Silver–Polyimide Nanocomposite Membranes: Macromolecular-Matrix-Mediated Metallization of an Aromatic, Fluorinated Polyimide Yielding Highly Reflective Films at Low Metal Concentrations

Luke M. Davis,[1] D. Scott Thompson,[1*] C. J. Dean,[1] M. Pevzner,[1] J. L. Scott,[2] S. T. Broadwater,[2] D. W. Thompson,[1] R. E. Southward[3]

[1]Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23187
[2]Department of Biology, College of William and Mary, Williamsburg, Virginia 23187
[3]Advanced Materials and Processing Branch, Langley Research Center,
National Aeronautics and Space Administration, Hampton, Virginia 23681

ABSTRACT: Highly reflective, surface-metalized, flexible polyimide films were prepared by the incorporation of a soluble silver-ion complex, (hexafluoroacetylacetonato)silver(I) (AgHFA), into dimethylacetamide solutions of poly(amic acid) prepared from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 2,2-bis[4-(4-aminophenoxy)-phenyl]hexafluoropropane. The thermal curing of solution-cast silver(I)–poly(amic acid) films to 300°C led to cycloimidization of the amic acid with concomitant silver(I) reduction and the formation of a reflective, air-side-silvered surface at very low (2 wt % and 0.3 vol %) silver concentrations. The reflective surface evolved only when the cure temperature reached about 275°C, although X-ray diffraction showed metallic silver in the hybrid film by 200°C. After a maximum specular reflectivity greater than 80% was achieved for the 2 wt % silver film, the specular reflectivity diminished sharply with further heating at a constant temperature of 300°C. Incorporating the AgHFA complex into the soluble, fully imidized form of poly{(1,3-dihydro-1,3-dioxo-2H-isoindole-2,5-diyl)[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene](1,3-dihydro-1,3-dioxo-2H-isoindole-5,2-diyl)-1,4-phenyleneoxy-1,4-phenylene[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4-phenyleneoxy-1,4-phenylene} gave films that were 25% less reflective than those beginning with poly(amic acid). Though highly reflective, the films were not electrically conductive. The metalized membranes were thermally stable and maintained mechanical properties similar to those of the parent polyimide. Transmission electron microscopy revealed an air-side, near-surface layer of silver that was about 40 nm thick; the interior of the film had well-dispersed metal particles with diameters mostly less than 2 nm. The near-surface silver layer maintained its integrity because of physical entrapment of the metal nanoparticles beneath a thin layer of polyimide; that is, the practical adhesion of the metal layer was good. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2409–2418, 2007

Key words: composites; inorganic materials; polyimides

INTRODUCTION

Surface-metalized polyimide films are an area of considerable interest, as summarized extensively by Matienzo and Unertl,[1] Strunskus et al.,[2] and Mittal.[3] Uses for such films encompass anti-infective tubing and coatings,[4–8] patterned conductive paths on dielectric bases (flexible circuitry),[9–11] enhancement of thermal conductivity,[12–18] flexible conductive tapes,[19–23] terrestrial concentration of solar radiation,[24–32] and selective gas permeability membranes.[33–39] The polymeric base offers advantages in weight, flexibility, elasticity, fragility, and deployability with respect to inorganic supports such as glass, metals, and ceramics. This makes metalized membranes especially germane to space applications, for which weight and packaging options are of special concern. Space applications include specularly reflective membrane reflectors and concentrators for solar propulsion and power generation,[40–43] reflectors for flat-panel solar-power arrays,[44,45] large-scale radio-frequency antennas for the management of electromagnetic signals,[46–49] solar sails,[50–52] and coatings (sunshields) for passive temperature control in devices such as the Next Generation Space Telescope.[53–61]
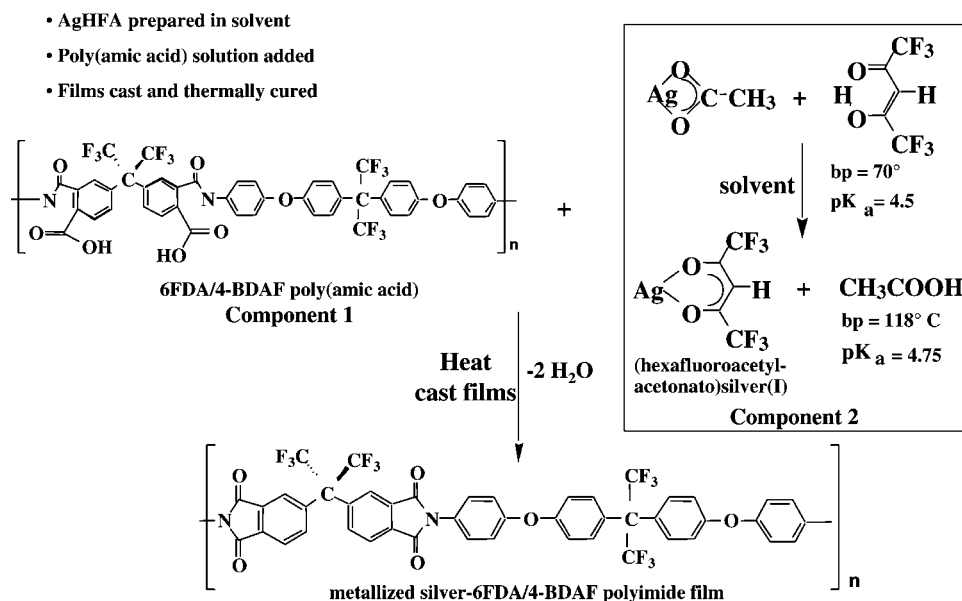
In this article, we report results for continuing studies on an unusual and distinctive single-stage, internal, macromolecular-matrix-mediated synthesis of surface-silvered polyimide films (see Fig. 1). Such films were originally disclosed by Endrey[22] (DuPont)

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Figure 1 Scheme for the synthesis of surface-metalized films from AgOAc and HFAH in a 6FDA/4-BDAF poly(amic acid) solution. The solvent is DMAc. Components 1 and 2 are mixed and cast as a film, which is then subjected to thermal curing. The cure cycle is 20 min to 135°C, 1 h at 135°C, 240 min to 300°C, and various times at 300°C.

and were elaborated significantly by Taylor and coworkers[62–64] and Southward and coworkers.[65–73] Depending on the materials and conditions, films that are highly reflective and/or surface (not bulk) electrically conductive can be fabricated. We use the term *single stage* to denote the fabrication of metalized films in a single step from a homogeneous solution containing a positive-valence silver precursor and a poly (amic acid). *Internal* and *matrix-mediated* refer to a film that is cast as a silver(I)-ion-doped poly(amic acid) solution, after which thermal treatment induces an internal metal-ion reduction to silver atoms that are first formed within the polymer matrix and subsequently concentrated, in part, at the membrane surface to give a 30–200-nm reflective, metallic layer. The reduction of the metal ions occurs without the addition of a distinct external reducing agent, such as sodium borohydride, hydrazine, or ultraviolet–visible (UV–vis) radiation, to give the metallic phase. Thermal curing also gives the final polyimide via cycloimidization of the amic acid precursor. Silver is of special interest because it has exceptional reflectivity and conductivity. Polyimides are advantageous because of outstanding thermooxidative stability and film-forming properties.[74]

A major motivation for pursuing single-step membrane metallization is that the formation of surface-metalized films via the vapor deposition of passive metals such as silver, gold, palladium, and even copper does not give strong adhesion between the organic and metallic phases.[75] This problem is usually overcome by the deposition of a seed layer with chemically active metals such as chromium and aluminum, which adhere strongly to polyimides. Generating metal atoms inside a curing polyimide matrix

means that the metal atoms/clusters must remain within the polymer as required by surface energy considerations and as amply demonstrated experimentally by Kovacs and Vincett[76–78] and Faupel et al.[79] Although the metal particles must remain in the polymer, they appear to have a striking tendency to form a layer of nanoparticles/crystallites very near (on the order of nanometers) the free (unbound or air-side) surface of a film, as shown experimentally and explained theoretically.[76–79] Thus, internally produced metal atoms and subsequent clusters and particles at the free surface of the film will be covered by the polymer, and this means that the encapsulated metal aggregates will have a high level of practical adhesion.

Recently, we reported studies for the silver metallization of the fluorinated polyimide poly{(1,3-dihydro-1,3-dioxo-2H-isoindole-2,5-diyl)[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene](1,3-dihydro-1,3-dioxo-2H-isoindole-5,2-diyl)-1,4-phenyleneoxy-1,4-phenylene[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4-phenyleneoxy-1,4-phenylene} (6FDA/4-BDAF; Fig. 1) with (hexafluoroacetylacetonato)silver(I) (AgHFA) and (trifluoroacetylacetonato)silver(I).[65,80] Silver concentrations in these systems ranged from 6 to 13 wt % and gave films with excellent specular reflectivity but without surface or bulk conductivity. In general, we have observed higher reflectivity values for extensively fluorinated 6FDA/4-BDAF than we have for numerous traditional nonfluorinated polyimides such as BTDA/4,4′-ODA (3,3′,4,4′-biphenyltetracarboxylic dianhydride/4,4′-oxydianiline). Thus, we were encouraged to investigate the formation of metalized films with 6FDA/4-BDAF with very low silver concentrations, and here we report studies that focus on preparing and charac-

terizing films with silver concentrations of 2–3 wt % (0.28–0.42 vol %), at which concentrations traditional polyimides exhibit only modest reflectivity.[68]

The synthetic protocol used in these studies is illustrated in Figure 1. Silver(I) acetate (AgOAc) and hexafluoroacetylacetone (HFAH) are allowed to react in the solvent dimethylacetamide (DMAc) or other solvents to give a solution of the AgHFA complex, which is not isolated from the solution. A DMAc solution of the poly(amic acid) form of 6FDA/4-BDAF is added to the DMAc solution of AgHFA. A colorless, homogeneous solution results. A film is cast. The thermal curing of the Ag(I)–poly(amic acid) film causes the reduction of Ag(I) to the native metal and ring closure to the imide to generate a surface-metalized polyimide membrane. The films of this study were characterized with X-ray diffraction, transmission electron microscopy (TEM), and scanning electron microscopy (SEM) and with conductivity, reflectivity, thermal, and mechanical measurements.

EXPERIMENTAL

Materials

4,4′-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis(1,3-isobenzofurandione) [alternatively, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride] was obtained from Chriskev (Leawood, KS) and vacuum-dried for 5 h at 150°C before use. The vacuum-drying process was essential for preparing resin solutions with adequate viscosity. 4,4′-{[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]-bis(4,1-phenyleneoxy)}bisbenzenamine {alternatively, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane} was purchased from Chriskev and used as received. A 6FDA/4-BDAF poly(amic acid) solution was prepared with a 0.5 mol % excess of dianhydride with 15% solids (w/w) in DMAc. The resin was stirred for 5 h. The inherent viscosity was typically in the range of 1.1–1.5 dL/g at 25°C. The fully imidized form of 6FDA/4-BDAF, which was chemically imidized with an acetic anhydride/pyridine (equal volumes) solution, was a gift from the Langley Research Center (Hampton, VA) of the National Aeronautics and Space Administration. HFAH, AgOAc (99.9%), DMAc (high-performance-liquid-chromatography-grade), dimethylformamide (DMF; 99.8% anhydrous), 2-methoxyethyl ether (diglyme; 99.5% anhydrous), and pyridine (99.8% anhydrous) were purchased from Sigma–Aldrich (Milwaukee, WI) and used as received, except for the storage of liquids over 4-Å molecular sieves.

Preparation of the metalized 6FDA/4-BDAF films

A representative procedure for the fabrication of a silvered AgHFA–6FDA/4-BDAF film follows. For a 2 wt % silvered film, an AgHFA-containing solution was prepared first by the slurrying of AgOAc (0.0456 g, 0.273 mmol) in a minimal amount of DMAc (1.0 g) in a 14-mL, wide-mouth vial followed by the addition via syringe of HFAH (0.0625 g, 0.300 mmol). The silver acetate went into solution as the AgHFA complex within seconds. The HFAH/Ag molar ratio was 1.1 : 1.0. A poly(amic acid)–DMAc solution (10.0 g of the solution with 15.0 wt % solids) was then added to an AgHFA solution with vigorous stirring. Stirring was continued for at least 30 min. During stirring, the sample was inverted numerous times to ensure complete mixing. Alternatively, the AgHFA complex solution could be syringed into the poly(amic acid) solution. The percentage of silver used to designate the metalized films was calculated on the basis of only silver metal and the final imidized polymer; the silver(I) ligand was assumed to be lost during thermal curing from the system along with water upon imidization of the amic acid moieties. The doped poly(amic acid) solution was cast as a film onto glass plates or 27 mm × 46 mm petrographic slides with a doctor blade set at 600 μm to obtain cured films 25–35 μm thick. After 15–18 h in an atmosphere of slowly flowing dry air (ca. 5% relative humidity), which gave a tack-free film, the film was heated in air in a Blue M forced-air oven (Watertown, WI). The cure cycle involved (1) heating over 20 min to 135°C and holding for 1 h, (2) heating to 300°C over 4 h, and (3) holding at 300°C as indicated in the figures.

Characterization

The surface resistivities of all films were measured with a Signatone (Gilroy, CA) four-point probe. TEM images were acquired on a Zeiss EM-109 instrument (Oberkochen, Germany); samples were embedded in epoxy and cut at 100 nm. SEM images were obtained on Hitachi S-4700 (Pleasanton, CA) or Amray 1810 instruments (Santa Barbara, CA); the samples were coated with about 5–10 nm of a palladium/gold alloy. Reflectivity measurements were made (with respect to a PerkinElmer polished aluminum mirror (Wellesley, MA) with a reflectivity coefficient of 0.92 at 531 nm) with a PerkinElmer Lambda 35 UV–vis spectrophotometer equipped with a variable-angle specular reflectance attachment with a wavelength of 531 nm. X-ray data were obtained with an XDS 2000 Scintag powder X-ray diffractometer (Cupertino, CA) on metalized films taken from the oven at various times and corresponding temperatures.

RESULTS AND DISCUSSION

Synthesis of the metalized films

Polymer 6FDA/4-BDAF

Previous metallization work has used traditional, that is, nonfluorinated polyimides such as BTDA/4,4′-

ODA and BPDA/4,4′-ODA. Recently, as mentioned previously, we extended single-stage silver metallization efforts[65,80] to highly fluorinated 6FDA/4-BDAF, which has hexafluoroisopropylidene groups in both the dianhydride and diamine units. This polyimide, like traditional polyimides, has excellent thermooxidative stability. Robust thermal properties for the polymer are crucial in silver-containing systems because silver metal catalyzes the air oxidation of organic functionalities at the temperatures (275–300°C) necessary to produce surface-metalized films. The presence of flexible, nonpolarizable, and spatially bulky trifluoromethyl groups lowers the effective symmetry of the dianhydride unit because of the availability of many low energy conformations, lowers the polarizability of chain segments, and increases steric constraints between chains. Such properties inhibit noncovalent inter- and intramolecular chain interactions, chain ordering, and crystallinity and thus allow the realization of polyimides with solid mechanical properties and good solubility in both the poly(amic acid) and polyimide forms while maintaining the excellent thermooxidative stability of traditional aromatic polyimides. Additionally, isopropylidene groups lead to reduced surface free energy, increased fractional free volumes, increased diffusion coefficients, reduced moisture absorptivity, reduced permittivity, reduced refractive index, and markedly reduced absorptivity in the visible region of the EM spectrum.[81–87] Indeed, 6FDA/4-BDAF is one of several fluorinated polyimides often called colorless.[88]

### AgHFA-doped polymer solutions and film fabrication

Silver(I)-doped polymer solutions are prepared readily at ambient temperatures without the need to isolate a solid AgHFA complex. As summarized in Figure 1, for each film synthesis, AgHFA was newly prepared in solution without isolation. The complex was prepared in DMAc, DMF, or diglyme from AgOAc and HFAH. HFAH was used in modest excess (HFAH/Ag molar ratio = 1.1 : 1.0) to ensure complete complex formation. Stirring for 3–5 min yielded a colorless solution of the complex, as indicated by the complete disappearance of the insoluble AgOAc starting material. We have previously shown that the AgHFA complex is indeed formed by this procedure.[89] The solution of the silver(I) complex was transferred into a solution of the 6FDA/4-BDAF in either the poly(amic acid) or polyimide form. It is not useful to add the complex-forming reagents directly to the polymer solution because AgOAc, before it reacts with HFAH, causes intractable gelation of the poly(amic acid). Because silver(I) complexes are often easily photolytically and thermally

degraded, our *in situ* preparation of the silver(I) complex ensures that a fresh, intact complex is available for each film fabrication. There is no difference in the final film properties according to the order of addition (the complex solution to polymer solution or vice versa). Before the films were cast, it was essential to stir thoroughly the viscous silver(I)-doped polymer solution to ensure homogeneity. To obtain highly reflective films, the silver(I) complex must remain soluble in the initial polymer solution and in the solvent-depleted polymer film that results during predrying in a film box at room temperature and during the thermal cure cycle. The silver(I) precursor must not undergo visual precipitation in the polymeric matrix at any time before or during the cure cycle or only micrometer-sized silver particles, which give surfaces without metallic conductivity or specular reflectivity, result.

Films were cast onto glass slides or plates and placed in a vented drying chamber with 5% relative humidity air flowing over the films at 100–150 scfh to evaporate the solvent so that film bubbling did not occur during the thermal treatment. Under the drying conditions, the films became tack-free in about 6 h, with about 80% of the solvent being lost. After 15 h in the drying chamber, about 91% of the solvent had evaporated from the cast film.[80] Only after predrying were the films cured to effect cycloimidization and silver(I) reduction. The cure involved heating the samples over 20 min to 135°C and holding them at this temperature for 1 h, then heating the film to 300°C over 4 h, and finally holding them constant at 300°C for various periods. The films that formed at 275, 300, and 300°C for 1 h exhibited the essential mechanical properties of the parent polyimide, as we have always observed in previous work with AgHFA polyimide films. All the films could be tightly creased without fracturing.

Silver(I) reduction

We do not know with absolute certainty the mechanism for the thermally promoted reduction of the silver(I) ion in the macromolecular matrix. However, from previous studies, it is unlikely that the HFAH ligand or solvent functions as the reducing agent.[90] Evidence from our previously cited work suggests that poly(amic acid) may function as the reducing moiety. The initiation of reduction takes place when the sample has been at a temperature of 135°C for less than 1 h. We determine this by taking a 2 wt % film from the oven after it has just reached 135°C, peeling the film from the glass side, and placing it in 2 vol % aqueous hydrazine hydrate. After a few minutes, the air-side surface of the film is brightly silvered with high electrical conductivity. Interest-
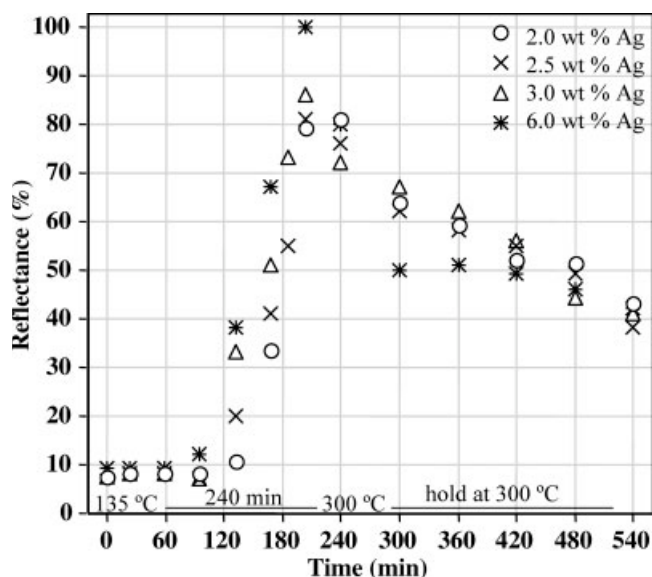
Figure 2 Reflectance versus time–temperature data for silver–6FDA/4-BDAF films prepared with silver acetate, HFAH, and a 6FDA/4-BDAF poly(amic acid) solution in DMAc. The silver concentrations were (*) 6.0, (△) 3.0, (×) 2.5, and (○) 2.0 wt % (see the Experimental section for the cure details).

ingly, the glass side of the films remains unchanged without visually apparent silver formation. After the film has been at 135°C for 1 h, immersion in hydrazine or borohydride does not give a silvered surface, nor is there any observed darkening of the film color. Thus, the reduction of silver(I) occurs relatively early in the thermal cure cycle.

Reflectivity, conductivity, and surface characterization

Reflectivity and conductivity

None of the films was electrically conductive. This is consistent with previous work[62–73] with traditional, nonfluorinated polyimides with AgHFA as the silver precursor. Although metallic silver particles are formed at the surface and throughout the polymer, the particles remain isolated and never form a continuous network. Only with the (trifluoroacetylacetonato)silver(I) complex have we been successful in preparing films that are both highly conductive (in the metallic range) and specularly reflective.[70,71]

Figure 2 displays the specular reflectance as a function of the cure time and temperature for a series of AgHFA–6FDA/4-BDAF films prepared in DMAc with low concentrations of silver (2.0, 2.5, 3.0, and 6.0 wt %). (The percentage silver is calculated on the basis of only silver metal and the final polyimide form. The ligand is assumed to be lost completely from the system; indeed, analytical data for analogous BTDA/4,4′-ODA systems show that a large majority of the fluorine from the ligand has been lost from the system.[64,91]) The silver-doped 6FDA/4-BDAF films begin to develop a metallic layer in the 200–225°C range, as evidenced by the emergence of measurable specular reflectivity. At 225°C, the 6.0 wt % film has the highest reflectivity at 38%; the reflectivities at 225°C for the 3.0, 2.5, and 2.0 wt % films are 33, 20, and 11%, respectively. The X-ray diffraction profiles for the set of 2.0 wt % films (Fig. 3) correlate with the reflectivity data, with the relatively intense 111 reflection emerging between 175 and 200°C in the thermal cure cycle. For
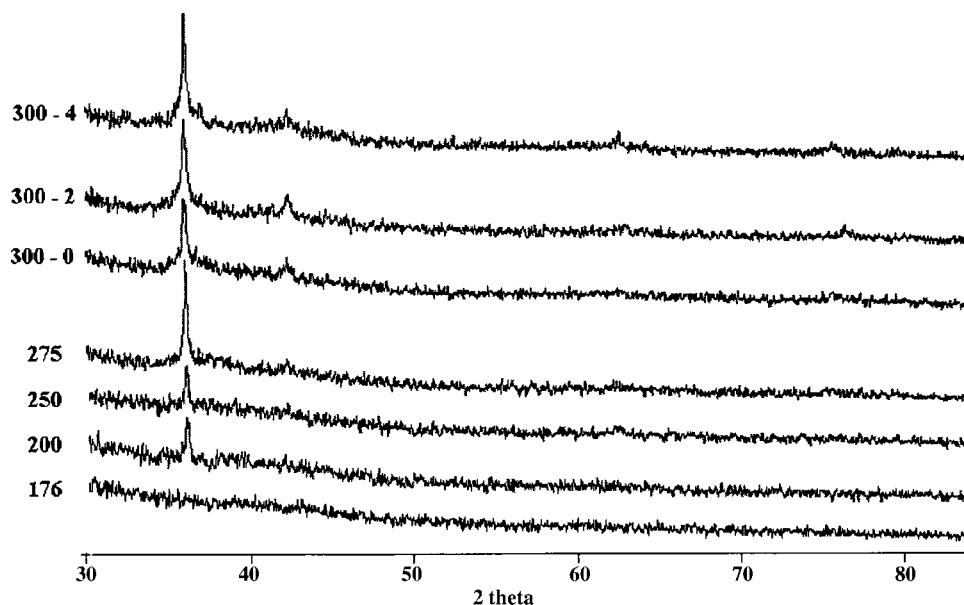

Figure 3 X-ray diffraction patterns for 2 wt % silver AgHFA–6FDA/4-BDAF films in DMAc as a function of the cure temperature and time. The temperatures are to the left (for the cure cycle, see Fig. 2).

the 2.5, 3.0, and 6.0 wt % films, the reflectivity achieves a maximum near 275°C. Thereafter, the reflectivity degrades gradually until after 5 h it is about 40%. At 2 wt % silver, the reflectivity is maximal at 82% at 300°C. (We have at times observed reflectance values of >90% for 2.0 wt % films but cannot reproduce these values consistently; this may be due to the lack of precise curing atmosphere control in the forced-air oven.) The observed reflectivities in the 80–90% range for 2–3 wt % silver films were unexpected, as our older work with traditional polyimides such as BTDA/4,4'-ODA showed a sharp drop in the reflectivity when the silver concentrations were below 5 wt %; for example, a 2.5 wt % AgHFA–BTDA/4,4'-ODA silvered film had a maximum reflectivity of 43%. Thus, with the heavily fluorinated 6FDA/4-BDAF, it is possible to produce highly specularly reflective films at very low silver concentrations. Why this is the case is unclear. We suggest tentatively that it may be related to the fact that the 6FDA/4-BDAF polyimide does not absorb in the visible, and thus there is no absorption of incident light by the polymer overlayer that must be present[76–79] (covering the silver particles) if no polyimide degradation has occurred.[70,92] On the other hand, the high reflectivity may be due to the greater ease of silver-atom/cluster migration in the heavily fluorinated polyimide, which is dominated by 12 nonpolarizable fluorine atoms per repeat unit. This would result in weaker van der Waals interactions between polyimide functionalities and silver atoms/clusters, so a surface silver layer would build more readily than for traditional, higher surface energy polyimides. The glass-transition temperature does not seem to influence the development of reflectivity, as we have reported recently.[93]

Electron microscopy and disposition/environment of the Ag nanoparticles

Figure 4 shows TEM micrographs of the 2.0 wt % film when it first reached 300°C, the point of maximum reflectivity. A surface layer of silver particles with a nominal thickness of about 40 nm is clearly visible. This is consistent with the SEM micrograph (Fig. 5, 2.0 wt % Ag), which shows the largest particles at the surface are about 40 nm, with the majority of the surface particles in the 30–40 nm range. (We use the term *surface* to mean any of the following: on the polyimide surface, partially embedded in the polyimide, or fully embedded in polyimide but only on the order of nanometers from the surface.) Though not completely unambiguous, a careful examination of the TEM micrographs at a higher magnification suggest strongly that the particles are embedded in the polymer bulk, with the top side of the quasispherical particles covered with about 5 nm of polyimide. We would, of course, expect that silver particles that are formed within the polymer matrix would remain encapsulated in the polymer matrix according to the work of Kovacs and Vincett,[76–78] who demonstrated experimentally that the thermodynamically stable state of a metal-nanoparticle/polymer system is for the particle to be fully embedded in the polymer. That is, when the surface free energy of the metal (γ_M) is greater than the interfacial free energy (γ_{MP}) plus the surface free energy of the polymer (γ_P), that is, $\gamma_M > \gamma_{MP} + \gamma_P$, a metal particle must embed itself in the polymer. For inorganic particles, this relationship appears to be general. Indeed, the practical adhesion of the silver particles to the surface is such that no silver is removed in
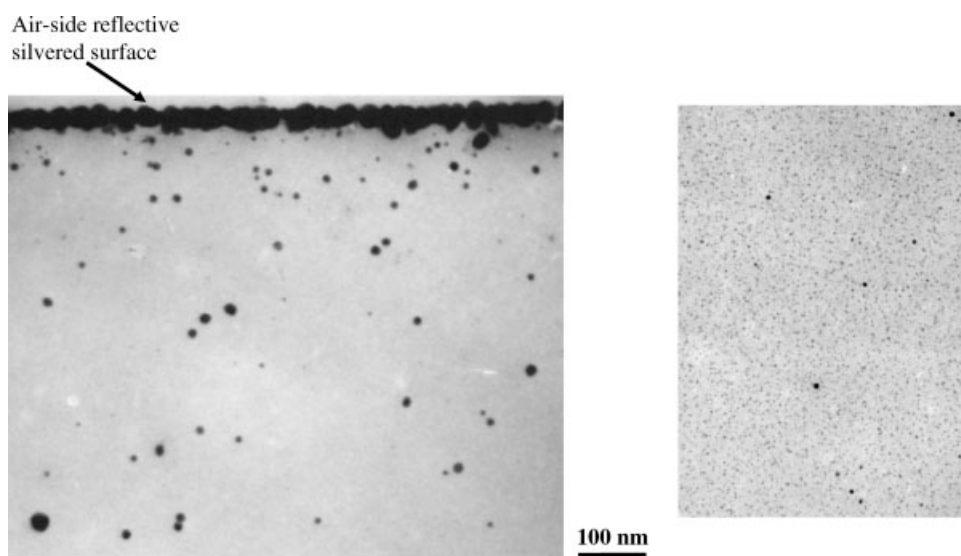
Figure 4   TEM micrographs for a 2 wt % silver AgHFA–6FDA/4-BDAF film in DMAc cured to 300°C, the point of maximum reflectivity (see Fig. 2). The film air-side surface is on the left; the film interior is on the right. The scale bar is for both films.
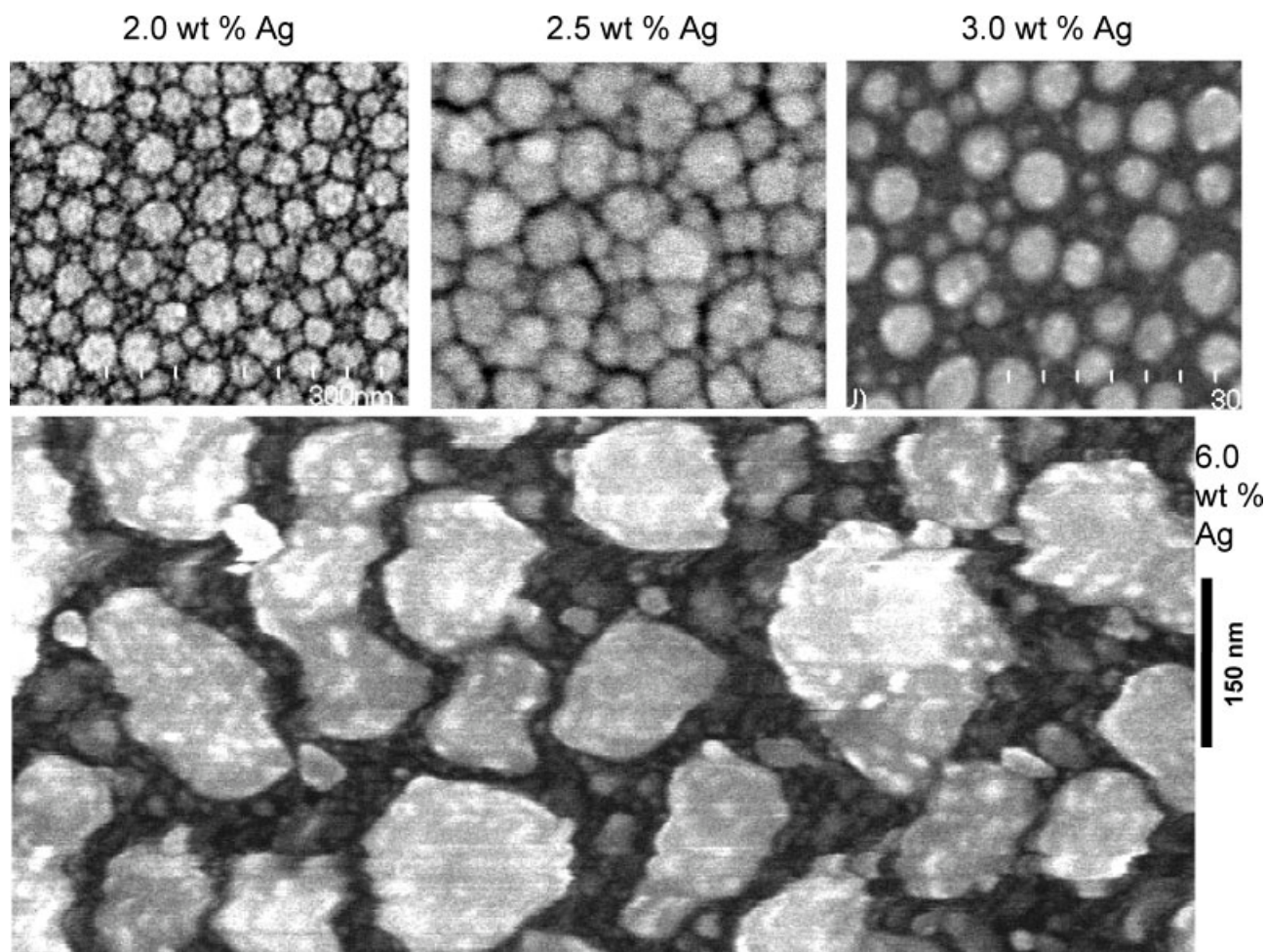
Figure 5 SEM micrographs as a function of the concentration for 2.0, 2.5, 3.0, and 6.0 wt % silver AgHFA–6FDA/4-BDAF films in DMAc. The scale bar is 150 nm and applies to all the micrographs.

the tape-test experiment done with common adhesives. By way of comparison, if silver is externally deposited on a polyimide film by Tollen's test, this silver layer is essentially removed onto the adhesive tape. Rubbing the silver layer with a polishing cloth was never observed to induce electrical conductivity in the metalized 6FDA/4-BDAF films. This is consistent with the silver particles being completely surrounded by the polymer. On the other hand, if the silver layer is rubbed firmly with a bare finger, the silver can be removed significantly. This may reflect that the particle depth is only a few nanometers, the thin surface polyimide being easily abraded. The fact that the silvered 6FDA/4,4′-ODA films of this study show no tarnish when in the ambient environment for several years is consistent with a polyimide overlayer protecting the metal surface.

Metal particles are spread rather uniformly throughout the bulk of the film. A few particles of substantial size, 10–25 nm, are seen about 1000 nm into the metalized air-side surface. In the bulk, the vast majority of the particles are very small, with

diameters of 2 nm or less and with only a few larger particles up to a maximum diameter of 7 nm. This is qualitatively consistent with the X-ray diffraction data, which show that the width at the half-height for the upper portions of 1,1,1 reflections from 200 to 300°C (Fig. 3) narrows slightly because of the increasing size, particularly of the near-surface particles. These larger particles contribute to the narrow upper part of the reflection peak, with the small particles, less than or equal to 2 nm, giving Scherrer-broadened reflections that are observed in a broadened portion of the reflection at the baseline, particularly for the samples at 300°C. That is, the observed 1,1,1 reflection peak is bimodal in character.

Figure 5 shows SEM micrographs for four 275°C samples with 2.0, 2.5, 3.0, and 6.0 wt % silver. The micrographs show a high density of quasispherical particles in the nanometer range. The 2.0 wt % film has an array of larger particles, about 30–40 nm, with somewhat textured surface structures. Between these larger particles are smaller clusters, with many in the range of 3–10 nm. The 2.5 wt % film appears to have
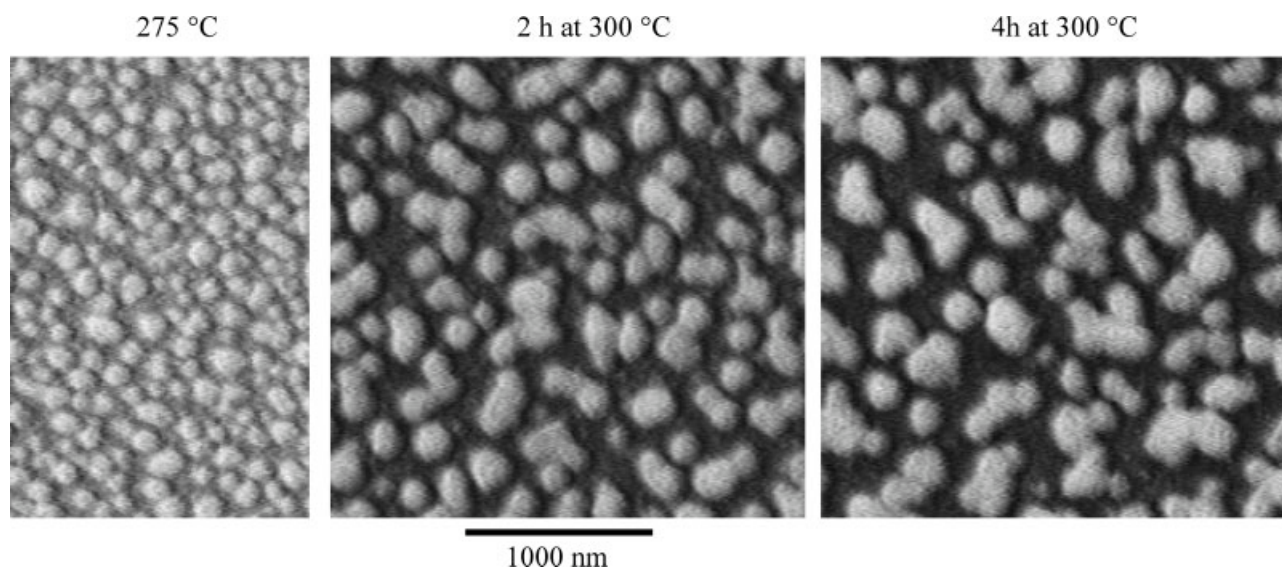
Figure 6 SEM micrographs for a 6.0 wt % silver AgHFA–6FDA/4-BDAF poly(amic acid)–DMAc film at three different time/temperature combinations as indicated. The scale bar is 1000 nm for all the micrographs.

a greater number of about 40-nm, closely packed particles with smoother surfaces and significantly fewer of the many smaller particles of the 2.0 wt % sample. At 3.0 wt %, the particle size and sphericity are increased, and the larger particles have moved further apart. There still appears to be modest density of smaller, spherical particles between the large ones. This slight tendency toward larger aggregates in the 2.0, 2.5, and 3.0 wt % films is confirmed by the micrograph of the 6.0 wt % film. Here numerous particles with diameters greater than 100 nm can be seen, although a number of smaller particles, about 30–50 nm, are also visible. Apparently, these larger particles of the 6.0 wt % film enhance the specular reflectivity markedly.

Figure 6 shows SEM images for the 6.0 wt % silver films of Figure 2 cured to 275 and 300°C for 2 h and to 300°C for 4 h. The maximum reflectance percentage of the 6.0 wt % films was about 100 at 275°C. The micrograph at this temperature shows mostly rather uniform and closely spaced globular particles at the air-side surface. The particles, however, are not in contact, and hence the film is not conductive. As the 6.0 wt % film is heated to 300°C and maintained at that temperature, a continuing increase in the particle size and shape diversity due to sintering and/or ripening effects can be seen. There is also a corresponding increase in the distance between particles. Diffuse reflectance measurements show only a slight increase in reflectivity above the specular component with increasing temperature, and so the decrease in the specular reflectivity must be associated with increasing polyimide absorption, perhaps significantly because of silver-catalyzed oxidative degradation of the polymer at and near the surface effected by heating at 300°C.

Poly(amic acid) versus polyimide as the starting macromolecular phase

One important option that fluorinated polyimides have with respect to their traditional, nonfluorinated congeners is that the imide form of the polymer is also soluble in solvents such as DMAc, DMF, and diglyme. Thus, the development of reflectivity can be examined as a function of the initial polymer structure. This has not been reported previously. Figure 7 shows reflec-
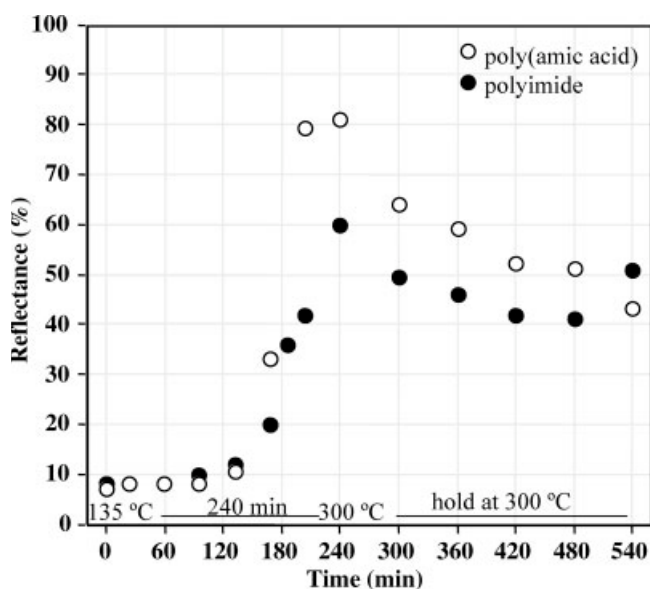
Figure 7 Reflectance versus the time–temperature data for silver–6FDA/4-BDAF films prepared with silver acetate, HFAH, and (●) 6FDA/4-BDAF polyimide or (○) 6FDA/4-BDAF poly(amic acid) in DMAc. The silver concentration was 2.0 wt % (see the Experimental section for the cure details).

tance plots for 2.0 wt % films prepared in an identical manner, except that in one case the polyimide form of 6FDA/4-BDAF was used in place of the poly(amic acid) form. The profiles of the two curves are very similar, with the exception that starting with the imide form gave a maximum reflectivity that was 25% less than that for the corresponding amic acid film. As for the poly(amic acid) films, none of the polyimide films was electrically conductive. We are currently investigating other soluble polyimide/poly(amic acid) pairs.

CONCLUSIONS

Highly reflective, surface-metalized, flexible polyimide films with low silver concentrations have been prepared by the incorporation of AgHFA into DMAc solutions of a 6FDA/4-BDAF poly(amic acid) solution followed by thermal curing to 300°C. Reflective surfaces appear maximal in the 275–300°C range; X-ray diffraction shows metallic silver in the polymer by 200°C. The specular reflectivity diminishes with further heating at 300°C. Incorporating the AgHFA complex into the soluble imide form of 6FDA/4-BDAF gives films that are 25% less reflective than those beginning with the poly(amic acid). None of the films of this study was electrically conductive. The silvered films are thermally stable and maintain mechanical properties similar to those of the parent polyimide. TEM has revealed an air-side, near-surface layer of silver, which is about 40 nm thick; the interior of the film has well-dispersed metal particles with diameters mostly less than 2 nm. The near-surface silver layer has high practical adhesion because of physical entrapment.

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