Structures and Properties of Polyimide with Different Pre-imidization Degrees

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Abstract A series of polyimide (PI) films derived from pyromellitic dianhydride (PMDA) and 4,4’-oxydianiline (ODA) were prepared with the employment of chemical pre-imidization, and the pre-imidization degree (pre-ID) was found influential on structures and properties of the films obtained. Specifically, a certain degree of chemical imidization could promote the in-plane orientation of molecular chains inside the film, which then enhanced the mechanical strength and reduced the coefficient of thermal expansion (CTE) of the films. Further, such pre-imidization process could expand the internal space gap inside the films, thereby lowering their dielectric constant and glass transition temperature. Our study provides a new approach for preparing high-performance PI films through chemical imidization.

Keywords Polyimide; Pre-imidization; Stacking model; In-plane orientation

INTRODUCTION

Polyimide films enjoy a great popularity in the application areas of aerospace, microelectronics, communication, machinery, etc., for they generally outperform the rival materials in terms of heat resistance, mechanical properties, insulation properties, and UV resistance. Despite the rapid advancement of PI films in the past decades, their properties under extreme circumstances require urgent improvement.

Polyimide films are typically prepared from poly(amic acid) (PAA), with imidization being the key step that plays a decisive role in the performance of the product. The imidization reactions mainly fall into two categories, thermal imidization and chemical imidization. The thermal method refers to the ring-closing reaction assisted by high-temperature heating and accompanied with a complete removal of solvents; multiple processes including solvent removal, ring closure, molecular chain packing, and drawing orientation proceed concurrently and overlap with each other, making the imidization procedure difficult to control. On the other hand, the chemical pathway utilizes chosen reagents to lower the energy barrier of imidization; poly(amic acid) precursors will be imidized at lower temperatures and a higher solvent content, which is advantageous to the control of molecular chain orientation in a drafting process. However, complete imidization can hardly be achieved in this way, and consequently, comprehensive performance of the final products might be largely compromised.

Previous studies have shown that proper arrangement of rigid structure and flexible segments is beneficial to a better alignment of molecular chains and thus enhances mechanical properties of the polymer products. This inspires us to perform pre-imidization on poly(amic acid) in order to delicately regulate the chain structure of the PI products; solvent removal through heating can further complete molecular chain packing and imidization. In this process, the already imidized segment has a relatively high rigidity and exists in an extended state, which can improve the in-plane regularity of the molecular chain and thereby the mechanical properties. In the meantime, the rigid segments restrict molecular chains from interplaner dense packing, so that the expanded free volume between planes should lead to lowered dielectric constant. In short, the preparation route we designed aims at endowing the PI films with both low dielectric constant and favorable mechanical properties, breaking the bottleneck of difficult balance between dielectric and mechanical properties.

To verify this idea, we started from PMDA/ODA-derived PAA and synthesized a series of PI-PAA solutions with different pre-imidization degrees (pre-IDs) by adding various amounts of acetic anhydride as the dehydrate agent and certain amount of pyridine as the catalyst. PI films were formed through a doctor blade approach. Solvent removal and imidization were completed by temperature programming, while no drafting was applied during the film preparation. Pre-IDs of the PI-PAA solutions were characterized by UV and IR spectrosopies, and basic mechanical properties and thermo-mechanical behavior of the PI films were characterized by universal material testing and static thermomechani-
cal analysis, respectively. The molecular chain arrangement was further analyzed by XRD, and variations in the free volume were revealed by dielectric measurement and DMA test. Finally, a stacking model of molecular chains was established based on the relationship between free volume and molecular chain compliance as demonstrated by molecular simulation.

EXPERIMENTAL

Materials
Pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) were supplied by Bohai Chemical, Wuxi, N,N-dimethylacetamide (DMAc) and acetone were purchased from Fuchen Chemical Reagents Co., Tianjin, China). Pyridine was obtained from Aladdin Bio-chem Technology Co., Shanghai, China. Acetic anhydride was provided by China National Pharmaceutical Group Co., China.

Preparation of PI-PAA Solution
To a three-necked flask equipped with a mechanical stirrer and an ice water bath was charged DMAc as the solvent to dissolve monomer ODA firstly. Then, the other monomer, PMDA, was introduced into the reaction system via multiple entries. Continuous stirring for 24 h afforded a PAA solution with 10 wt% solid content, which was then divided equally into 5 portions to be added separately with different amounts of dehydration agents and catalysts. The reaction mixtures were stirred for another 24 h at room temperature to give homogeneous PAA-PI solutions with different pre-IDs. For clarity, the solutions prepared from 0, 10 mol%, 20 mol%, 30 mol%, and 40 mol% of dehydration agents relative to the original amino groups were abbreviated as PI-0, PI-10, PI-20, PI-30, and PI-40, respectively. The synthetic route is concisely outlined in Scheme 1.

Preparation of Polyimide Films
For film formation, the PAA-PI solutions prepared were cast onto glass plates and baked in a vacuum oven successively at 135 °C for 2 h and then 300 °C for another 2 h.

Characterization
For accurate and handy measurements, the PI-PAA solution was coated on a glass slide and immersed in acetone for 30 min to replace DMAc with acetone. The PI-PAA mixture precipitated out was stored in a 60 °C oven for 30 min to give a PI-PAA film free of solvent.

Infrared spectroscopy was performed using a Fourier transform infrared spectrometer (iS5) from Thermo Nicolet, USA. The test conditions were 16 scans with a resolution of 4 cm⁻¹ and a spectral range of 4000−400 cm⁻¹. A strong absorption band at 1500 cm⁻¹, which is assigned to the stretching vibration of para-substituted benzene ring, kept almost unchanged in the cyclization process, while the band at 1776 cm⁻¹ derived from the in-phase (symmetric) stretching vibration of two carbonyl groups on the five-membered imine ring of PI was taken as a characteristic absorption band of PI. The area ratio of these two bands was used to calculate the pre-ID of the PI-PAA system using the following equation,

\[
ID = \frac{S_{1776}}{S_{1500}}
\]

where \(S\) is the band area of absorption, and \(T = 350 °C\) is taken as the temperature that ensured complete imidization.

Ultraviolet (UV) absorption spectrum was produced on a UV-visible spectrophotometer (UV-2550) manufactured by SHIMADZU, Japan. The absorption mode was adopted, and the spectral range was 600−200 nm.

Mechanical properties of the films were evaluated on a universal material testing machine (SANS CMT-4101) at room temperature.

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temperature with the crosshead speed of 10 mm/min.

X-ray diffraction (XRD) was performed on an X-ray diffractometer (D/max-2550PC) from Bruker AXS in Germany for structural analysis. The radiation source used in the instrument was Cu Ka (λ = 0.154 nm), the tube voltage and the tube current were 40 kV and 40 mA, respectively, the scanning rate was 10°/min, and the scanning range was 5°−90°.

The glass transition temperature (Tg) was tested on a dynamic thermal mechanical analyzer (Q800). Samples were heated from 25 °C to 450 °C at a heating rate of 5 °C/min under a nitrogen atmosphere. Tg was taken as the peak temperature of the tanδ curve.

Dielectric permittivity and loss tangent were measured on a precision impedance analyzer (Agilent 4294A). Film samples coated with platinum on both sides as the electrode (1 cm × 1 cm) were scanned from 10³ Hz to 10⁷ Hz at room temperature.

Coefficient of thermal expansion (CTE) of the films was acquired from thermomechanical analysis (TMA, TA Q400EM) under a tension mode (tension force 0.05 N); the heating rate was 5 °C/min and temperature range was 50−200 °C. Data were collected from the second heating scan after thermal history of the films was eliminated via annealing.

The fractional free volume (FFV) of PAA and PI was calculated by molecular dynamics (MD) simulation (Materials Studio 2017). For modelling, molecular chains composed of PAA and PI with 20 units were assessed in the COMPOSS force field. A cubic simulation cell for PAA and PI matrix with 10 molecular chains was constructed using the Amorphous Cell module, and a series of MD calculations were carried out in either NPT (fixed number of atoms, pressure, and temperature) ensemble or NVT (fixed number of atoms, cell volume, and temperature) ensemble.

RESULTS AND DISCUSSION

Characterization of PI-PAA Solutions

In the presence of acetic anhydride and pyridine, poly(amic acid) was partially converted into polyimide through dehydrolysis, and the structural changes during dehydration were well tracked by infrared spectroscopy. The asymmetric stretching band of carbonyl group (1776 cm⁻¹) was taken as an indicator of the imide structure, and an enhanced band intensity suggested an increased imide content, i.e. an improved degree of pre-imidization (Fig. 1). To further quantify the pre-ID values, band area at 1776 cm⁻¹ was normalized against that at 1500 cm⁻¹, which is assigned to the stretching vibration of benzene ring, due to its stability in the reaction process. The sample fully imidized via thermal treatment at 350 °C was taken as a reference, and pre-ID of other samples was thus calculated according to Eq. (1). As listed in Table 1, the degree of pre-imidization was nearly proportional to the amount of acetic anhydride added into the system, which demonstrates the reactions were well controlled.

The conjugation effect of imide and benzene rings could promote the movement of electrons, which causes the films to absorb more visible light at low wavelengths (Fig. 2). The yellow color of the polymers came from this mechanism, and with increasing pre-ID, the enhanced conjugation effect led to the darkened colors (Fig 3).

Characterization of PI Films

Mechanical properties of PI films with different pre-IDs were firstly investigated. As shown in Fig. 4, the higher the pre-ID, the greater the modulus and tensile strength. Such improvement in mechanical performance may be caused by the orientation of molecular chains inside the films. Linear CTE in film plane

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direction is another important measure of chain alignment, and a higher degree of in-plane chain orientation typically leads to lower CTE values. CTE is temperature dependent and therefore, the average between 50 and 200 °C was reported for each sample. Data collected in Fig. 5 reveal a downtrend of CTE with enhanced pre-ID, which suggests that chain orientation inside PI films was getting better gradually. This observation also conforms to the variation in mechanical properties mentioned above.

To look closely into the arrangement of molecular chains, X-ray diffraction was performed on the PI films (Fig. 6). The pattern of PI film without pre-imidization (PI-0) exhibits a typical dispersion peak, indicative of an amorphous state of the polymer at room temperature. In comparison, the application of pre-imidization sharpens the diffraction peak, namely, the PI chains were better ordered and existed with higher alignment.

Measurements on dielectric properties of the PI films are summarized in Fig. 7. Dielectric constant and dielectric loss of all the samples varied little at lower frequencies, but the former dropped slightly while the latter raised as the scanning frequency was further increased (Figs. 7a and 7b). This is due to the fact that most dipole orientations can keep up with the alternating electric applied field of lower frequencies, so the higher degree of dipole orientation endows the PI samples with a relatively high and stable dielectric constant. Conversely, dipoles can hardly follow the applied electric field if the frequencies are much too high. As a result, the heat losses produced would cause decrement in dielectric constant and increment in dielectric loss.

To further investigate the effect of pre-IDs on dielectric properties, dielectric constants at 1 MHz were compared among these samples (Fig. 7c). Intriguingly, a downward tendency was observed as the pre-ID increased. Since no fluorine-containing groups existed in our PI system, we speculated that the decrease in dielectric constant was caused by an increase in the free volume of the film. Then, DMA was conducted to test this conjecture. Glass transition temperature (T_g) of PI films was defined as the peak temperature of the tanδ curves and collected in Fig. 8 inset. Samples with higher pre-ID exhibited lower T_g, which suggests that pre-imidization could enlarge the free volume among PI molecules.

Molecular dynamics (MD) simulation is an intuitive method for depicting the internal structure of a polymer. Fig. 9 compares the simulated results of PAA and PI, in which the blue and gray regions in the simulation unit stand for the free volume and possession volume of the sample, respectively. Based on the optimized model structure, the fractional free volume (FFV) of a polymer could be calculated from its specific volume and occupied volume using the following equation:

\[
FFV = \frac{V_f}{V_o} = \frac{V_f}{V_f + V_o}
\]
where \( V, V_0 \), and \( V_W \) are the specific volume, the occupied volume, and the van der Waals volume of a polymer, respectively.

According to the calculation results gathered in Table 2, PI possesses a larger free volume than PAA. In other words, a higher degree of pre-imidization would cause a greater free volume inside the film, so that the dielectric constant and glass transition temperature were correspondingly decreased.

As discussed above, the variation of mechanical properties and CTE of the PI films suggests an improved regularity of molecular chain alignment as well as a tighter packing pattern when the degree of pre-imidization was enhanced, but contrarily, the analyses on dielectric constant, glass transition temperature, and free volume lead to the very opposite conclusion. Considering that the films in this study were only subjected to solvent removal and imidization but no drawing process, we thus proposed a specific model to rationalize the packing behavior of molecular chains. As depicted in Fig. 10,

Table 2  Theoretical density, specific volume, occupied volume, and calculated FFV for PI and PAA samples.

| Sample | Density (g/cm\(^3\)) | Specific volume (Å\(^3\)) | Occupied volume (Å\(^3\)) | FFV  |
|--------|-----------------------|----------------------------|-----------------------------|------|
| PAA    | 1.3953                | 99604                      | 66977                       | 0.3276|
| PI     | 1.3148                | 96955                      | 60722                       | 0.3737|

Fig. 7  (a) Dielectric constant and (b) dielectric loss spectra of PI films with different pre-IDs; (c) Dielectric constant of the PI films at 1 MHz.

Fig. 8  \( \tan \delta \) curves of PI films with different pre-IDs.

Fig. 9  Simulation models of (a) PAA and (b) PI.
during the gradual removal of solvent in a neat PAA solution, the flexibility of PAA chains allow them to closely pack and fill as much space as possible via conformational rotation; therefore, free volume of the resultant PI product is relatively low. In comparison, chemical pre-imidization converts amic acid partially into imide, and this five-membered ring structure rigidifies the molecular chain locally. When the molecular chains consisting of both soft segments and rigid segments undergo solvent removal, they tend to align in the planar direction, which contributes to better mechanical properties and thermal dimensional stability. In the meantime, enhanced chain rigidity limits the chains from conformationally rotating and sufficiently filling the interchain space. Consequently, larger free volume is formed between layers, leading to decrement in dielectric constant and glass transition temperature.

CONCLUSIONS

In this research, a series of PI films polymerized from PMDA and ODA were prepared with the employment of chemical pre-imidization. Tensile strength and Young’s modulus of the PI films showed an increasing trend with enhanced pre-ID while their CTEs were reduced. These observations were explained by the improved regularity of molecular chain alignment, as confirmed by X-ray diffraction patterns. On the other hand, higher pre-ID was found inductive to lowered dielectric constant and $T_g$ of the PI films. According to MD simulations, this might result from an expanded free volume of PI relative to PAA the precursor. Specifically, the stacking of molecular chains with different flexibility during thermal cyclization could generate a larger free volume. To summarize, pre-imidization can exert a significant effect on the aggregate structure of PI films and therefore break the bottleneck of improving simultaneously the significant effect on the aggregate structure of PI films and thereby free volume of the resultant PI product is relatively low. In comparison, chemical pre-imidization converts amic acid partially into imide, and this five-membered ring structure rigidifies the molecular chain locally. When the molecular chains consisting of both soft segments and rigid segments undergo solvent removal, they tend to align in the planar direction, which contributes to better mechanical properties and thermal dimensional stability. In the meantime, enhanced chain rigidity limits the chains from conformationally rotating and sufficiently filling the interchain space. Consequently, larger free volume is formed between layers, leading to decrement in dielectric constant and glass transition temperature.

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