A Comparison of Physical and Mechanical Properties of Polyimide Films Containing Different Metal Ions

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Synopsis

Metal ions have been incorporated into linear polyimide films in order to improve the potential of these materials for applications in space. Various metals such as Al, Pd, Ag, Au, and Sn in a variety of chemical states were added to a polyamic acid prepared from 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride and 4,4′-oxydianiline. Films of the metal ion-filled polyamic acids were prepared and cured to the corresponding polyimides by heating at 300°C in air. The cured films were characterized for such properties as glass transition temperature, electrical conductivity, and thermal stability. Modulii and tensile strengths of the metal-containing polyimide films were obtained at both ambient and elevated temperatures. Comparison of the physical and mechanical properties of these polyimide films as a function of metal additive is made.

INTRODUCTION

Modification of the physical and chemical properties of polymers is a broad and rapidly expanding area of science.[1] The doping of polymers with nonmetal or metal additives constitutes one method whereby the properties of a specific polymer might be modified. The polymers which have received the most study in this regard contain no ionizable groups and include polyamides, polyimides, poly(alkylbenzimidazoles), poly(vinyl alcohol), polyethers, polyesters, polyacetylene, poly(*p*-phenylene), polyethylene, and poly(methylphenylsiloxane). Nonmetal dopants such as oxygen, iodine, and AsF_5 have been investigated with "poly(hydrocarbons)." Metals, metal salts, metal complexes, and organometallic compounds have been primarily employed with heteroatom containing neutral polymers. The latter phase of this area of research has been recently reviewed.[2] From the very limited number of studies available, it is quite apparent that metallic additives can have a profound effect on polymer properties. Different metals as well as different additives of the same metal can induce a variety of physical and chemical changes in a given polymer. Subtle differences in the polymer backbone can even significantly alter the metal dopant effect for a certain class of polymers. Needless to say, the modification of polymer properties via metal incorporation justifiably requires additional study.

Palladium[3–6] and lithium[7] containing polyimide films have been recently prepared and partially characterized in our laboratory. Several combinations of dianhydride and diamine were studied and a number of palladium and lithium additives were screened. Best results todate have been obtained with Li_2PdCl_4, $Pd(S(CH_3)_2)_2Cl_2$, and LiCl and the polyimide derived from 3,3′,4,4′-benzophe-

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none tetracarboxylic acid dianhydride (BTDA) and 4,4′-oxydianiline (ODA). Electrical resistivity lowering was realized in several films; however, this phenomenon was found to depend on numerous factors such as the monomer combination, the particular additive, the imidization atmosphere, and surface moisture on the film. In another study,[8,9] aluminum ion addition to the polyimide derived from BTDA and 3,3′-diaminobenzophenone (DABP) has been shown to improve high temperature adhesive properties of the polyimide with respect to bonding titanium surfaces. Thermal and mechanical properties of these high quality doped BTDA–ODA thin films have not been extensively explored.

In this regard, we wish to describe the evaluation of BTDA–ODA polyimide films containing the following metal ions: Al(III), Pd(II), Ag(I), Au(III), Sn(II). A single additive for each metal was employed. The specific compound was chosen because of its ready availability; however, it may not necessarily be the best dopant for that particular element. Our emphasis here will be on the gross comparison of several metals with a particular polyimide. A determination of electrical, mechanical, and thermal properties for each film will serve as our approach in this evaluation. The importance of this study, aside from its fundamental interests, rests on the potential of these materials as applicable high temperature films and coatings for the aerospace and electronics industries.

EXPERIMENTAL

Materials. 3,3′,4,4′-Benzophenone tetracarboxylic acid dianhydride (BTDA) was obtained from commercial sources and purified by sublimation at 215°C at less than 1 torr, melting point 558°K. 4,4′-Oxydianiline (ODA) was obtained from commercial sources and purified by recrystallization. *N,N*-dimethylacetamide (DMAC) was obtained from Burdick and Jackson and used as received. The solvent was reagent grade, distilled in glass, and packed under N_2. Lithium tetrachloropalladate(II) (Li_2PdCl_4) was prepared by a previously reported procedure.[10] All other chemicals [$Al(acac)_3$, $AgNO_3$, AuI_3, $SnCl_2 \cdot 2H_2O$ were of reagent grade or equivalent and were obtained from commercial sources.

Polymerization. Polymerizations were carried out in solutions containing 20% solids (w/w) by adding diamine (0.005 mol) and DMAC to a flask flushed with dry nitrogen. The appropriate dianhydride (0.005 mol) was then added as a solid in a single portion and the solution was stirred at room temperature for 8–24 h. At this point the appropriate metal complex or salt (0.001 mol) was either added directly or added as a solution in a minimum amount of DMAC to the polyamic acid–DMAC solution. In most cases polymerization conducted *in situ* with the appropriate metal complex gave similar results.

Preparation of Films. Polyamic acid–metal dopant solutions were poured onto soda-lime glass plates. Solutions were spread using a doctor blade with a 8–16 mil gap to insure a final film thickness of approximately 1 mil. Films of the polyamic acid–metal dopant were dried in static air at 60°C for 2 h. Imidization was thermally achieved by heating in a forced air oven 1 h each at 100°C, 200°C, and 300°C. Polyimide–metal dopant films were removed from the glass plate by soaking several hours in warm water.

Characterization. Thermochemical analyses (TMA) were performed on

films in static air at a 5°C/min temperature program on an E. I. DuPont Model 990 Thermomechanical Analyzer. Thermogravimetric analyses (TGA) were obtained on films at 2°C/min in static air. Surface and volume resistivities were measured following the standard ASTM method of test for electrical resistance of insulating materials (D 257-66) employing a Keithley voltage supply, electrometer, and three-point probe. Film densities were measured by a density-gradient technique, ASTM D 1505-60T. Tensile testing of the polyimide films were performed on an Instron Universal Testing Instrument Model TT-6 according to ASTM Designation D 882-61T. Specimens were tested at a crosshead speed of 0.51 cm (0.2 in.)/min using a gauge length of 7.62 cm (3 in.). Elevated temperature testing at 200°C was conducted in an Instron Environmental Chamber wherein each film specimen was soaked for 10 min at temperature before testing. Young's modulus of films was obtained on an IMASS Autovibron Dynamic Viscoelastometer.

RESULTS AND DISCUSSION

Polyimides derived from 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA) and oxydianiline (ODA) containing metal compounds have been prepared. The synthetic procedure that was employed involved (1) formation of the polyamic acid (20% solids) in *N,N*-dimethylacetamide (DMAC), (2) addition of the metal complex to the polyamic acid in a 1:5 mole ratio, (3) fabrication of a film of the polyamic acid–metal dopant mixture, and (4) thermal conversion (300°C) of the polyamic acid to the metal containing polyimide. Five different metal dopants were employed: $Al(acac)_3$, Li_2PdCl_4, $AgNO_3$, AuI_3, and $SnCl_2 \cdot 2H_2O$. Each metal film retained the high flexibility characteristic of the polymer alone. Inherent viscosities of the polyamic acid solutions measured at 35°C ranged from 1.4 to 1.5, indicating formation of high molecular weight polymer. The apparent glass transition temperatures (T_g) of the metal-ion-containing films increased approximately 30–40°C compared to the polymer alone with the exception of the $SnCl_2$-containing film (Table I). The increased T_g's do not correlate with added metal content since the mol % (~9%) of each metal dopant was constant. T_g also does not follow the experimentally determined metal weight percentages. For example, T_g increases 29°C for $Al(acac)_3$

TABLE I
Properties of Metal/Polyimide Films

Polymer/metal film	T_g (°C)	Electrical resistivity: Volume (Ω-cm)	Electrical resistivity: Surface (Ω)	% Metal: Found	% Metal: Calcd[a]
Polymer alone	283	1.8×10^{16}	$>10^{18}$	—	—
Polymer + $Al(acac)_3$	312	1.2×10^{16}	$>10^{18}$	Al = 0.9	0.9
Polymer + $AgNO_3$	320	1.7×10^{16}	$>10^{18}$	Ag = 4.0	4.0
Polymer + Li_2PdCl_4	341	3.5×10^{10}	1.5×10^{9}	Li = 0.1	0.5
				Pd = 7.7	3.8
Polymer + AuI_3	320	7.5×10^{15}	$>10^{18}$	Au = 0.2	6.4
Polymer + $SnCl_2 \cdot 2H_2O$	283	2.9×10^{14}	2.4×10^{10}	Sn = 2.7	4.3

[a] Weight of metal added ÷ combined weight of monomers plus metal dopant less calculated weight of H_2O of imidization released.

TABLE II
Density of Films[a]

Polymer/metal film	Density (g/cc)
Polymer + polymer alone	1.3794
Polymer + Li_2PdCl_4	1.4410
Polymer + $AgNO_3$	1.4431
Polymer + $Al(acac)_3$	1.3880
Polymer + AuI_3	1.4116
Polymer + $SnCl_2 \cdot 2H_2O$	1.4160

[a] Measured at 23°C.

(% Al = 0.9) addition, whereas the T_g does not change for $SnCl_2$ (% Sn = 2.7) doping. Film densities (Table II) have been measured at 23°C; yet, correlation with T_g is again not obvious. It is interesting to note that, in general, film density increases with metal content by weight, albeit not in a linear fashion with Al and Au additives being the exception.

The noncorrelation of these properties with metal weight percentage suggests that these dopants are more than just inert fillers in the polyimide backbone. X-ray photoelectron spectroscopic data[11] suggest that Pd, Ag, and Au reside predominantly in the metallic state, whereas Li, Al, and Sn are ionic in their respectively doped polyimide. The presence of different ligands and/or counterions and their effect on these properties has not been considered. In addition to any coordinative interaction between metal and polymer, different metal species may influence the degree of polymerization and thermal curing of the polyimide, which in turn would probably affect film density and T_g.

While the softening temperature of these doped polyimides are in general greater, significant thermal stability has been sacrificed in the $AgNO_3$ and Li_2PdCl_4 cases (Fig. 1). Al, Au, and Sn, films possess excellent thermal stability, just as the polymer alone, as evidenced by their TGA profiles obtained in air. The lowered thermal stability of the $AgNO_3$ film may reflect the presence of the highly oxidizing nitrate ion. The film containing Li_2PdCl_4, of course, possesses

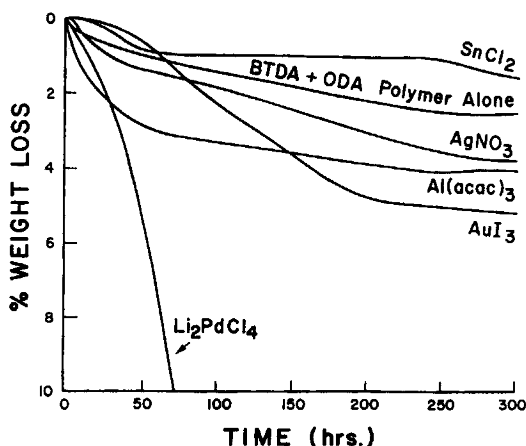

Fig. 1. Isothermal TGA's of metal/polyimide films (300°C in N_2).

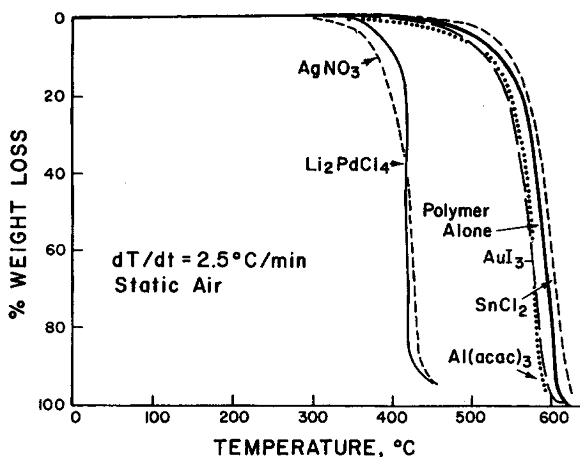

Fig. 2. Dynamic TGA of metal/polyimide films curved at 300°C in air.

two different metals as well as the highest metal weight percentage. Independent studies with Li dopants alone have shown reduced thermal stability over polymer alone; however, not to this extent. The Li_2PdCl_4 film exhibits infrared detectable moisture which may also enhance polymer decomposition.

These observations on thermal stability are further dramatized by isothermal measurements on these films. Originally all films were aged at 200°C for 300 h in an inert atmosphere, but none of them lost significant weight. This temperature was chosen because stability at 200°C is required for space applications. In order to observe differences in each film, accelerated aging experiments at 300°C were conducted. The Li_2PdCl_4 film was the only film that did not survive this environment (Fig. 2). Even though $AgNO_3$ and Li_2PdCl_4 films exhibit about the same polymer decomposition temperature by dynamic TGA, the $AgNO_3$ film is noticeably more thermally stable by isothermal TGA measurement (i.e., ~4% weight loss after 300 h).

Reflection upon these thermal properties and the preparative thermal curing process employed to prepare these films may reveal in part why several of these films have quite different metal percentages from the theoretical value (Table I). Au, Li, and Sn have a much lower metal content than calculated. No doubt vaporization of AuI_3, LiCl, and $SnCl_2$ occurs during imidization at 300°C in flowing air. The amount of Pd, on the other hand, is double what is predicted. The ready decomposition of the polyimide film when doped with Li_2PdCl_4 indicates that some polymer "breakdown" occurs during thermal imidization, thereby, raising the % Pd in the film. The curing process apparently affects neither the metal additive nor polymer in the presence of $AgNO_3$ and Al-(acac)$_3$.

Surface and volume resistivity measurements have been performed on films of polymer alone and polymer with dopant added (Table I). Special care was taken to insure that only films of uniformly high quality were measured. Only films containing $SnCl_2$ and Li_2PdCl_4 exhibited greatly reduced resistivities relative to the polymer alone. Why these dopants were effective is not entirely clear. Surface moisture on these films does appear to be more prevalent. The Li_2PdCl_4 film on drying in vacuum at 100°C also exhibits a significantly higher

TABLE III
Mechanical Properties of Metal/Polyimide Films (Instron Tensile Testing)

Polymer film	Test temp (°C)	Yield strength at 2% (psi)	Tensile strength (psi)	Tensile modulus (psi)	% Elongation
Polymer	RT	10,700	16,500	284,000	10
	200	5,900	6,800	178,000	26
Polymer +	RT	9,100	16,100	454,000	6
$Al(acac)_3$	200	6,000	7,900	257,000	6
Polymer +	RT	9,400	12,000	486,000	3
$AgNO_3$	200	4,500	8,300	215,000	4
Polymer +	RT	11,300	13,900	492,000	4
Li_2PdCl_4	200	7,700	10,600	336,000	5
Polymer + AuI_3	RT	10,000	19,100	494,000	8
	200	7,300	9,900	311,000	15

resistivity, which decreases on exposure to the laboratory atmosphere. Further work needs to be carried out on these dopants in light of the wide applicability of these materials as conductive space films, industrial films and coatings, and as a replacement for costly metal sputtering techniques.

Mechanical tensile properties of these metal-containing polyimide films have been measured and are given in Table III. Films were pulled in the 0° direction (as cast) at a rate of 0.2 in./min at both room temperature and 200°C. With the exception of $AgNO_3$ the tensile and yield strengths are excellent. At elevated temperature all metal-containing films have surprisingly increased strengths relative to the polymer alone. Incorporation of metal ions into polyimide films in order to improve their space applicability offers a distinct advantage over the addition of heavy metal fillers or carbon microspheres. These latter additives not only add unwanted weight to the film, but greatly lower tensile strengths making them unfit for space applications. For each metal-containing film, the tensile modulus increased and the percent elongation decreased relative to the polymer alone both at room temperature and 200°C. Although hand-cast films are more subject to flaws and premature breaks, it is reasonable to expect tensile modulus to increase upon metal incorporation. The modulii of these films are on the order of that of DuPont's Kapton® film (400,000 psi). Further evidence of an increase in film stiffness is offered by Young's modulus data (Table IV). Regardless of the test temperature or metal dopant, an increase in modulus is

TABLE IV
Mechanical Properties of Metal/Polyimide Films by Autovibron

Polymer/metal film	Young's modulus $E \times 10^{10}$ dyn/cm^2		
	RT	100°C	200°C
Polymer alone	3.52	2.81	2.02
Polymer + $Al(acac)_3$	4.49	3.61	2.59
Polymer + $AgNO_3$	4.89	3.97	3.10
Polymer + Li_2PdCl_4	4.31	3.67	2.88
Polymer + AuI_3	4.06	3.39	2.57
Polymer + $SnCl_2$	4.66	3.77	2.70

TABLE V
Effect of Dopant Concentration on Thermal and Resistivity Properties

Metal additive	Mole ratio metal:polymer	T_g (°C)	PDT (°C)	Electrical resistivity Volume (Ω-cm)	Electrical resistivity Surface (Ω)	% Metal found	
$AgNO_3$	1:17	286	429	10^{16}	10^{18}	Ag = 1.4	
	1:5	320	406	10^{16}	10^{18}	Ag = 3.80	
	1:2	301	390	10^{15}	10^{18}	Ag = 3.95	
Li_2PdCl_4	1:22	321	426	10^{15}	10^{18}	Pd = 0.92	Li = 0.06
	1:5	341	415	10^{10}	10^{9}	Pd = 7.73	Li = 0.11
	1:2	334	420	10^{10}	10^{8}	Pd = 7.79	Li = 0.16

observed. Again a correlation with the weight percentage of each metal is not possible.

A limited study of the effect of variable metal ion concentration on thermal, electrical, and mechanical properties was conducted. $AgNO_3$ and Li_2PdCl_4 were selected for this investigation (Table V). Metal to polymer ratios ranged from approximately 1:20 to 1:2. Surprisingly, the found metal content did not change appreciably on going from the 1:5 to 1:2 formulation for either $AgNO_3$ or Li_2PdCl_4. In general, T_g increased with an increase in metal content. No significant effect on polymer decomposition temperature, however, was noted with different concentrations of either $AgNO_3$ or Li_2PdCl_4. Electrical resistivity of polyimide films containing $AgNO_3$ was not affected by changes in Ag ion concentration. On the other hand, resistivity of Li_2PdCl_4 films was reduced by increasing the metal ion/polymer ratio from 1:22 to 1:5. No further decrease in resistivity was measured on going to a 1:2 ratio. From these thermal and electrical data, it would appear that the 1:5 metal/polymer ratio is optimal. Dopant concentration also impacts on mechanical properties (Table VI). Room temperature tensile strengths decrease with an increase in metal concentration. Amazingly tensile strengths at 200°C were found to increase with increasing metal content for both $AgNO_3$ and Li_2PdCl_4. Tensile modulus, both at room temperature and 200°C, increases with increasing metal content with the exception of the 1:5 $AgNO_3$ formulation.

TABLE VI
Effect of Dopant Concentration on Mechanical Properties

Metal additive	Mole ratio metal:polymer	Test temp (°C)	Tensile strength (psi)	Tensile modulus (psi)	% Elongation
$AgNO_3$	1:17	RT	16,600	467,000	7
		200	7,500	271,000	8
	1:15	RT	12,000	486,000	3
		200	8,300	215,000	4
	1:2	RT	13,500	511,000	3
		200	10,500	352,000	4
Li_2PdCl_4	1:22	RT	18,800	462,000	7
		200	9,800	285,000	8
	1:5	RT	13,900	492,000	4
		200	10,600	336,000	5

SUMMARY

In conclusion, metal-containing polyimides exhibited improved properties over polyimide alone for certain applications. In most cases thermal stability is not sacrificed upon metal ion doping. Electrical resistivity is reduced for specific dopants. All metal-containing films show increased mechanical strength at elevated temperatures. Modulus of films containing metal dopants is consistently greater than the polymer alone. Additional study of different metals, different additives of the same metal, and various dianhydride–diamine combinations is desirable toward optimizing specific polymer properties.

References

1. C. E. Carraher and M. Tsuda, Eds., *Am. Chem. Soc. Symp. Ser.*, **121**, (1980).
2. A. K. St. Clair and L. T. Taylor, *J. Macromol. Sci., Chem.*, **A16**, 95 (1981).
3. T. L. Wohlford, J. Schaaf, L. T. Taylor, T. A. Furtsch, E. Khor, and A. K. St. Clair, *Conductive Polymers*, R. B. Seymour, Ed., Plenum, New York, 1981, p. 7.
4. L. T. Taylor, A. K. St. Clair, V. C. Carver, and T. A. Furtsch, NASA Langley Research Center, "Electrically Conductive Palladium Containing Polyimide Films," U.S. Pat. 4,311,615 (1982).
5. A. K. St. Clair, V. C. Carver, L. T. Taylor, and T. A. Furtsch, *J. Am. Chem. Soc.*, **102**, 876 (1980).
6. L. T. Taylor, V. C. Carver, T. A. Furtsch, and A. K. St. Clair, "Electrically Conductive Palladium Containing Polyimide Films," U.S. Pat. 4,311,615 (1982).
7. E. Khor and L. T. Taylor, *Macromolecules*, **15**, 379 (1982).
8. L. T. Taylor, A. K. St. Clair, and NASA Langley Research Center, "Aluminum Ion Containing Polyimide Adhesives," U.S. Pat. 4,284,467 (1981).
9. L. T. Taylor, V. C. Carver, T. A. Furtsch, and A. K. St. Clair, *Am. Chem. Soc. Symp. Ser.*, **121**, 71 (1980).
10. A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, **90**, 911 (1968).
11. T. A. Furtsch, L. T. Taylor, T. W. Fritz, G. Fortner, and E. Khor, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 1287 (1982).

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