

Preparation of Highly Uniform Self-Standing Submicrometer Polyimide Films and an Investigation of Their Antibulging Capabilities

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ABSTRACT: Aiming for X-ray astronomy applications, we prepared large-area submicrometer polyimide (PI) films [diameter (Φ) = 8 cm] with great thickness uniformity via the spin-coating technique by using a PI precursor, poly(amic acid) (PAA) derived from 3,3',4,4'-biphenyltetracarboxylic dianhydride, and *p*-phenylenediamine as the starting materials. The effects of the spinning speed, apparent viscosity of the PAA solution (η), and spinning time on the PI film thickness and its uniformity, as characterized by the measurement of the film thickness every 0.5 cm along the diameter direction, were investigated. By optimizing the spin-coating conditions, we prepared final submicrometer PI films with average thicknesses in the range of 200–850 nm and with film thickness fluctuations of less than 1.3%. The pressure bulge test results indicate that at a thickness of 805 nm and an inside test aperture diameter of 2.64 cm, the prepared PI films reached a final burst pressure of 20.2 KPa; this suggested excellent mechanical performances in the self-standing submicrometer PI film. This study makes a contribution by providing a typical example and opening the way for the preparation of robust self-standing submicrometer PI films with great thickness uniformities for X-ray astronomy applications. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39977.

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INTRODUCTION

Polyimide (PI) has been extensively used in the fields of high-performance engineering plastics, electronics, and aerospace applications such as X-ray astronomy^{1,2} because of its outstanding thermal stability and mechanical and dielectric properties. The thickness of the PI film is typically a few thousand angstroms for the use in X-ray astronomy, where flat films with no pinholes are also required. Currently, the commonly used techniques used to prepare such submicrometer films are spin coating^{3,4} and vapor deposition polymerization.^{5,6} They differ in the way that the film is coated onto the substrate. Vapor deposition polymerization is a solventless technique in which the monomers are codeposited by evaporation onto the substrate where they react to form PI. *Spin coating* refers to the preparation of PI films by the direct spreading of a presynthesized PI solution onto the substrate via a spin coater or by the spreading of a poly(amic acid) (PAA) precursor solution onto a substrate followed by thermal cyclization to convert PAA into PI. The film thickness and its uniformity strongly depend on the spin parameters. The orientation of the molecular chains is directly influenced by the way that the film is prepared. Therefore,

variations in the preparation strategies are expected to produce PI films with different properties. Powell⁷ once measured the mechanical properties of submicrometer PI films prepared by the previous two techniques through the bulge test method.⁸ The results indicate that the burst pressure strength of the vapor-deposited material was much lower than that of spin-coated material at the same thickness. Therefore, the spin-coating technique was selected in this study to prepare submicrometer PI films.

Norrman et al.⁹ reviewed the main progress in the spin theory. The angular velocity, solution viscosity, and solution concentration were found to affect the film thickness significantly. The spin-coating process for the deposition of the PI film was also studied specifically. Jenekhe³ estimated the relative magnitude of non-Newtonian flow effects by characterizing the Deborah number of the PAA flow on a spin disk. Skrobis et al.¹⁰ compared five different solvents used in the spin coating of PI precursor solutions. They concluded that the spin speed constant was directly related to the relative evaporation rate of the employed solvent. Levinson et al.¹¹ investigated the spin-coating behavior of pyromellitic dianhydride/4,4'-oxydianiline based

PAA solutions. Also, a simple equation relating the film thickness to the spin parameters was experimentally determined. Chang et al.¹² indicated that the convective flow caused by the centrifugal force played a dominant role in the thickness of the coated films. The thickness of the films derived from *N*-methyl-2-pyrrolidone solutions of PAA depended largely on the solution density, spinning speed (ω), and spinning time. However, these studies only provided information on the average film thickness. The uniformity of the film thickness, which is the major concern with the spin-coating technique, has rarely been reported.

Hence, in this study, we focused our efforts on the preparation of submicrometer PI films with highly uniform contours and investigated the various factors that might have influenced the film thickness uniformity. PAA solutions synthesized through the polycondensation of 3,3',4,4'-biphenyltetracarboxylic dianhydride (sBPDA) and *p*-phenylenediamine (pPDA) were chosen for the preparation of the submicrometer PI films. The influence of ω , the apparent viscosity of the PAA solution (η), and the spinning time on the film thickness and its uniformity and the defect control in the spin-coated films were investigated. A bulge test device was designed in our laboratory to characterize the mechanical properties of the prepared submicrometer films. The effects of the thermal imidization procedures on the burst pressure of the submicrometer PI films were evaluated.

EXPERIMENTAL

Materials and Measurements

sBPDA and pPDA were obtained from Acros and were used as received. Dimethylacetamide was obtained from Acros and was dried over 5-Å molecular sieves. η was measured with a Brookfield DV-C viscometer. The film thickness was measured with a Dektak 150 surface profiler. The mechanical properties were tested by a self-designed bulge test device. All of the experiments were performed in class 100 clean room conditions. Fourier transform infrared (FTIR)-attenuated total reflection (ATR) spectra of the thin films were collected with a Nicolet Nexus 670 IR spectrometer. Atomic force microscopy (AFM) micrographs were collected with a Digital Instruments NanoScope IIIA multimode scanning probe microscope (Santa Barbara, CA) under tapping mode.

Synthesis of PAA

The synthesis of PAA was carried out by the reaction of sBPDA and pPDA in dimethylacetamide. For each experimental setup, a three-necked flask was equipped with a magnetron and a nitrogen inlet and outlet. The flask was charged with 20 mL of solvent and 2.5 mmol of pPDA. The mixture was stirred at room temperature until the solid was completely dissolved. Then, the solution was cooled to 0°C, and 2.5125 mmol of sBPDA was added to the flask. The reaction mixture was stirred for 6 h at 0°C to yield a viscous PAA solution. The chemical structure and synthetic process for the sBPDA/pPDA-based PAA are shown in Figure 1.

Preparation of the PI Film

The synthesized PAA solution was filtered through a membrane filter (pore size = 0.4 μm) and kept under ambient conditions for several hours to eliminate the bubbles. We then prepared

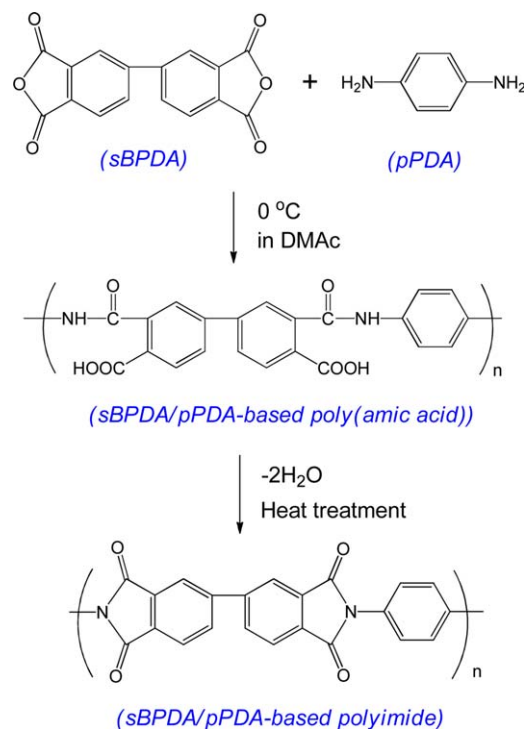


Figure 1. Synthesis of the sBPDA/pPDA-based PI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thin PAA films via spin coating by spreading the PAA solutions at 500 rpm for 15 s onto a substrate; this was followed by rotation at a higher speed. Circular float glass [diameter (Φ) = 8 cm] was used as the substrate. After they were kept for 1 day on a horizontal stage placed in a clean box programmed at a constant temperature (25°C) and humidity (20%), the prepared films were thermally treated in a forced-air oven to convert the PAA into its final imide form. The thermal conditions for imidization were heated at 80°C for 60 min, heated from 80 to 230°C over 150 min, kept at that temperature for 120 min, heated from 230°C to the final curing temperature at 1°C/min, and kept at that temperature for 120 min. Figure 1 shows the illustrative diagram for the thermal cycloimidization of the sBPDA/pPDA-based PAA to its final PI form.

RESULTS AND DISCUSSION

Defect Control

Submicrometer PI films are delicate and must be treated with special care. In the spinning process, many different kinds of defects, including air bubbles on the film surface, comets, streaks or flares, swirl patterns, chuck marks, and pinholes, may be unintentionally introduced into the films; this always causes damage to the thin films. To prepare submicrometer PI films with as few defects as possible, in this study, the whole experimental process was completed in class 100 clean room conditions. Also, the PAA solutions were filtered through a 0.4- μm pore membrane filter to eliminate the insoluble purities before spin coating. Also, all of the substrates were pre-cleaned strictly with concentrated sulfuric acid and successively ultrasonicated in MilliQ water, acetone, chloroform, and isopropyl alcohol. They were then used in 0.5 h after they were dried with an N₂

gun. Contamination control was performed at all times during the film preparation process. The characterization results indicate that under these conditions, PI films with no defects could be successfully prepared with a high reproducibility.

Film Thickness and Its Uniformity

Film thickness uniformity is one of the most important parameters for characterizing the thin-film qualities. However, it has rarely been mentioned in previous publications. For a quantitative evaluation of the film thickness uniformity, circular float glasses with a diameter of 8 cm were selected as the substrate for the submicrometer PI film preparation in this study. The center of the glass was set as the origin coordinates (radial position = 0), and the film thicknesses were then measured every 0.5 cm along the axial direction to show the fluctuations. The degree of nonuniformity (NON%) with respect to the film thickness could be defined as follows:

$$\text{NON}\% = \frac{h_{\max} - h_{\min}}{h_{\max} + h_{\min}} \times 100\% \quad (1)$$

where h_{\max} and h_{\min} represent the maximum and minimum values of the film thickness, respectively. Because of the influence of the edge bead effect,¹³ the outmost point (i.e., edge) was abandoned in the evaluation of film uniformity. The effect of the spinning parameters on the film thickness uniformity were then investigated by comparisons of NON%.

As pointed out by Lock et al.,¹⁴ the increase in ω will always cause a decrease in the film thickness. However, this never means the simultaneous maintenance of the film uniformity. Acrivos et al.¹⁵ found that an initial uniformly deposited fluid layer remained uniform when the fluid was Newtonian. For non-Newtonian fluids, coating uniformity was virtually impossible. Nitta et al.¹⁶ pointed out that spin coating in the shear-thinning regime resulted in significant thickness nonuniformities from the film center to the edge and also suggested that spin-coating procedures be performed when the rheology of the solution was in the Newtonian regime. For the PI precursor, PAA, rheological characterizations from Jenekhe³ suggested that the non-Newtonian flow of the PAA solution was in the shear rate range 30–400 s^{-1} . Simple modeling suggested that spinning at lower rates would reduce the shear rate and subsequently weaken the non-Newtonian behavior of the PAA solutions. In addition, it was already demonstrated by Levinson et al.¹¹ that a solution becomes more Newtonian as it becomes less concentrated. Thus, to obtain PI films with a good thickness uniformity, PAA solutions with low η s were used in our study to prepare the submicrometer PI films. Relatively low ω s were also used to prevent the non-Newtonian flowing behavior of the PAA solutions.

Figure 2 shows the thickness variations along the axial direction for the submicrometer PI films prepared for different spinning times. η was 760 cp. The results indicate that the spinning time had significant effects on the film thickness of the submicrometer PI films and their thickness uniformity. With a constant ω at 1000 rpm, the thickness of the submicrometer films decreased rapidly from 820 to 532 nm when the spinning time was increased from 1 to 5 min. However, the film thickness uniformity was seriously affected. At a spinning time of 1 min,

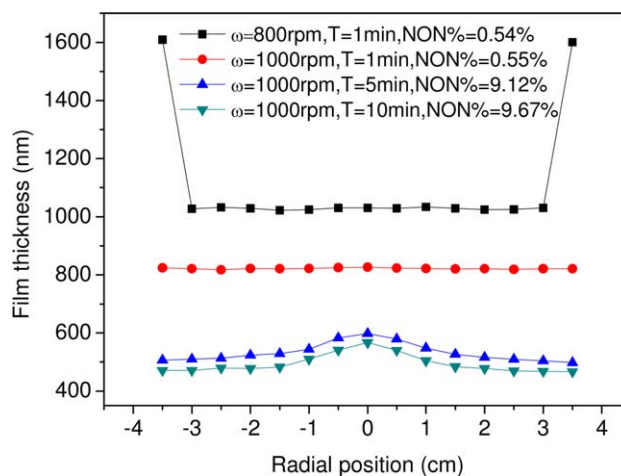


Figure 2. Thickness variations along the axial direction for the PI films prepared under different ω s and spinning times ($\eta = 760$ cp), where T is spinning time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

considerably uniform films with almost no thickness fluctuation were obtained, whereas when the spinning time was increased to 5 min, the film exhibited a humplike thickness contour along the axial direction, and thicker films were formed in the center of the glass substrate. When the spinning time was further extended to 10 min, neither resulted in any significant thinning effect on the film nor in any improvement in the film uniformity; this indicated that a balance was basically formed between the centrifugal force and the viscous force at a spinning time of around 5 min.¹¹ In addition, when the ω was reduced to 800 rpm, the results shown in Figure 2 suggest that uniform films with 1028-nm thicknesses were also prepared at a spinning time of 1 min. However, the film thickness on the edge was much thicker than that in the center. This suggested that the viscosity and surface tension effects made it difficult for the solution to detach from the substrate;¹³ this resulted in the attachment of small liquid beads around the entire perimeter and the consequent formation of thicker coatings in this rim zone.

Figure 3 shows the thickness variations of the thin PI films prepared from a diluted PAA solution with an η of 288 cp. A lower ω (500 rpm) was selected for this dilute PAA solution. Similar with what has been observed in Figure 2, films with excellent thickness uniformity were also prepared at short spinning time, that is, 1 min (with disregard of the edge effect). Thus, the results shown in both Figures 2 and 3 demonstrate that submicrometer PI films with good thickness uniformity could be prepared at selected ω s and spinning times. For PAA solutions with low η , a low ω was necessary. Also, in both cases, the spinning time had to be limited to a short period (e.g., 1 min) to obtain uniform films.

However, in contrast to what is shown in Figure 2, where humplike films were formed, when the spinning time was increased to 5 or 10 min, Figure 3 shows that the film thickness exhibited a muldelike contour, and thinner films were formed in the center. The reason for the generation of the completely inverse humplike and muldelike film contours is discussed later.

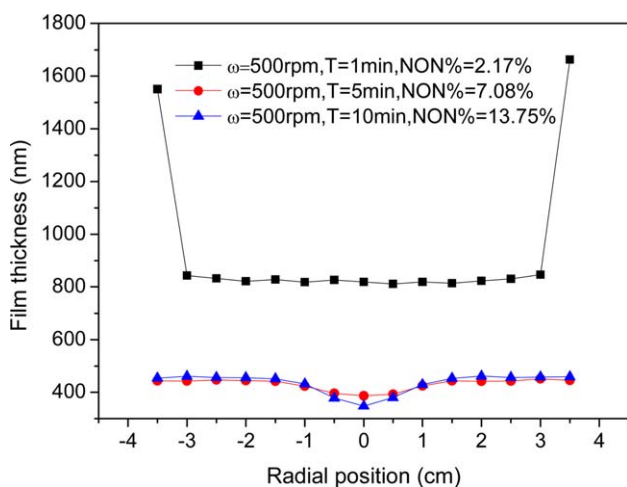


Figure 3. Thickness contours for the submicrometer PI films prepared under different spinning times ($\eta = 288$ cp), where T is spinning time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The decrease in the film thickness during spinning basically originated from convective flow induced by centrifugal force. The centrifugal force on the polymer solution at a given ω was proportional to the distance of the PAA solution from the substrate center. Under the same preparation conditions, greater centrifugal force resulted in the formation of thinner films. Thus, a humplike thick liquid film was soon formed in the initial stage of the spin-coating process. During the further spreading process, the polymer solution flowed to the edge of the substrate. However, the rate of this flow was proportional to the cube of the thickness of the coated liquid film.¹⁷ The thicker the liquid film was, the faster the convective outflow was. So, the initially formed humplike thick film of the coated liquid gradually became uniform. There should have been a best spinning time at which the liquid film was completely uniform. Once the spinning time was prolonged, the film became nonuniform again under the continued centrifugal force; this resulted in the formation of either a humplike thin film (Figure 2) or a muldelike thin film (Figure 3) that primarily relied on the viscosity of the polymer solutions used, as explained later.

For polymer solutions with high viscosities, humplike films were usually formed at prolonged spinning times because film thinning at prolonged times was mainly caused by centrifugal forces. The larger centrifugal force at the outer radial position resulted in the formation of thinner films in the outer film region and the corresponding humplike contours, as shown in Figure 2. However, when η was reduced to a certain level, the effect of air shear induced by disk rotation on the film thickness fluctuations, which is usually neglected at high viscosities, had to be taken into consideration. According to refs. 18–21, when a circular disk rotates in its plane, it behaves like a centrifugal pump, induces an axial air flow toward the disk, and hence radially outwards. The air flow provides a shear stress at the liquid–air interface, which will accelerate the thinning of the liquid film on the disk. During the spinning process, the air flow above the substrate, which first blows down from the aperture on the cover of the spin coater and then flows to the edge along

the substrate radius, drives the dilute PAA solution on the substrate center to flow outward along the radial direction and the formation of thinner films on the center. In addition, the surface tension of the dilute polymer solution will also help to induce a more significant thinning effect in the central area than in the outer region, and this might provide another reason for the formation of muldelike film contours (Figure 3), as pointed out by Dandapat.²²

At this point, we concluded that the uniformity of the film thickness was mainly influenced by the spinning time, ω , and η of PAA. Our experimental results indicate that the suitable η of the PAA solutions for obtaining uniform submicrometer PI films via spin coating was in the range 180–800 cp. Both the film thickness and its uniformity were affected significantly by the spinning time. To obtain PI films with a high uniformity, it was better that the spinning time was confined within 1 min. The film thickness could be effectively adjusted by the variation of η of the PAA solutions and ω . In addition, to prepare thin PI films with a high uniformity, it was necessary that the spin-coating process was carried out in forced-air conditions; this ensured a constant air flow. Also, this could have been realized by the application of a cover or the blockage of the holes on the top of the spin machine.

Finally, by taking all of the previous factors into consideration, we prepared highly uniform PI films with different thicknesses, the results of which are shown in Figure 4. NON% was limited within 1.3% for all of the prepared films; this completely meets the requirements for X-ray astronomy applications. The successful fabrication of perfectly uniform submicrometer PI films were further verified by the AFM three-dimensional image shown in Figure 5, with the observation of an almost negligible surface roughness ($R_a = 0.49$ nm).

Bulge Test

As basic parameters, the mechanical properties of thin films are always of primary concern. However, with decreasing film thickness into the submicrometer level, the conventional standard characterization methods became inapplicable because the

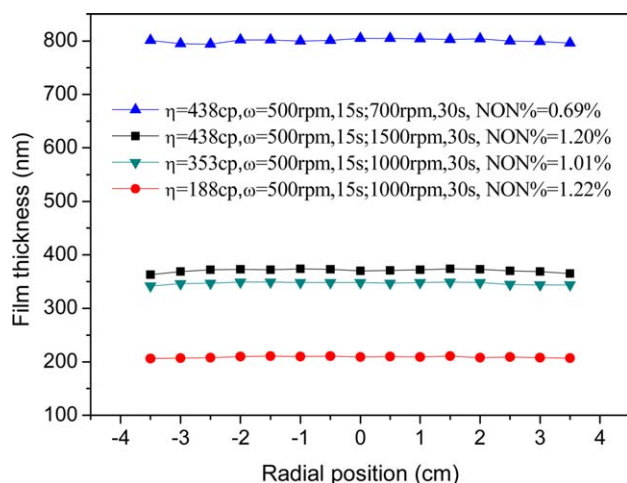


Figure 4. Radial film thickness profiles of the submicrometer PI films prepared under different spinning conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

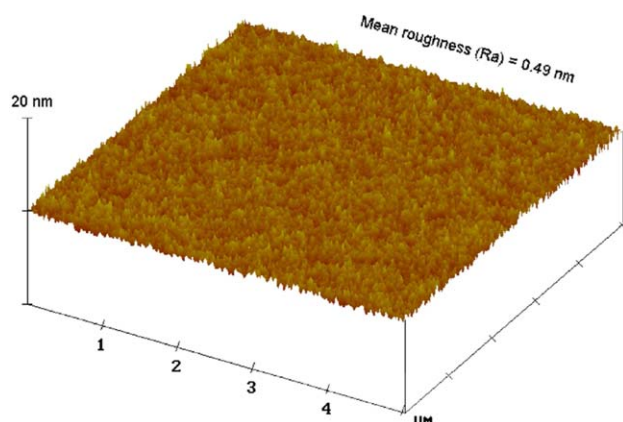


Figure 5. AFM three-dimensional image for the surface of the 200 nm thick PI film in Figure 4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

problems associated with sample handling, mounting, and measurements appeared. Alternatively, the bulge test⁸ is generally used as a common method for testing the mechanical properties of submicrometer thin films, and a burst pressure was used as an indication for the relative strength of the thin films. Figure 6 shows the self-designed bulge test device used in our research.

The properties of the PI films depended not only on the chemical structures of PAA but also on how they were cured or imidized. Ree et al.²³ studied the influence of imidization conditions on the properties of PI films. The results indicate that PI films with low residual stress were obtained when they were heated under multistep thermal imidization cycles at a low heating rate. Accordingly, a heating rate as low as 1°C/min was selected in this study, and the thin films were thermally imidized at 80°C for 1 h and at 230°C for 2 h, respectively, followed by heating at higher temperatures in the range 300–380°C for 2 h.

Figure 7 shows the FTIR-ATR spectra for the PAA film and the corresponding submicrometer PI films obtained at different

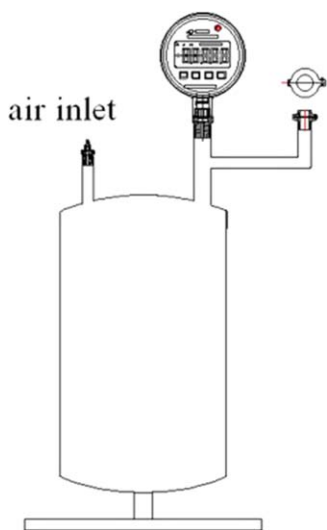


Figure 6. Schematic diagram for the bulge test device. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

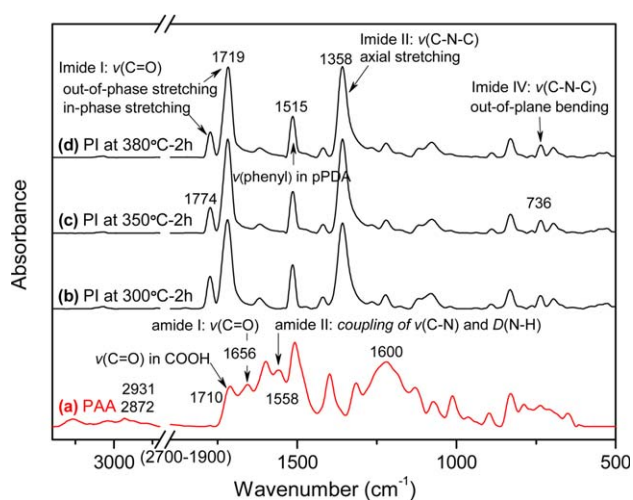


Figure 7. FTIR-ATR spectra for (a) the PAA film and (b–d) the corresponding PI films prepared after thermal treatment of the PAA film to (b) 300°C for 2 h, (c) 350°C for 2 h, and (d) 380°C for 2 h. The thermal cycles were as follows: RT $\xrightarrow{1^\circ\text{C}/\text{min}}$ 80°C/1 h $\xrightarrow{1^\circ\text{C}/\text{min}}$ 230°C/2 h $\xrightarrow{1^\circ\text{C}/\text{min}}$ (300–380°C)/2 h, where RT is room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

final curing temperatures. The amic acid characteristics of the PAA precursor were characterized by the observation of three absorbance bands centered at 1710, 1656, and 1558 cm^{-1} , as shown in Figure 7(a); this corresponded to the carbonyl stretching vibrational mode of carboxylic acid, the amide I band (carbonyl stretching), and amide II band (the coupling of C–N stretching and N–H deformation), respectively.²⁴ After 2 h of curing at 300°C, as shown in Figure 7(b), the appearance of the absorbance bands at 1780 and 1720 cm^{-1} , which were related to the symmetric and antisymmetric stretching vibrations of the imide carbonyl groups (imide I), and the observation of two new absorbance peaks centered at 1358 and 736 cm^{-1} , which were related to C–N–C axial stretching (imide II) and out-of-plane bending (imide IV), respectively,^{24,25} together with the complete disappearance of the amic acid peaks (1710, 1656 and 1558 cm^{-1}) indicate that PI films with well-defined imidization structures were prepared. The IR spectra in Figure 7(c,d) for the films cured to 350 and 380°C for 2 h did not show any significant variations from that in Figure 7(b) for the 300°C-cured films. However, quantitative evaluation of the absorbance peak intensity ratios indicated that I_{1358}/I_{1515} (i.e., the ratio of the IR absorbance intensity at 1358 and 1515 cm^{-1}), which could be used to characterize the degree of cycloimidization,²⁶ increased from 1.96 at 300°C to 2.26 at 350°C; this suggested an increase

Table I. Burst Pressure for Thin PI Films Prepared under Different Thermal Treatment Cycles

Imidization procedure	Burst pressure (KPa)
80°C, 1 h; 230°C, 2 h; 300°C, 2 h	13.341
80°C, 1 h; 230°C, 2 h; 325°C, 2 h	15.024
80°C, 1 h; 230°C, 2 h; 350°C, 2 h	20.207
80°C, 1 h; 230°C, 2 h; 380°C, 2 h	18.265

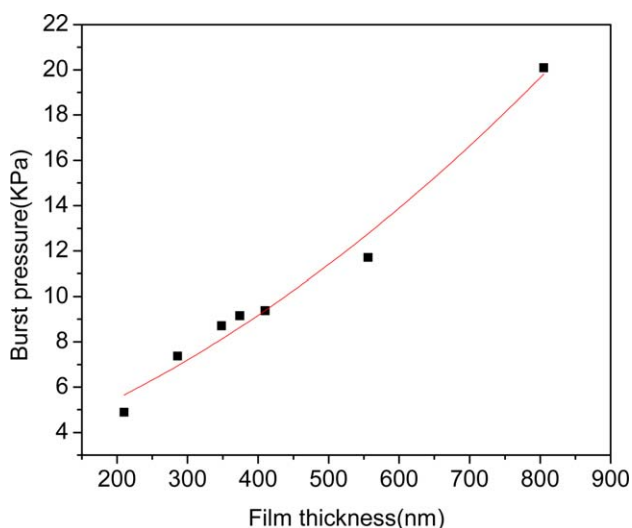


Figure 8. Burst pressure versus the thickness of the thin PI films. (The final curing temperature was 350°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in the imidization degree at higher temperatures. However, when the final thermal treatment temperature was increased to 380°C, I_{1358}/I_{1515} showed a slight decrease to 2.21; this was probably due to the slight degradation occurring in the polymer chains at elevated temperatures in air.^{27,28}

Table I shows the mechanical properties for our submicrometer PI films (805 nm) prepared under different ultimate imidization temperatures. The PI films were peeled from the substrate by the method developed by S. F. Powell.²⁹ The burst pressure was measured on the bulge test device with an inside test aperture diameter of 2.64 cm. As observed, with the increase in the ultimate thermal treatment temperature from 300 to 350°C, the burst pressure of the films increased rapidly from 13.3 to 20.2 KPa. This was reasonable and was attributed to the formation of better imide structures under high temperatures consistent with the IR characterization results shown in Figure 7. However, the film subsequently exhibited a slightly reduced burst pressure when the temperature was increased to 380°C. This seemed strange but was not unexpected because thermooxidative degradation may occur at enhanced temperatures in air²⁷ and lead to a decrease in the mechanical properties in accordance with the observation of a slight decrease in I_{1358}/I_{1515} of the IR curve, as shown in Figure 7(d) (380°C). The results shown here suggest that the ultimate imidization temperature played an important role in determining the final mechanical properties (burst pressure) of the submicrometer PI films. To obtain submicrometer PI films with desirable mechanical properties, it was better to control the final imidization temperatures at around 350°C.

Figure 8 shows the burst pressure variations for the submicrometer PI films as a function of the film thickness. The results indicate that at a final imidization temperature of 350°C, the burst pressure of the submicrometer PI films increased almost proportionally with the film thickness; this suggested that great compactness and uniformity were realized in the prepared films. The 210-nm PI thin films exhibited a burst pressure around 4.9 KPa. When the film thickness was increased to 805 nm, submicrome-

ter PI films with a burst pressure of over 20 KPa were finally obtained. This demonstrated the availability of spin coating to produce robust, large-area, and highly uniform submicrometer self-standing PI films for X-ray astronomy applications.

CONCLUSIONS

Submicrometer PI films with a high thickness uniformity were successfully prepared via spin-coating techniques. The experimental results indicate that the PI film thickness and its uniformity were strongly dependent on the spinning time, ω , and η of the PAA solutions. Highly uniform PI films with thickness fluctuations of less than 2% were successfully prepared when the PAA solutions with η values in the range 180–800 cp and a spinning time within 1 min were used. Bulge test results show that the mechanical properties of the submicrometer PI films increased almost proportionally with the film thickness, and the 805-nm films cured at a final imidization temperature of 350°C exhibited optimum properties with a burst pressure over 20 KPa at an inside test aperture diameter of 2.64 cm. This work demonstrated that spin-coating technique could be applied in the preparation of robust and highly uniform self-standing submicrometer PI films with fairly large areas ($\Phi = 8$ cm) for X-ray astronomy applications.

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