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### Chemical Factors That Influence the Production of Conductive and/or Reflective Silver-Doped Polyimide Films

A. F. Rubira<sup>a</sup>; J. D. Rancourt<sup>b</sup>; L. T. Taylor<sup>b</sup>; D. M. Stoakley<sup>c</sup>; A. K. St Clair<sup>c</sup>

<sup>a</sup> Departamento de Quimica, Universidade Estadual de Maringa, Maringa, PR, Brazil <sup>b</sup> Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA <sup>c</sup> Materials Division, NASA Langley Research Center, Hampton, VA

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## CHEMICAL FACTORS THAT INFLUENCE THE PRODUCTION OF CONDUCTIVE AND/OR REFLECTIVE SILVER-DOPED POLYIMIDE FILMS

**A. F. Rubira**

Universidade Estadual de Maringa  
Departamento de Quimica, Av. Colombo 5790  
87020-900- Maringa-PR. Brazil

**J. D. Rancourt and L. T. Taylor\***

Virginia Polytechnic Institute and State University  
Department of Chemistry  
Blacksburg, VA 24061-0212

**D. M. Stoakley and A. K. St. Clair**

Materials Division  
NASA Langley Research Center  
Hampton, VA 23665

Key Words: Polyimide, Silver, Reflectivity, Conductivity

### ABSTRACT

Doping a poly(amide acid) resin with a silver containing additive (1,5-cyclooctadiene-hexafluoroacetylacetonato)-silver(I) [Ag(COD)(HFA)] resulted, after thermal cure, in either a highly reflective or highly electrically conductive polyimide film. The combination of monomers, which render films with low  $T_g$  ( $\sim 210^\circ\text{C}$ ), and contained sulfur, produced films with surface resistance in the range  $10^1$ - $10^3$  ohms. On the other hand, films with specular reflectivity (relative to a silver mirror) in the range of 65-48% were obtained using both high  $T_g$  polyimides and polyimides void of sulfur in the polyimide backbone with low  $T_g$ . Our understanding regarding the structure-property relationship on these polyimide films and also the characterization of the doped-films are discussed.

## INTRODUCTION

Polyimides have found numerous uses in such industries as aerospace and electronics [1, 2]. Polyimides, however, have shortcomings in certain potential applications [3]. The incorporation of metallic species into polyimides has been attempted in order to address some of these deficiencies. Silver is especially attractive in this regard since under appropriate conditions, the thermal stability and electrical conductivity of polyimide can be enhanced [4]. Furthermore, silver-coated polyimides have been proposed as candidates for mirrored surfaces in NASA's proposed dynamic power system [5].

Traditionally, polymers that contain a silver surface have been produced by either chemical vapor deposition, sputter technology, or lamination [6]. Better adhesion between the polymer substrate and silver has been predicted to occur if the polymer contained a donor group such as thioether to interact with the silver [7]. Sen *et al.* have used this idea in the synthesis of polymer immobilized nanoclusters of chromium and iron oxides. In this manner, a homogeneous distribution of nanoclusters in the cured polyimide matrix was generated [8]. Mazur *et al.* have used a deposition process to create a silver layer within a polyimide film [9, 10]. By adjusting the experimental variables, the location of the electrically conducting and reflective silver layer within the film could be changed. In another study, Huang *et al.* have prepared metallized plastics by reduction of polymer/AgNO<sub>3</sub> chelate films [11, 12].

For several years, we have taken a less traditional *in situ* approach in the preparation of both silver-coated and silver-incorporated polyimide films. The *in situ* process involved doping a pre-polyimide (e.g. polyamide acid) solution with an organometallic silver compound followed by a thermal cure of the cast film which promoted both imidization of the polymer and reduction of the silver compound to silver metal [13]. Unlike the more traditional approaches, good adhesion between the polyimide and silver (which appeared only on the air-side film surface) was observed. Unique properties were preliminarily shown to depend on the dianhydride-diamine combination. For example, when the dianhydride was 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride, a highly reflective silver surface was produced on the film. If the dianhydride was 4,4'-bis(3,4-dicarboxyphenoxy)-diphenyl sulfide, an electrically conducting silver-polymer surface resulted [14-16].

We now wish to report an extension of this study to other dianhydride-diamine combinations in order to see how changes in polyimide chemical structure influence the properties of silver-doped polyimides [17, 18]. Specifically, sulfur and

non-sulfur containing polyimides have been studied which exhibit glass transition temperatures close-to and far-removed from the temperature of imidization. Our discussion here will attempt to focus on those polyimide features that enhance the production of either silver-containing reflective films or silver-containing surface conductive films.

## EXPERIMENTAL

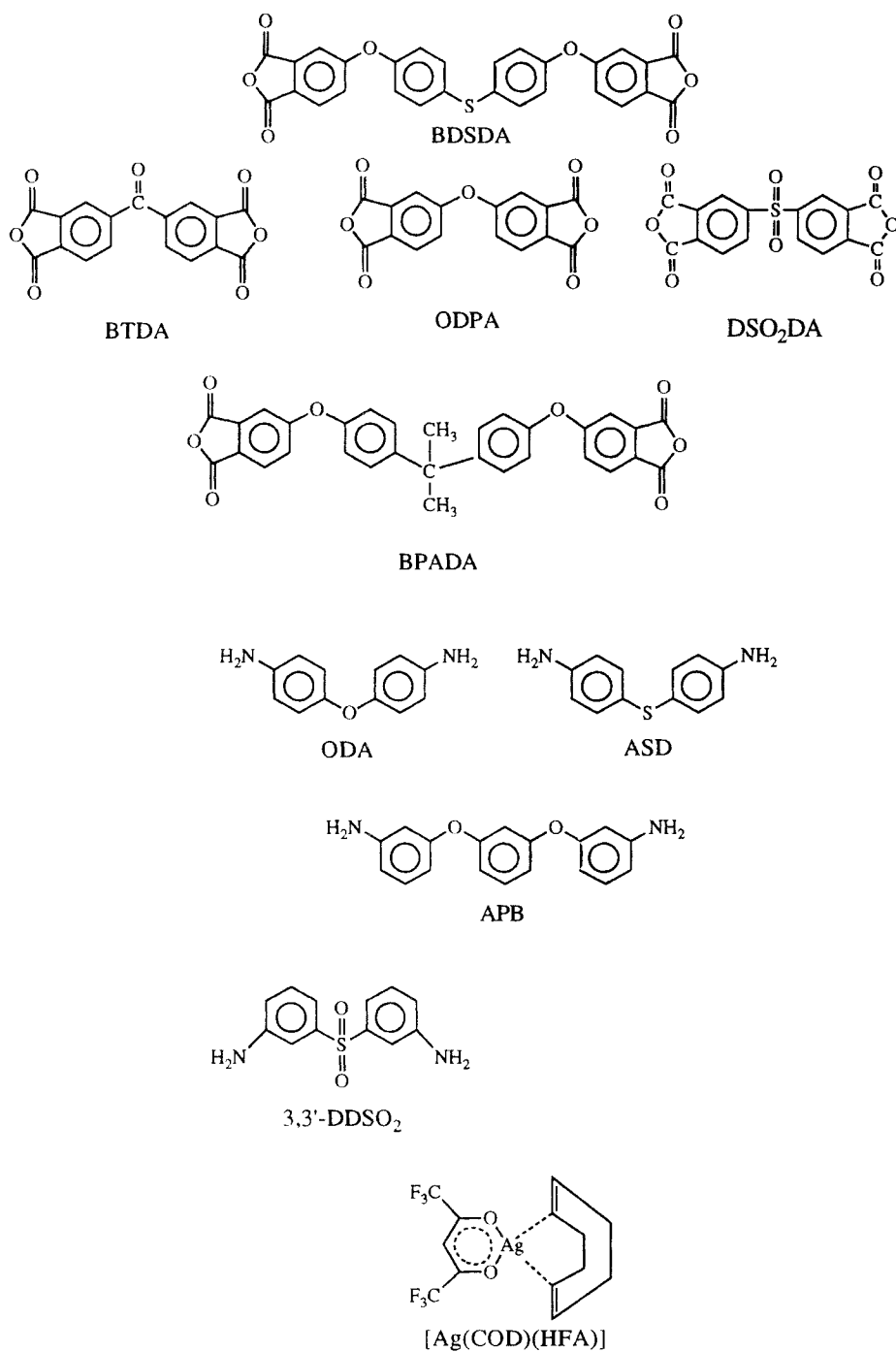
### Chemicals

The following monomers (Figure 1) and purification procedures<sup>1</sup> were used in this study: (a) 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA), Chriskev Inc. (Leawood, KS) vacuum dried overnight at 110°C; (b) 4,4'-bis(3,4-dicarboxyphenoxy) diphenyl sulfide dianhydride (BDSDA) NASA Langley Research Center (Hampton, VA), recrystallized twice from 2-butanone, and vacuum dried overnight at 120°, (c) 4,4'-oxydiphthalic anhydride (ODPA), (d) 3,3',4,4'-diphenylsulfonetetracarboxylic acid dianhydride (DSO<sub>2</sub>DA), (e) bisphenol A dianhydride (BPADA) General Electric (Schenectady, NY) vacuum dried overnight at 120°C; (f) 4,4'-oxydianiline (ODA), Chriskev Inc. (Leawood, KS) sublimed at 185°C and less than 1 torr pressure then vacuum dried at 70°C, overnight; (g) 4,4'-diaminodiphenyl sulfide (ASD), Chriskev Inc. (Leawood, KS) vacuum dried at 80°C overnight; (h) 1,3-bis(aminophenoxy) benzene (APB), Mitsui-Toatsu Inc. (Tokyo, Japan) vacuum dried overnight at 70°C, and (i) 3,3'-diaminodiphenyl-sulfone (3,3'DDSO<sub>2</sub>), Chriskev Inc. (Leawood, KS) vacuum dried overnight at 70°C. N,N-Dimethylacetamide (DMAC) was obtained from Aldrich Chemical Co. (Milwaukee, WI) in a Sure-Sealed bottle under N<sub>2</sub>. The silver additive (1,5 cyclo-octadiene hexafluoro-acetylacetonato) silver(I) [Ag(COD)(HFA)] was obtained from Aldrich Chemical Co. (Milwaukee, WI) and was used as received. The dopant was stored in the dark in a refrigerator. The additive structure is also shown in Figure 1.

### Synthesis

Poly(amide acid) solutions were synthesized at room temperature by first adding diamine (4.0 mmol) to a nitrogen-purged glass bottle containing 30 mL of dry DMAC. Next, dianhydride (4.0 mmol) was added to the diamine with an additional 30 mL of DMAC. The resulting solution was stirred for 2 hours at room

<sup>1</sup>No additional data regarding the extent of purity of each monomer was obtained.



**Figure 1.** Monomers and additive used in this study.

temperature. Solid Ag(COD)(HFA) (0.5-2.0 mmol or 210 mg-840 mg) was then added to the pre-polymer solution with an additional 5 mL of DMAC, thereby resulting in a 10-20 wt% solids solution depending on the monomer combination. The silver containing poly(amide acid) solutions were then stirred for an additional 2 hrs. at room temperature. Films were next prepared by spreading the silver-containing poly(amide acid) solution (10-20 wt%) onto a clean, dust-free soda glass plate, using a doctor blade (16 or 20 mil gap), followed by heating 20 minutes at 80°C, then heating at 100, 200, and 300°C each for 1 hour under a dynamic (30 SCFH) atmosphere of dry breathing air (Air Products and Chemicals, Inc., Allentown, PA). The surface of the film in contact with the soda-lime glass plate during imidization is referred to as the glass side, while that in contact with the atmosphere of the curing oven is referred to as the air side.

### Measurements

Thermal analysis for the purpose of determining glass transition temperature was performed on a Perkin Elmer Model DSC-4 differential scanning calorimeter at 10°C/min heating rate under a nitrogen atmosphere. To determine the polymer decomposition temperature (PDT), thermogravimetric analysis was performed with a Perkin Elmer Model TGS-2 thermogravimetric system at 10°C/min heating rate in a dynamic air or nitrogen atmosphere. A Polymer Laboratories MK II dynamic mechanical thermal analyzer (DMTA) that was equipped with a bending/shear head was also employed.

X-ray photoelectron spectra (XPS) were obtained via a Perkin-Elmer Phi Model 5300 ESCA system. A magnesium anode ( $K\alpha=1253.6$  eV) operating at 400 W was used. The samples were attached to mounts by double-stick tape. The binding energies cited have been referenced to the polyimide aromatic carbon photoelectron transition (C 1s) at 284.6 eV. Scanning electron micrographs (SEM) were taken with an ISI Model SX-40 scanning electron microscope. The samples were attached to mounts by double-stick tape and were coated with a thin layer of gold in order to dissipate charge. Transmission electron micrographs (TEM) were taken with a Phillips Model 420 transmission electron microscope. Samples were imbedded in Polyscience ultra low viscosity epoxy medium and were cured for 8 hours at 70°C. Using a Reichert-Jung ultramicrotome with a microstar diamond knife, cross sections (500-800 Å) of the samples were obtained. These sections were placed on 200 mesh copper grids prior to analysis. Surface electrical resistance at room temperature was measured using Keithley equipment consisting of a voltage supply (model 240A), electrometer (model 617 C), and a four point probe

TABLE 1. Characteristics of Ag(COD)(HFA) Doped Polyimide Films.<sup>d</sup>

Polymer	Appearance		T <sub>g</sub> (°C)		% Reflectivity (at 20°, 531 nm) <sup>e</sup>	Surface Resistance (Ohms) <sup>f</sup>
	air side	glass side	On doped	Doped		
BTDA-ODA <sup>a</sup>	Silvery	Brown	270	265	65.2±0.8	>10 <sup>11</sup>
BTDA-ASDA <sup>a</sup>	Silvery	Tan	270	270	55.0±1.2	>10 <sup>11</sup>
ODPA-ODA <sup>b</sup>	Opaque	Brown	264	268	48.5±1.2	>10 <sup>11c</sup>
DSO <sub>2</sub> DA-ODA <sup>c</sup>	Silvery	Tan	273	268	52.7±1.8	>10 <sup>11c</sup>
BSDA-ODA <sup>a</sup>	Opaque	Red	214	221	3.9±2.1	3-20
BSDA-ASDA <sup>a</sup>	Opaque	Red	218	221	4.2±1.9	10 <sup>4</sup>
BPADA-ODA <sup>c</sup>	Silvery	Tan	219	227	54.6±1.8	>10 <sup>11</sup>
BPADA-ASDC <sup>c</sup>	Opaque	Green	217	225	4.8±1.9	10 <sup>4</sup>

<sup>a</sup>Reference 13

<sup>b</sup>Reference 14

<sup>c</sup>Reported here for first time

<sup>d</sup>Mole ratio (monomer:dopant) was 2:1

<sup>e</sup>Relative to an optical mirror which was used as a 100% reflectivity standard.

<sup>f</sup>Four-point probe assembly.

assembly. Surface reflectivity measurements at 531 nm relative to a silver mirror were performed on a Perkin-Elmer Lambda 5 UV-VIS spectrophotometer equipped with a variable-angle reflectance accessory. Measurements were taken at a 20° angle.

## RESULTS AND DISCUSSION

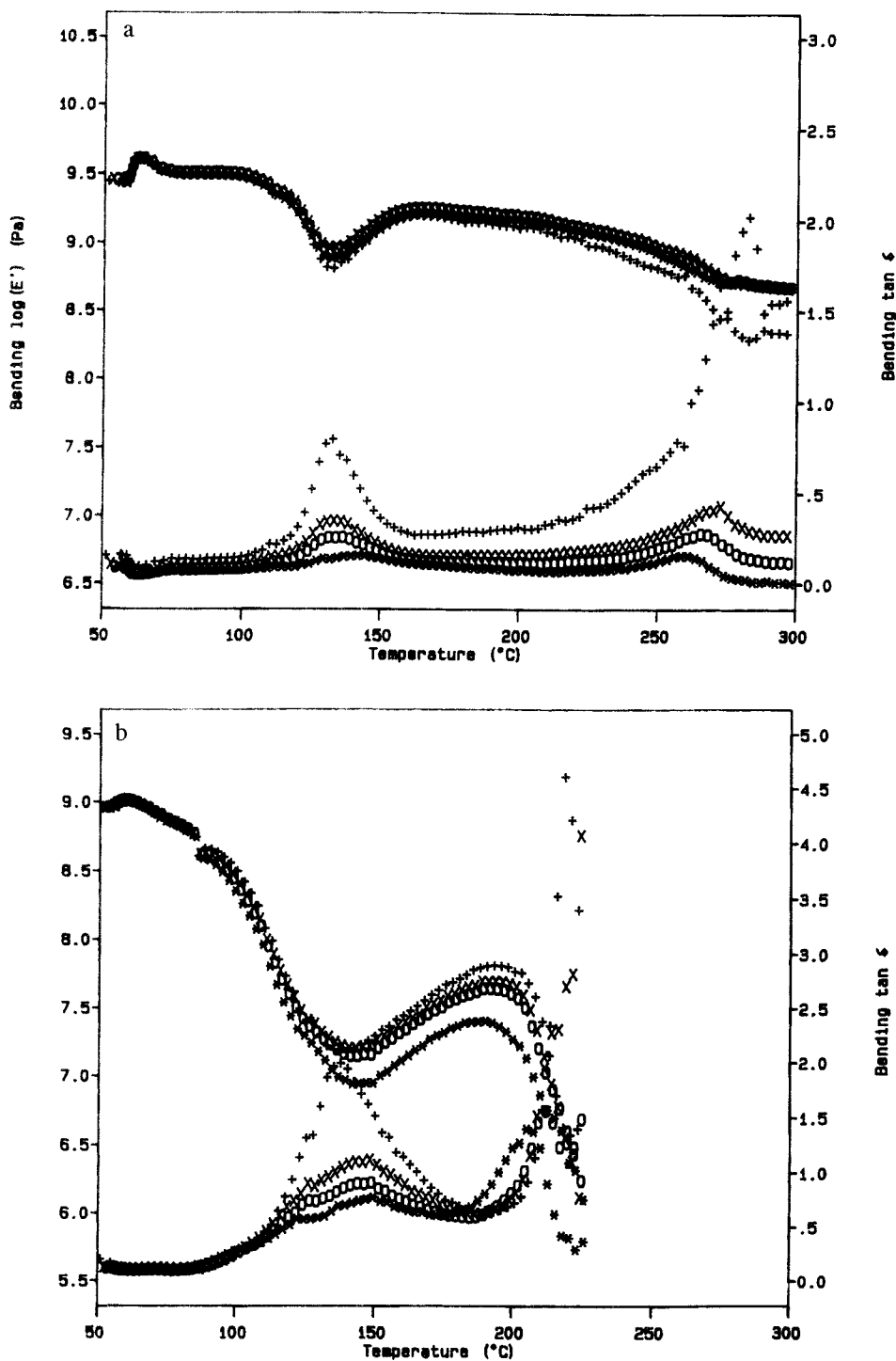
In our previously reported studies with Ag(COD)(HFA) and selected polyimides, we postulated that electrically conductive films would result if the polyimide exhibited low T<sub>g</sub> (~200°C) and contained sulfur. Furthermore, we hypothesized that specular reflective films would result if sulfur were absent in the polyimide

regardless of the  $T_g$ . Additional combinations of diamines and dianhydrides have now been researched in order to provide support for our postulates. The new silver-doped films and their general characteristics are shown in Table 1. They are ODPA-APB, DSO<sub>2</sub>DA-ODA, BPADA-ODA, and BPADA-ASD. Only the later film which contained sulfur and exhibited a low  $T_g$  proved to be electrically conductive. True to our postulate the three remaining films were specular reflective. They either exhibited high  $T_g$  and contained sulfur or exhibited low  $T_g$  and contained no sulfur.

Reflectivity and surface electrical conductivity data on both the new and previously reported silver-doped polyimide films are also shown in Table 1. One can see that doped polyimide films containing BTDA showed better optical properties than other dianhydride systems (e.g. BDSDA, DSO<sub>2</sub>DA, ODPA and BPADA). The best reflective film was obtained with a combination of BTDA and ODA. On the other hand, BDSDA-derived films yielded an opaque conducting surface and a low reflectivity (4%) regardless of the diamine. Silver-doped BPADA-ASD films were also cloudy but surface resistance was approximately 10<sup>4</sup> ohms although when the surface was rubbed with tissue paper the film surface resistance dropped to nearly 50 ohms. On the other hand, BPADA-ODA which contained no sulfur yielded a reflective surface when doped with Ag[COD][HFA].

In order to better understand the influence of  $T_g$ , sulfur content, and dopant concentration on film properties, we carried out XPS, TEM, and DMTA (see Experimental) measurements. Reflective and conductive films exhibited differences in DMTA measurements taken during the curing process of the resin precursor (e.g. polyamide acid). BTDA-ODA poly(amide acid) resin was studied as a representative example of a reflective film. It showed a behavior characterized by solvent decomplexation at 115°C and a precipitous drop in modulus apparently due to an abrupt plasticization. At 142°C, the modulus increased again due to the combined effects of solvent evaporation and imidization. Near 270°C, a small drop in modulus was observed which was attributed to the glass transition of the polyimide. The behavior of the BDSDA-ODA poly(amide acid) resin (i.e. representative of a conductive film) under the same conditions differed significantly (Figure 2b). The precursor softened continuously thus allowing the evaporation of solvent until 140°C. At around 150°C, the modulus started increasing smoothly due to the combined effects of solvent evaporation and imidization to 200°C. At this point a sharp drop in modulus occurred which was attributed to the glass transition of the polyimide. Compared to BTDA-ODA, the overall temperature width of this last





**Figure 2.** Storage modulus and  $\tan \delta$  vs. temperature obtained by DMTA of the thermal cure of a) BTDA-ODA and b) BDSDA-ODA poly[amide acid] [ $+ = 20$ ;  $x = 10$ ;  $0 = 5$ ;  $* = 1$  Hz].

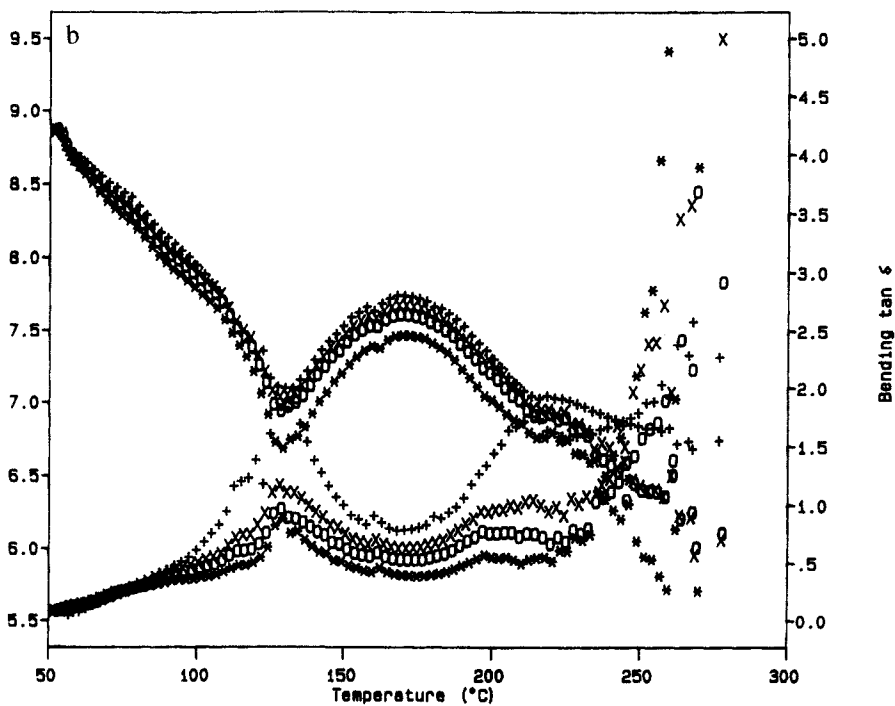
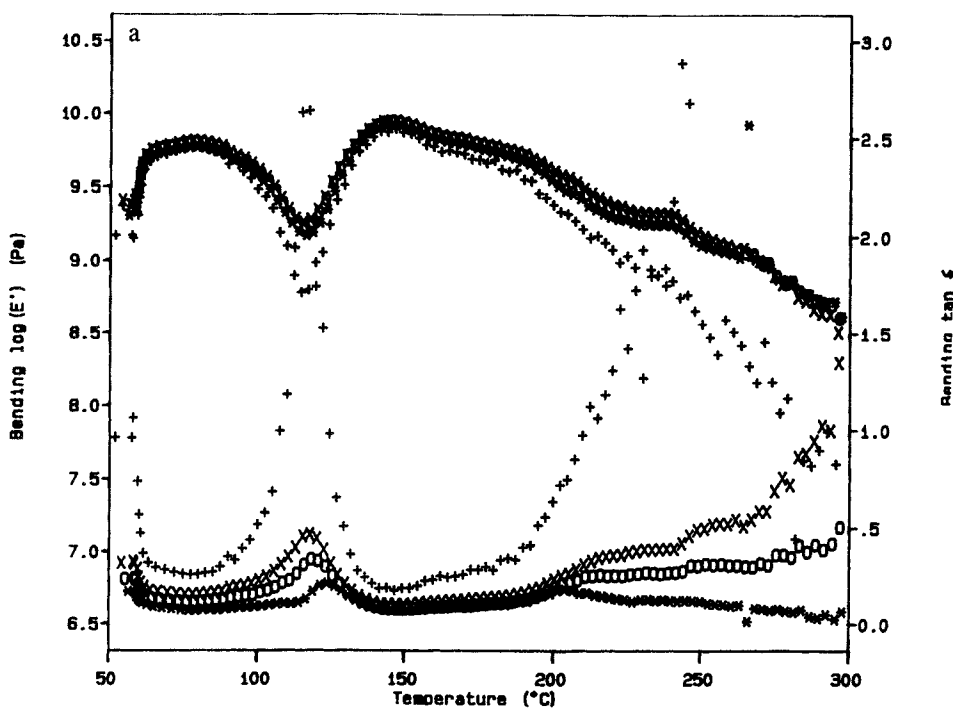
step was much broader and the softening which was attributed to the glass transition of the polyimide was more prominent.

The curing behaviors of silver-doped precursor resins are shown in Figures 3a and 3b. Basically they showed similar behavior as the non-doped precursors except they softened at a lower temperature. Based on the data discussed above, we can postulate that migration of the silver additive occurs rapidly in the highly flexible state, which is more favorable with BDSDA derived films, since they have a glass transition temperature near the solvent evaporation/imidization step temperature.

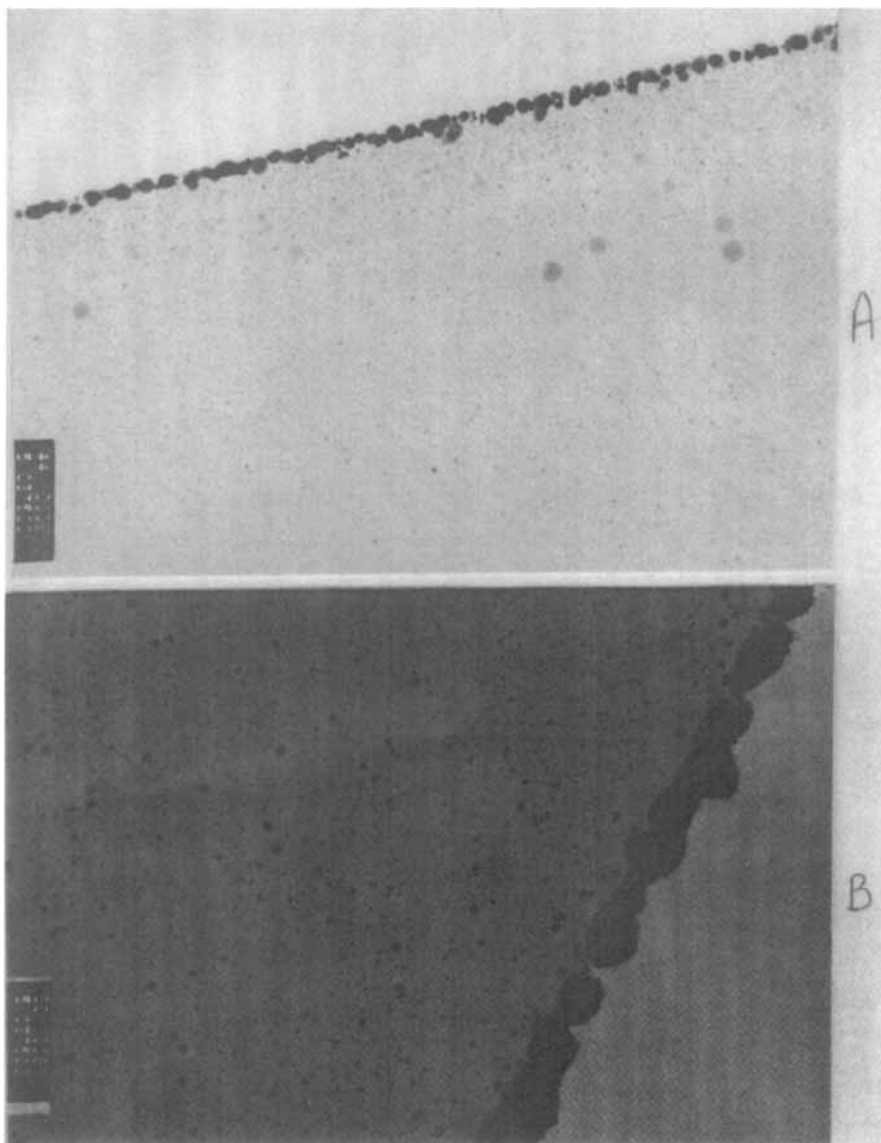
Transmission electron micrographs were obtained on a conductive (BDSDA-APB) and a reflective (BTDA-APB) film. The reflective film (Figure 4a) exhibited a well defined surface layer of uniform sized Ag particles. On the other hand, the conductive film (Figure 4b) had a surface layer of nonuniform sized silver particles. The transmission electron micrograph of silver-doped BDSDA film illustrated a much higher density of particles, and the surface layer had a less discontinuous surface since particles were smaller and better intermixed with polyimide. Views of the cross-sectional area of silver-doped BPADA-ODA show a well defined surface layer of silver particles, similar to other silver-doped reflective polyimide films [14]. BPADA-ASD conductive film had a surface layer of nonuniform sized silver particles similar to conductive BDSDA-derived films [16].

To ascertain the chemical state and surface elemental composition of the silver-doped films, X-ray photoelectron spectroscopy (XPS) measurements in conjunction with argon ion etching were made on reflective (BTDA-derived) and conductive (BDSDA-derived) films. The atomic concentration of silver was fairly constant for both types of polymer films regardless of the mole ratio of monomer to dopant. Approximately 30% less silver appeared on the surface of the film, however, when the ratio was 8:1 as opposed to ratios of 2:1 and 4:1. The same trends were found using variable XPS photoelectron take-off angles (e.g. 15°, 45°, and 90°). It is noteworthy that both silver and polyimide nitrogen were detected on the surface which suggests that either the silver layer is not continuous or there is intermixing of silver and polyimide on the surface. If the latter assumption is correct, then the depth to which this intermixing occurs would be of interest.

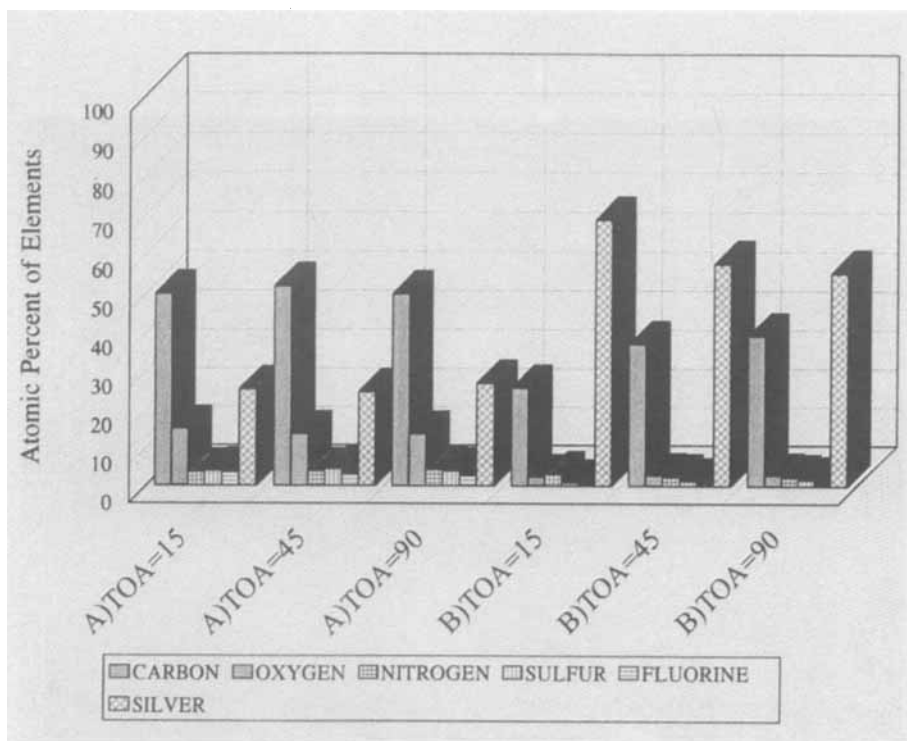
To determine if the intermixing between polymer and silver was constant in the films, surface sputtering with argon ion etching for 10 minutes (~5 Å/min.) was done on conductive BDSDA-ASD films in conjunction with Auger electron spectroscopy at different take-off angles (Figure 5). The silver concentration was higher at a take-off angle of 15° than 45° and 90°. Results obtained after sputtering reflective BTDA-ODA films also showed a similar increase in silver signal. These



**Figure 3.** Storage modulus and  $\tan \delta$  vs. temperature obtained by DMTA of the thermal cure of silver-doped a) BTDA-ODA and b) BDSDA-ODA poly(amide acid) (+=20; x=10; o=5; \*=1 Hz).



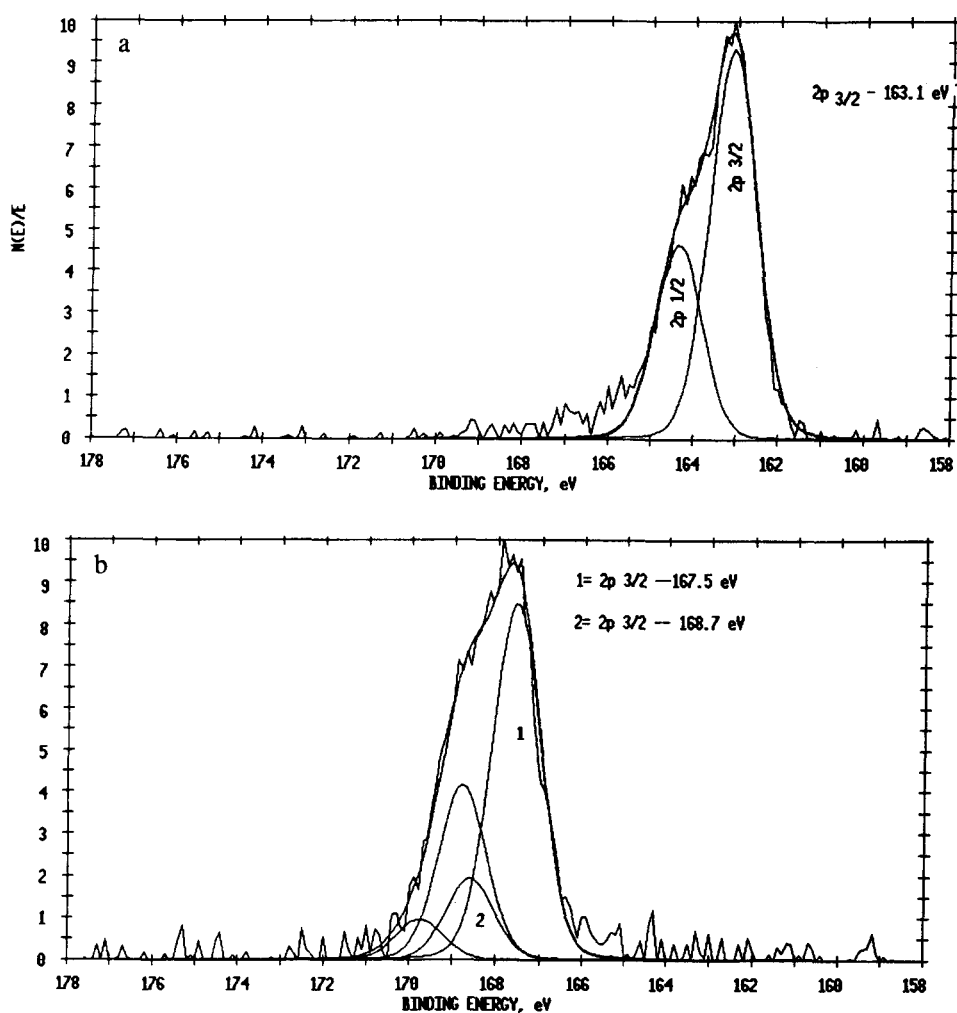
**Figure 4.** Transmission electron microphotographs of silver-doped A) BTDA-APB and B) BDSDA-APB. 2:1 mole ratio monomer:dopant, magnification 65,625x.



**Figure 5.** Relative atomic concentration of silver-doped BDSDA-ASD film with 2:1 mole ratio monomer:dopant at different take-off angle (TOA), before (A) and after (B) 10 minutes of ion argon sputtering.

results suggest that the silver concentration is approximately 100% greater at the sub-surface as opposed to the “true” surface since the atomic concentration of silver is approximately 100% greater after sputtering regardless of the take-off angle.

Evaluation of the sulfur 2p photopeaks in the silver-doped BPADA-ASD film suggested the presence of a new sulfur specie which was not observed in the polyimide alone (Figure 6). Specifically new peaks were seen at 167.9 and 168.5 eV (Figure 6a) in addition to the expected functionality at 163.3 eV (Figure 6b) (19-21). The new sulfur signals are believed to be indicative of a sulfone/sulfate moiety. As there is not a sulfone/sulfate peak detected in the undoped sulfur-containing polyimide film, it is proposed that thioether oxidation promoted by silver has occurred. Similar observations have been made by Ellison *et al.* (22) in iron-doped BDSDA-ODA films and by Gerenser *et al.* (20) with silver and poly(p-phenylene sulfide).



**Figure 6.** Sulfur 2p XPS photopeaks of the air side of a) BPADA-ASD and b) silver-doped BPADA-ASD.

We summarize here our findings with representative reflective and conductive films. The surface layer on the air side of silver-doped BTDA-derived films has more uniform sized particles than the other silver-doped polyimide films. BTDA-ODA films with mole ratio [monomer:dopant] of 2:1 also exhibited a cluster of silver particles near the glass side surface. These silver clusters were not present in the same proportion and with the same dimension as other BTDA-ODA films of a different mole ratio. In contrast, BTDA-ASD films with mole ratio

(monomer:dopant) of 2:1 showed a better distribution of metal particles within the polymer, and the uniformed size particles on the surface were 1.5 times bigger than the BTDA-ODA case. On the other hand, the BDSDA-derived films (2:1 and 4:1 mole ratio, monomer:dopant) had no clusters within the film, and the surface was composed of nonuniform sized, larger particles bonded together which no doubt accounts for the lower electrical resistance of these films. The 8:1 mole ratio (monomer:dopant) BDSDA-ODA film had a metal distribution on the surface and within the bulk polymer that was similar to BTDA-derived films. It showed reflectivity around 48% which was a value near to that for the 8:1 mole ratio (monomer:dopant) BTDA-ODA film. The new BPADA-ODA film exhibited properties which were similar to BTDA-derived films since it had a high surface resistance ( $>10^{11}$  ohm) and a high ( $\sim 55\%$ ) reflectivity. The opposite behavior was found for the new silver-doped BPADA-ASD film which showed low optical reflectivity ( $\sim 5\%$ ) and relatively low ( $10^4$  ohm) electrical conductivity properties similar to the BDSDA-derived films.

## CONCLUSION

Silver-surfaced polyimide films with either high reflectivity or low electrical resistance can be obtained with different combinations of dianhydride and diamine. In order to obtain electrically conductive films, dianhydride and diamine combinations that yield low  $T_g$ , contain sulfur, and exhibit a monomer:dopant mole ratio of no greater than 4:1 must be used. Reflective films can be obtained when polyimides with high  $T_g$ , regardless of the presence of sulfur and also with low  $T_g$ , but with no sulfur were utilized.

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