

# Synthesis and characterization of polyimide thin films obtained by thermal evaporation and solid state reaction

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In this research polyimide films were prepared by physical vapor deposition (PVD), using solid state reaction of pyromellitic dianhydride (PMDA) and p-phenylene diamine (PDA) to form poly(amic acid) (PAA) films. The resultant films were converted to polyimide by thermal treatment, usually below 300 °C. For this study, a FT-IR spectrometer has been used to measure the effect of imidization temperature on the chemical structure of the vapor-deposited thin films of aromatic PI. When temperature increased, an increase in all absorption peaks was observed. This suggests that residual PAA monomers continued to be converted into PI. The surface topology of the PI films obtained at imidization temperatures of 150, 200, 250 °C for 1 hour was further examined by using AFM atomic force microscopy. It can be clearly seen that the surface became rougher with increasing imidization temperature. The thermal stability of polyimide was also studied by using thermogravimetric analysis (TGA).

Keywords: *polyimide thin films; thermal imidization temperature; thermal evaporation; polycondensation reactions*

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## 1. Introduction

Polyimides are very important polymers, thermally very stable, having wide practical applications. From that reason, the knowledge about relations between synthesis and structure, including physicochemical properties of the compounds is essential [1]. Innovative polyimide design led to their use in aerospace, microelectronics, automotive and packaging industries [2]. Polyimides, due to their excellent thermal stability and mechanical strength, high stability to ionizing radiation, good film forming ability and superior chemical resistance, became important materials in the manufacture of a large number of technical products, e.g. varnishes, coatings etc. [3]. Since the excellent properties of polyimides are a result of combination of both chemical structure and final morphology of the product, it is important to understand the structural evolution within the material during imidization process, which directly affects the final thermal, mechanical and optical properties [4].

Polyimides are step or condensation polymers derived from both aliphatic or aromatic dianhydrides and diamines [5].

Vapor deposition of the precursors and solid state reactions of imidization are of a greater priority than the spin coating and dipping methods. The physical vapor deposition as a “dry” method provides high purity material for producing thin polymer films of controlled thickness, ratio of precursors and composition [6]. In this paper results of physicochemical investigations of polyimides received from dianhydride (PMDA) and P-phenylene-diamine (PDA) at different temperatures are presented.

## 2. Experimental

The polyimide was synthesized by a two-step reaction, as shown in Fig. 2. We used pyromellitic dianhydride (PMDA) and p-phenylene diamine (PDA), commercially available from Sigma-Aldrich. These two monomers, 2 g each, were evaporated from two separate boats to form a poly(amic acid) (PAA) thin film on a substrate.

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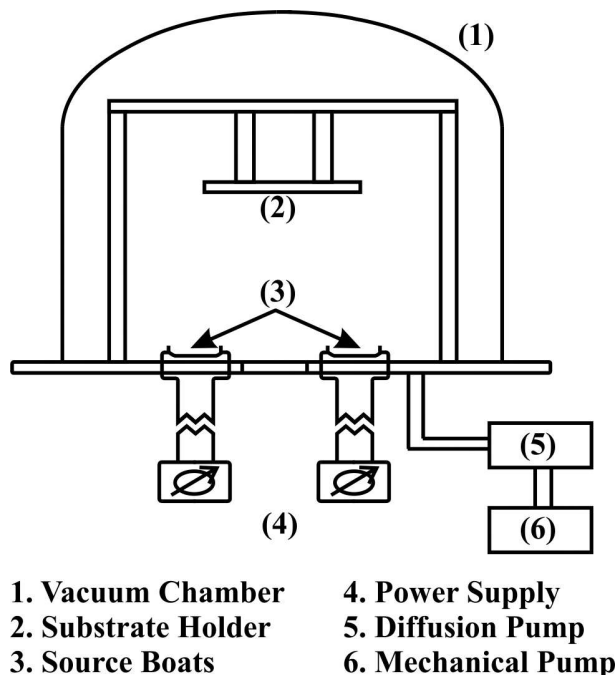


Fig. 1. Schematic illustration of the PVD chamber.

The substrates used were silicon wafers and glass. The deposition process was carried out in vacuum of  $2 \times 10^{-3}$  Pa. Fig. 1 shows the scheme of the PVD apparatus [4]. The resultant polyamic acid PAA film was then soft baked to remove the  $H_2O$  from the substrate followed by a thermal treatment at 150, 200 and 250 °C for 1 h in an air circulating oven.

In the case of PI, the purpose of thermal treatment was to run polycondensation reactions in solid state till completion of the PI formation. As a consequence of these reactions a release of water and imidization took place. The final thickness of the films was  $5 \pm 0.1$   $\mu\text{m}$ .

### 3. Results and discussion

#### 3.1. FT-IR analysis

FT-IR measurements have been performed for the films obtained at different imidization temperatures to determine the completion of imidization reaction of the polyimide films. The changes in transmission peak magnitude of the functional groups or in the characteristic linkages during the

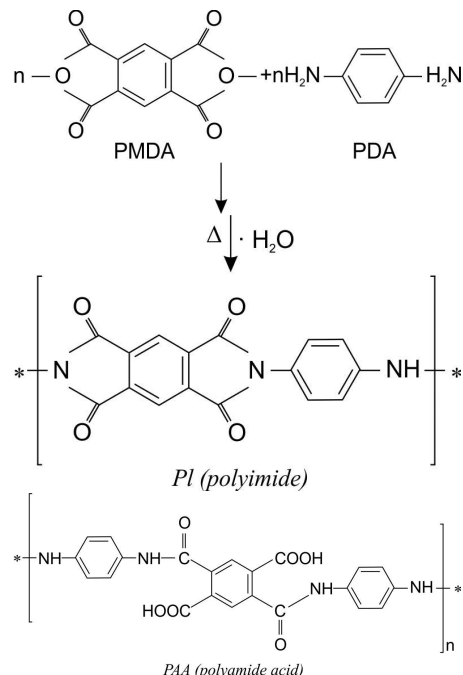


Fig. 2. Two-step synthesis of polyimide.

reaction were analyzed. Fig. 3 shows the changes in FT-IR spectra of PMDA-PDA obtained at different imidization temperatures of 150, 200 and 250 °C for 1 h.

When temperature increases, an increase in all the absorption peaks is observed. This suggests that residual PAA monomers continue to be converted into PI. This evolution is stabilized after exposure to temperature above 250 °C [3, 7].

The spectra have been normalized to the classical aromatic ring  $C=C$  absorption band appearing around  $1500 \text{ cm}^{-1}$ , and the absorption peak at  $1365 \text{ cm}^{-1}$ ,  $C-N$  stretching vibration of imide ring, was monitored during the curing, leading to transformation of PAA to PI. The absorption peaks at  $1790 \text{ cm}^{-1}$  and  $1730 \text{ cm}^{-1}$  indicate that there is asymmetry and symmetric stretching vibration of  $C=O$  bonding. The absorption peak at  $710 \text{ cm}^{-1}$  corresponds to the flexural vibration of  $C=O$  bonds [8, 9].

#### 3.2. Atomic force microscopy (AFM)

The AFM analysis provided information on the changes in the surface morphology and roughness

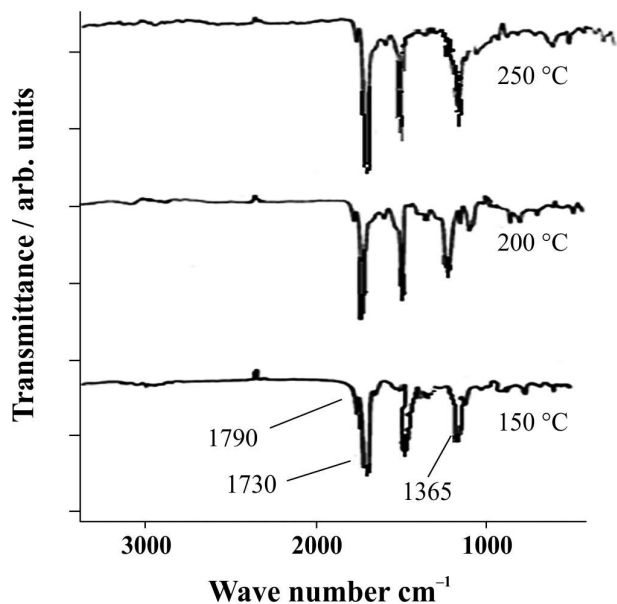


Fig. 3. FT-IR spectra of PMDA-PDA obtained at different imidization temperatures.

caused by the heat treatment. Fig. 4 shows the AFM topographic images of the polyimide films subjected to imidization at temperatures of 150, 200 and 250 °C for 1 h.

It can be clearly seen that the surface became rougher with increasing imidization temperature, creating a distinctive surface structure [10]. This indicates that the films of PAA and fully cured PI have comparable roughness and thickness uniformity; i.e. curing has significantly roughened the surface in the conditions used in this work.

The surface topology of the PI films was further examined by using AFM (Fig. 5). Nodular aggregates are aligned in several rows [11]. Moreover, the area of the dark spots, indicating the troughs on the surface increased when the imidization temperature was increased, for instance, some kind of decomposition occurred at the elevated temperatures before the imide chain decomposition took place [6, 12].

### 3.3. Thermal stability

Fig. 6 shows the weight loss of the PI films with temperature at a heating rate of 10°/min as measured by TGA in air.

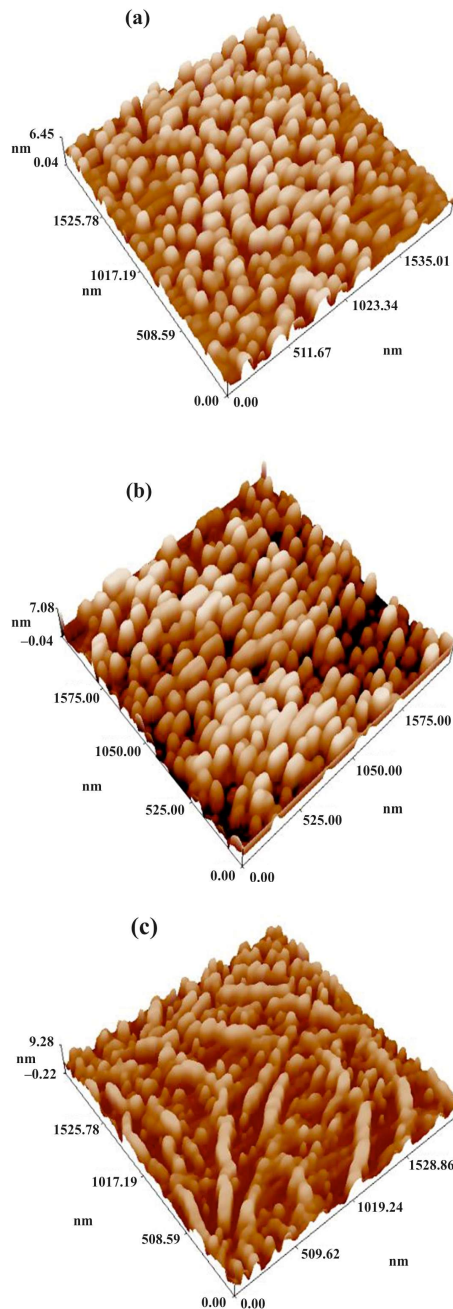


Fig. 4. 3-D AFM images of PI thin films obtained at imidization temperatures of (a) 150, (b) 200 and (c) 250 °C.

The three curves in the figure indicate the thermal stability of PI films obtained at imidization temperatures of (a) 150, (b) 200 and (c) 250 °C.

It can be observed from Fig. 6 that the temperatures, at which the weight loss has occurred are

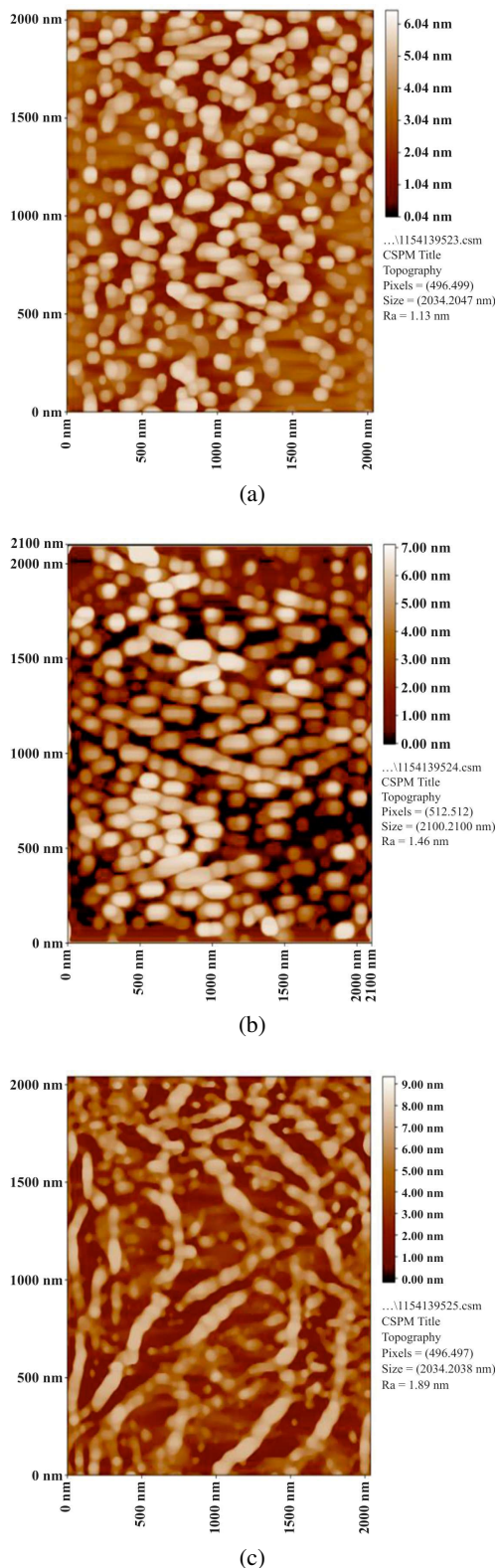


Fig. 5. 2-D AFM images of PI thin films obtained at imidization temperatures of (a) 150, (b) 200 and (c) 250 °C.

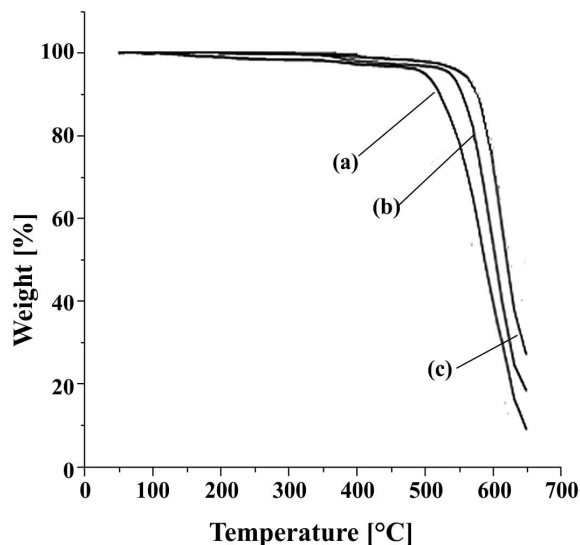


Fig. 6. TGA curves for PI thin films obtained at imidization temperatures of (a) 150, (b) 200 and (c) 250 °C.

500, 530 and 560 °C for PI-a, PI-b and PI-c, respectively. The continuous weight loss in the initial stage may be attributed to the evaporation of the preabsorbed water and solvent from the films [9]. It was also found that the temperature of thermal weight loss increased with the increasing of thermal imidization temperature of PAA. The weight loss became more pronounced, indicating the occurrence of imidization.

This result implies that imidization temperature had a significant influence on the thermal weight loss [13, 14]. At temperature above 580 °C, the samples started to decompose drastically. For the typical film, as shown in Fig. 6, the rapid weight loss above 490 °C may result from solvent evaporation and imidization. A complete decomposition took place at 585 °C [4, 15].

#### 4. Conclusions

In this research polyimide films were prepared by the vapor deposition using the reaction of a PMDA-p-PDA mixture, which was converted to polyimide by solid state reaction at different imidization temperatures. When temperature increased, an increase in all the absorption peaks was

observed in FT-IR spectra. The AFM analysis provided information on the changes in the surface morphology and roughness introduced by the heat treatment. The thermal properties of all polyimides varied, depending on the structure of the monomer.

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