

Formation of Double-Surface-Silvered Polyimide Films via a Direct Ion-Exchange Self-Metallization Technique: The Case of BPADA/ODA and $[\text{Ag}(\text{NH}_3)_2]^+$

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ABSTRACT: Double-surface-silvered polyimide (PI) films have been successfully fabricated via a direct ion-exchange self-metallization method using silver ammonia complex cation ($[\text{Ag}(\text{NH}_3)_2]^+$) as silver resource and bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride/4,4'-oxydianiline (BPADA/ODA)-based poly(amic acid) (PAA) as the PI precursor. The alkaline characteristic of the silver precursor dramatically improves the efficiency of the ion exchange and film metallization process. By using an aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution with a concentration of only 0.01M and an ion-exchange time of only 5 min, metallized films with desirable performance could be easily obtained by simply heating the silver(I)-

doped PAA films to 300°C. The strong hydrolysis effect of the basic $[\text{Ag}(\text{NH}_3)_2]^+$ cations on the flexible and acidic BPADA/ODA PAA chains was observed during the ion exchange process by the quantitative evaluation of the mass loss of PAA matrix. Nevertheless, under the present experimental conditions, the final metallized film essentially retained the basic structural, thermal, and mechanical properties of the pristine PI, which make it a truly applicable material. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: films; ion exchange; metal-polymer complexes; polyimides; silver

INTRODUCTION

As a class of materials with excellent dielectric properties, high-temperature stability, chemical inertness, and superior thermal and mechanical properties, polyimide (PI) has been widely applied in aerospace and electronics industry.^{1–6} Particularly, surface-silvered PI received much attention for its combined excellent chemical and physical properties of the PI matrix and optical and electrical properties of the surface silver layers and has prospected for potential applications in flexible printed circuit board,⁷ magnetic data storage,^{8,9} catalysts,^{10,11} electromagnetic interference shielding filters,¹² highly reflective thin-film reflector,¹³ and large-scale radio frequency antennas,¹⁴ among many other materials.

Many conventional methods have been established to prepare the surface-silvered PI films, including physical vapor deposition, chemical vapor deposition, electrodeposition, and electroless chemical reduction.^{13,15} However, these methods are usually labor-intensive and give films with very poor adhesion at the silver-PI interface.^{16,17} These problems were successfully resolved by the so-called *in situ* single-stage, internal, self-metallization technique developed by Southward and Stoakley.¹⁸ The method works by simply thermal treating the precursor hybrid films cast from the homogeneous mixture solution of an organometallic silver complex and the desired poly(amic acid) (PAA). Highly reflective and conductive silvered films with excellent adhesion have been prepared. However, silver metallization was only realized on the air surface and the glass side of the film remains neither reflective nor conductive. What is more, successes were achieved only when the complex silver precursors such as (1,1,1-trifluoroacetylacetonato) silver (I)^{17,19} and (1,1,1,5,5,5-hexafluoroacetylacetonato) silver(I)¹⁹ were used, which are unstable and expensive compared to simple silver salts.

With the aim to obtain surface-silvered PI films with high reflectivity and conductivity on both film sides in a cost-effective route, a new direct ion-exchange self-metallization (DIESM) method has been developed in our group. And by using simple

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inorganic silver salts as the precursor, double-surface-silvered PI films with desirable surface performances have been synthesized.^{20,21} This method works by doping metal ions into the PAA film through the ion exchange of the PAA carboxyl groups with metal ions in aqueous solution. Subsequent thermal treatment of the silver(I)-doped PAA films under tension converts the PAA into the final PI form with concomitant silver reduction and aggregation forming metallic layers on the polymer surface. This general protocol has demonstrated considerable successes in different PI matrixes using different silver precursors.^{21–23} For the 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride/4,4'-oxydianiline (BTDA/ODA)-based PI with silver nitrate (AgNO_3)²¹ as the silver source, the hybrid films were prepared with optimum reflectivity of 71 and 84% and surface resistances of 4.1 and 1.3 $\Omega \text{ sq}^{-1}$ on the air side and glass side, respectively. Similarly, by using silver fluoride,²² reflectivity higher than 80 and 100% and electrical resistance less than 0.6 and 0.2 $\Omega \text{ sq}^{-1}$ on the air side and glass side of the silvered films were achieved. In addition, a more effective silver species, silver ammonia complex cation ($[\text{Ag}(\text{NH}_3)_2]^+$)²³ was found in our recent work on BTDA/ODA-based matrix, which make it possible to produce superior silvered PI films using very short ion-exchange time and very dilute silver ion solution.

In this work, we extend the application of our DIISM technique to a more flexible and available PI matrix, BPADA/ODA, by using the effective $[\text{Ag}(\text{NH}_3)_2]^+$ as the silver source. We report on the successful preparation of highly reflective and conductive silvered PI films in the case of BPADA and $[\text{Ag}(\text{NH}_3)_2]^+$ and the structural, morphological, and thermal mechanical characterization of the hybrid films with ATR-FTIR, dynamic mechanical thermal analysis (DMTA), scanning electron microscope (SEM), and thermal gravimetric analysis (TGA). The ion-exchange process including the damaging effect of $[\text{Ag}(\text{NH}_3)_2]^+$ on PAA, the silver(I) loading, the structural variation before and after ion exchange were examined. Optimized ion-exchange time and proper silver concentration were determined for the preparation of hybrid films with desirable surface properties. The results further demonstrated the extensibility and controllability of our DIISM technique.

EXPERIMENTAL

Materials

Both bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA), or bisphenol A dianhydride, and 4,4'-ODA were purchased from the Shanghai Research Institute of Synthetic Resins. BPADA was used as received, and ODA was recrystallized in ethyl acetate

before use. Dimethylacetamide (DMAc; analytically pure, $\leq 0.1\%$ water) was purchased from Tianjin Fu Chen Chemicals Reagent Factory and used after distillation. AgNO_3 (analytically pure, $\geq 99.8\%$) was produced by Beijing Chemical Works and used as received. Aqueous silver ammonia complex cations ($[\text{Ag}(\text{NH}_3)_2]^+$) solution was prepared by adding dilute ammonia solution dropwise to the aqueous AgNO_3 solution until a transparent solution was obtained. In this work, 0.005 and 0.01M aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solutions were used.

Preparation of silvered BPADA/ODA film: Ion exchange and film metallization

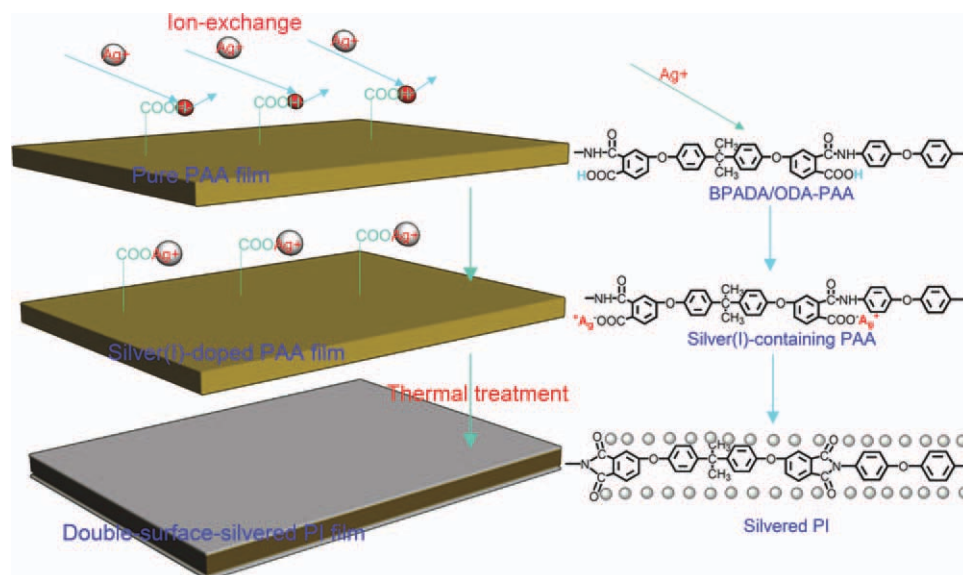
The BPADA/ODA PAA was synthesized by first dissolving the 4,4'-ODA in DMAc followed by adding a 1-mol % offset of BPADA gradually. A yellow viscous homogeneous solution with a solid content of 15 wt % was then obtained after being stirred at ambient temperature for 5 h. Damp-dry PAA films with thickness of 40–45 μm were subsequently prepared by casting the viscous resin solution on a clean glass plate followed by solvent evaporation in ambient atmosphere. The damp-dry PAA film was then peeled from the glass substrate and immersed into the 0.005 or 0.01M aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution to load silver(I) ions into the PAA precursor via ion exchange. The silver(I)-doped PAA film was then washed with a large amount of deionized water to remove the free silver ions followed by thermal treatment under tension in a forced-air oven. The thermal cycles are heating over 1 h to 135°C and holding for 1 h, raising to 300°C over 2 h, and keeping at 300°C. Thermal curing cycloimidizes the PAA to PI and simultaneously induces an internal silver reduction and subsequent aggregation giving thin silver metallic layers on the polymer surfaces, as depicted in Scheme 1. For evaluation and comparison of the surface difference, the surface of the PAA film in contact with the glass substrate was marked as underside, while that exposed to the atmosphere was referred to as upside.

The ion exchange process of BPADA/ODA PAA in aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution, including the mass changes, silver loading and structural variation before and after ion exchange, was also investigated following the procedures reported in our previous publication.²⁴

Characterization

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of the films were collected using a Nicolet Nexus 670 IR spectrometer.

Silver(I)-loadings in the PAA films were quantified by a Seiko Instruments SPS 8000 inductively



Scheme 1 Illustrative protocol for the preparation of silvered BPADA/ODA-based polyimide films via the direct ion-exchange self-metallization process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coupled plasma-atomic emission spectrometer (ICP-AES). The measurements were performed by dissolving the silver-doped PAA films in a 5-wt % nitric acid solution.

Surface reflection spectra (relative to a BaSO_4 mirror set at 100% reflectivity) of the metallized film were obtained on a Shimadzu 2501PC UV/vis spectrophotometer at an incidence angle of 8° in the 200–800 nm wavelength range. Surface electrical resistances were measured with a RTS-8 four-point-probe meter produced by Guangzhou Semiconductor Material Research Institute in China.

Thermal mechanical behaviors of the films were characterized using a DMTA system (Rheometric Scientific) at a heating rate of 5 K min^{-1} .

Surface images of the hybrid films were recorded on a Hitachi S-4300 field emission SEM (FE-SEM) operated at 15 KV. Samples used for surface morphology observations were coated with $\sim 5 \text{ nm}$ platinum before measurements.

TGA were conducted on a NETZSCH STA449C system at a heating rate of 10 K min^{-1} . Mechanical properties were evaluated by an Instron-1185 system.

RESULTS AND DISCUSSION

Structural properties of PAA before and after ion exchange

The ideal protocol for the synthesis of the silver-metallized PI films is illustrated in Scheme 1. The presence of many active carboxyl groups allows the *in situ* reaction of the PAA macromolecules with the salts of noble metals possessing labile anions to generate a metal-polymeric blend.²⁵ Accordingly, a

silver-polycarboxylate salt (silver polyamate) was supposed to be formed *in situ* when the damp-dry PAA films were immersed into the aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution to undergo the silver(I)-doping process. Figure 1 shows the ATR-FTIR characterization results of the PAA films before and after ion exchange. The appearance of a strong new absorbance peak at 1366 cm^{-1} and the broadening of the band near 1600 cm^{-1} in the spectrum of the silver(I)-doped PAA film (in 0.01 M $[\text{Ag}(\text{NH}_3)_2]^+$ for 5 min), represent the characteristic absorptions of the carboxylate symmetric and asymmetric stretching

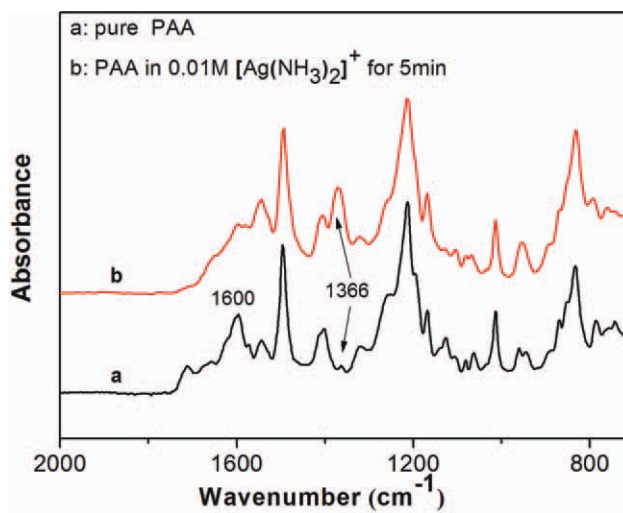


Figure 1 ATR-FTIR spectra for the pure poly(amic acid) film and the silver(I)-doped poly(amic acid) film obtained after being immersed in 0.01 M aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution for 5 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

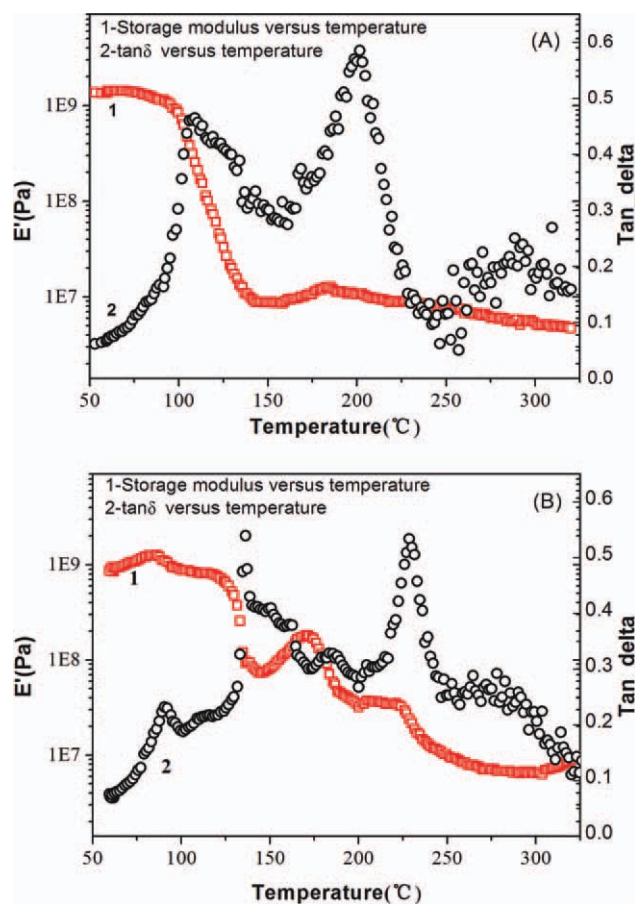


Figure 2 DMTA curves of (A) pure poly(amic acid) and (B) the silver(I)-doped poly(amic acid) film obtained after ion exchange in 0.01M aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution for 5 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vibrations, providing very strong evidence for the formation of silver polyamate in the PAA films after the ion exchange.^{26–28}

To further evaluate the structural variation, thermal curing profiles of the PAA films before and after ion exchange were examined by DMTA, as shown in Figure 2. As illustrated in Figure 2(A), the pure PAA film exhibits a dramatic decrease in storage modulus near 100°C, reflecting the abrupt softening of the PAA film at this temperature. Simultaneously, a distinct loss peak was observed on the $\tan \delta$ curve at 110°C, which is corresponding to the glass transition of the PAA molecules. Further increase in temperature results in an increase in storage modulus from 150°C due to the cyclimidization of the PAA into its PI form,²⁹ while the softening of the formed PI molecules at higher temperature (>180°C) leads to the decrease in modulus conversely. Correspondingly, a second loss peak was emerging at 200°C on the $\tan \delta$ curve attributing to the glass transition of the PI molecules.

For the silver(I)-doped PAA films, as shown in Figure 2(B), the evident loss peak at 130°C on $\tan \delta$

curve indicates that the glass transition of the PAA molecules in the silver(I)-doped PAA films is $\sim 20^\circ\text{C}$ higher than that in the pure PAA films (110°C). It is suggested that it is the incorporated silver ions that block the motion of the PAA segments by forming physical crosslinking in the ion-exchange films as demonstrated in our previous work,²⁴ which consequently enhance the glass transition temperature (T_g) of the PAA molecules.

As is similar with the pure PAA, the storage modulus of silver-doped PAA film also begins to increase at 150°C due to thermal imidization. Whereas the glass transition temperature of the PI molecules in the silver(I)-doped films shifted to $\sim 235^\circ\text{C}$, which is $\sim 35^\circ\text{C}$ higher than that of the pure PI film. This is completely different from the results that we have observed in the BTDA/ODA-²⁴ and PMDA/ODA-based³⁰ PI/silver films, for which the T_g of the PI molecules are usually evidently decreased after silver hybridization due to the destructive effect of silver on the thermal imidization process. However, the increase in T_g in this work is not unexpected since when compared with BTDA/ODA and PMDA/ODA, BPADA/ODA-based PI is much more flexible, and therefore, the presence of silver might not affect the thermal imidization of the PI precursor but will definitely block the motion of the PI segments leading to the positive shift of the T_g .

Mass variation and silver loading in PAA during ion exchange

Because of the presence of massive amide groups in the PAA macromolecules, the loading of silver into PAA via ion exchange inevitably accompanies the hydrolysis and degradation of the PAA molecule, especially, when free reactive metal ions are involved.²⁵ To clarify the damaging effect of $[\text{Ag}(\text{NH}_3)_2]^+$ on PAA molecules during ion exchange, the mass variation of the PAA film was measured according to the method reported in our previous publication,²⁴ the results of which are shown in Figure 3(A). As a reference, the mass variation of the PAA film after being treated in deionized water for the same time was also measured, as shown in Figure 3(A) (curve 1). The results indicate that the mass loss of PAA after being treated for 20 min in deionized water is no more than 1 wt %, reflecting the weak hydrolysis effect of water on PAA. However, in aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution, as shown in Figure 3(A) (curve 2), the PAA film shows an almost linearly increased mass loss with the ion exchange time. And in 20 min, 46 wt % PAA was dissolved into the aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution, suggesting that $[\text{Ag}(\text{NH}_3)_2]^+$ has a very strong accelerating effect on the hydrolysis of PAA molecule. To partially avoid the strong damaging effect of silver ions on PAA matrix, in present experiment, an ion exchange time no more

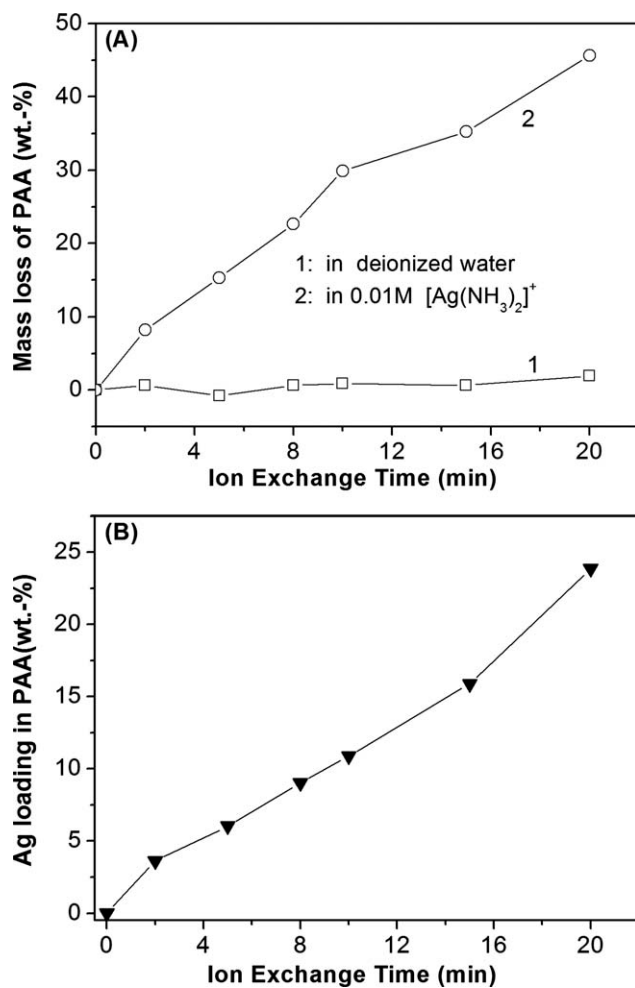


Figure 3 (A) Mass losses of PAA as a function of treatment time in (1) deionized water, (2) 0.01M aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution. (B) Silver ion loading as a function of ion exchange time for PAA in 0.01M aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution.

than 5 min was selected for the synthesis of the silvered PI films. Nevertheless, as many as 15 wt % PAA was also lost during the ion exchange.

The amount of silver ions loaded into the PAA films was determined by ICP during the ion exchange process. As shown in Figure 3(B), the amount of silver ions increases linearly with the ion exchange time and approaches about 24 wt % on 20 min treatment in 0.01M aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution, suggesting that $[\text{Ag}(\text{NH}_3)_2]^+$ is a rather effective silver source for ion exchange. In addition, 5-min ion exchange introduced 6.4 wt % of silver into PAA films, which is adequate for the formation of continuous silver layers on PI surfaces, as will be shown later.

Surface properties and surface morphology of the silvered films

Thermal treatment of the ion-exchanged films cyclomizes the PAA to its final PI form and reduce

silver(I) to silver, resulting in the formation of silver layers on both PI surfaces. Figure 4 shows the variation of the surface reflectivity with the cure time/temperature for the hybrid films ion exchanged in 0.005 and 0.01M aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution for 5 min. As can be observed, the surface reflectivity of the silvered films developed gradually with the increasing cure time and temperature in a stepwise manner. For the films ion exchanged in 0.01M aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution for 5 min, it is exciting to note that an optimum reflectivity over 80% was achieved on both film sides. The reflectivity shows a slight decrease when the aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution was diluted to 0.005M. Whereas the film still achieved a maximum reflectivity more than 70%.

Table 1 displays the surface electrical resistances of both the upside and underside of hybrid films cured at different stages of thermal cycle. Before 300°C for 4 h, characterization data indicate that electrical conductivity was only achieved on the

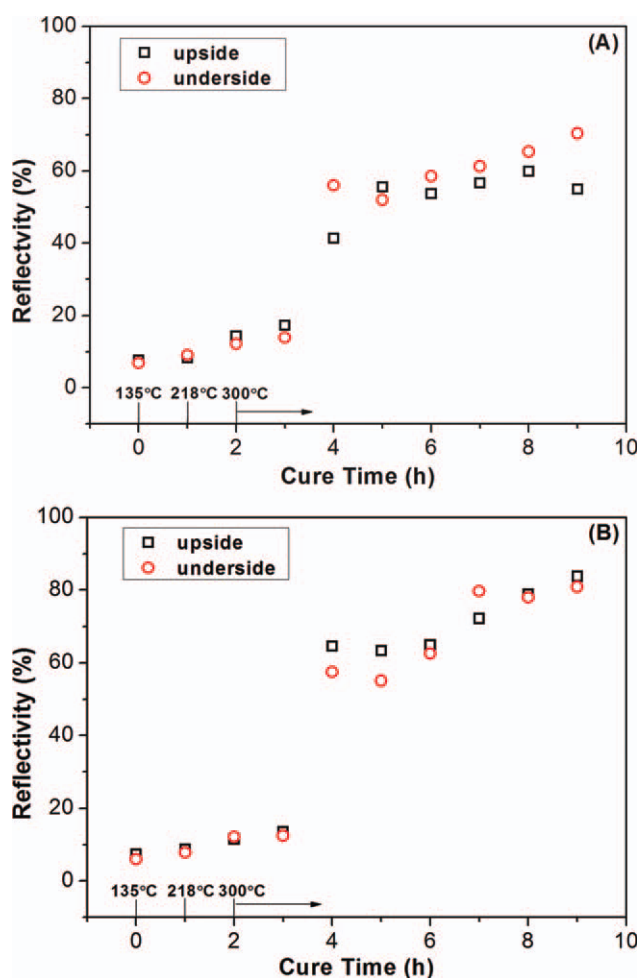


Figure 4 Surface reflectivity of the upside and underside as a function of the cure cycle for the silvered films ion exchanged in (A) 0.005M and (B) 0.01M aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution for 5 min. (Time zero is at 135°C after 1 h.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Surface Resistance for the Silvered BPADA/ODA Films
(5 min in 0.01M [Ag(NH₃)₂]⁺)

Thermal history	Surface resistance ($\Omega \text{ sq}^{-1}$)	
	Upside	Underside
300°C for 3 h	>10 ⁶	12
300°C for 4 h	>10 ⁶	9
300°C for 5 h	1.5	0.8
300°C for 6 h	0.6	0.4
300°C for 7 h	0.5	0.5

underside of hybrid film with surface resistances about $10 \Omega \text{ sq}^{-1}$. The upside surface was not conductive. However, double-surface-conductive films were soon obtained after an additional thermal treatment of 1 h. And after thermal treatment at 300°C for 7 h, the surface resistances of the hybrid film decreased to $0.5 \Omega \text{ sq}^{-1}$ on both upside and underside, implying the formation of well-defined continuous silver layers on both film sides. However, for the films ion

exchanged in 0.005M [Ag(NH₃)₂]⁺ solution, conductivity was never achieved on either side of the final silvered films, even after being cured at 300°C for 7 h.

Figure 5 shows the surface topographies of the metallized PI films. As has been proved in our previous works,²¹⁻²⁴ the continuous metal layers on the surface of the final hybrid film mainly exist in the form of native silver. As shown in Figure 5(B,C), well-established continuous silver layers have been formed on both the upside and underside surfaces for the hybrid films ion exchanged in 0.01M aqueous [Ag(NH₃)₂]⁺ solution for 5 min and then thermally treated to 300°C for 5 h and 300°C for 7 h, which accounts for the excellent surface reflectivity and conductivity mentioned above. While for the hybrid films derived from the PAA precursor films ion exchanged in 0.005M aqueous [Ag(NH₃)₂]⁺ solution for 5 min, the images in Figure 5(A) indicate that continuous metal layers have never been formed, consistent with the nonconductivity.

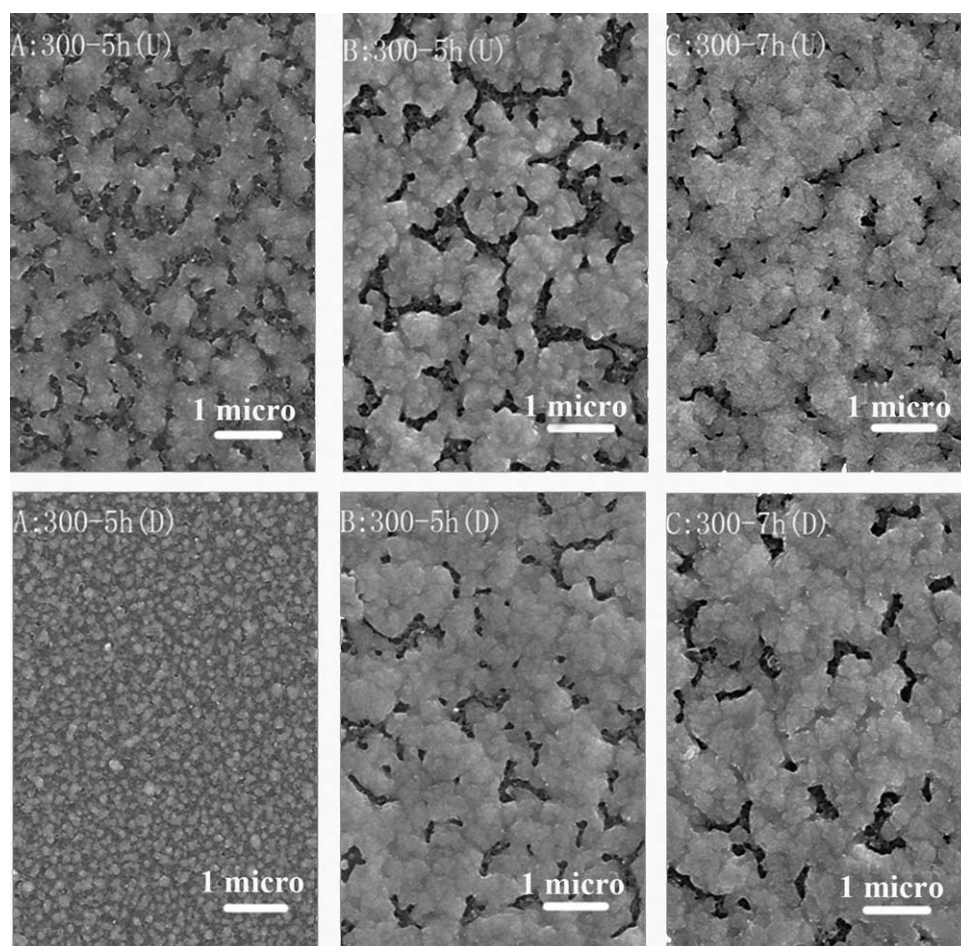


Figure 5 FE-SEM images of double-surface-silvered PI films. (A) Ion exchanged in 0.005M [Ag(NH₃)₂]⁺ solution for 5 min and cured to 300°C for 5 h; (B) Ion exchanged in 0.01M [Ag(NH₃)₂]⁺ solution for 5 min and cured to 300°C for 5 h; (C) Ion exchanged in 0.01M [Ag(NH₃)₂]⁺ solution for 5 min and cured to 300°C for 7 h. (U, upside of the film; D, underside of the film.)

TABLE II
Thermal and Mechanical Properties of the Polyimide-Silver Composite Films

Film samples	$[\text{Ag}(\text{NH}_3)_2]^+$ Concentration (mol L ⁻¹)	Tensile strength (MPa)	Modulus (MPa)	Percent elongation (%)	Temperature at which 10 wt % loss reached in N ₂ (°C)	Temperature at which 10 wt % loss reached in air (°C)
Pristine PI 300°C for 3 h	0	94.2	2313.2	9.43	542	520
PI-silver 300°C for 3 h	0.005	99.4	2346.7	8.62	560	458
PI-silver 300°C for 3 h	0.01	86.3	2377.4	6.98	580	440

In summary, surface-silvered hybrid films with high reflectivity and conductivity on both film sides have been successfully prepared after thermally treating the PAA films ion exchanged in 0.01M aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution for 5 min at 300°C for over 5 h. The failure to achieve surface conductivity by using the 0.005M silver precursor solution might be due to the inadequate silver loadings in the PAA matrix. A more concentrated silver precursor solution would readily load enough silver ions into the PAA matrix; however, it would inevitably result in a serious degradation on the PAA matrix. Thus, to produce double-surface-silvered films with high reflectivity and conductivity, silver precursor species with a concentration of 0.01M is suggested to be the best.

Mechanical and thermal properties of the final metallized polyimide films

As mentioned previously, the PAA chains might be seriously hydrolyzed by the alkaline aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution during ion exchange, causing significant compromise to the mechanical properties of the metallized films. In addition, the incorporation of silver into the PI matrix might also diminish its high-temperature thermal stability because silver particles have a significantly catalytic and oxidative decomposition effect on the PI matrix at a high temperature.^{17,29}

Table 2 displays the mechanical and thermal characterization data for the metallized films and pristine PI. As can be observed, the tensile strength and modulus for the silvered films are grossly similar to that of the pure PI films. The percent elongation of the hybrid films slightly decreased after metallization, while it is still around 7%. The thermal data shown in Table 2 suggest that in nitrogen atmosphere, the temperatures at which there is a 10-wt % loss for the hybrid films were never lowered and contrarily enhanced after silver metallization. Whereas in air, the 10%-weight-loss temperature was about 62–80°C degraded as compared to that of the host PI film, but it is still above 440°C, which could also meet many practical requirements. Thus, although the high-temperature thermal stability of silvered films in air was diminished to some extent,

the metallized films basically retained the excellent mechanical and thermal properties of pristine PI film, and the remaining mechanical and thermal properties are still adequate for most purposes.

CONCLUSIONS

This work demonstrates that double-surface-silvered PI films could be fabricated by simply heating the BPADA/ODA-based PAA to 300°C, which were ion exchanged in a 0.01M aqueous $[\text{Ag}(\text{NH}_3)_2]^+$ solution for 5 min. Silvered PI films with an optimum reflectivity of 81/80% and surface resistance of 0.5/0.4 $\Omega \text{ sq}^{-1}$ on the upside/underside have been prepared. The metallized films are among the highly reflective and conductive catalogues sufficient for many practical applications. The alkaline silver ion solution has very strong hydrolysis effect on the PAA precursor films, resulting in a significant mass loss of PAA during the ion exchange process. Nevertheless, under the present experimental conditions, characterization results suggested that the final metallized films basically maintained the thermal and mechanical properties of pristine PI. Finally, the extensibility and controllability of our DIEM technique have been confirmed that it is applicable to a flexible and available PI(BPADA/ODA) matrix.

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