Highly Reflective Polyimide Films Created by Supercritical Fluid Infusion of a Silver Additive

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ABSTRACT: Supercritical fluid infusion of a silver-containing additive [1,5-cyclooctadiene silver(I)-1,1,1,5,5,5-hexafluoroacetylacetonate] into a fully cured polyimide was achieved with moderately high-density carbon dioxide at 110°C for the first time. The polyimide was derived from 4,4′-oxydianiline and 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride. After infusion for approximately 60 min, the resulting film was then recured at 300°C in air. During this time, a silver mirror formed on both film surfaces. The nature of the silver and its distribution within the film and on the film surface were established via microscopy and surface analysis techniques. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1309–1317, 1997

INTRODUCTION

It has been found that CO_2 accelerates the absorption of many low molecular weight additives into a number of polymers. This effect is due, in part, to the high diffusivity, solubility, and plasticizing action of compressed CO_2 in polymers. Upon release of the pressure, absorbed CO_2 rapidly diffuses from the polymer while other compounds desorb more slowly.[1] The amount of additive absorbed can be determined from the weight change of the sample after most of the CO_2 has escaped. This infusion process can be described as a partitioning of the additive between the CO_2- and polymer-rich phases. Consequently, the relative solubility of the additive in CO_2 and in the polymer is a major factor governing the amount of additive absorbed. Poly(vinyl chloride) (PVC) with dimethyl phthalate (DMP) has been used to explore the effects of CO_2 on the transport kinetics and equilibria of an additive in a glassy polymer.[2] The amount of DMP infused into a PVC film (0.1–1.0 mm) after a 71 h exposure to liquid CO_2 ranged between 8 and 37% (w/w). In the same study, films of polycaprolactone (PCL), ethyl cellulose (EC), and cellulose acetate (CA) were contacted with their own weight of aspirin in the presence of liquid CO_2 for 64 h at room temperature. The absorption of aspirin was 8% for PCL, 12% for EC, and 3% for CA.

In another study,[3] poly(ethylene glycol)diacrylate and 4,4′-dichlorobenzophenone were infused into polycarbonate as a CO_2 solution. Following depressurization and removal from the autoclave, UV photolysis initiated a reaction that consumed ~ 25% of the acrylate residues. The CO_2-assisted impregnation of fragrances and pharmaceuticals in thermoplastic polymers such as polyethylene and polypropylene has also been disclosed.[4]

The impregnation of organometallic compounds into a polymer matrix with supercritical phases leaves no solvent residues within the polymer be-
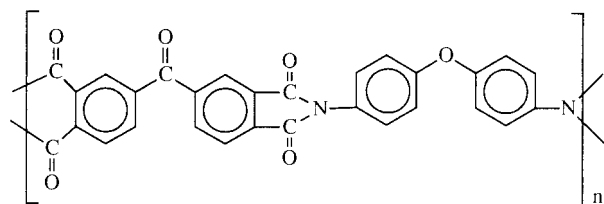
Figure 1 The repeat unit for the BTDA–ODA polyimide.

cause the CO_2 can diffuse out. Once impregnated into the polymer, the compound can be induced to react with certain polymers without any side reactions with solvent residues. The photochemical C—H activation of polyethylene by $[Cp*Ir(CO)_2]$ $(Cp*=C_5(CH_3)_5)$ serves as one example of this type of study.[5,6] Clearly, the impregnation of other organometallic compounds into polymers offers considerable possibilities for the modification or tailoring of specific polymer properties.

In a recent article, Watkins and McCarthy[7a] used supercritical CO_2 to infuse an inorganic additive, $(COD)Pt(CH_3)_2$, into poly(4-methyl-1-pentene) (PMP) and polytetrafluoroethylene (PTFE). Following chemical reduction of the additive, small (ca. 50 nm) clusters of platinum metal were distributed throughout the polymer. The same authors[7b] 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 study involves the infusion of CO_2 solutions of styrene into a variety of polymer substrates where thermally initiated radical polymerization within the swollen substrates generated polystyrene–substrate polymer blends. Poly-

Table I   Mass Change and Thermal Data for BTDA–ODA Polyimide Films Upon Extraction with SC-CO_2 at Varying Times

Time (min)/ Temp (°C)/ Pressure (psi)	T_g (°C)	PDT (°C)[a]	Mass Change[b]
Original film	276	585	—
30/110/5000	277	520	−0.1%, 0.0%
120/110/5000	276	516	0.0%, +0.9%

[a] Polymer decomposition temperature taken as the temperature after 10% weight loss of the sample.
[b] Each value represents a separate piece of the same film.

Table II   Reflectivity Data for Fully Cured BTDA–ODA Films Upon Infusion with $(COD)AgF_6acac$ at 100°C and 5000 psi for 30 and 120 Min, Then Cured a Second Time to 300°C[a]

|	Additive Level (Wt/Wt)			
	10%		20%	
Angle	30 Min	120 Min	30 Min	120 Min
20°	47.1%	43.1%	43.1%	50.4%
45°	34.7%	33.1%	41.6%	43.9%
70°	19.3%	14.6%	22.2%	27.4%

[a] Measured by NASA Langley Research Center, Hampton, VA, at 531 nm using a Perkin-Elmer Lamfda 9 UV-visible spectrophotometer equipped with a variable-angle reflectance accessory. Measurements were taken at 20°, 45°, and 70° angles and are relative to an optical mirror taken as 100% percent reflection.

mer samples were placed in high-pressure stainless-steel reactors that consisted of ~ 1.2 cm (i.d.) $X \sim 10$ cm sections of $\frac{1}{2}$ in. schedule 160 seamless pipe with a plug at one end and a high-pressure needle valve at the other. The initiator was dissolved in styrene, and the solution was introduced into the reactor via a syringe. CO_2 was introduced via a high-pressure manifold to the desired pressure mix. Both dense structures and expanded foamlike materials were prepared.

Table III   Data for Partially Cured BTDA–ODA Films Upon Infusion by $(COD)AgF_6acac$ with SC-CO_2; Values in Parentheses Are Those After the 300°C Cure Cycle and Are the Total Mass Change

Time (min)/ Temp (°C)/ Pressure (psi)	Additive Level	Mass Change	PDT
180/110/5000[a]	8.7%	−1.6%	—
30/110/5000	10.0%	−0.8% (−13.7%)	497°C
60/110/5000	10.0%	−2.2%	—
120/110/5000	20.0%	−1.1% (−13.3%)	515°C
120/110/5000	20.0%	−2.9% (−14.0%)	494°C
180/110/5000[a]	28%	−5.0%	—

[a] A larger piece of film was used but it cracked badly after infusion; the mass after the cure cycle could not be determined.
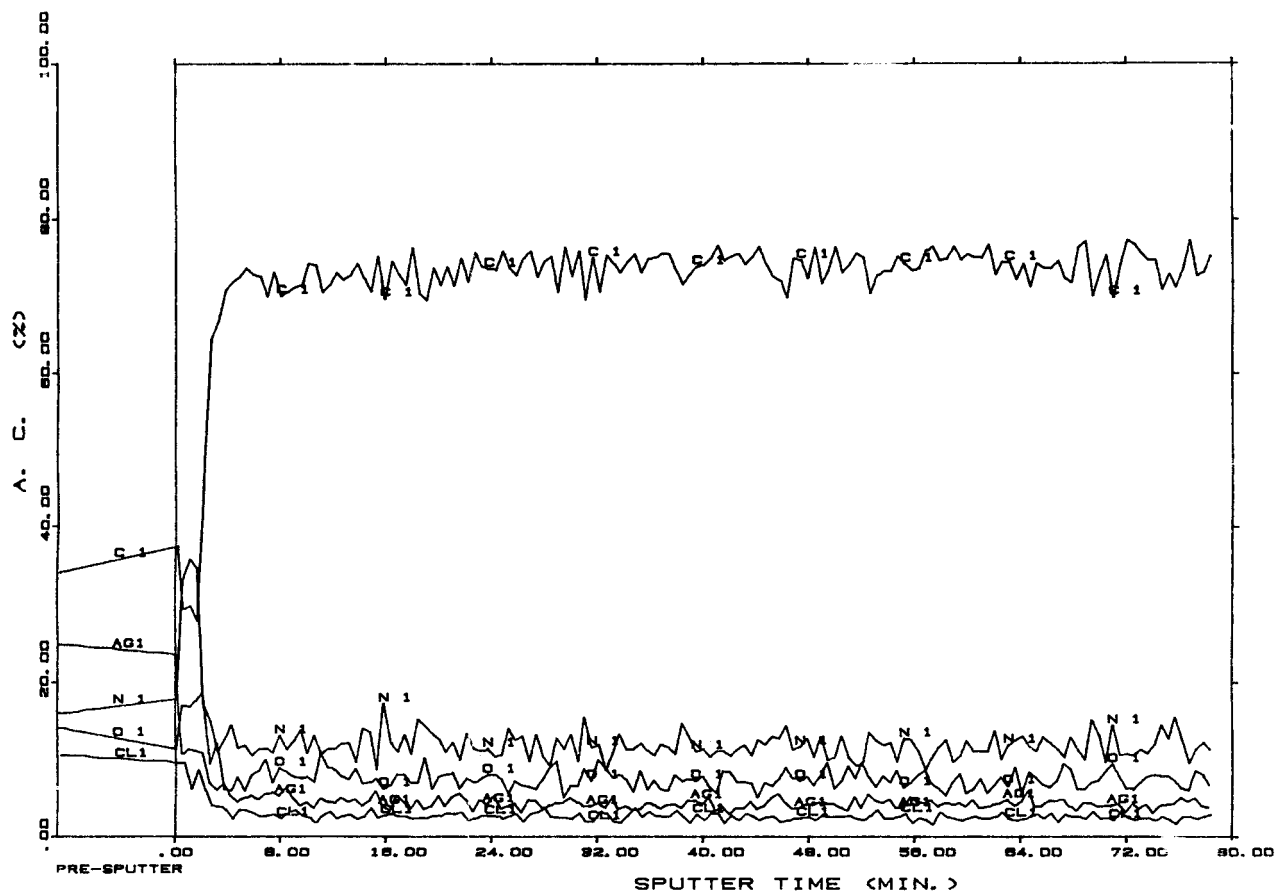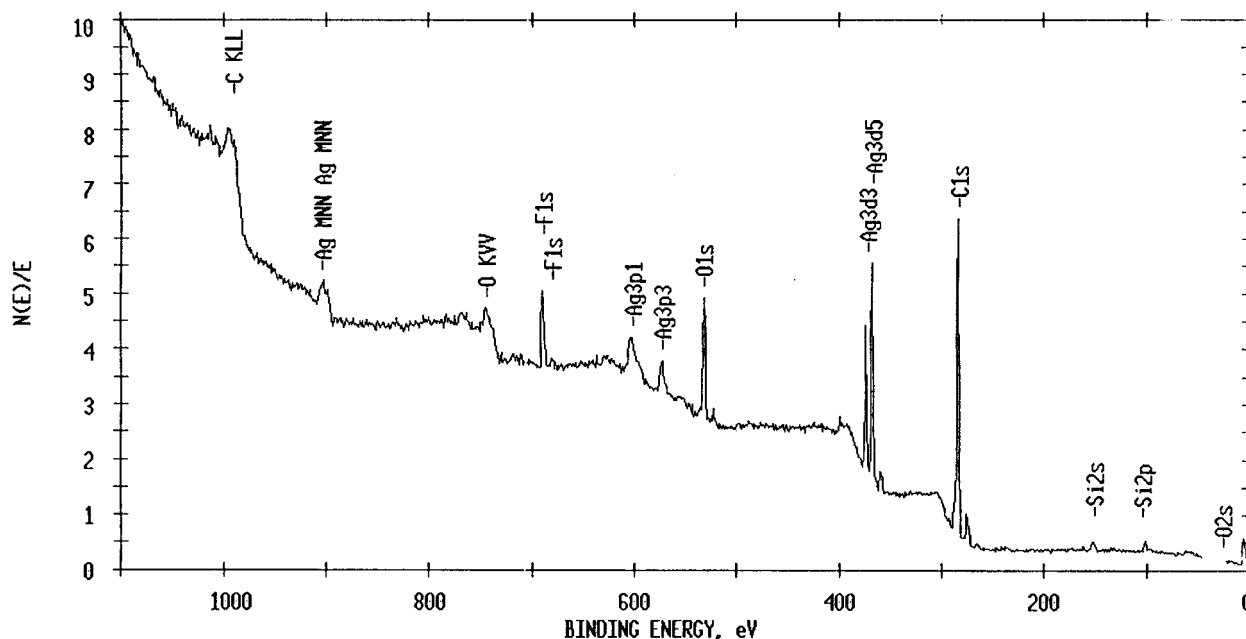
Figure 2 Auger depth profile of the air side of the BTDA–ODA polyimide film cured to 100°C. The additive, $(COD)AgF_6acac$, is at the 20% level. The sputter rate is ca. 50 Å per minute.

The feasibility of using supercritical fluids to impregnate and densify a variety of carbon/carbon composites with a ceramic precursor has been successfully demonstrated.[8] Polycarbosilane and polysilane were employed as silicon carbide precursors. The carbon/carbon apparent 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 polymeric ceramic precursors was demonstrated as a means to control physical properties and char yield.

Polyimides have found wide applicability in areas such as integrated electronic circuits and aerospace devices.[9] Some aerospace applications require high reflectivity and, thus, polyimides with a reflecting surface promise to have numerous applications.[10–12] Efforts from this laboratory over the past 10 years have concentrated on plac-

ing either metallic or metallic oxide layers on the surface of polyimides.[13–19] This has been accomplished by the addition of a soluble metal salt to a homogeneous solution containing the poly(amide acid), then casting a thin film of the solution and heating to 300°C to form the polyimide. During the cure cycle, the metal salt usually migrates to one surface of the film as the solvent evaporates. The metallic additive converts either to the metallic oxide or to the metallic state.

It has been shown via Fourier transform IR spectroscopy that polymers possessing electron-donating functional groups exhibit specific interactions with CO_2, most probably of a Lewis acid–base nature.[20] Evidence of the 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 ke-

Figure 3 The ESCA survey spectrum of the air side of the BTDA−ODA polyimide film cured to 100°C. The additive, (COD)AgF$_6$acac, is at the 20% level.

tone), and poly(2-vinylpyridine), exhibited the suggested splitting. These results suggested that CO_2 might act as an electron acceptor rather than as an electon donor. Stern et al.[21] proposed specific CO_2−fluorine interactions to explain the increased solubility of CO_2 in polymers that contain fluorine groups.

Several supercritical fluids have been used to transport organometallic precursors to the surface of a solid substrate for the purpose of preparing a thin film of either a metal or a metal oxide.[22] However, the deposition temperature was reported to be between 600 and 800°C, well above the glass transition temperature and the polymer decomposition temperature of most organic polymers. Where lower temperatures for the deposition of a metal oxide were desired, supercritical N_2O was used and a high-energy plasma inside the deposition chamber decomposed the fluid and the precursor compound. Efforts are now underway in our laboratory to infuse the metal precursor directly to both a poly(amide acid) film and a polyimide film using supercritical carbon dioxide (SC-CO_2) and to ascertain the optimal conditions to produce a reflecting film. The large number of carbonyl (e.g., Lewis base) groups in the polyimide led to high CO_2 solubility and additive infusion. The results of this investigation allow us to report the first use of a supercritical fluid to infuse a metal additive into a polyimide.

EXPERIMENTAL

Chemicals and Syntheses

Sources for all dianhydrides, diamines, 1,5-cyclo-octadienesilver(I)1,1,1,5,5,5-hexafluoroacetyl-acetonate, (COD)AgF$_6$acac, and solvents and the preparation of the polyimide films have been reported elsewhere.[19] (COD)AgF$_6$acac was added to the films on a weight-of-additive/weight-of-film basis. In a typical experiment at the 10% additive-to-film level, 5.0 mg of the additive (MW 423.1, 0.0118 mmol) and a 50-mg section of 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride−4,4′-oxydianiline (BTDA−ODA) polyimide film (MW 504.4 for the repeat unit, 0.0991 mmol) were placed in the supercritical vessel, supercritical CO_2 (SC-CO_2) was added to a preselected pressure, and then the vessel was heated at a selected temperature for a given time. For (COD)-AgF$_6$acac and BTDA−ODA, the 10% weight/weight level gives a mol ratio of polyimide-to-additive of 8.4 : 1.0. This is considerably *less* doping than the typical ratios of 4 : 1, 2 : 1, and 1 : 1 for the in situ method typically employed. The upper end of the doping (20%) employed in this work is at the lower end (4 : 1) of doping by conventional methods.

Infusion of poly(amide acid) films was done in the same manner as for the polyimides except
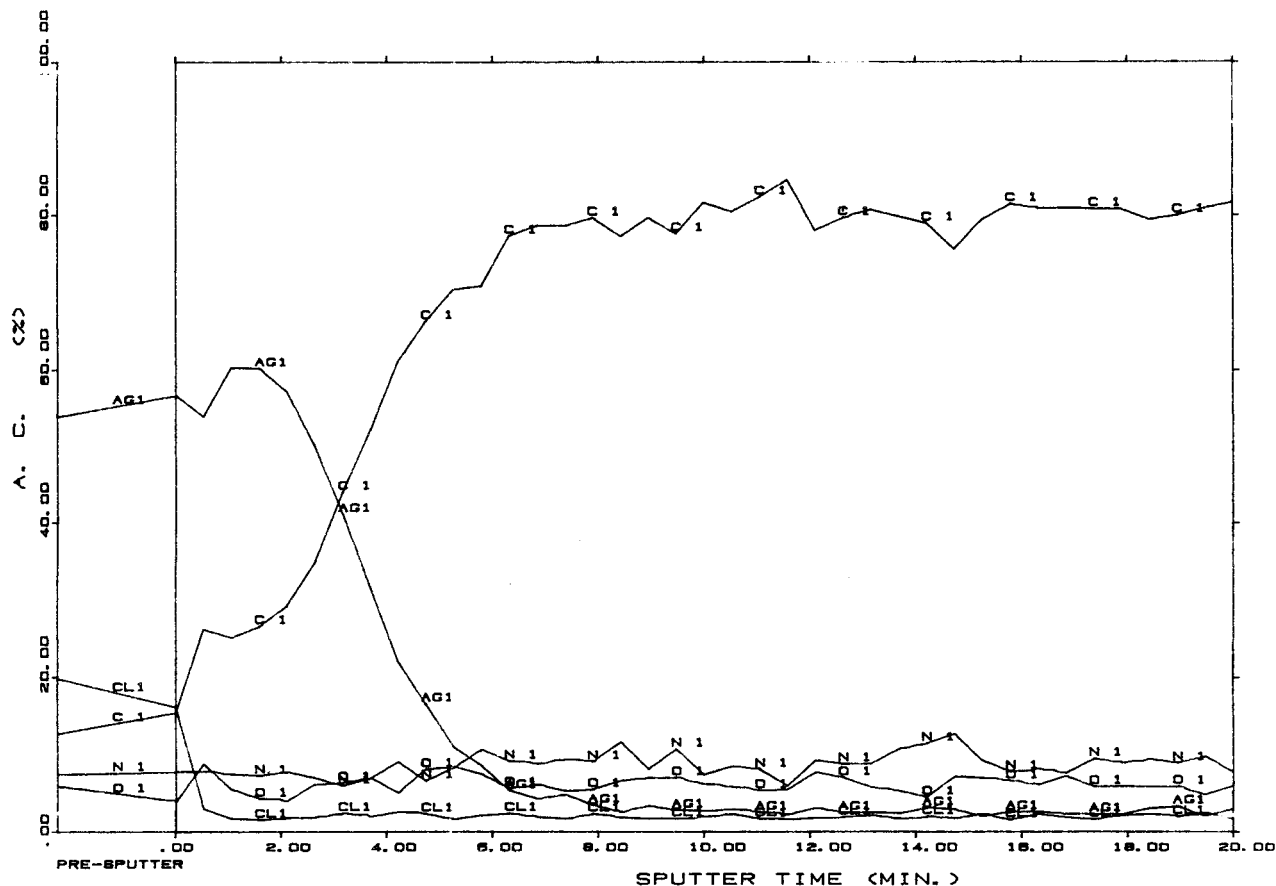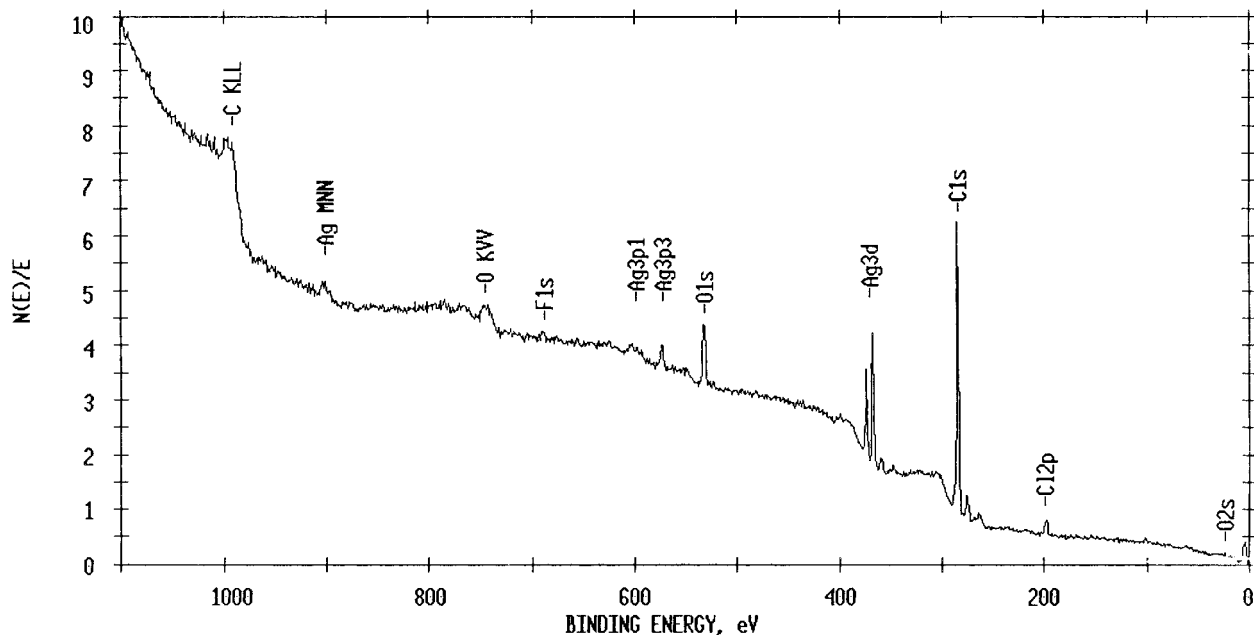
Figure 4 Auger depth profile of the air side of the BTDA–ODA polyimide film after curing to 300°C. The additive, (COD)AgF$_6$acac, is at the 20% level. The sputter rate is ca. 50 Å per minute.

that the film was removed from the oven after 1 h at 100°C. When the poly(amide acid) is infused with SC-CO$_2$, it is not possible to calculate a true mol ratio since the composition of the film is unknown. A film is typically cast at ca. 18% solids; assuming the film after the 100°C cure to be 25% poly(amide acid) due to loss of the solvent, a level of 10% additive-to-poly(amide acid) corresponds to an approximate mol ratio of 2 : 1 and a level of 20% to an approximate mol ratio of 1 : 1.

Sections of infused films (usually between 20 and 100 mg in mass) that had been removed from the glass plates on which they were originally cast and cured were placed in a 20 cm Petri dish with a glass cover plate. The cover plate had been drilled with five (0.25 in.) holes to allow air circulation through the Petri dish. The dish was then placed in the oven and the films taken through an entire cure cycle.

Measurements

A description of all measurements and instrumentation was reported elsewhere.[19] The analysis for silver was performed by Desert Analytics, Tucson, AZ. The supercritical extractor was an Applied Separations Spe-ed SFE. All extractions and infusions were carried out in a 3 mL cell with a diameter of approximately $\frac{1}{2}$ in. Of necessity, the film was curled and one side (identified as the outside of the film) was against the wall of the SCF vessel. The film (and additive if infusion was the purpose of the experiment) was placed in the cell, SC-CO$_2$ was introduced into the cell to the desired pressure, and the cell was then heated to the desired temperature for a selected time. Upon completion of the experiment, the cell was cooled to room temperature, then decompressed to room pressure. The films were usually weighed before and after the extraction or infusion experiment. A few films

Figure 5 The ESCA survey spectrum of the air side of the BTDA–ODA polyimide film after curing to 300°C. The additive, $(COD)AgF_6acac$, is at the 20% level.

weighed several weeks after the experiments showed no additional mass changes. Thermal measurements were made by Polymer Solutions, Blacksburg, VA.

DISCUSSION

Supercritical fluids have been used for extraction of analytes from a wide variety of matrices.[23] In recent years, a few reports have discussed the use of supercritical fluids to infuse a substance into a
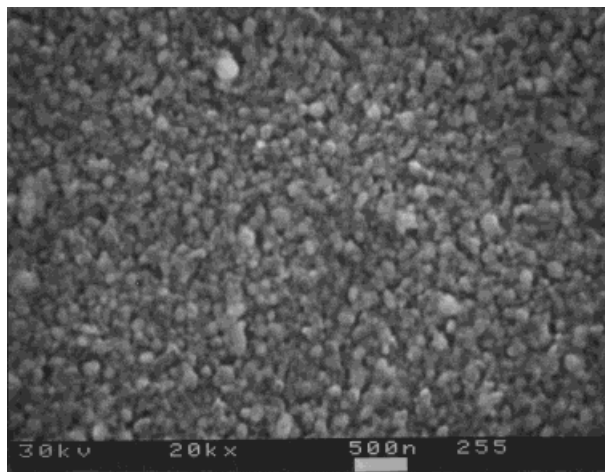
Figure 6 SEM of the air side of the BTDA–ODA film.

matrix, often a polymer.[2] It was the intent of this work to investigate whether $SC\text{-}CO_2$ could be used to infuse additives into polyimides and, if so, to determine the crucial parameters for the infusion. A dianhydride–diamine combination commonly used for commercial polyimides is BTDA–ODA (Fig. 1) and this polyimide was the focus of this study. The only additive investigated was 1,5-cyclooctadienesilver(I) 1,1,1,5,5,5-hexafluoroacetylacetonate, $(COD)AgF_6acac$, which was found to be soluble in $SC\text{-}CO_2$.

Polyimides, once formed, are thought to be relatively impervious to many materials.[24] Thus, the first set of experiments was designed to determine if $SC\text{-}CO_2$ could penetrate the surface of the polyimide. BTDA–ODA polyimide films were prepared and cured to 300°C on a glass plate in a normal fashion[25] (80°C for 20 min, then at 100, 200, and 300°C for 1 h each). Sections of this film were then subjected to 5000 psi CO_2 pressure and 110°C for 30 and 120 min (Table I). There was no apparent change in the color or the texture of the film and only a slight change in mass was observed. Thus, $SC\text{-}CO_2$ may penetrate the polyimide but little CO_2 remained when the pressure was reduced to room pressure and it does not appear that any component of the polyimide, including residual solvent if present, was extracted. Thermal analyses were performed to determine if any degradation
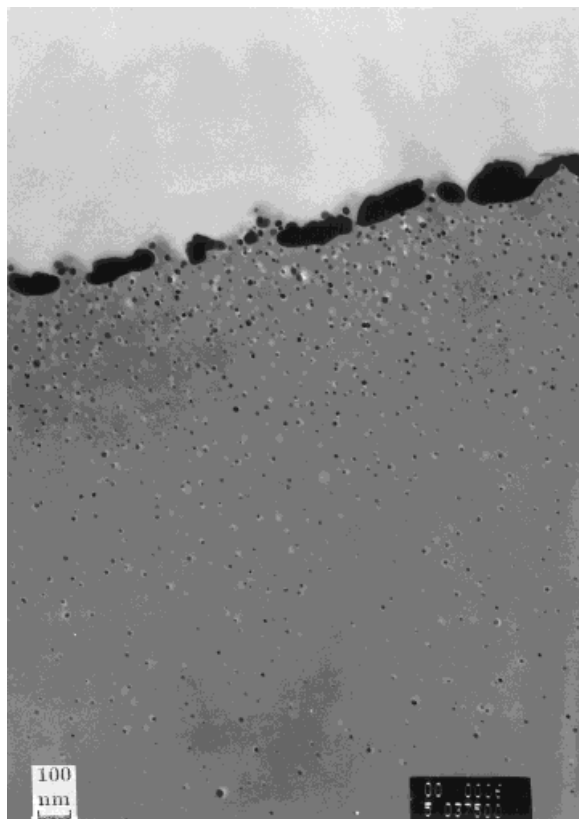
Figure 7 TEM of the air side of the BTDA–ODA film at 37,500× magnification.

had occurred. A comparison of the glass transition temperature (T_g) and the polymer decomposition temperature (PDT) of the polyimide before and after supercritical fluid extraction with CO_2 does indicate that the film did, in fact, undergo some change. The T_g of the polyimide remained constant upon extraction with SC-CO_2 but the PDT decreased by approximately 70°C.

After this first set of experiments, infusion of the additive directly into the polyimide was attempted. Using sections of the same film, the additive level (10 and 20% weight of additive-to-weight of film) and time (30 and 120 min) for infusion were varied (Table II). There was a slight increase in the weight of each film, implying that some additive and/or CO_2 had indeed infused into the film and a slight darkening of the film was observed. At the conclusion of the supercritical fluid infusion (SFI) experiments, each film was placed in a Petri dish and taken through the entire normal cure cycle to determine if the silver additive had indeed infused and, if so, would it form a silver mirror? All four BTDA–ODA polyimide films of Table II had a very silvered appearance on both sides of the film which could not be easily removed by mechanical means. Maximum reflectivity of the films (Table II) was between 40 and 50%. These values compare very favorably to other films prepared by the in situ method.[19] Thus, fully cured BTDA–ODA *can* be infused with additive to produce silvered surfaces. Compared to the original film, there was a small decrease in mass, probably due to the decomposition of the additive or slight decomposition of the polyimide, when the film was cured.

It was of interest to determine if the additive could also be infused into a poly(amide acid), or a prepolyimide, film and, if so, to compare results with the infused polyimides above. A BTDA–ODA film was prepared and cured through the 100°C portion of the normal cycle. Sections of the partially cured BTDA–ODA poly(amide acid) film were then infused with $(COD)AgF_6acac$ under different conditions of time, temperature, pressure of SC-CO_2, and relative amounts of the additive and then each section was taken through the entire normal cure cycle (Table III). The weight of each film was determined prior to the infusion, after the infusion, and after the cure cycle. Visual inspection of the films after infusion showed that each had darkened. Upon curing to 300°C, a silver surface was present on all films but incomplete silvering of a surface was generally noted for the side of the film touching the glass bottom of the Petri dish.

The extent of infusion of the additive into the poly(amide acid) film was determined by Auger depth-profiling and ESCA spectra before and after taking the film through the final cure cycle. A poly(amide acid) film was doped at the 20% level for 120 min at 110°C and 5000 psi (Table III). During the SFI, the glass side of the film was in contact with the supercritical fluid vessel. For the air side of this film, Auger depth-profiling of selected elements showed carbon near a constant atomic concentration of 70%, nitrogen near 10%, and oxygen and silver between 5 and 10% (Fig. 2). The film was sampled at several spots and all gave essentially the same result. An ESCA survey of the binding energies (Fig. 3) showed a fairly large peak near 690 eV for F_{1s}, two peaks at 374.9 and 368.9 eV for $Ag_{3d3/2}$ and $Ag_{3d5/2}$, respectively, and the Auger silver peaks near 904 and 898 eV in addition to the elements of the polyimide. A section of this film was then taken through the entire cure cycle and a silver surface was produced on both sides of the film. Auger depth-profiling of the same side as above showed an altered

distribution of the components (Fig. 4) as silver became the predominant element at the surface of the film, accounting for nearly 60% of the atomic concentration within the first 100 Å of the surface. After the first 100 Å, the concentration of silver decreased rapidly, and by 300 Å, its atom concentration was only about 5% and carbon accounted for nearly 80% of all atoms with nitrogen and oxygen each accounting for ca. 10%. The ESCA survey (Fig. 5) showed little fluorine on the surface of the film. The binding energies of the $Ag_{3d3/2}$ and $Ag_{3d5/2}$ peaks each have decreased by 0.5 eV and the Auger peaks were centered near 903 and 897 eV, respectively. All the changes are consistent with the migration of the additive to the surface of the film and the subsequent decomposition of the additive and reduction of the silver to its elemental state. The glass side of the film, which was in contact with the wall of the SCF vessel during the infusion experiment, did not produce as uniform a surface as did the air side of the film but gave essentially the same results.

A second film with the additive level at 20% was infused for 180 min at 150°C and 5000 psi, then taken through the entire cure cycle, also produced a silver surface on both sides of the film. This film, which contained 2.67% silver, was analyzed by scanning electron microscopy and transmission electron microscopy as well as by Auger depth-profiling and ESCA. The original air side or glass side was not identified, but from the ESCA results, the side with the higher sodium concentration is assumed to be the original glass side. The original air side of the film was against the wall of the SCF vessel during the infusion of the additive.

Scanning electron micrographs (SEMs) show that the original glass-side surface has a grainy appearance with most particles approximately 100–200 nm across (Fig. 6). The surface is a discontinuous metallic silver layer as shown by transmission electron micrographs (TEMs) of a cross section of the polyimide (Fig. 7). The TEMs show the layer to be approximately 100 nm (1000 Å) thick and most of the silver in the film is part of this layer. However, there are particles of silver, most less that 20 nm (200 Å) in diameter, that extend several hundred nanometers into the polyimide. Auger depth-profiling of a spot approximately 1 μm (1000 nm or 10,000 Å) in diameter also showed a high concentration of silver on the surface, accounting for 60–80% of the atoms within the first 150 Å of the surface. However, by 300 Å, the silver concentration had dropped to

less than 20%. The two techniques give somewhat different information concerning the thickness of the silver layer. ESCA survey data show strong silver peaks as expected, but also show carbon, oxygen, and nitrogen peaks; together, these four elements account for more than 95% of the atoms within the surface depth analyzed, with fluorine and sodium accounting for most of the remaining 4%. When this film was placed in the supercritical vessel, it was this side of the film that was away from the wall of the vessel and the results above suggest more silver on this surface than on the surface in contact with the wall of the vessel.

TEMs on the original air side of the film (which was against the wall of the supercritical vessel during the infusion) show approximately the same thickness to the silver layer but perhaps with a few more gaps in the layer. ESCA survey data support this notion as the carbon and oxygen peaks compared to the silver peaks are much stronger on this side of the film. Auger depth-profiling provides additional support as the relative amounts of silver, carbon, and oxygen are vastly different for two spots. For one spot, the percent silver never reached 20% but approached 80% for a second spot. For both spots, there was relatively little silver at the surface of the film and the maximum concentration was approximately 150–350 Å into the polyimide. SEMs were also different for this side of the film and indicated the surface to be less particulate in nature. The TEMs were consistent in showing that the film had very little silver in the bulk of the polyimide.

All previous work from this laboratory dealing with polyimides has involved curing the polyimide on a glass plate. Thus, it was decided to determine if the additive could be infused into the polyimide without removing it from the glass plate. A BTDA–ODA sample was cast on a glass plate and taken through the 100°C portion of the cure cycle, then removed from the oven. Small sections of glass ($\frac{1}{4} \times 3$ in.) were cut from the plate with the polyimide still attached. A sample extracted for 180 min at 110°C and 5000 psi showed no weight change. However, most of the mass is that of the glass plate and the section of poly(amide acid) probably weighed less than 5 mg. Thus, it would be difficult to observe any mass loss of the poly(amide acid). A second sample infused with additive under identical conditions also showed no noticeable weight change; however, when this sample was taken through the entire cure cycle, a slight decrease in mass was noted and the air side

of the film had a silver surface. Thus, a polyimide attached to a glass plate can also be infused using SC-CO_2.

CONCLUSIONS

The CO_2-assisted infusion process is feasible for incorporating a silver additive into a polyimide film. CO_2 absorption into the film was not as great as previously predicted but this feature has been turned into an advantage. In other words, since only surface deposition as opposed to bulk deposition was desired, the limited infusion placed the additive exclusively near the film surface. A second advantage is that both sides of the film can be made reflective as opposed to only one side when prepared by the in situ method. Further studies with different additives and polyimide combinations are in progress.

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