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Silver-Polyimide Nanocomposite Films Yielding Highly Reflective Surfaces

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ABSTRACT

Highly reflective surface-metallized flexible polyimide films have been prepared by the incorporation of the soluble silver ion complex (1,1,1-trifluoroacetylacetonato)silver(I) into dimethylacetamide solutions of the poly(amic acid) prepared from 2,2-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA) and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoro-propane (4-BDAF). Thermal curing of solution cast silver(I)-poly(amic acid) films leads to cycloimidization of the amic acid with concommitant silver(I) reduction and formation of a reflective surface-silvered film at 8 and 13 weight percent silver. The metallized films are thermally stable and flexible with mechanical properties similar to those of the parent polyimide. TEM reveals that the bulk (interior) of the polyimide composite films have 5-20 nanometer-sized silver particles with a surface layer of silver metal ca. 80 nm thick. Neither the bulk nor the surface of the films is electrically conductive. Adhesion of the surface metal to polyimide is excellent.

INTRODUCTION

The fabrication of specularly reflective and electrically conductive surface metallized polyimide films is of enormous interest as reviewed by Matienzo and Unertl [1]. Applications are numerous including: anti-infective coatings, contacts and circuit lines in microelectronics, enhancement of thermal conductivity, flexible surface conductive tapes, patternable conductive surfaces on dielectric bases, the terrestrial concentration of solar radiation for power generation, and gas permeability barriers. Of particular interest to us are space applications of metallized polyimides. These include highly reflective thin film reflectors and concentrators in space environments for solar thermal propulsion [2] and solar dynamic power generation [3,4], reflectors for flat panel solar power arrays for satellites [5], large scale radiofrequency antennas for the management of EM signals [6], solar sails [7,8], and sunshields to control device temperatures for projects such as the Next Generation Space Telescope. Polymeric supports offer advantages in weight, flexibility, elasticity, fragility, and deployability relative to inorganic supports such as glass and ceramics.

Southward et al. [9] and Taylor et al. [10] have have been successful in preparing surface-metallized, in particular silver-metallized, polyimide films by a novel single-stage, internal metallization technique which leads to flexible films with excellent specular reflectivity and/or electrical conductivity. "Single-stage" denotes the fabrication in one step of metallized films from a homogeneous solution of a positive valent metal precursor and a poly(amic acid). In contrast to traditional metallized film preparation protocols, in the present work the polyimide film is not prepared in a first stage and subsequently coated with metal (vapor deposition, sputtering, etc.) in a discrete second stage. "Internal metallization" refers to a film that is cast as a homogeneous silver ion-doped poly(amic acid) solution and then thermally treated to induce metal ion reduction to give the metallized surface with concomitant cycloimidization of the amic acid to the final polyimide. During the thermal cycle a portion of metal atoms and small clusters formed in the polyimide film aggregate at the surface to give a 50-200 nm metallic layer. Silver is the metal of interest since it has exceptional reflectivity and conductivity [11]. Polyimides were chosen as substrates owing to their excellent thermal-oxidative stability and film-forming properties [12,13].

The synthetic protocol with respect to the system reported herein is illustrated in Figure 1. Silver(I) acetate and trifluoroacetylacetone (TFAH) are allowed to react in the solvent dimethylacetamide (DMAc) to give an *in situ* solution of the (trifluoroacetylacetonato)silver(I) complex, AgTFA. A DMAc solution of the poly(amic acid) form of 6FDA/4-BDAF is added to the DMAc solution of AgTFA. A colorless homogeneous solution results. A film is then cast. Thermal curing of the Ag(I)-poly(amic acid) film effects reduction of Ag(I) to native metal and ring closure to the imide. During the cure silver atoms/clusters aggregate in part at the surface to give reflective films, usually with excellent adhesion of metal to polyimide.

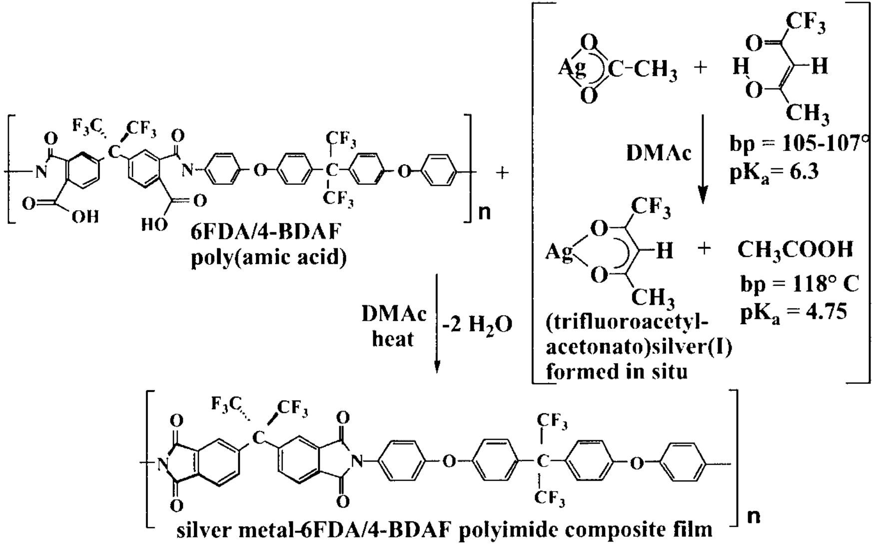


Figure 1. Synthetic route to a polyimide metallized film.

For present study described herein we chose the 6FDA/4-BDAF polymer because it has been reported to have high thermal stability, radiation resistance, and low absorption in the visible [14]. The low color of this polyimide is of importance since in previous studies of metallized polyimides exhibit a thin polyimide overlayer or significant polyimide at the surface. Since tradition polyimides such as PMDA/ODA, BTDA/ODA, BPDA/ODA, etc. absorb strongly in the visible, some of the loss of reflectivity has been due to surface polymer absorption.

EXPERIMENTAL DETAILS

Materials. All chemicals were obtained from commercial sources. 6FDA/4-BDAF poly(amic acid) solution was prepared with a 0.5% offset of dianhydride at 15% solids (w/w) in DMAc. The resin was stirred for 5 h. The inherent viscosity was 1.2 dL/g at 35° C.

Preparation of BTDA/4,4′-ODA metallized films. Ag(I)-containing solutions were prepared by first dissolving silver(I) acetate in DMAc containing trifluoroacetylacetone. The 15% poly(amic acid) solution was then added to give the desired Ag to polymer ratio. Doped poly(amic acid) solutions were cast as films onto glass plates using a doctor blade set at 500-650 µm to obtain cured films 20-25 µm thick. After remaining in an atmosphere of slowly flowing dry air for 18 h, the films were cured in a forced air oven. The cure cycle involved heating over 20 min to 135 °C and holding for 1 h, heating to 300 °C over 4 h, and holding at 300 °C varying times.

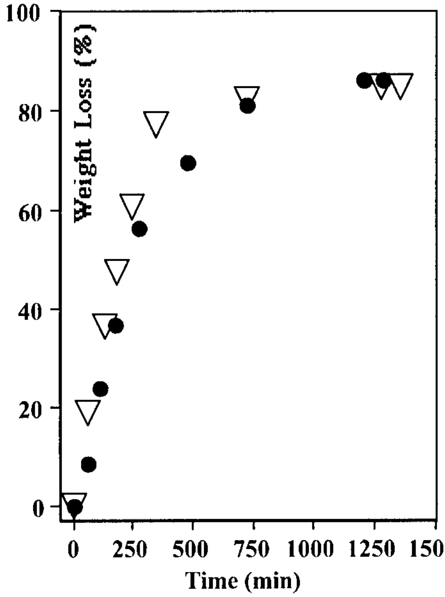
RESULTS AND DISCUSSION

As seen in Figure 2, poly(amic acid)-DMAc or diglyme (2-methoxyethyl ether) films retain a substantial portion of solvent which cannot is not lost by evaporation at 25 °C. Thus, thermal cure of Ag ion-doped films occurs in a solvent rich state; the solvent then may play a role in metal ion reduction and also serve as a plasticizing agent. Figure 3 shows the development of reflectivity as a function of time/temperature for 8 and 13 wt% silver-6FDA/4-BDAF polyimide films. For the 8% film maximum reflectivity is observed after 2 h at 300 °C. The 13% film achieves maximum reflectivity after only 1 h at 300 after which the reflectivity diminishes dramatically due to metal promoted oxidative degradation of the polyimide. The observed reflectivities (relative to an optical Al mirror) are high and do not show a strong concentration dependence (8 versus 13%). The metal is firmly adhered to the polyimide and cannot be removed by adhesive tape test protocols.

Figure 4 displays TEM data for the 13% film. The surface silver is ca. 80 nm thick and composed of particles of globular shape. The bulk of the film contains silver particle with sizes in the 5-20 nm range. Thus, only a limited quantity of the original silver appears at the surface. While the 8 and 13% films have excellent reflectivity, neither is electrically conductive. The SEM for the 13% film (Figure 5) shows the globular form of the silver particles and reveals that the particles do not form a continuous network. Intervening polyimide keeps the nanoparticles effectively isolated.

While significant reflectivity for the two films is not observed until 300 °C, X-ray data shown in Figure 6 for the 13% films make clear that reduction to silver metal is occurring at temperatures as low as 175 °C. Thus, sufficient silver aggregation at the surface to form a mirror is much slower than silver(I) reduction. Interestingly, the early low temperature silver reflections are significantly broadened which is consistent with Scherrer broadening due to very small nanometer-sized particles. As curing temperature and time increase the reflections narrow with the larger particle sizes seen in the TEM and SEM at 300 °C for 1 h.

The metallized exhibited tensile moduli and strength which are not significantly different from those of the parent polyimide. This is consistent with the relatively low concentration of silver metal and with the fact that silver is a passive metal which does not interact strongly with polyimide functional groups. Thus, the metallic silver particles appear to behave as a inert nano-filler in the polymer. The glass transition temperature in the metallized films is unchanged from that of the parent. However, while thermal stability remains high, the temperature at which there is 10% weight loss in air is *ca.* 125 °C lower than for the parent polyimide. In nitrogen the thermal stability is the same as the parent indicating that silver metal, as expected, catalyzes polyimide degradation at higher temperatures.



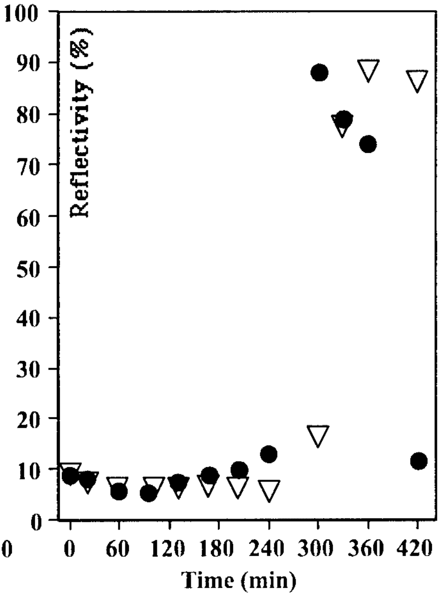


Figure 2. (Left) Evaporative solvent loss (DMAc-circle and diglyme-triangle) as a function of time under slowly flowing dry air.

Figure 3. (Right) Specular reflectivity as a function of time and temperature for 8% (triangle) and 13% (circle) silver-6FFDA/4-BDAF films

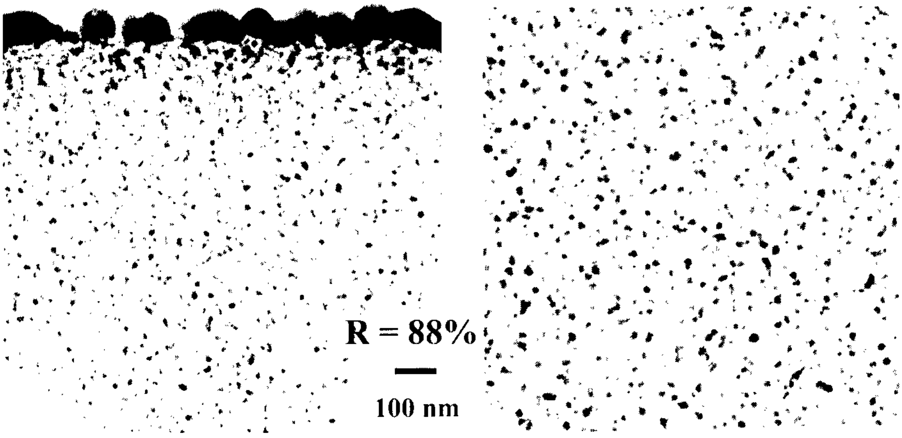
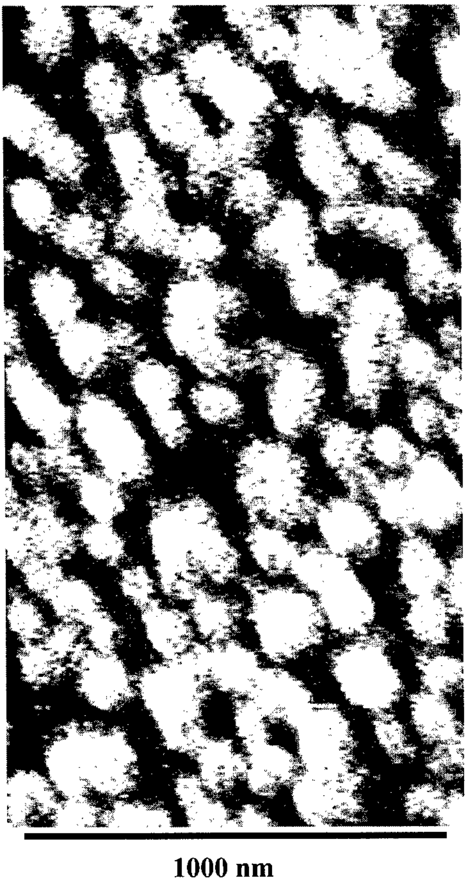


Figure 4. TEM micrographs for the 13% silver-6FDA/4-BDAF film cured to 300 °C for 1 h. Left - surface view; Right - bulk view.



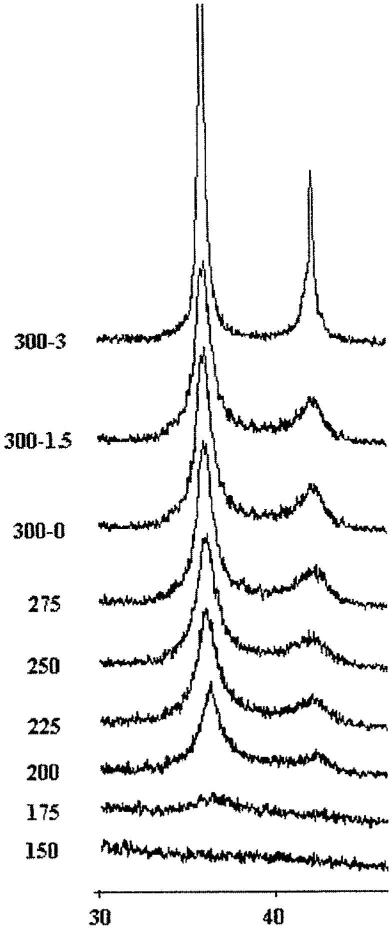


Figure 5. (Left) SEM micrograph for the 13% silver-6FDA/4-BDAF metallized film cured to 300 °C for 1 h.

Figure 6. (Right) X-ray reflections for a series of 13% silver-6FDA/4-BDAF metallized films as a function of cure temperature and time. The abscissa is in units of two theta; the ordinate is the temperature in °C at which the sample was withdrawn from the oven; at 300 °C samples where withdrawn after 0, 1.5, and 3 h. (See experimental section for cure cycle details.)

CONCLUSIONS

Silver surface-metallized films with high reflectivities can be prepared from AgTFA with the fluorinated polyimide 6FDA/4-BDAF in a thermally promoted single-stage process. These metallized films are not electrically conductive. Metal-polyimide adhesion is excellent, and thermal and mechanical properties of the composite films remain near those of the parent polymide.

ACKNOWLEDGMENT

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REFERENCES

1. Matienzo, L. J.; Unertl, W. N. "Adhesion of Metal Films to Polyimides,"in *Polyimides: Fundamental and Applications*, ed. Ghosh, M. K.; Mittal, K. L., Marcel Dekker, New York, 1996. pp. 629-696.
2. Gierow, P. A. in *Proceedings of the ASME-JSME-JSES Solar Energy Conference*: Reno, NV, 1991; pp 1-7.
3. Ehricke, K. in *Meeting of the American Rocket Society*: Cleveland, OH, June 18-20,1956; pp ARS paper 310-56.
4. Gulino, D. A.; Egger, R. A.; Bauholzer, W. F. *NASA Technical Memorandum 88865*, **1986**.
5. Naval Research Laboratory, "Solarcon - Concentrator Reflector System," described online: code8200.nrl.navy.mil/solarcon.html.
6. Freeland, R. E.; Bilyou, G. in *43rd Congress of the International Astronautical Federation, IAF-92-0301*: Washington, D.C., 1992
7. McInnes, C. R. *Solar Sailing Technology: Dynamics and Mission Applications*, Springer-Verlag, London, 1999.
8. Garner, C.; Diedeich, B.; Leipold, M. A Summary of Solar Sail Technology Developments, *AIAA/ASME/SAE/ASEE, 35th Joint Propulsion Conference and Exhibit*, Los Angeles, CA, June 21-23, 1999. Available online: techreports.jpl.nasa.gov
9. Southward, R. E.; Stoakley, D. M. *Progress in Organic Coatings*, **2001**, *41*, 99-119 and references therein.
10. Rubira, A. F.; Rancourt, J. D.; Taylor, L. T.; Stoakley, D. M.; St. Clair, A. K. *J. Macromolecular Sci., Pure and Applied Chemistry* **1998**, *A35*, 621-636 and references therein.
11. Jorgensen, G.; Schissel, P. in *Metallized Plastics*; Mittal, K. L.; Susko, J. R., eds.; Plenum: New York, 1989; Vol. 2, pp 79-92.
12. Bower, G. M.; Frost, L.W. *J. Polym. Sci., A* **1963,** *1*, 3135.
13. Sroog, C. E.; Endrey, A. L.; Abramo, S. V.; Berr, C. E.' Edwards, W. M.; Olivier, K. L. *J. Polym. Sci., A*, **1965**, *3*, 1373.
14. Clair, A. K. S.; Clair, T. L. S.; Slemp, W. S. “Optically Transparent/Colorless Polyimides:” in *Recent Advances in Polyimide Science and Technology*; Weber, W. D., Gupta, M. R., eds.; Society of Plastic Engineers, Mid-Hudson Section: Poughkeepsie, 1987, pp.16-34.