catalyst to adhesives[17]. The utilization of a polymer in a specific application is redominantly based upon the polymer's chemical and physical properties. The high diffusivity of supercritical carbon dioxide in many solid polymers, for example has implications in polymer modification. A sampling of these studies includes: 1) polymer controlled precipitation[18], 2) polymer fractionation[19], 3) polymer plasticization[20], and 4) medium for polymer synthesis[21]. Swelling of many polymers in supercritical CO_2 suggests a high permeation rate of CO_2.

There is a great interest in obtaining materials having a surface layer of metal. Some uses for these materials are for optical and structural conductive purposes; while, others are intended for electrical and magnetic applications[22]. Traditionally metal-coated polymers have been achieved by a variety of external processes such as chemical vapor deposition, lammination, and sputter technology[23]. The work described here will demonstrate the preparation of a highly reflective metal coated poly(ether ether ketone) film by supercritical infusion of a silver additive. The effect of different additive concentrations, infusion conditions, and curing conditions on the metallized surface of PEEK will be studied.

2. Historical Background

Few reports have discussed the use of supercritical fluids to infuse a substance into a matrix such as a polymer[24]. The additive must dissolve in carbon dioxide first. The basis of this process is to expose a polymer sample to an additive substance and CO_2 under high pressure. The additive carried by the CO_2 rapidly diffuses into the polymer. When the CO_2 pressure is released, the gas rapidly diffuses out of the polymer, sharply reducing the additive diffusivity; the additive would then be left in the polymer to desorb at a slow rate governed by its diffusivity in the CO_2-free polymer. The terms "CO_2- assisted impregnation "or simply " infusion" for brevity is often used in referring to this process.

Berens[24] and Sand[25] demonstrated in 1986 that polymer substrates could be impregnated by swelling the polymer with a solution of penetrant in CO_2 followed by rapid venting of the supercritical solution. A variety of polymers (e.g. poly(vinyl chloride), polycarbonate, poly(methylmethacrylate), poly(vinyl acetate)) and additives such as dimethyl phthalate, octane, n-butanol, and naphthalene were used in this study. The penetrant having lower diffusivity than gaseous CO_2 was retained by the polymer. The amount of penetrant absorbed was determined from the weight change of sample after most of the CO_2 had escaped. Chemical reactions may be carried out in the swollen solid polymer substrate or the CO_2 may only function as an aid whereby the physical properties of the polymer are regained after processing. This approach has obvious advantages over liquid solvent infusion which may be time consuming and where potentially toxic, residual solvent may be left in the product. Although supercritical infusion (or impregnation) has only been studied in a very limited fashion, both organic and organometallic penetrants have been explored. Berens found that CO_2 accelerated the absorption of many low molecular weight additives into a number of polymers. The infusion process may also be described as a partitioning of the additive between the CO_2-and polymer-rich phases. Consequently, the relative solubility of the additive in both the CO_2 and in the polymer is a major factor governing the amount of additive absorbed. Poly(vinyl chloride) (PVC) with dimethyl phthalate has been used to explore the effects of supercritical CO_2 on the transport kinetics and equilibria of an additive in a glassy polymer[24].

In another study[26], poly(ethylene glycol) diacrylate and 4,4'-dichlorobenzophenone were infused into polycarbonate in the presence of CO_2. Following depressurization and removal from the autoclave, UV radiation initiated a reaction that consumed ~25% of the acrylate residue. It was shown that by controlling the infusion time one could control the amount of acrylate residue which was consumed. For example, the time of infusion could be designed in such a way that only 1% of the acrylate residue was consumed.

Watkins and McCarthy[27] have modified solid organic polymers by carrying out chemical reactions within supercritical fluid - swollen solid polymer substrates. The reactions can be run either in the presence of the supercritical fluid solution or subsequent to removal of the solution by depressurization. One illustrative study involved the infusion of CO_2 solutions of styrene into a variety of polymer substrates where thermally initiated radical polymerization within the swollen substrate generated polystyrene- substrate polymer blends. The advantages of supercritical fluids as reaction media for this study were: 1) they increased (significantly) diffusion rates of penetrants in solid polymers; 2) the solvent strength could be adjusted over wide ranges by manipulating temperature and pressure; therefore the degree of swelling and the partitioning of reagents between the swollen polymer matrix and the supercritical fluid solution were controllable; 3) since common supercritical fluid solvents are gases at atmospheric pressure; the solvent rapidly dissipated upon release of pressure thus trapping penetrants in the polymer substrate.

CO_2- assisted impregnation of fragrances and pharmaceuticals in thermoplastic polymers such as poly(ethylene) and poly(propylene) has also been disclosed[25]. The thermoplastic polymer was impregnated by 1) dissolving an impregnation material such as a fragrance or pharmaceutical material in a near critical or supercritical fluid and 2) reducing the pressure so that the critical fluid agent diffuses out of the thermoplastic polymer. The amount of fragrance or pharmaceutical material in the thermoplastic polymer was controlled by the concentration of impregnation material in the critical liquid.

It has been shown via Fourier transform infrared spectroscopy that polymers possessing electron donating functional groups exhibit specific molecular interactions with CO_2, most

probably of a Lewis acid-base nature[28]. The evidence for interaction was the observation of the splitting of the band corresponding to the CO_2 bending mode. This splitting was not observed with polymers such as polyethylene and polystyrene which lacked electron-donating functional groups. A series of polymer films, such as polyesters, poly(vinyl methyl ketone), and poly(2-vinyl pyridine) exhibited the splitting suggested. Higher solubility of CO_2 into the polymer could be correlated with the CO_2 band splitting. These results suggested that CO_2 might act as an electron acceptor rather than an electron donor.

Supercritical fluid infusion has been demonstrated with organometallics[29] by infusion of polyethylene with C_P*$Ir(CO)_2$ where C_P* = η^5- $C_5(CH_3)_5$ via supercritical CO_2. Infusion attempts also employed CO_2 saturated with a fluoroalcohol. The infused polyethylene provided a new opportunity for investigating the equilibrium process by matrix isolation / FT-IR. In this study the photochemical C-H activation of polyethylene by C_P*$Ir(CO_2)$ and C_P*$Ir(CO_2)$…HORF were compared. Clearly, the impregnation of other organometallic compounds into polymers offers considerable possibilities for the modification or tailoring of specific polymer properties.

The feasibility of using supercritical fluids to impregnate a variety of carbon/carbon composites (as opposed to polymers) with a ceramic precursor has been successfully demonstrated[30]. Polycarbosilane and polysilane were employed as silicon carbide precursors. The apparent carbon/carbon porosity varied from 4% to 85% . The conditions required to dissolve, transport, and precipitate the ceramic precursors were not provided. Significant improvements in oxidative resistance and mechanical properties were measured. Supercritical fluid fractionation of the ceramic precursors was demonstrated as a means whereby to control physical properties and char yield of the composite.

The synthesis of polymer/metal composites containing isolated metal nanoclusters distributed homogeneously through a polymeric substrate was recently reported[31]. A platinum organometallic precursor, (1,5- cyclooctadiene) dimethylplatinum(Π), $(COD)Pt(CH_3)_2$, was dissolved in supercritical CO_2 and infused into both solid poly(4-methyl-1-pentene) (PMP) and poly(tetrafluorethylene) (PTFE). Reduction to platinum metal followed infusion by either

hydrogenolysis before (4hr.) or after (24hr.) decompression or by thermolysis (20hr.) in CO_2 by raising the temperature to 140°C prior to decompression. Regardless of the post-infusion treatment, dark- colored composites were produced that contained platinum clusters with a maximum particle diameter of 15 nm. Uniform distribution of platinum clusters throughout both films was reported. A significant amount of platinum metal was also deposited at the PTFE surface. The effect of different infusion conditions on metal distribution was not investigated.

The placement of thin metal films on a solid inorganic surface via supercritical fluid transport of organometallic precursors has also been demonstrated[32]. In this process, precursor reagent(s) (e.g. $Al(HFA)_3$, $Cr(acac)_3$, $In(acac)_3$) were dissolved in a supercritical fluid (e.g. pentane, acetone, CO_2) and then this solution, under high pressure, was passed through the restrictor into a deposition chamber where the rapid expansion of super- critical fluid caused vaporization of the solute(s). The vaporized precursor compounds were then induced to react at or near a substrate surface (usually Si or SiO_2) to form a thin film. Unfortunately the decomposition temperature of the precursor (600-800°C) was well above the decomposition temperature of most polymers thus resulting in polymer degradation prior to metal reduction.

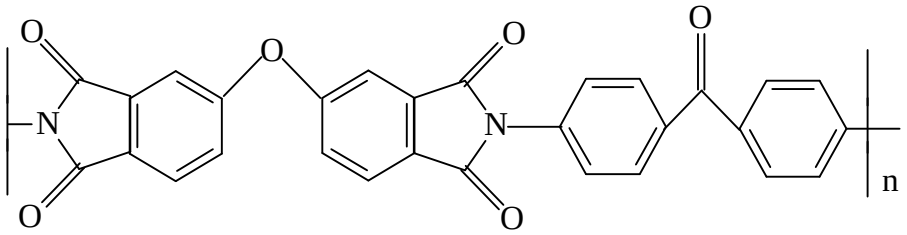
Boggess et al. have studied the infusion of a silver complex into both poly(amide acid) and fully cured polyimide films using supercritical CO_2. Optimal conditions for the production of a reflecting film were established[33] as 110°C/5000psi/120min for infusion and 100°C/60min/30 SCFH for cure process. The polyimide on which this feasibility was demonstrated was derived from 3,3',4,4'- benzophenonetetracarboxylic acid dianhydride (BTDA) and 4,4'- oxydianiline (ODA). Supercritical fluid infusion of the (1,5-cyclooctadiene-1,1,1,5,5,5-hexafluoroacetonate) silver(I), $[Ag(COD)HFA]_2$ was into the fully cured BTDA-ODA polyimide. Thermal treatment of the infused film resulted in a reflective silver surface. The infused film showed no apparent change in texture or color, and only a slight change in mass was observed relative to the polyimide before infusion. Thus, supercritical CO_2 was believed to penetrate the polyimide but little CO_2 remained when the pressure was reduced to one atmosphere.

Later on, this process was expanded to a number of polyimides such as PMDA-ODA, 6FDA-ABP, ODPA-DABP (Figure 1) to see whether a reflective surface could be formed using the silver complex[34]. It was interesting that not all of the polyimides after infusion with the silver additive and subsequent heating gave rise to a reflective surface. The explanation of failure to form a reflective surface on some polyimides such as 6FDA-ABP stated to result from lack of a ketonic carbonyl oxygen in the polymer. Combinations of several other dianhydride-diamine pairs were studied in order to further test the suggestion that a ketonic carbonyl group was necessary for the formation of a reflective surface. Each polyimide with a ketonic carbonyl group in the dianhydride and or the diamine formed a reflective silver surface; while if no ketonic group were present no reflective surface was forthcoming. Also, this study determined that the infusion process was not unique to supercritical CO_2 since a reflective film could be obtained via using supercritical CHF_3 as the carrier of the silver complex.

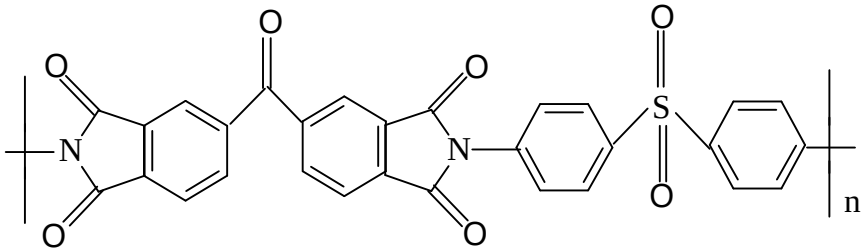
The feasibility for preparation of novel thin silver films on a variety of polymer substrates such as polycarbonate(PC), polysulfone(PS) and polymethylmethacrylate (PMMA) via supercritical infusion of a silver precursor under relatively mild conditions has been reported[35]. Resulting films were (a) reflective, (b) maintained their flexible nature and (c) had a surface resistance higher than 10^{11} ohms in spite of their metallic appearance. It was determined that silver infused PS films could be either reflective or conductive just by controlling the temperature of the thermal treatment. Temperatures above the PS glass transition temperature (T_g) resulted in low surface electrical resistance (~3-20Ω); while a reflective surface formed at cure temperatures below the PS glass transition temperature . Chemical structures for some of these polymers are shown in Figure 1.

The objective of this M.S. thesis was to extend this silver-mirror technology to additional polymer films via supercritical fluid infusion of a silver precursor under relatively mild conditions. The polymer on which this feasibility has been conducted is poly(ether ether ketone), (PEEK).

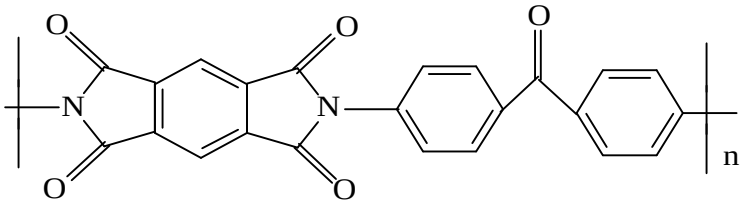
Depending on the additive concentration, infusion conditions (e.g. temperature, pressure and time), and curing conditions (e.g. temperature and time), silver surface films with varied



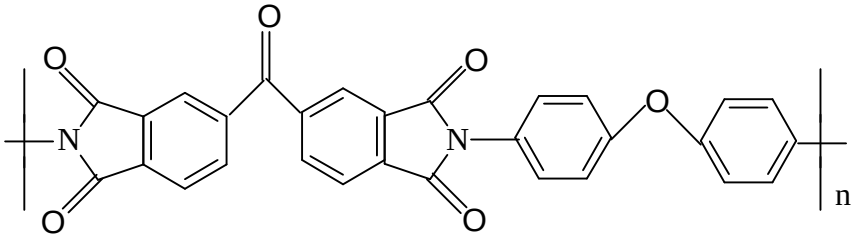
ODPA/DABP



BTDA/DDSO2

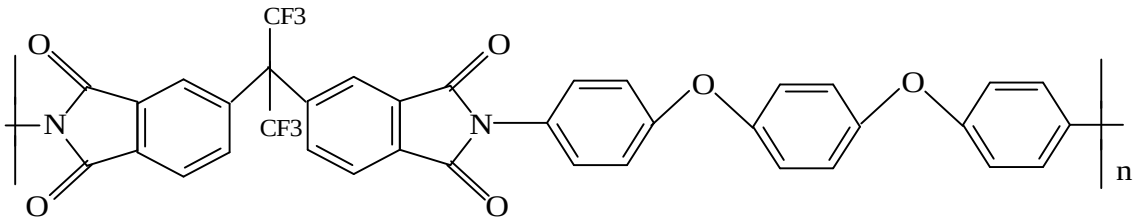


PMDA/DABP

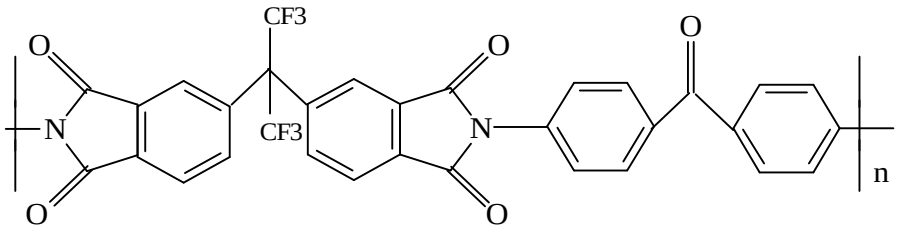


BTDA/ODA

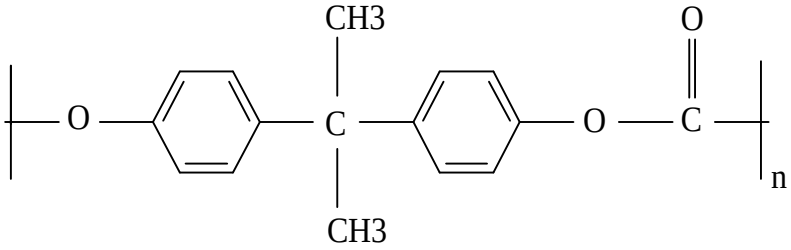
Figure 1: Chemical structure of some polymers



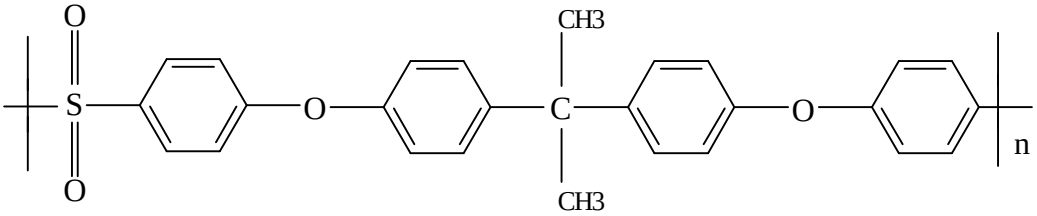
6FDA/APB



6FDA/DABP



PC



PS

Figure 1: Chemical structure of some polymers

reflectivity were produced. The nature of the silver and its distribution within the polymer and on the surface of the film were obtained via microscopy and surface analysis techniques such as x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and auger electron spectroscopy (AES). In addition, thermogravimetric analyses (TGA) and reflectivity measurements were conducted. The application of this work is in the space where large area antennas and reflectors desirable.

3. Experimental

3.1 - Materials

3.1.1. Polymer Film

Poly(etheretherketone), PEEK, film was obtained from McMASTER-CARR supply company (Dayton, NJ.) and used as received (Figure 2). The thickness of the film was 0.003″. It had a smooth surface on one side and a much rougher surface on the other film side. PEEK has been described as a tough, semi crystalline thermoplastic. The common grade of PEEK is ca 35% crystalline and has a density of 1.32 g/ml. PEEK is an inert polymer under normal storage conditions.

3.1.2. Additive

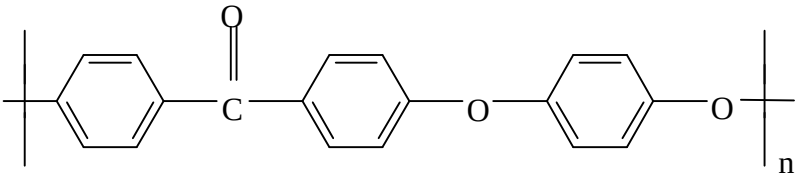
The additive (1,5-cyclooctadiene-1,1,1,5,5,5-hexafluoroacetonato)silver(I), $[Ag(COD)HFA]_2$, was obtained from Aldrich Chemical Company (Milwaukee, WI.) and was used as received (Figure 2). It has a boiling point of 200°C and a melting point of 122-124°C.

3.2 - Instrumentation

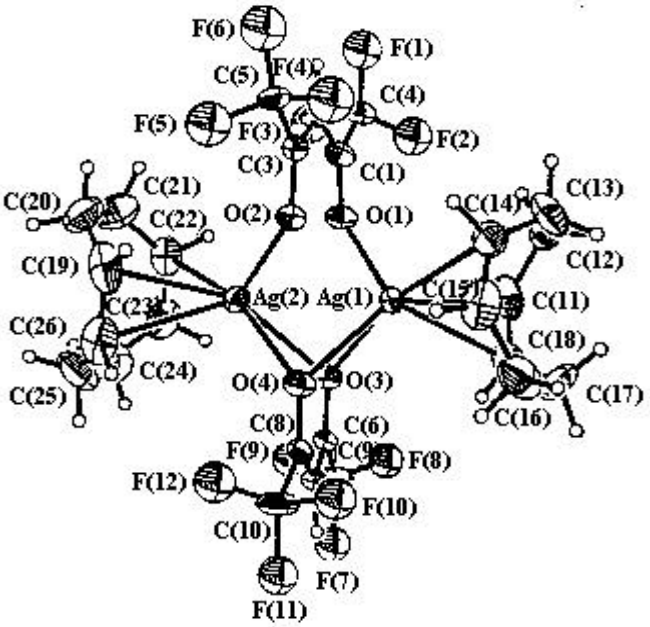
All supercritical fluid infusion (SFI) experiments were performed using an Applied Separations (Allentown, PA.) supercritical fluid system (Spe-ed SFE) equipped with an air-driven piston pump to achieve a maximum pressure of 10,000 psi (Figure 3). The oven module of the Spe-ed SFE can reach temperatures as high as 250°C. A 10 ml stainless steel supercritical fluid extraction vessel (Keystone Scientific, Bellefonte, PA.) was used for each infusion. Following each infusion experiment, the vessel was returned to ambient conditions by releasing pressure through a heated valve. All infusion experiments were performed using SFE/SFC grade CO_2 (Air Products and Chemicals Inc., Allentown, PA.) padded with 2000 psi of helium.

3.3 - Supercritical Fluid Infusion and Cure Procedure

The film and the additive were placed together in the vessel. The average weight of film



PEEK



$[Ag(COD)HFA]_2$[36]

Figure 2: Molecular structure of PEEK and additive used in this study

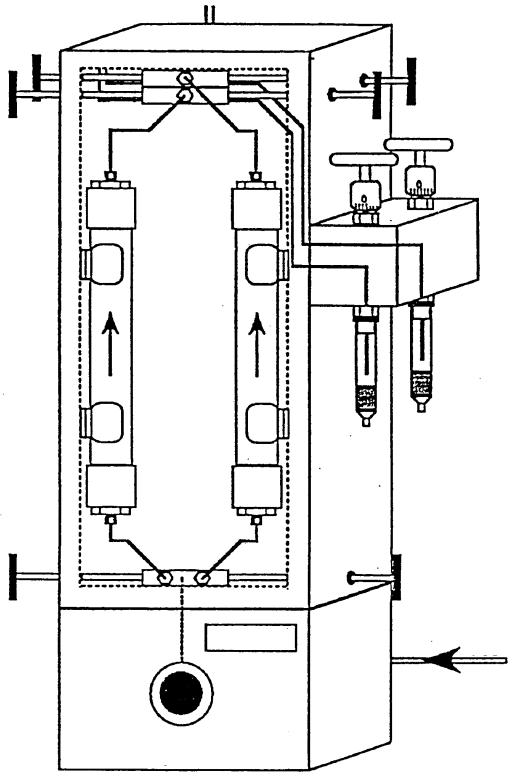


Figure 3: Applied Separations SFE Spe-ed

was 70 ± 2 mg. The additive was introduced on a weight of additive/ weight of film basis. CO_2 was added to the selected pressure and the vessel was heated to the desired temperature for a given time to achieve supercritical conditions. Upon completion of the experiment, the vessel was decompressed to ambient pressure. After allowing the vessel to cool to room temperature, the film was removed. The edges of the film were then clamped between two glass plates, and heated in a Blue M (Wilmington, DE.) oven Model DCI-146C at a selected time and temperature with compressed air circulation at 100 SCFH. The oven temperature can reach as high as 316°C/600°F. The air flow rate was in the range of 0-100 standard cubic feet per hour (SCFH). After thermal cure a silvery surface was formed on both sides of the PEEK film.

3.4 – Characterization

3.4.1. X-Ray Photoelectron Spectroscopy (XPS)

X- Ray Photoelectron Spectra were obtained via a Perkin-Elmer Phi Model 5400 ESCA system. A magnesium anode (Kα = 1253.6 eV) operating at 400W was used. The operating pressure typically was less than 5×10^{-7} torr. The sample was attached to aluminum or copper mounts by a piece of double-stick transparent tape. The specimen stage was set at a 45° exit angle. Survey scans from zero to 1100 eV were obtained. Cited binding energies were relative to the assumed aromatic carbon signal at 284.6 eV [37]. XPS data were acquired and stored on an Apollo 3500 computer with Perkin-Elmer software.

3.4.2. Transmission Electron Microscopy (TEM)

Transmission Electron Micrographs were taken with a Philips Model 420T transmission electron microscope. Samples prepared for TEM were embedded in Polyscience's Ultra low-viscosity medium and cured for 12 hours at 60°C. Using a Reichert-Jung ultra-microtome with a microstar diamond knife, cross sections of the samples between 500 and 1000 angstroms were obtained. These sections were placed on 200-mesh copper grids prior to analysis.

3.4.3. Scanning Electron Microscopy (SEM)

An ISI Model SX-40 scanning electron microscope (SEM) was used to obtain all scanning electron micrographs. The samples were attached to aluminum mounts using double-stick tape coated with a thin layer of gold in order to dissipate charge.

3.4.4. Auger Electron Spectroscopy (AES)

A Perkin – Elmer Phi Model 610 Scanning Auger Microprobe System was used to record depth profiles of modified films. A typical electron beam voltage was 3 kV with a beam current of 0.1 μA. The ion beam used for concurrent argon sputter etching was operated with an accelerating voltage of 4 kV and an ion current of 5μA/cm^2. The ion gun was rastered within a 2mm×2mm square. Samples were mounted on aluminum mounts using double-stick transparent tape. Silver paint was applied to the corner of the samples to reduce charging on the surface of the sample.

3.4.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed using a TA Instrument, Inc. (New Castle, DE) Hi-Res Model TGA 2950 Thermogravimetric Analysis. The heating rate was 10 °C/min with a dynamic airflow of 20 ml/min. The system's internal calibration procedure was followed to calibrate the system.

3.4.6. Reflectivity Measurements

All reflectivity determinations were performed at NASA Langley Research Center. Measurements were obtained at 531 nm on a Lambda 9 UV/VIS/NIR spectrophotometer with a variable angle reflectivity attachment. Measurements at 531 nm were used since this is the solar maximum value and these materials are of interest for aerospace applications.

4. Results and Discussion

4.1 – Preliminary

Incorporation of a silver additive into PEEK film via a supercritical fluid to form a reflective mirror surface of silver was found to be strongly dependent on both the infusion and curing conditions. The first set of experiments was designed to determine if supercritical CO_2 could penetrate the surface of the PEEK. After this experiment, infusion of the additive directly into the PEEK was performed. The first attempt was the infusion of 20 percent additive while temperature, pressure and time were varied. After the infusion process, the film was cured to reduce the infused silver and to hopefully give rise to formation of a silver mirror. All infused samples were cured at 225°C for 30 minutes and for another 30 minutes at 250°C; while, the flow rate of air during the cure cycle was 100 standard cubic feet per hour. Since a reflective mirror surface formed as a result of 20% additive, the amount of additive to film level (wt./wt.) was reduced to 10 and 5% to determine whether reflective mirror surfaces could also be formed. For 10 % additive a reflective mirror surface formed. Using 5% additive a reflective mirror surface also formed but only at 110°C/120min/2200psi and 140°C/120min/2200psi for infusion. The cure conditions were the same as noted previously. The objective of this chapter is to describe the synthesis and characteristics of silver modified films made via infusion using supercritical fluid CO_2 and to optimize the conditions for formation of a reflective surface.

4.2 - General Characterization

Fully cured PEEK is a transparent, colorless, flexible film which has a smooth side and rough side. It has a glass transition temperature (T_g)=143°C, melting point (T_m)=334°C and is stable in the melt at 400°C in air[38].

Infusion by supercritical CO_2 containing silver additive generated in some cases films, which appeared metallic silver on both sides after cure. All films maintained their flexibility after surface coverage with silver. The appearance of the silvery surface on the film depended solely on the infusion conditions since the cure conditions were the same in all experiments described in this section.

4.2.1- Basic Considerations in Light Scattering Theory

Often materials are modified by coating them to create new materials for different purposes, i.e. coating of paper to cover the base sheet and to form a new design primarily for printing[39]. The optical properties of coated materials depend on the characteristics of the coating pigment. Usually the high reflectance results mainly from light scattering within both the coating and base stock. When a ray of light enters the sheet it rapidly becomes diffused in the spatial direction. At each interface between a pigment particle and air, the phenomena of reflection, diffraction, interference and refraction occur. These are the basic mechanisms of light scattering. In view of irregular shapes and depositions of the particles making up the coating and base stock it is easy to see how these phenomena, involved in multiple scattering, result in diffusion of the light. The technical measurement of the light scattering power is the specific scattering coefficient. Scattering coefficient, s, may depend on the properties of particles such as particle size, particle shape and refractive index. Concerning the particle size one should mention that the extent of reflection and refraction will depend upon the amount of surface area per unit mass (the specific surface). If the linear dimensions of the space are large enough to permit to consider a scattering coefficient of the mass of particles, it should be very small in magnitude, and the reflectivity of the mass would also be low. This follows the fact that the specific surface of subdivided matter varies inversely with the particle diameter, the “constant” depending on particle shape. As the particles are made smaller, the specific surface area becomes larger, and the scattering coefficient and the reflectivity increase substantially. The index of refraction of pigment particles also has an effect on the scattering coefficient particularly, when the particles are in contact with, a liquid or solid.

During the transmission of light through pigment particles, some of the radiation is absorbed and transformed to thermal form. In any case light is absorbed by all materials in varying degrees, and the measure of absorbing power is the specific absorption coefficient. Absorption coefficient (k) is a function of natural and added coating materials, and may be a strong function of wavelength[39].

Kubelka and Munk[40] showed the relationship between the reflectance (where the reflectance defined as a ratio of the intensity of reflected light over the intensity of incident light) of an opaque layer (theoretically infinitely thick) and the coefficients s and k (scattering coefficient and absorption coefficient, respectively) by the following equation:

$$\mathbf{R = 1 + (k/s) - \text{Square root}[\,2\,(k/s) + (k/s)^2\,]}$$

where the reflectivity (R) is a function of the ratio of (k/s). Further, if the reflectivity is to be very high this ratio must be very low. For imperfectly opaque films this equation becomes more complicated.

4.3 –PEEK in the Presence of Supercritical CO_2

To determine if supercritical CO_2 could penetrate the surface of the PEEK a strip of PEEK film was subjected to 2200 psi CO_2 at 110°C for 120 minutes. There was no apparent change in the color or the texture of the film and only a slight change in mass was observed (Table 1) after decompression. Thus, supercritical CO_2 may penetrate the PEEK but if it does we concluded that little CO_2 remained when the pressure was reduced to ambient pressure. Furthermore, it didn't appear that any component of the PEEK was extracted during the CO_2 treatment.

4.4 – Synthesis of the Metalized Film

A thin strip of PEEK film and 20wt.% $[Ag(COD)HFA]_2$ were placed together in a stainless steel vessel. CO_2 was added to a pre-selected temperature and pressure. Table 2 lists the various infusion conditions and times that were employed. Upon completion of the experiment, the vessel was decompressed to ambient pressure. After allowing the vessel to cool to room

Table 1: Mass change for PEEK film upon treatment with supercritical CO_2 and then decompression

(Infusion conditions: 110°C/2200psi/120min.)

Time (min)	Mass change
Exactly after decompression	+0.6%
1 day after decompression at room temperature	+0.4%
2 days after decompression at room temperature	+0.3%
7 days after decompression at room temperature	+0.3%

Table 2: Supercritical infusion conditions and appearance of the PEEK with 20 wt. % $[Ag(COD)HFA]_2$ after infusion/cure

Sample	Infusion conditions			Surface
	T(°C)	t(min)	P(psi)	
A-1	60	60	2200	Brown
A-2	60	120	2200	Brown
A-3	60	120	5000	Brown
A-4	80	60	2200	Brown
A-5	80	120	2200	Silvery mirror
A-6	80	60	4000	Brown
A-7	80	120	5000	Brown
A-8	110	60	2200	Silvery mirror
A-9	110	120	2200	Silvery mirror
A-10	110	60	5000	Brown
A-11	110	120	5000	Brown

temperature, the film was removed. No apparent changes were observed in the color or texture of the infused film. The edges of the film were then clamped between two glass plates, and heated in an oven at 225°C for 30 minutes and for another 30 minutes at 250°C; while, the flow rate of air during the cure cycle was 100 standard cubic feet per hour (SCFH). A silvery surface formed on both sides of the PEEK film (Table 2) during the cure in three instances (e.g. A-5: 80°C/2200psi/120min, A-8: 110°C/2200psi/60min, and A-9: 110°C/2200psi/120min.).

Since a reflective mirror surface did not form at 60°C infusion for the 20 wt.% level of additive/ polymer, experiments for 10 wt.% level of additive/ polymer were carried out above 60°C (Table 3). Again a silvery surface was obtained on both sides of PEEK in three instances (e.g. B-4:110°C/2200psi/60min, B-5: 110°C/2200psi/120min, and B-8: 140°C/2200psi/120min.). For the same reason the infusion experiments for 5 wt.% of additive /polymer were begun at 110°C (Table 4). Silvery surfaces were observed at 110°C/2200psi/120min for C-1 and at 140°C/2200psi/120min for C-3. All PEEK films before infusion had a thickness of 0.003″ mm and a dimension of 5×1 cm. and the dimensions remained constant after cure.

4.5 - Surface Analysis of the Films

X-ray photoelectron spectroscopy (XPS) was used to investigate the surface properties of silver containing films prepared by the method outlined in Section 3.3. Depth profiling via Auger electron spectroscopy (AES) in conjunction with argon ion etching was utilized to gain additional knowledge regarding the distribution of particles in the bulk of the films. A detail analysis of the surface density of particles and the distribution of particles in the films were obtained via scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively.

Elemental surface atomic compositions from XPS for selected films which exhibited a silver mirror are presented in Table 5. A comparison of films A-5 and A-9 (20 wt.% of additive/polymer) revealed that at constant pressure and time (2200 psi and 120 minutes), as the infusion temperature increased from 80°C to 110°C, silver atomic concentration on the film

Table 3: Supercritical infusion conditions and appearance of the PEEK with 10 wt.% $[Ag(COD)HFA]_2$ after infusion/cure

Sample	Infusion conditions			Surface
	T(°C)	t(min)	P(psi)	
B-1	80	60	2200	Brown
B-2	80	120	2200	Brown
B-3	80	120	5000	Brown
B-4	110	60	2200	Silvery mirror
B-5	110	120	2200	Silvery mirror
B-6	110	120	5000	Brown
B-7	110	180	5000	Brown
B-8	140	120	2200	Silvery mirror

Table 4: Supercritical infusion conditions and appearance of the PEEK with 5 wt.% $[Ag(COD)HFA]_2$ after infusion and cure

Sample	Infusion conditions			Surface
	T(°C)	T(min)	P(psi)	
C-1	110	120	2200	Silvery mirror
C-2	110	120	5000	Brown
C-3	140	120	2200	Silvery mirror
C-4	140	120	5000	Brown

Table 5: Atomic concentrations of selected elements via XPS of infused/cured metalized reflective films

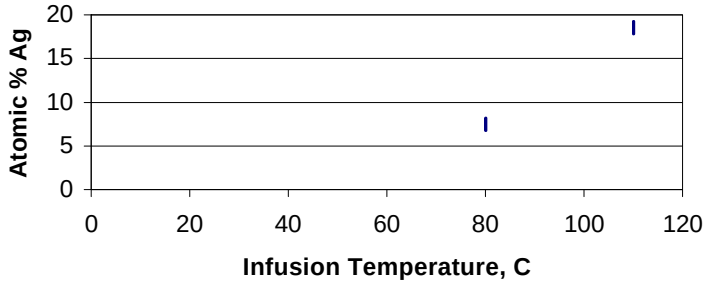
(Cure conditions: 225,250°C/30+30min/100 SCFH)

Sample	% additive	Infusion Conditions (°C/psi/min)	%C	%O	%F	%Ag
A-5	20	80/2200/120	75.9	13.9	2.7	7.5
A-9	20	110/2200/120	68.6	12.3	0.6	18.5
B-4	10	110/2200/60	76.1	13.1	1.4	9.6
B-5	10	110/2200/120	67.0	14.8	2.7	15.5
C-1	5	110/2200/120	81.2	14.7	0.2	3.9

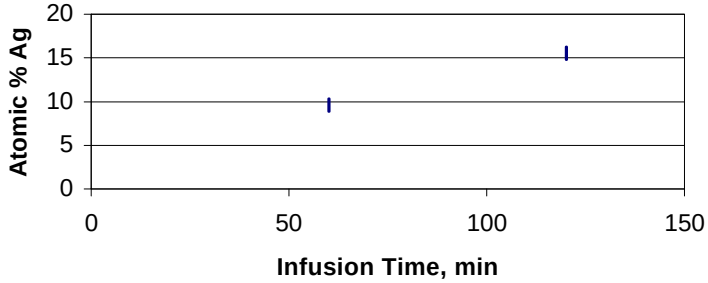
surface increased from 7.5 to 18.5% and fluorine concentration decreased from 2.7 to 0.6%. At 10 wt.% of additive/polymer and constant temperature and pressure (110°C and 2200 psi), the amount of silver increased from 9.6 to 15.5% and the amount of fluorine increased from 1.4 to 2.7% in going from 60 to 120 minutes infusion. At constant infusion conditions (110°C, 2200 psi, 120 min.) the amount of silver on the surface decreased as the wt.% level of additive/polymer changed from 20% to 10% to 5%. The plots of silver atomic concentration versus infusion temperature, infusion time and %wt. additive have been shown separately (Figure 4).

Reflectivity results for infused silvered films are summarized in Table 6. The angle of incidence defined as an angle of incoming light measured perpendicularly to the surface (Figure 5). Reflectivity measured at 20°, 45° and 70° relative to the incident light of 531 nm (i.e. the most intense wavelength of solar radiation) was taken as the criterion for evaluation. The results of these measurements yielded reflectivity values of the film compared to an optical silver mirror assigned a reflectivity value of 100%. The highest reflectivity was 65% measured on the 20 wt.% additive/polymer for an infusion temperature, pressure, and time of 110°C, 2200 psi and 120 minutes, respectively. The second highest reflectivity was 45% at 10 wt.% additive/polymer for the same infusion conditions. Also, for the same infusion conditions using 5 wt% additive the reflectivity of 11.1% observed. These reflectivity results support the XPS results mentioned previously in that a higher atomic concentration of silver on the surface gave rise to films with higher reflectivity (all samples cured at 225,250°C/30+30min/100 SCFH). The plot of %reflectivity versus percent atomic concentration of silver for selected elements at constant infusion conditions (110°C/2200psi/120min.) and constant cure conditions (225,250°C/30+30min/100 SCHF) is shown in Figure 6.

Despite the formation of reflective mirror surfaces at both 20 and 5 wt.% additive/ polymer, our future work focused on films that incorporated 10% additive. At this point, the best infusion condition using 10% additive with subsequent formation of high reflectivity films was 110°C, 2200 psi and 120 minutes; while, the cure condition was T=225,250°C for t=30,30



(A)



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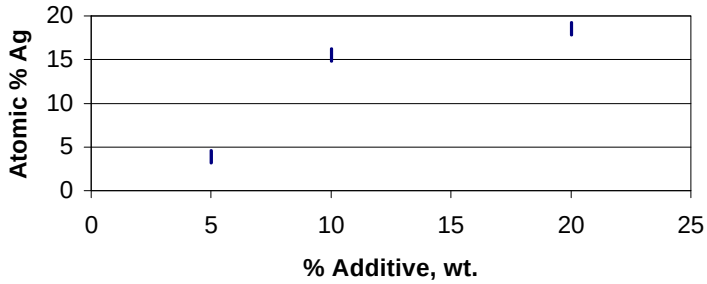


(C)

Figure 4: Surface silver atomic concentration versus: (A) infusion temperature using 20 wt% additive, (B) infusion time using 10 wt.% additive, (C) % additive

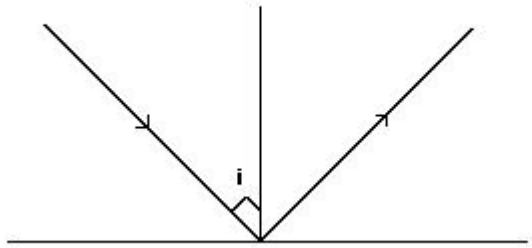


Figure 5: Angle of incidence (i)

Table 6: Percent reflectivity of selected silver infused/cured PEEK films

(Cure conditions: 225,250°C/30+30min/100 SCFH)

Sample	% additive	Infusion conditions (°C/psi/min.)	% Reflectivity		
			20°	45°	70°
A-5	20	80/2200/120	44.2	39.7	16.8
A-9	20	110/2200/120	65	50	45
B-4	10	110/2200/60	41.1	38.1	19.8
B-5	10	110/2200/120	45	41.7	21.1
C-1	5	110/2200/120	11.1	10.1	7.5

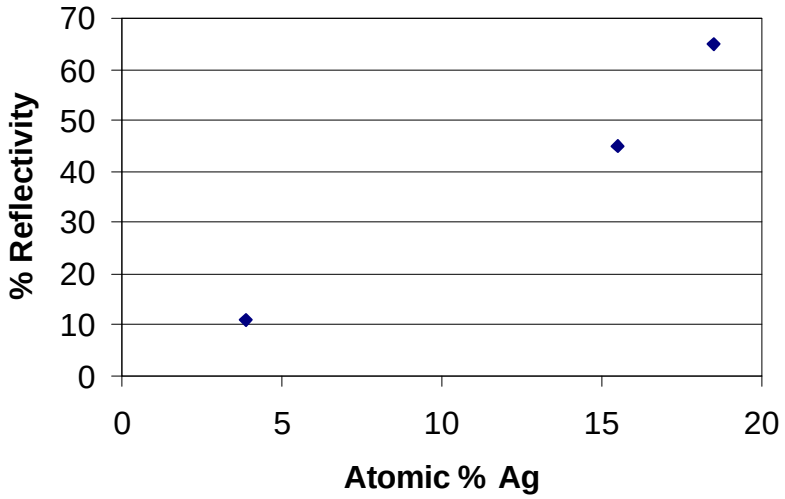


Figure 6: %Reflectivity versus surface silver atomic concentration at 20° for 5, 10, 20 wt.% additive

minute with an air flow rate of 100 SCFH. Under these conditions and taken from the oven the atomic concentrations of silver and fluorine as stated previously were 15.5 and 2.7%, respectively (Table 5). It was thought that the surface of the silvery film might be covered with unconverted additive since fluorine was on the surface. It was reasoned that if the surface were cleaned of fluorine a higher reflectivity might result. We tried to remove the fluorine from the surface by dipping the sample in acetone for 1 minute since the additive is very soluble in acetone. Four films were studied in order to investigate if the amount of fluorine on the surface could be reduced by cleaning the surface in this way (Table 7). The placement of the washing step within the infusion/cure process was varied. All resulting films were infused/cured in the same way and each had a reflective surface.

The XPS analysis as stated earlier for the unwashed silver film found 15.5% silver and 2.7% fluorine on the surface (see Figure 7 for XPS profile); while, it had a reflectivity of 45% at 20°. A second sample was infused, cured, and dipped in acetone after the cure. The atomic concentrations of silver and fluorine on the surface were 16.6% and 0.8%, respectively while the surface had a reflectivity of 59% at 20°. The XPS analysis showed that dipping the sample in the acetone for one minute after cure caused reduction in the amount of fluorine from 2.7% to 0.8% and an increase in the amount of silver from 15.5% to 16.6% (Figure 8). It was interesting to observe that by cleaning the surface after curing the reflectivity changed from 45% to approximately 59% (Table 8). The third sample was infused, washed after infusion, and then cured. It showed 16.1% silver and 1.1% fluorine on the surface with a reflectivity of 46.7%.This observation suggests that a wash step after curing is more effective than before curing. The fourth sample was infused, washed after infusion, cured, and again washed after cured. The XPS data for this sample detected 14.9% silver and 1.1% fluorine, while its reflectivity was around 53.1%. It may be speculated that washing the film after infusion causes reduction in the amount of infused additive. Washing a single time after curing appears to be the method of choice. It should be noted that XPS analysis of the backside (e.g. rougher side) of the film which had been washed after curing showed different atomic concentrations than the smooth side: 72.3%

Table 7: Atomic concentrations (XPS) of infused/cured PEEK/silver films as a function of order of treatment

Order of film treatment*	%C	%O	%F	%Ag
I / C	67.0	14.8	2.7	15.5
I / C/ W	68.1	14.5	0.8	16.6
I / W/ C	68.1	14.8	1.1	16.1
I / W/ C/ W	70.5	13.6	1.1	14.9

* I= Infuse, C= Cure, W= Wash

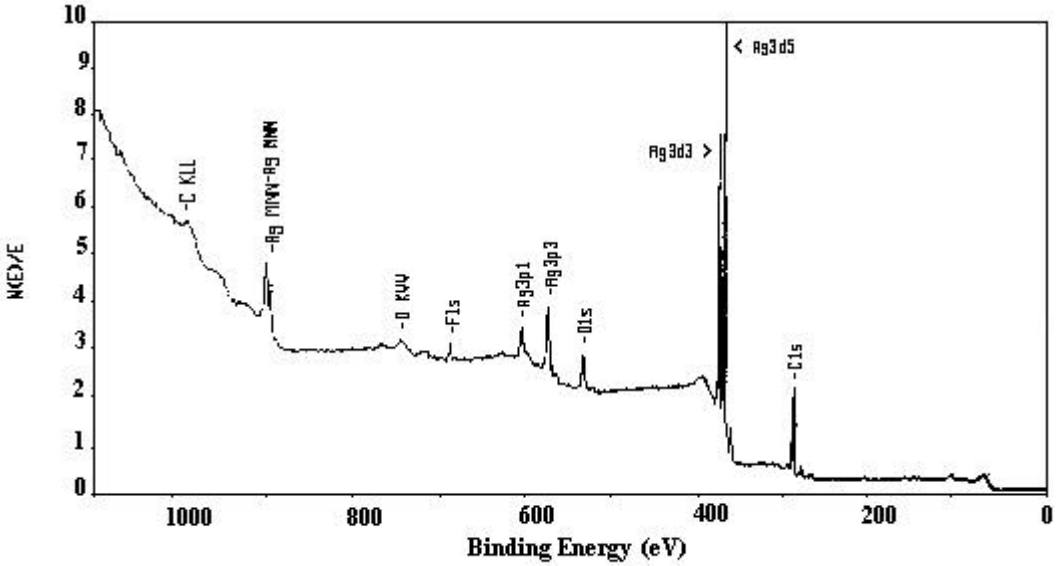


Figure 7: XPS profile of infused and cured sample before being dipped in acetone

(Infusion conditions: 110°C/2200psi/120min.)

(Cure conditions: 225,250°C/30+30min/100 SCFH)

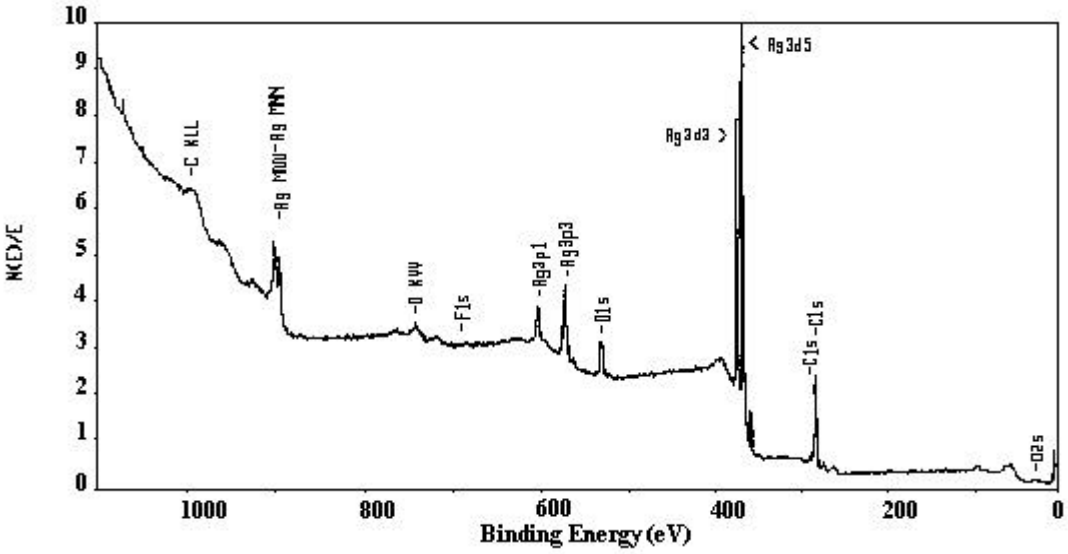


Figure 8: XPS profile of infused and cured sample which had been dipped in acetone after cure

(Infusion conditions: 110°C/2200psi/120min.)

(Cure conditions: 225,250°C/30+30min/100 SCFH)

Table 8: Percent reflectivity of infused/cured PEEK/silver films as a function of order of wash treatment

Order of film treatment	% Reflectivity		
	20°	**45°**	**70°**
I/C	45	41.7	21.1
I/C/W	59.4	54.3	26.8
I/W/C	46.7	41.2	16.1
I/W/C/W	53.1	46.3	17.6

carbon,14.1% oxygen, 3.4% fluorine and 10.3% silver. No reflectivity measurements on the reflective rough film side were measured. Since washing the sample just after cure showed the highest reflectivity and the least amount of surface fluorine all samples were dipped in acetone for one minute in the following experiments.

4.5.1-Effect of Cure Air Flow Rate

Three important factors during the cure cycle might affect the formation of a reflective surface: 1) air flow rate, 2) temperature, and 3) time. A discussion of the effect of cure air flow rate follows. A piece of film infused at 110°C,2200psi and 120 minutes was cut into three pieces and cured separately. The cure conditions for each film were T=225,250°C at t=30,30 minutes while the air flow rate was either 0, 30, 100 SCFH. After curing, all three reflective samples were washed by dipping the films in acetone for one minute.

XPS results (e.g. atomic concentrations) for these films are shown in Table 9. Some air flow appears to be essential to get high atomic concentration of silver on the surface. At an airflow rate of 30 SCFH, silver concentration was 17.2% and when there was no airflow the silver value was 2.3%. The fluorine concentration was 0.1% and 1.7% on the surface for flow rates of 0 and 30 SCFH, respectively. Reflectivity results surprisingly appear to not be affected by flow rate. At 0, 30 and 100 SCFH, the percent reflectivity was 55.6, 56.4 and 59.4, respectively at 20°. The same behavior was observed when reflectivity measurements were obtained at both 45° (e.g. 49.8, 50.2 and 54.3% at 0, 30, 100 SCFH, respectively) and 70° (e.g. 24.8, 26.2 and 26.8% at 0, 30, 100 SCFH, respectively). Since the reflectivity was slightly higher at 100 SCFH, this air flow was used for the following studies.

4.5.1.1 -Mass Transfer During the Cure Process

Mass transfer usually refers to any process in which diffusion plays a role. Diffusion is the spontaneous intermingling or mixing of atoms or molecules by random thermal motion. It gives rise to motion of species relative to the motion of the mixture. During the cure process two

Table 9: Atomic concentrations (XPS) and percent reflectivity of selected elements comparing different air flow rates during cure cycle

(Infusion conditions 110°C/2200psi/120min.)

Cure conditions		Atomic concentration				% Reflectivity		
(°C / min)	**SCFH**	**%C**	**%O**	**%F**	**%Ag**	**20°**	**45°**	**70°**
225,250/30,30	0	68.5	29.2	0.1	2.3	55.6	49.8	24.8
225,250/30,30	30	68	13.2	1.7	17.2	56.4	50.2	26.2
225,250/30,30	100	68.1	14.5	0.8	16.6	59.4	54.3	26.8
225,250/30,30	100	-	-	-	-	60.5	53.3	26.6

steps for mass transfer are possible: 1) diffusion of volatile product (such as HFA and COD) through the PEEK film. Molecules within a single phase will always diffuse from regions of higher concentration to regions of lower concentration[41]. This gradient results in a molar flux of the species, W, in the direction of concentration gradient. The molar flux, W, is the result of two contributions: the molecular diffusion flux, produced by a concentration gradient, J, and the flux resulting from the bulk motion of the fluid, B, so:

$$\mathbf{W=B+J}$$

Because there is no bulk motion of the fluid (B=0), the flux will be only that resulting from the concentration gradient. So the constitutive equation for J, the diffusional flux, resulting from a concentration difference is related to the concentration gradient by Fick's first law:

$$\mathbf{J= -D(\eth c/\eth z)}$$

Where D is a diffusivity or diffusion coefficient.

2) diffusion/convection of volatile product from the surface of PEEK film to the air phase. This behavior could be determined in terms of a molar flux from the bulk to the surface:

$$\mathbf{W_{ext}=k(C_{surf} - C_{air})}$$

where k is the mass transfer coefficient. Since in our system C_{air}= 0, the above equation is reduced to:

$$\mathbf{W_{ext}= kC_{surf}}$$

It should be note that the mass transfer coefficient (k) is a function of convection. In convection the fluid coming into contact with a hot surface heats up and moves away, thereby distributing the heat. When the motion of the fluid is brought about by external forces it is called forced convection[42]. This form of heat transfer is very important technically. It is to be expected that the heat transfer coefficient will rise as velocity increases, because the more rapid the fluid flows the more rapid will the parts of the fluid be heated up and be replaced by new ones. Since changing the air flow rate from 0 to 30 SCFH showed a large increase in surface silver atomic concentration (Table 9). It concluded that convection from the surface was a rate-limiting step.

4.5.2 – Effect of Cure Temperature and Time

In hopes of improving the surface reflectivity, the effect of temperature and time during the thermal treatment was considered. Up to now the usual cure conditions were 225°C for 30 minutes and another 30 minutes at 250°C. To study the effect of cure temperature and time, 3 sets of experiments were performed wherein temperature was varied from 225 to 250°C and time was varied from 30 to 120 minutes. The infusion conditions were the same for all samples (T=110°C, P=2200psi and t=120 min.).

Initially three samples were cured at fixed temperature (e.g. 225, 250°C) while the cure time varied from 15+15, 30+30, and 60+60 minutes, respectively (e.g. samples were again dipped in acetone for one minute after cure) at 100 SCFH air flow(Table 10). There was an increase in silver concentration and in reflectivity (Table 10) when the cure time increased from 15+15 to 30+30 minutes. But increasing the cure time from 30+30 to 60+60 minutes resulted in a decrease in both silver concentration and in reflectivity, as well. While the changes in silver atomic concentration were significant, the changes in reflectivity were considered to be minimal. This behavior could be explained by nucleation of particles at 30+30 minutes; however, there was no nucleation at 60+60 minutes and just growth of particles observed. Turkevich[43] defined growth as a process in which additional material deposits on the particle causing it to increase in size. Thus, in this manner the medium became more discontinuous and as a result less reflective. Nucleation defined as a process whereby a discrete particle of a new phase forms in a previously single-phase system.

In a second study, 3 samples were cured separately for 30, 60, and 120 minutes at a fixed temperature of 225°C rather than for half the time at two different temperatures and then dipped in acetone for 1 minute. All three samples formed reflective surfaces. Table 11 lists the atomic concentrations of carbon, oxygen, fluorine and silver on the surface of each film as determined

Table 10: Atomic concentrations (XPS) and percent reflectivity of selected elements at fixed cure temperature and different times

(Infusion conditions 110°C/2200psi/120min.)

Cure conditions		Atomic concentration				% Reflectivity		
T(°C)	**t(min)**	**%C**	**%O**	**%F**	**%Ag**	**20°**	**45°**	**70°**
225,250	15+15	72.4	14.9	0.9	11.8	55.8	50.3	15.7
225,250	30+30	68.1	14.4	0.8	16.6	59.4	54.3	26.8
225,250	60+60	77.5	14.4	0.5	7.7	53.4	51.3	20.8

Table 11: Atomic concentration (XPS) and percent reflectivity of selected elements at fixed cure temperature and different times

(Infusion conditions 110°C/2200psi/120min.)

Cure conditions		Atomic concentration				% Reflectivity		
T(°C)	**t(min)**	**%C**	**%O**	**%F**	**%Ag**	**20°**	**45°**	**70°**
225	30	71.2	14.7	0.6	13.6	39.3	32.7	20.1
225	60	69.3	14.7	0.4	15.6	42.8	36.3	23.7
225	120	64.9	15.9	0.6	18.8	62.8	54.4	26.3

via XPS. Also it lists the reflectivity data which suggest that the reflectivity and silver concentration increased as the cure time increased. It is believed that at 225°C and 120 minutes better intermixing of polymer and additive were obtained and nucleation process happened relative to the 225,250°C and 60+60 minutes which seemed growth of particles observed. Scanning electron microscopy (SEM) of this film showed a surface which exhibited different size particles distributed on the surface (Figure 9). In terms of particles size and shape if assumed particles had a spherical shape and since they were small it followed the suggestion in light scattering theory that for small particles, the specific surface became large and as a result the scattering coefficient and the reflectivity would increase. To obtain a view of the internal physical structure of the film, transmission electron microscopy (TEM) of a film cross- section was used. The TEM showed the silver layer to be approximately 400 angstrom (40 nm) thick and most of the silver in the film was part of this layer (Figure 10). However, there were particles of silver, most less than 50 angstrom (5 nm) in diameter, that extended several hundred nanometers into the PEEK.

In order to find the chemical state of elements for silver infused PEEK films X-ray photoelectron spectroscopy (XPS) was applied to both non-infused PEEK and to silver infused PEEK to compare the result. The carbon (C1s) photoelectron spectrum for non-infused PEEK (smooth side) exhibited the pattern displayed in Figure 11-A. This signal may be curve resolved into three separate carbon environments that would be expected based on the chemical structure of PEEK (Figure 11-B). The calculated carbon ratio for PEEK is 1:5:12, corresponding to the carbonyl, ether, and aromatic carbons, respectively. Experimental ratios obtained from the area gave a ratio of 1:3:12.5. The oxygen (O1s) photopeak, as expected, exhibits two types of oxygen species (carbonyl and ether, Figure 12-B). Theoretically, one would expect a 2:1 ratio between ether and carbonyl oxygen. Experiment yielded a 2:1 ratio, which shows excellent agreement with theory.

Changes in surface composition relative to the non-infused PEEK film were noticeable

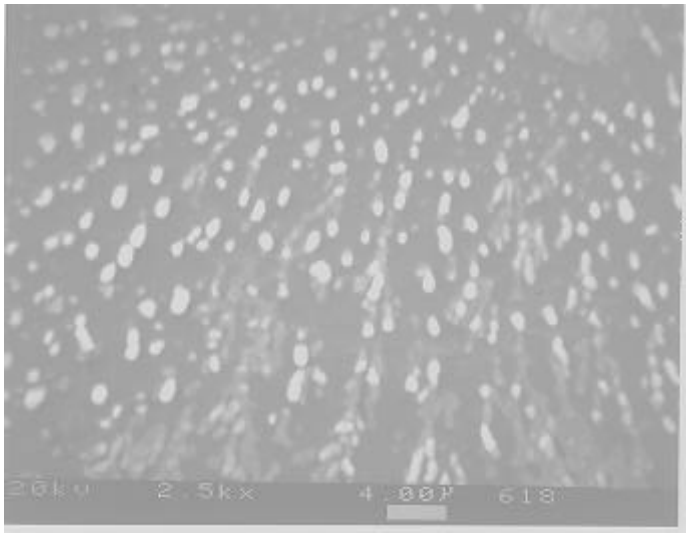


Figure 9: Scanning electron microscopy (SEM) of silver - infused PEEK which was cured at 225°C/120min/100 SCFH

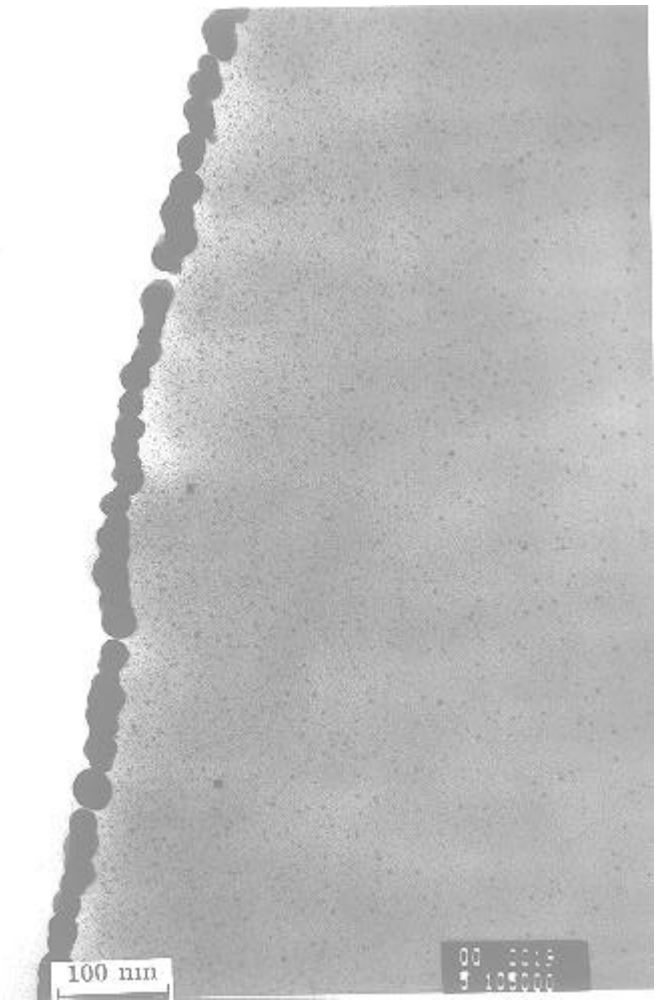


Figure 10-A: Transmission electron microscopy (TEM) of silver - infused PEEK which was cured at 225°C/120min/100 SCFH (magnification: 187,500x)

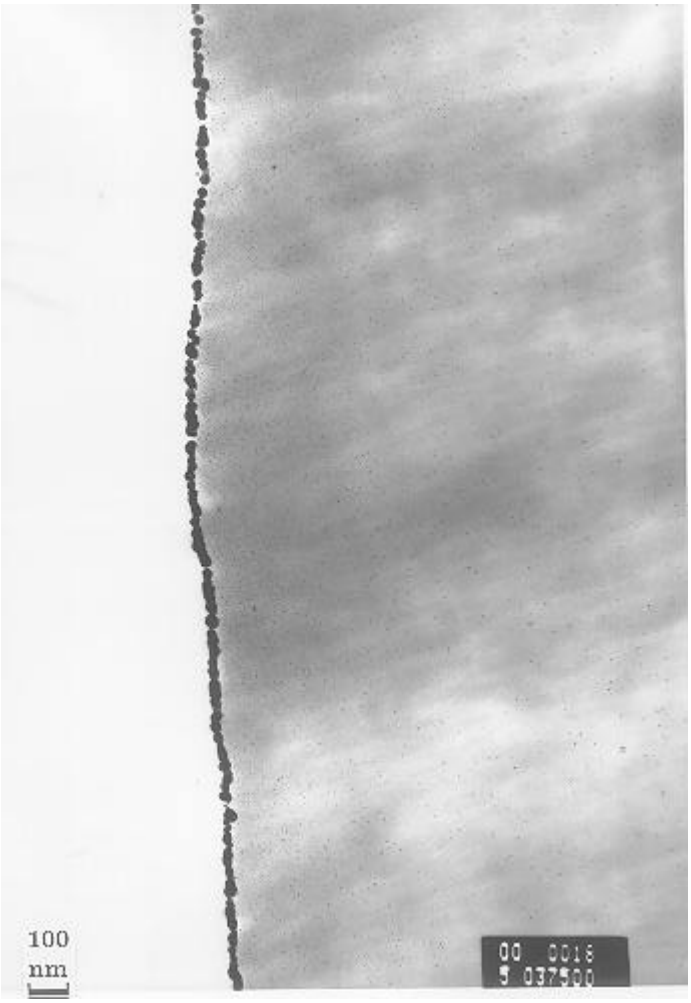
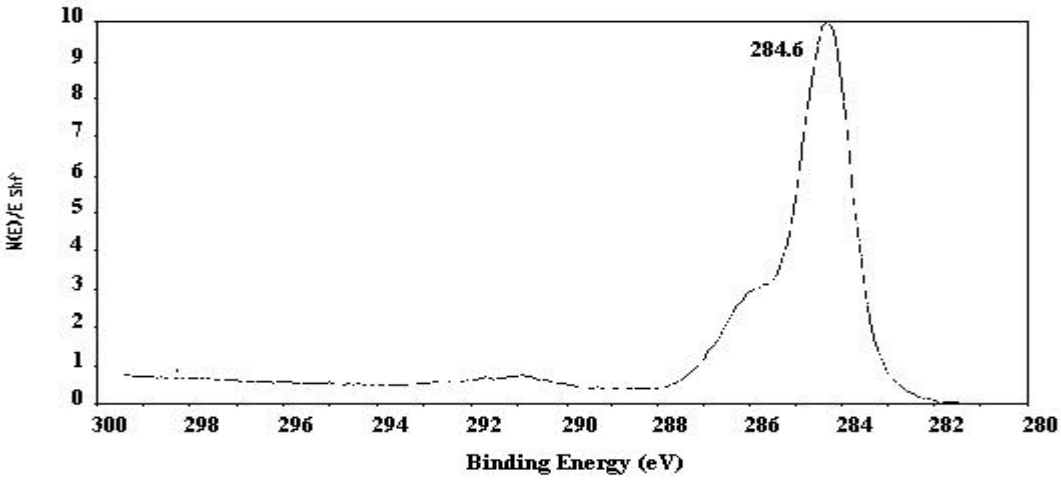
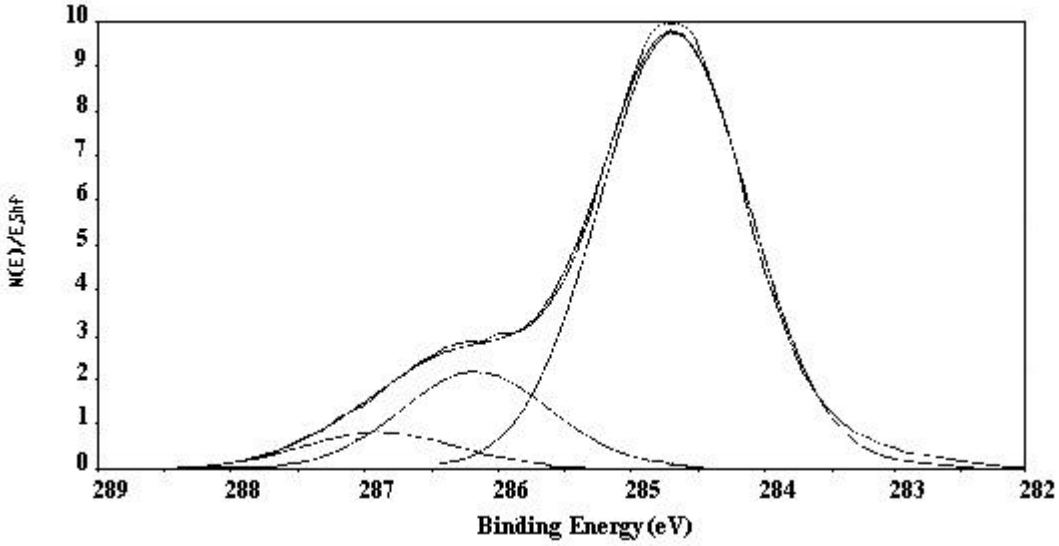


Figure 10-B: Transmission electron microscopy (TEM) of silver - infused PEEK which was cured at 225°C/120min/100 SCFH (magnification: 67,000x)

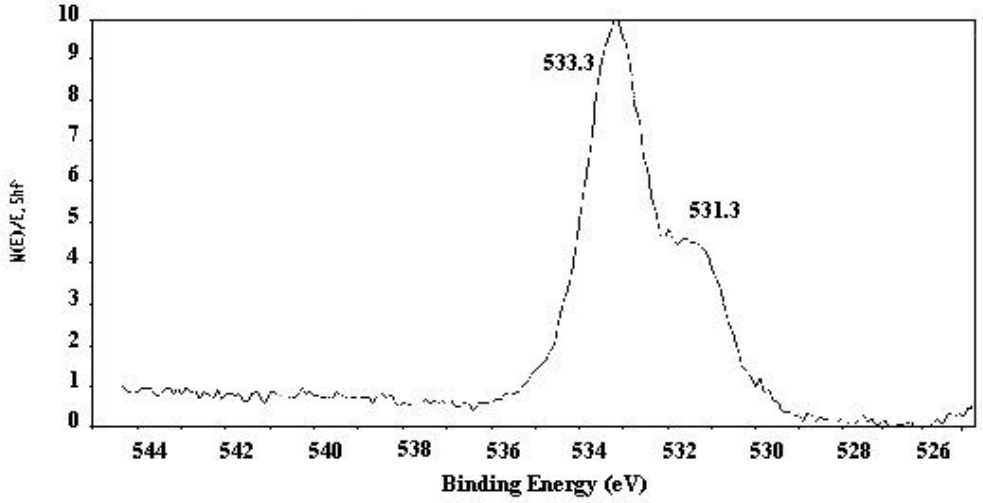


(A)

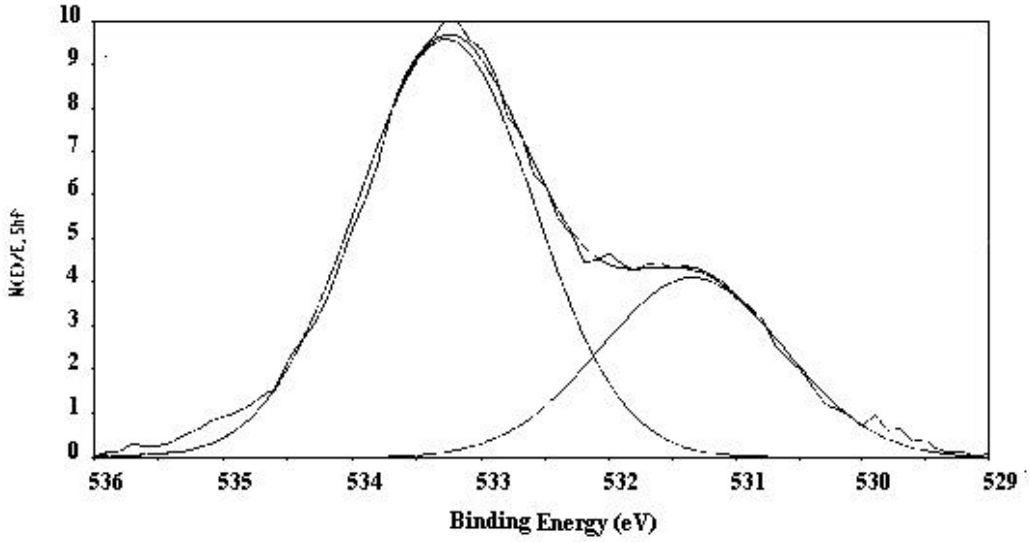


(B)

Figure 11: Carbon (C1s): (A) photoelectron spectrum, (B) curve resolved for non infused PEEK



(A)



(B)

Figure 12: Oxygen (O1s): (A) photoelectron spectrum, (B) curve resolved for non infused PEEK

for silver infused films. For infused PEEK film, which was cured continuously at 225°C and 120 minutes, the XPS profile is shown in Figure 13. The carbon (C1s) photoelectron spectrum for this sample exhibited the same pattern which was shown for non-infused PEEK (Figure 14-A). Surprisingly, the oxygen (O1s) photopeak for this same sample showed three rather than two types of oxygen atoms present on the surface (Figure 15-B). Oxygen 1 and 2 corresponded to the carbonyl and ether oxygen, respectively. Oxygen 3, was probably due to surface contamination. The photopeak (Figure 16-B) at 688.4 eV suggested that fluorine was present as a fluorocarbon (CF_2), either formed by a chemical reaction between the silver additive with PEEK or by incomplete decomposition of $[Ag(COD)HFA]_2$ on the surface of the PEEK.

The Chemical state of the silver was of interest in the same film (Figure 17). The obtained from the silver 3d photo peak was not sufficient to determine the chemical state of silver because silver metal and silver (I) have nearly identical binding energies. Schon[44] and Larson[45] have shown that Auger shifts (MNN) are frequently more revealing than XPS shifts for different chemical states of silver. The chemical state of silver was estimated from the Auger line (Figure 18) versus the binding energy of the photoelectron line[37].The kinetic energy was calculated by subtracting the Auger peak binding energy (896.4 eV) from the $K\alpha$ of magnesium (1253.6 eV) to obtain the value of 357.2 eV. The Auger parameter was then calculated by adding the values of the kinetic energy (357.2 eV) and the binding energy of $Ag(3d_{5/2})$ (368.5) to give 725.5 eV. This indicated that the most of the silver was present in the zero oxidation state, since the Auger parameter of silver metal is 726 eV.

Depth profiling via Auger electron spectroscopy (AES) in conjunction with argon ion etching (sputtering rate was 50 angstrom/min.) was utilized to gain additional knowledge regarding the distribution of particles in the bulk of the silver infused PEEK film at 225°C/120 min/100 SCFH. By looking at the depth profile (Figure 19) one can observe nearly 50% and 42% atomic concentrations of silver and carbon, respectively, within the first 40 angstroms of the surface. This finding supports the early TEM results which suggested that the silver layer was not continuous. After the first 40 angstroms, the concentration of silver decreased and the concent

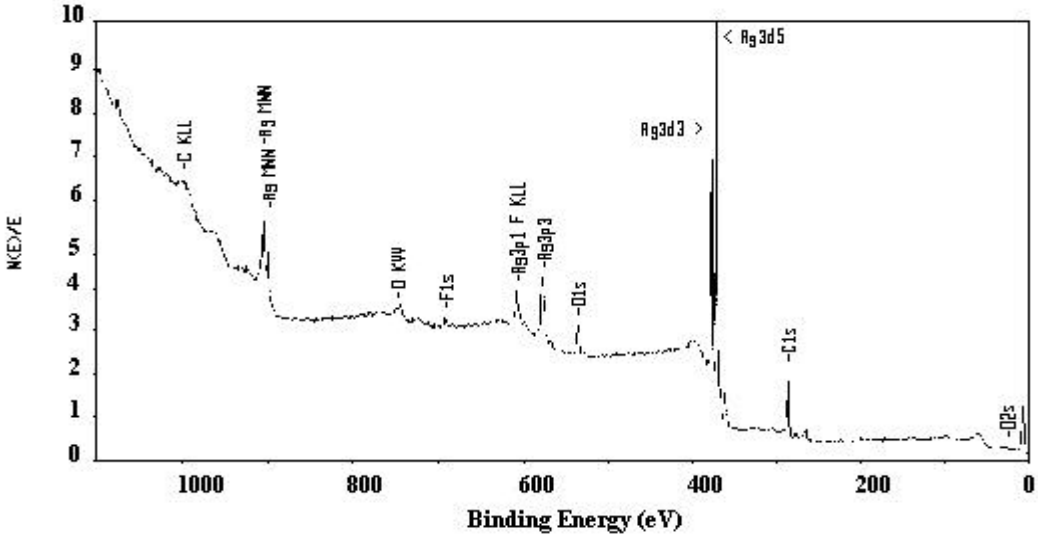
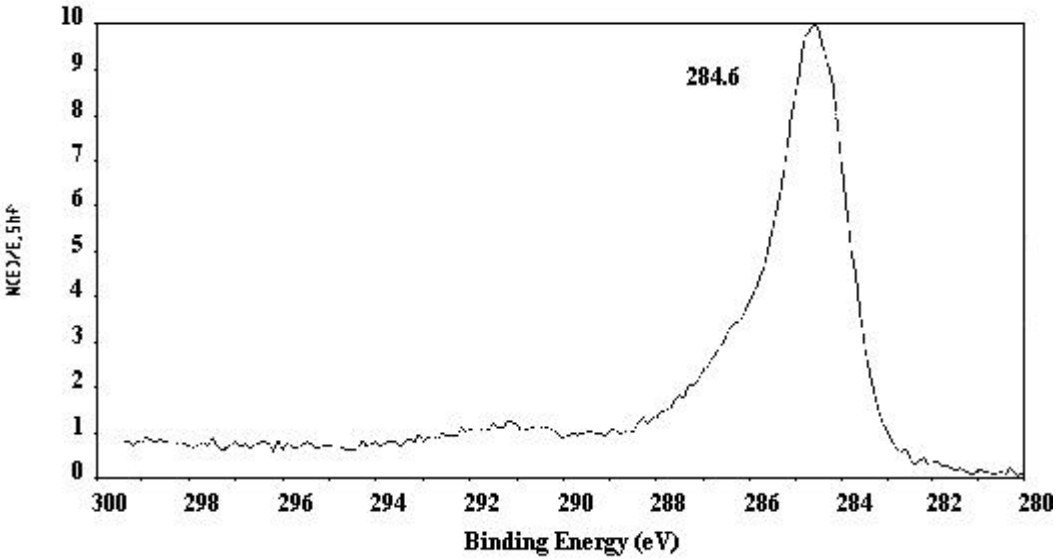
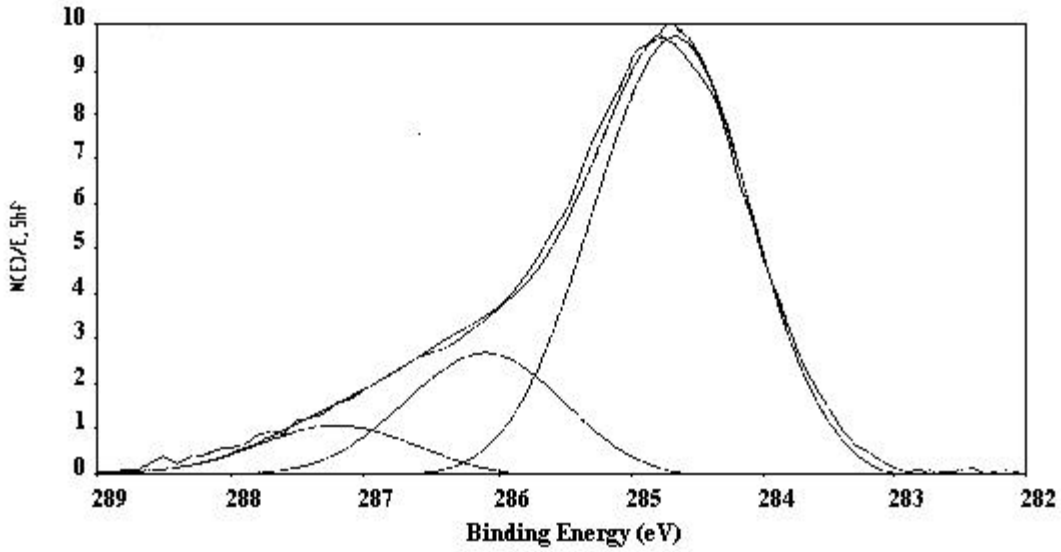


Figure 13: XPS profile of infused film which was cured at 225°C/120min/100 SCFH

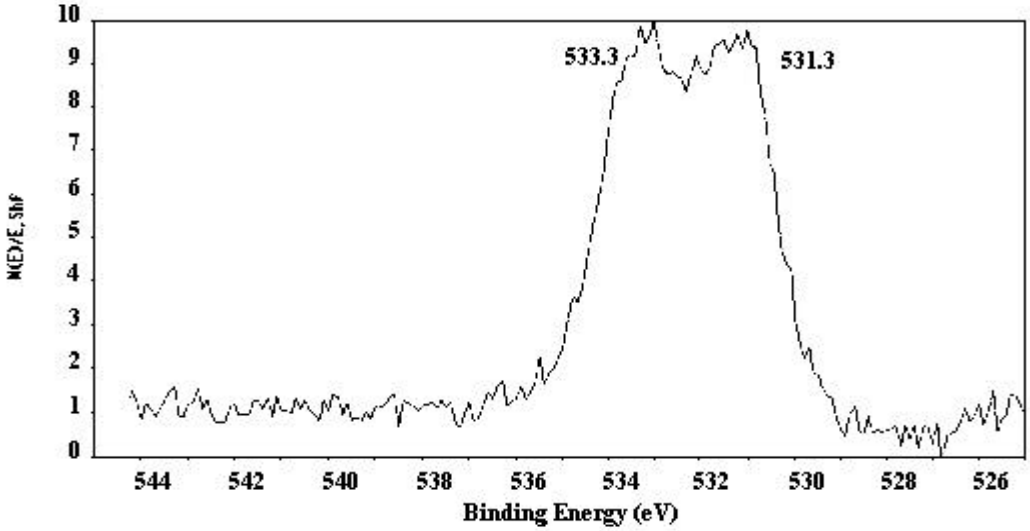


(A)

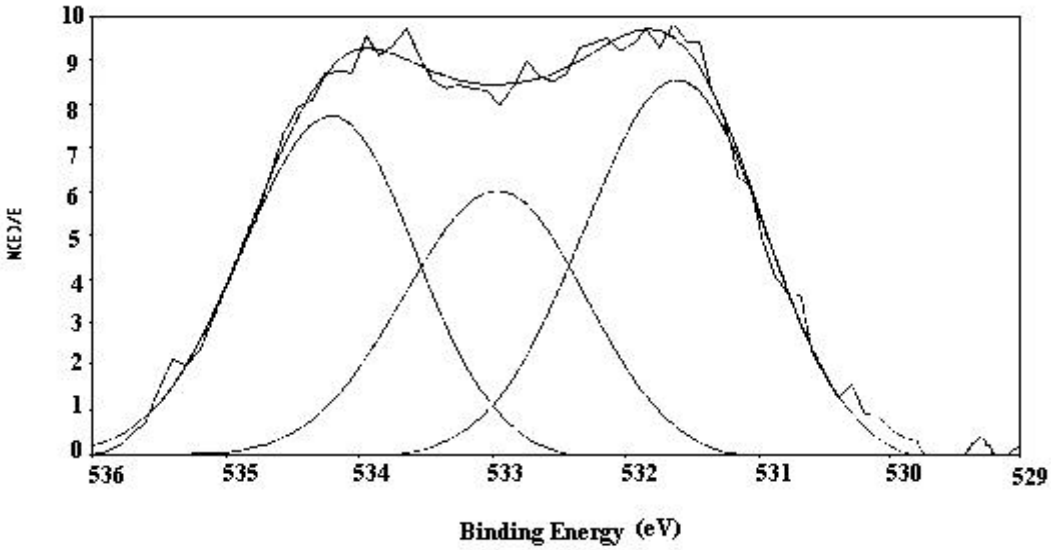


(B)

Figure 14: Carbon (C1s): (A) photoelectron spectrum, (B) curve resolved for infused and cured PEEK

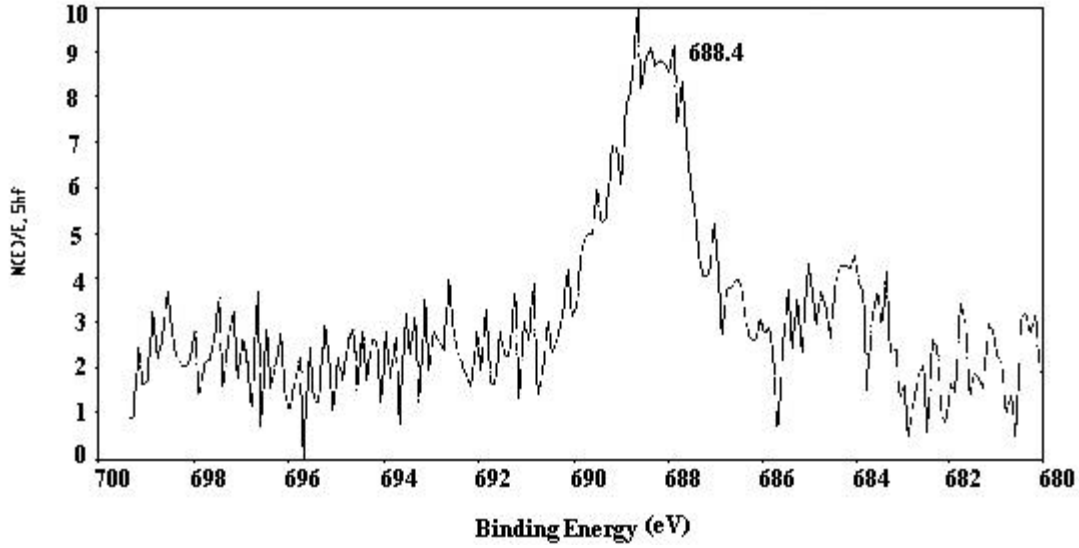


(A)

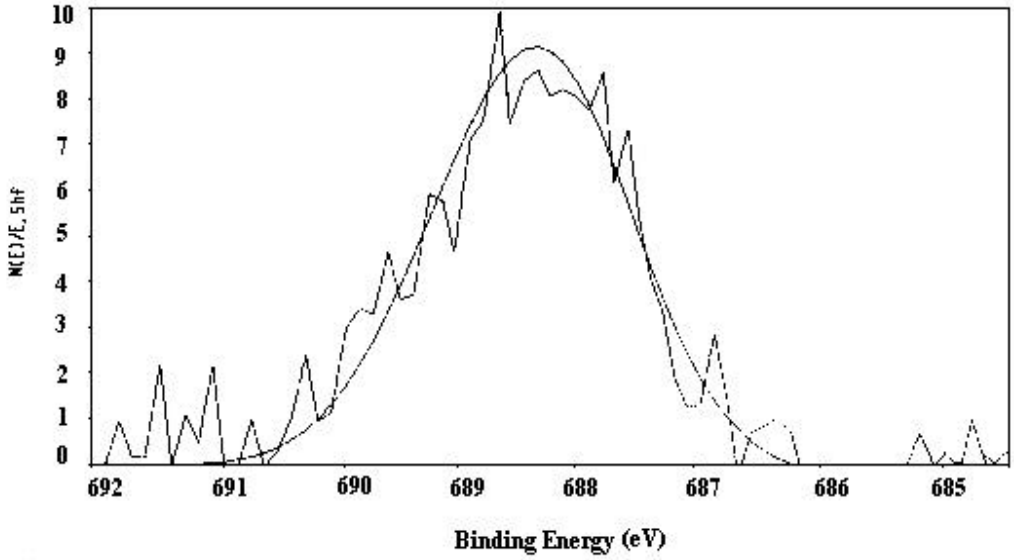


(B)

Figure 15: Oxygen (O1s): (A) photoelectron spectrum, (B) curve resolved for infused and cured PEEK



(A)



(B)

Figure 16: Fluorine (F1s): (A) photoelectron spectrum, (B) curve resolved for infused and cured PEEK

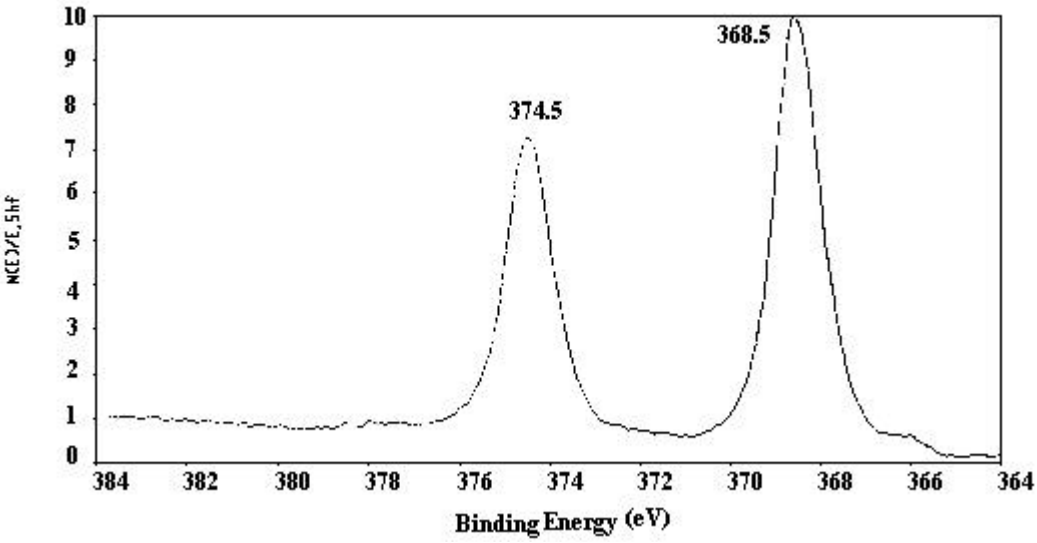


Figure 17: Silver (Ag 3d) photoelectron spectrum

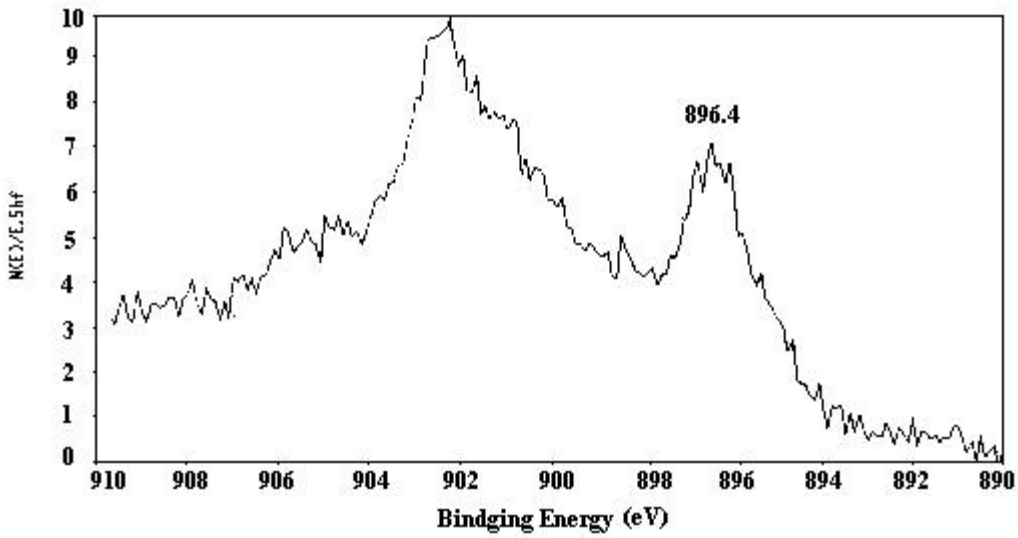


Figure 18: Silver (Ag 3d) Auger spectrum

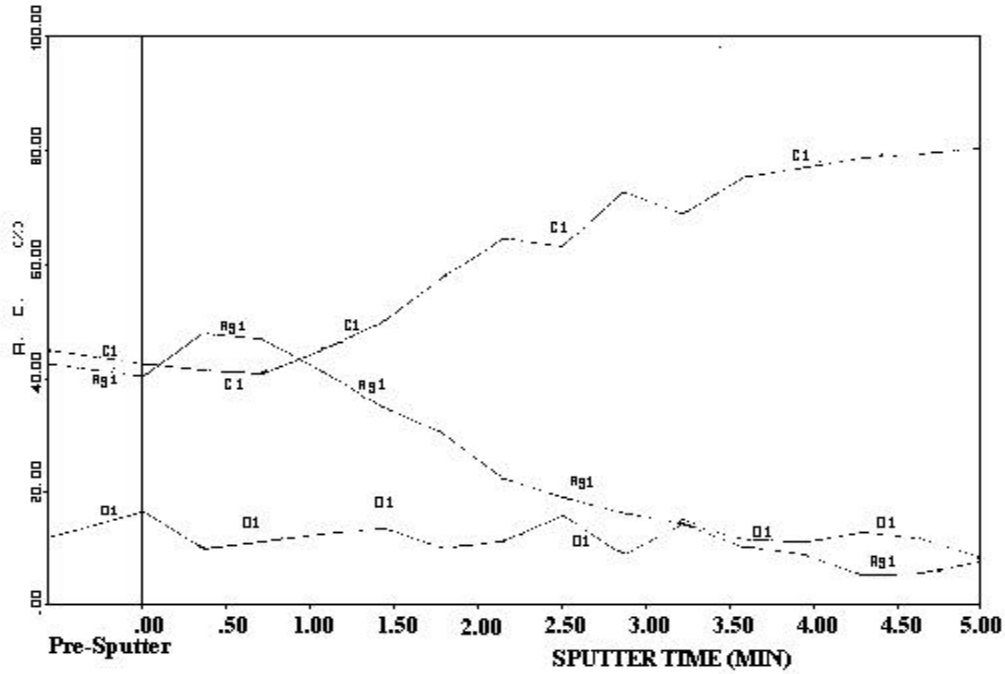


Figure 19: Depth profiling via Auger electron microscopy (AES) of silver - infused film which was cured at 225°C/120min/100 SCFH

concentration of carbon increased as one goes deeper into the surface. for example, at the depth of 250 angstroms the atomic concentrations of silver and carbon are about 10% and 82%, respectively. The atomic concentration of oxygen remains nearly constant through the film (e.g. nearly10%).

Finally, three samples were cured separately for 30, 60 and 120 minutes as before but at a fixed temperature of 250°C rather 225°C and then dipped in acetone for one minute after cure (Table 12). All three samples formed reflective mirror surfaces. There was an increase in both silver concentration and reflectivity when the cure time increased from 30 to 60 minutes. But increasing the cure time from 60 to 120 minutes resulted in a slight increase in silver concentration and a large decrease in reflectivity. Here again this behavior could be explained by " nucleation and continued growth of particles which lead to greater discontinuity of the medium". It appeared at 30 and 60 minutes nucleation dominates-leads to high reflectivity and at 120 minutes particle growth dominates-leads to lower reflectivity. Transmission electron microscopy (TEM) showed discontinuity of the metallic silver layer for infused film which was cured at 250°C for an hour (Figure 20). The TEM profiles of this sample revealed the silver particles on the surface were approximately between 500 to 900 angstrom (50 to 90 nm) in diameter while much smaller particles of silver with diameter less than 150 angstrom (15 nm) appeared at several hundred nanometers into the film. Scanning electron microscopy (SEM) of this film showed a surface with bigger particles (Figure 21) relative to the samples which cured at 225°C,120 min and 100 SCFH. The oxygen (O1s) photopeak for this sample showed two types of oxygen: carbonyl and ether oxygen (Figure 22). Since the area under the peak at 531.3 eV was higher than the area under the peak at that position for original PEEK it was believed that a little bit oxygen exist as an oxide oxygen. Note that no signal that could be attributed to fluorine.

From the previous experiments, one can conclude that reflectivity of the film is dependent on both time and temperature of thermal treatment. At lower cure temperature (225°C) it was

Table 12: Atomic concentration (XPS) and percent reflectivity of selected elements at fixed cure temperature and different times

(Infusion conditions 110°C/2200psi/120min.)

Cure conditions		Atomic concentration				% Reflectivity		
T(°C)	**t(min)**	**%C**	**%O**	**%F**	**%Ag**	**20°**	**45°**	**70°**
250	30	72	13.7	0.5	13.7	40.8	36.8	16.2
250	60	71.5	14.3	0.1	14.1	61.8	55.3	24.9
250	120	69.8	14.9	0.01	15.3	43.5	36.3	13.8

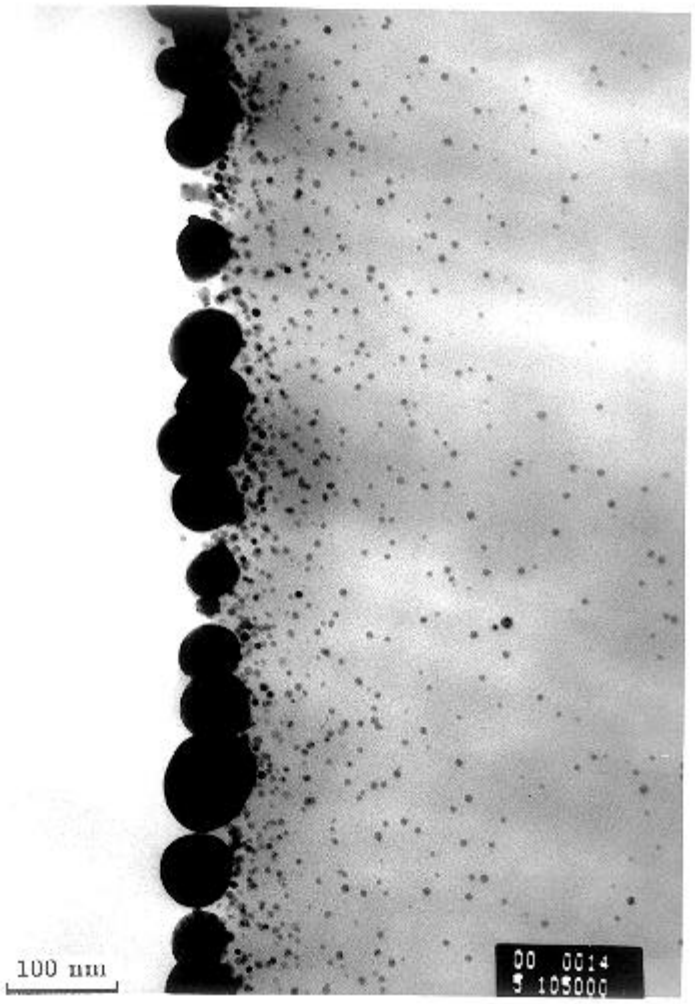


Figure 20-A: Transmission electron microscopy (TEM) of infused film which was cured at 250°C/60min/100 SCFH (magnification: 187,500x)

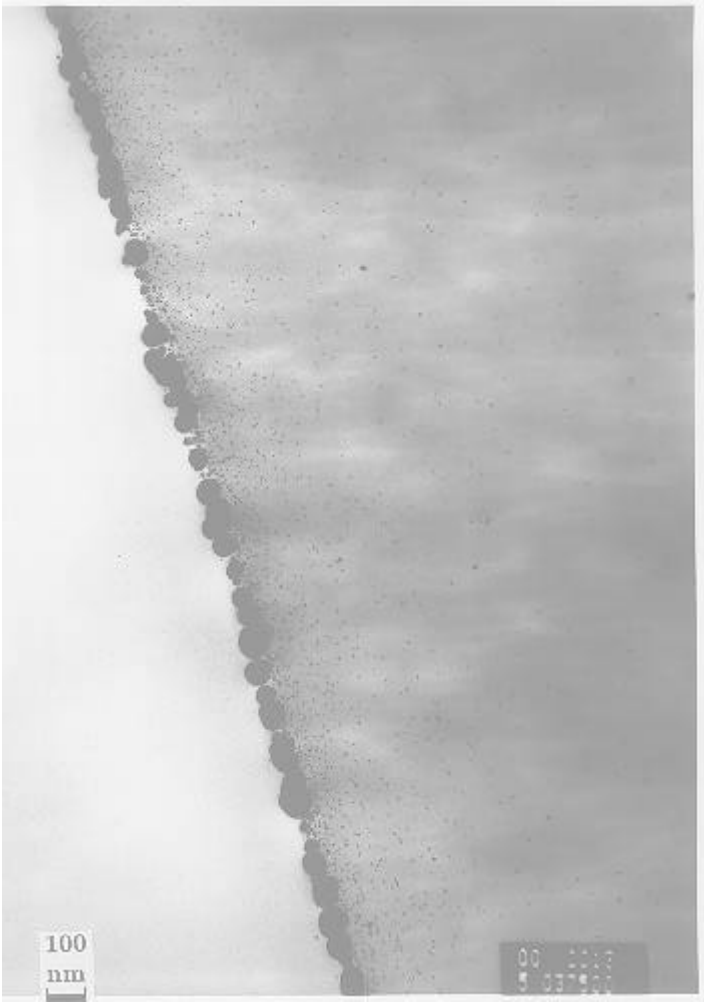


Figure 20-B: Transmission electron microscopy (TEM) of infused PEEK which was cured at 250°C/60min/100 SCFH (magnification: 67,000x)

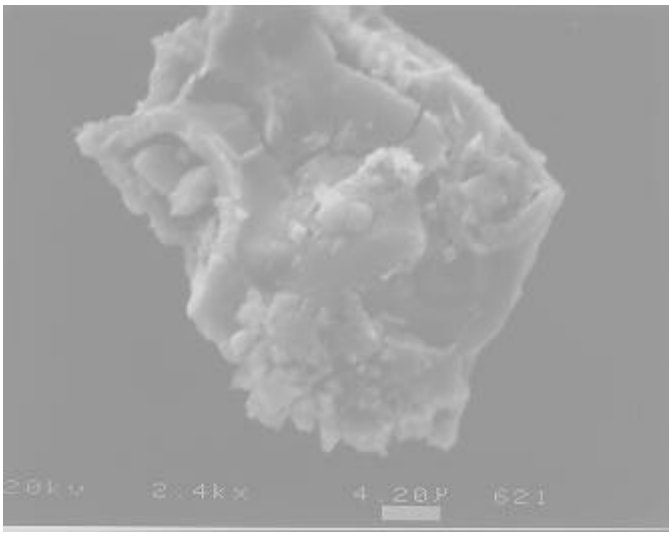
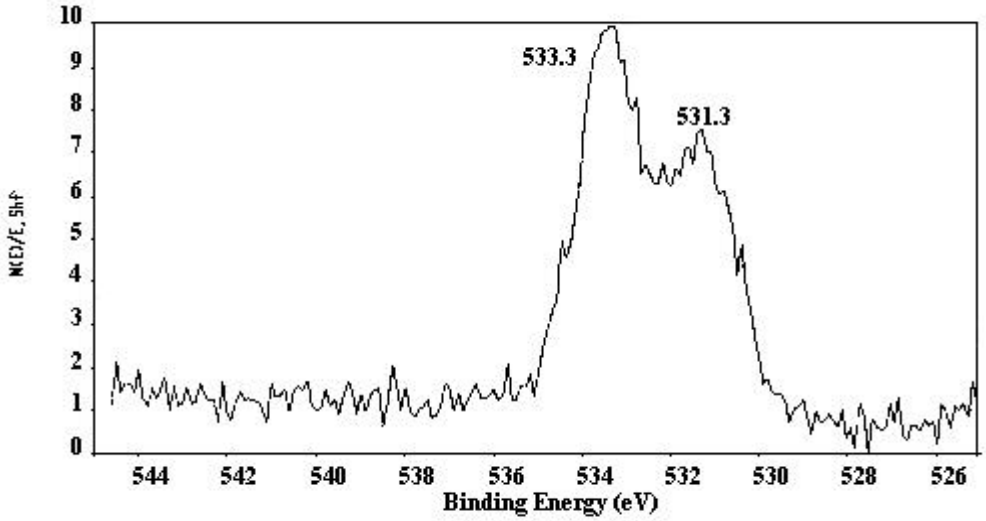
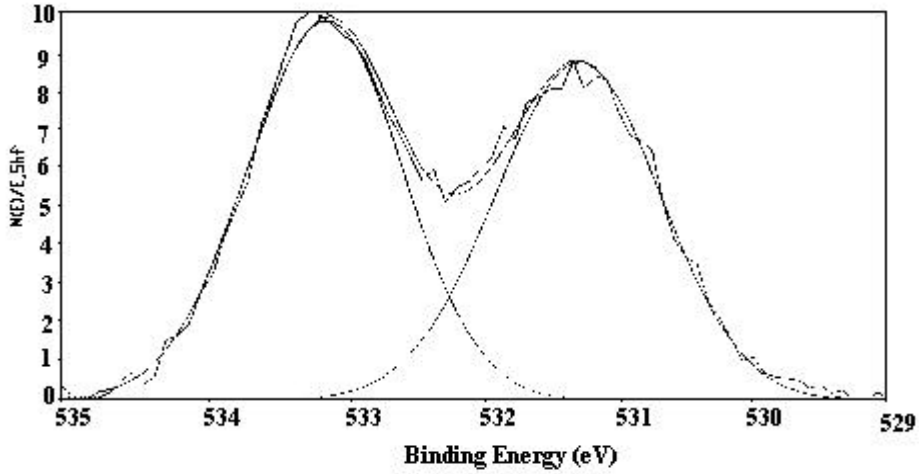


Figure 21: Scanning electron microscopy (SEM) of infused film which was cured at 250°C/60min/100 SCFH



(A)



(B)

Figure 22: Oxygen (O1s): (A) photoelectron spectrum, (B) curve resolved for infused film which was cured at 250°C/60min/100 SCFH

demonstrated that long cure (120 min.) time is necessary to obtain high reflectivity, while at a higher cure temperature (250°C) shorter cure time (60 min.) is required. However, one must recognize that at lower cure temperatures, very long cure times may also cause the medium to become more continuous and result in more reflective surface.

4.6 – Thermal Analysis of the Film

Thermal methods of analysis are well suited for the characterization of these materials. Estimates of PEEK film thermal stability were obtained by performing thermal gravimetric analysis (TGA) in air atmosphere. Stabilities are commonly referenced to the polymer decomposition temperature (PDT). PDT_{10} is a parameter corresponding to the temperature at which 10% weight loss occurs[46,47]. Thermal gravimetric analysis (TGA) is dependent on the type of atmosphere, flow rate of atmosphere, positioning of the film within the furnace, and the heating rate[48].

The PDT_{10} in air for non-doped PEEK was 560°C. The observed PDT_{10} for an infused film (110°C/2200psi/120min) with 10 wt.% additive/polymer which was cured at 225°C/120 min/100 SCFH was 450°C (Figure 23). The large difference between the polymer decomposition temperatures (PDT) for infused films versus original films suggested the incorporation of silver into film lowered the polymer decomposition temperature (PDT). It seemed that the presence of silver serves to catalyze the oxidative degradation of the PEEK. However, the knee that was present in the TGA curve of the infused PEEK film could be described by this hypothesis that silver species were only present in the surface or near surface region of the infused PEEK film[46]. Porta had reported that residual metal species within a polymer acted as a catalyst in the polymer decomposition mechanism and was responsible for reduced stability of the polymer film[49,50].

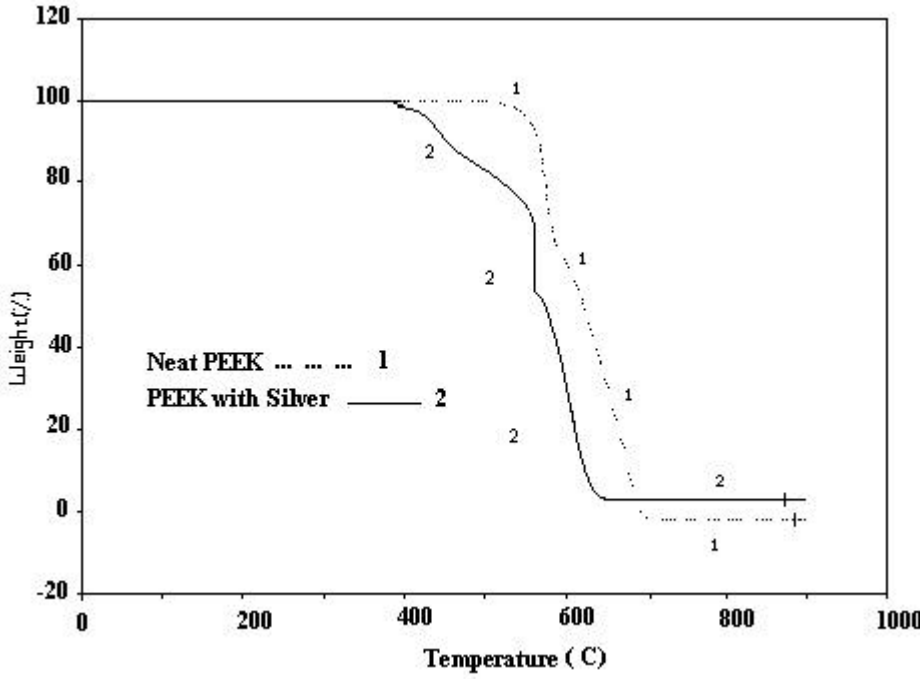


Figure 23: Thermogravimetry analysis (TGA) of infused film which was cured at 225°C/120min/100 SCFH

(analysis done in air 20ml/min, heating rate 10°C/min)

4. Conclusions

The focus of this research was the preparation of highly reflective polymer surfaces. The CO_2-assisted infusion process was feasible for incorporating a silver additive into a PEEK film. Reflective silver-surfaced PEEK was prepared by infusion and thermal reduction of (1,5-cyclooctadiene-1,1,1,5,5,5 hexafluoroacetylacetonato) silver (I), $[Ag(COD)HFA]_2$. No chemical reducing agent was needed to effect silver reduction. Reflectivity of the surface was dependent both on the infusion and cure conditions.

The first goal of this work was to determine the best infusion conditions at fixed cure conditions. In this regard the influence of infusion parameters studied. This goal was achieved by evaluating different additive concentrations at different temperatures, pressures, and times**.** The result of this study demonstrated that:

I - At constant pressure and time, the reflectivity of the surface increased as the temperature increased due to high diffusivity of CO_2 at high temperature.

II - At constant temperature and pressure, the reflectivity increased as the time increased due to infusing more CO_2 at longer time.

III - At constant time and temperature, increasing the pressure caused the reflectivity to decrease.

Optimal infusion condition were determined to be at 110°C/2200psi/120min for 10wt% additive/polymer. To improve the reflectivity of the surface, samples were dipped in to acetone for one minute in order to remove fluorine from the surface. The second portion of this work focused on the effect of the cure parameters such as airflow rate, temperature, and time at fixed infusion conditions on reflectivity. It was observed that the highest reflectivity was obtained when the airflow rate had its maximum value. The optimal cure condition was at 225°C/120min/100 SCFH for infusion condition at 110°C/2200psi/120min. The reflectivity of the surface which employed these infusion/ cure conditions was about 62%. Analysis by TEM revealed a surface layer of silver particles 40 angstrom thick which was determined by XPS to

contain up to 18 atomic percent of silver. Thermal gravimetric analysis (TGA) showed the presence of the knee in the curve which suggested that silver particles were present in the surface or near surface region of the infused PEEK. Polymer decomposition temperature (PDT) for this film was 450°C. Auger electron spectrum explained that most of the silver exist as silver metal on the surface. Depth profile via AES showed most of silver appeared within the first 40 angstrom. Analysis by SEM determined that silver particles distributed with different size throughout the surface of the PEEK. Results of the study of effect of cure parameters suggested that:

I - At lower cure temperature, long cure time is necessary to obtain high reflectivity, which at higher cure temperature shorter cure time is required.

II - Lower cure temperature and long cure time may cause the medium become more continuos and causes higher reflective surface.

The advantage of the infusion of additive into polymer by supercritical CO_2 described in this way: since only surface deposition as opposed to bulk deposition was desired, the limited infusion placed the additive exclusively near the film surface.

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Vita

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