

## Comparison of Different Methods for Determining the Imidization Degree of Polyimide Fibers<sup>\*</sup>

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**Abstract** In this study, polyimide fibers at different stages of imidization were characterized by TGA, DSC, and FTIR. The imidization degree (ID) calculated by TGA was based on the weight loss of each sample, which was caused by the imidization of residual amic acid groups. The results of TGA showed good regularity with the thermal treatment temperature of the PI fibers. For DSC, the ID was calculated based on the area of endothermal peak of each sample. Compared with TGA, DSC showed a relatively higher value because the endothermal peak was reduced by the exothermic re-formation of polyamic acid which may be partially degraded during thermal treatment. The IDs obtained by the FTIR spectra generally showed poorer regularities than those obtained by both TGA and DSC, especially for the results calculated using the 730 cm<sup>-1</sup> band. Based on the 1350 cm<sup>-1</sup> band, the obtained IDs showed better agreement with the TGA or DSC results. The results obtained by these three methods were compared and analyzed. The ID obtained by TGA showed much more reliability among these three methods.

**Keywords:** Imidization degree; Polyimide fibers; Polyamic acid; Polyimide; Characterization.

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## INTRODUCTION

Aromatic polyimide (PI) is a high-performance material with good thermal stability, chemical resistance, and excellent mechanical properties. Aromatic PI has important applications in the fields of constructional or functional materials, such as high-performance fibers and films, thermosetting or thermoplastic resins, heat-resistant adhesives and coatings, and foamed plastics<sup>[1–6]</sup>. Most aromatic PIs can only be produced *via* two-step method because they exhibit relatively poor solubility, whereas their precursor, polyamic acid (PAA), is soluble in common solvents, such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP)<sup>[7–10]</sup>. In the two-step method, PAA is synthesized first and then imidized into PI through chemical or thermal routes. Thus, the imidization process considerably influences the final properties. In

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fiber manufacturing, a reliable way of measuring the imidization degree (ID) of fibers is also of great importance in developing the fabrication technology.

The conversion ratio of PAA into PI during imidization is a frequently discussed research topic. FTIR is the most commonly used method to determine the ID<sup>[11–14]</sup> or characterize the chemical change during imidization<sup>[15]</sup>. Pryde<sup>[11, 12]</sup> studied the imidization of BPDA-PDA and BTDA-ODA-MPDA PAA using FTIR from 1780, 730, and 1350 cm<sup>-1</sup> bands, and found that only the results obtained by 1350 cm<sup>-1</sup> band can offer a reliable way to follow the imidization, and the former two bands are influenced either by the bands attributed to anhydride or by the dichroic effect. Wu *et al.*<sup>[16]</sup> studied the effect of hydrogen bonds on properties of PI fibers containing 2-(4-aminophenyl)-6-amino-4(3H)-quinazolinone moieties by deconvoluting the FTIR absorption band between 1750 and 1700 cm<sup>-1</sup>. Moreover, the content of hydrogen-bonded imide was evaluated by the area of the deconvoluted peaks. In addition, with help of *in situ* devices, real-time FTIR shows a more powerful application in exploring the imidization process<sup>[17, 18]</sup>. Recently, Cakmak *et al.*<sup>[18]</sup> utilized a custom *in situ* device for real-time measurements of thermal imidization kinetics of PMDA-ODA films and evaluated the IDs by considering the dichroic effect.

TGA and DSC are also effective techniques to characterize the imidization process. Brekner<sup>[19, 20]</sup> has applied TGA and DSC techniques to study the complexes between amic acid groups and NMP solvents. Both the model molecules of diamic acid and PAA of PMDA-ODA were investigated, and a ratio of 1/4 and 1/2 was found between the amic acid units and NMP molecules at different curing temperatures. Ree<sup>[21]</sup> and Nakamae<sup>[22]</sup> measured  $T_g$  of several kinds of PAAs (*i.e.*, PMDA-ODA, BPDA-PDA, and BPDA-ODA) using temperature-modulated DSC and studied the influences of the contents of NMP solvents on  $T_g$ .

In the present study, PAA fiber synthesized by 3,3',4,4'-biphenyltetra-carboxylic dianhydride (BPDA) and *p*-phenylenediamine (PDA) was applied to study the ID using TGA, DSC, and FTIR techniques. The results obtained by these three methods were compared and analyzed to find a reliable approach for measuring ID.

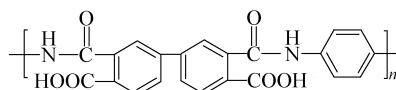
## EXPERIMENTAL

### Materials

3,3',4,4'-Biphenyltetra-carboxylic dianhydride (BPDA) and *p*-phenylenediamine (PDA) were all purchased from Shanghai Research Institute of Synthetic Resins. And the BPDA was dried at 200 °C for 20 h. The PDA was purified by recrystallization. DMAc as the solvent was purchased from Tianjin Fine Chemical Company and used as received.

### Preparation of Polyamic Acid Fibers

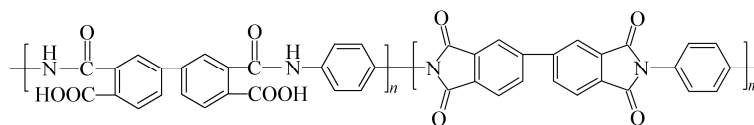
PAA was polymerized by BPDA and PDA in DMAc at a low temperature. This PAA solution was filtered and degassed before fiber spinning. As-spun PAA fibers were prepared *via* dry-jet wet-spinning technology by extruding PAA solution through a spinneret (50 holes, 80 μm) into air first and then drawn into coagulation bath. The air gap between spinneret and coagulation bath is about 4 cm. And the coagulation bath was a mixture of water and DMAc ( $V/V = 5/4$ ). After five times of washing by deionized water, the as-spun PAA fibers were dried in an air oven at 80 °C for 12 h. The structure of PAA fibers is shown in Scheme 1.



**Scheme 1** Chemical structure of PAA fiber

### Sample Preparation

PI fibers with different imidization degrees were obtained by heating PAA fibers from room temperature to different end temperatures under nitrogen atmosphere at a rate of 5 K·min<sup>-1</sup>. All PI fibers were denoted by its end temperatures as PI-*temp*, for example PI-180 means the PAA fiber was treated from room temperature to 180 °C. The structure of PI fibers at different imidization stage is shown in Scheme 2.



**Scheme 2** Chemical structure of PI fibers with different imidization degrees

### TGA Coupled with Mass Spectrometry (TGA-MS)

To study the imidization process, PAA fiber was characterized in TGA (TA, STD-Q600) at a heating rate of  $15 \text{ K} \cdot \text{min}^{-1}$  from room temperature to  $400^\circ\text{C}$ . And the off-gas was collected and analyzed by an MS detector (Pfeiffer Vacuum, THERMOSTAR).

### $^1\text{H-NMR}$ Spectroscopy

The  $^1\text{H-NMR}$  spectra of PAA fibers were performed in  $\text{DMSO-d}_6$  with a 400 M NMR spectrometer (Bruker AV-400). The content of DMAc in fiber was estimated by aromatic protons of PAA and all protons of DMAc.

## METHODS

### TGA Measurements of ID

Measurement of ID by TGA (Q50, TA Instruments) was based on the weight loss which was caused by the imidization of residual polyamic acid chains in PI fibers. The measurement was performed from  $60^\circ\text{C}$  to  $400^\circ\text{C}$  with a heating rate of  $15 \text{ K} \cdot \text{min}^{-1}$  under nitrogen atmosphere. For stable measurements, the fiber sample was placed into an alumina cup ( $40 \mu\text{L}$ ), which was then placed on the platinum pan.

To calculate the ID, the mass of fiber sample before and after imidization must be obtained. However, both the initial and end points of imidization were not easily recognized for the raw PAA fibers after washing and drying in production, as in Fig. 1(a). The residual solvents (actually only water, and this will be discussion later) in fiber may induce a notable weight loss, which will overlap with the process of imidization. Thus, all the samples were kept at  $100^\circ\text{C}$  for 20 min to eliminate the influence of the residual water before regular measurements. After this pre-drying process, the weight retention of PAA fibers began to decrease obviously at about  $150^\circ\text{C}$  as shown in Fig. 1(a), indicating a thorough elimination of the residual water. For the end point of imidization, two points were chosen for calculation and comparison. As shown in Fig. 1(b), the first end point was selected at the temperature that was the minimum of the DTG curve at about  $300^\circ\text{C}$ , and the second one was the minimum at about  $400^\circ\text{C}$ .

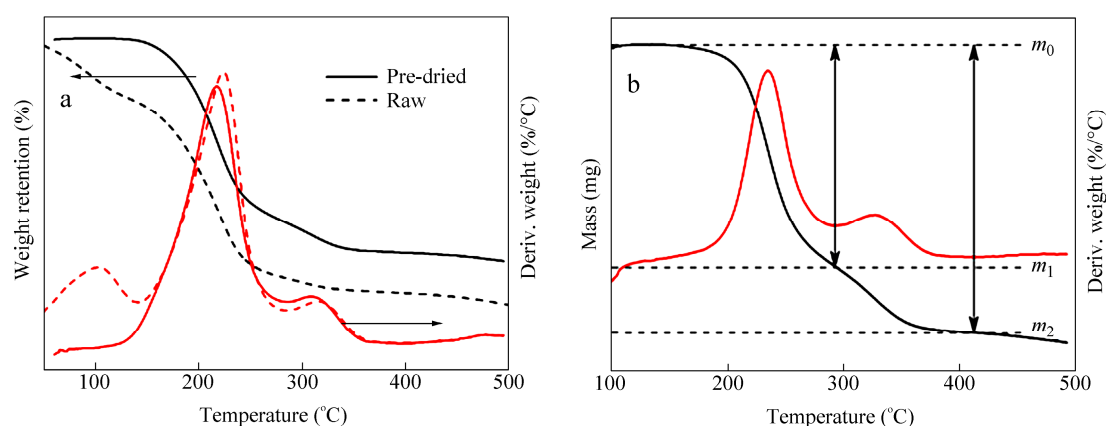


**Fig. 1** (a) TGA and DTG curves of raw PAA fibers after washing and drying in production (dash line) and the above PAA fibers pre-dried before the TGA measurement (solid line), (b) selection of the imidization end points of PI-200 as an example

The weight change caused by imidization was normalized according to the following formula:

$$w_1 = \frac{(m_0 - m_1)}{m_2} \times 100\% \quad (1)$$

$$w_2 = \frac{(m_0 - m_2)}{m_2} \times 100\%$$

where  $m$  stands for the sample mass and the subscripts, 1 and 2, represent the end points at about 300 °C and 400 °C, respectively. The ID was obtained using the following equation

$$I_1 = \frac{(W_1 - w_1)}{W_1} \times 100\% \quad (2)$$

$$I_2 = \frac{(W_2 - w_2)}{W_2} \times 100\%$$

where  $w$  and  $W$  are the normalized weight changes in PI and PAA samples, respectively.

### DSC Measurements of ID

Measurement of ID by DSC (Q2000, TA Instruments) was based on the endothermal peak which was caused by the evaporation of released water during imidization of the residual polyamic acid chains in PI fibers. Each sample was performed on DSC at a heating rate of 15 K·min<sup>-1</sup> from 60 °C to 400 °C under nitrogen atmosphere. The ID was calculated according to the following formula:

$$I = \frac{(A_{\text{PAA}} - A_{\text{PI}})}{A_{\text{PAA}}} \times 100\% \quad (3)$$

where  $A$  stands for the area of the endothermal peak. Identical to TGA measurement, the same problem also arises from the residual water in PAA fiber. As shown in Fig. 2(a), a strong peak at about 100 °C overlapped with that of imidization at 200 °C. Thus, a drying process was also necessary before DSC measurement as in TGA. The dried PAA fibers showed only one endothermal peak at 200 °C and the baseline kept stable until about 150 °C, implying the content of residual water in fiber were negligible. Another problem that should be considered is that the sample mass determines the peak area and continues to change during the drying process. Thus, the sample should be weighed immediately after regular measurement. The mass of the after-measured sample was used to evaluate the peak area.

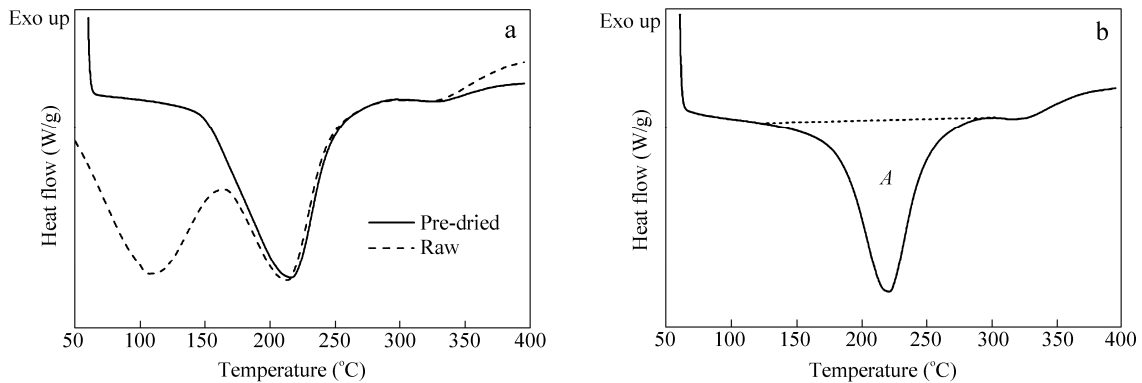


**Fig. 2** (a) DSC curves of raw PAA fibers after washing and drying in production (dash line) and the above PAA fibers pre-dried before the DSC measurement (solid line), (b) selection of the endothermal peak of PI-190 as an example

### FTIR Measurements of ID

Measurement of ID by FTIR (Bruker, Vertex 70) was based on the area or height of specific absorption bands which were assigned to imide groups on the IR spectra of PI fibers. FTIR measurements were performed at ambient temperature with an ATR accessory. Prior to measurement, all of the samples were dried under vacuum at 80 °C for 6 h. Five absorption bands at about 1850, 1780, 1520, 1350, and 730  $\text{cm}^{-1}$  were related to ID calculation<sup>[11, 12]</sup>, as shown in Fig. 3.

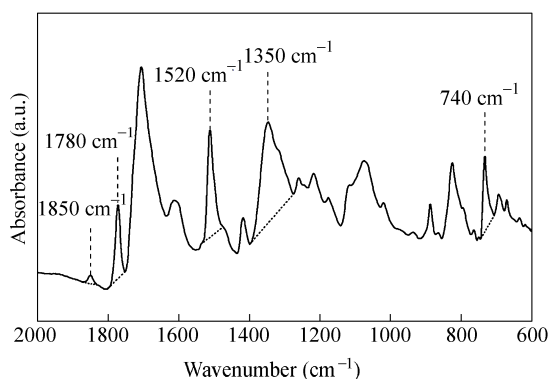


**Fig. 3** Absorption bands related to ID calculation and the baseline selection of PI-210 as an example

For each related absorption band, the area and height must be normalized by the 1520  $\text{cm}^{-1}$  band which is related to the stretching of benzene ring and acts as the inner standard. The absorption bands at 730 and 1780  $\text{cm}^{-1}$  are attributed to carbonyl groups in both imide and anhydride rings. In order to evaluate ID by these two bands, a correction must be made by subtracting the ingredients of anhydride from these two bands. The 1850  $\text{cm}^{-1}$  band, another absorption band of anhydride carbonyl groups, can be used to make this correction as in Eq. (4). As for 1350  $\text{cm}^{-1}$  band, it is assigned to C—N stretching of imide and can be used directly to estimate ID without a correction. For all related bands, the normalization and correction can be made as follows:

$$A = \frac{a - p \cdot a_{1850}}{a_{1520}} \quad (4)$$

where  $a$  stands for the band area or height, and  $p$  represents the correction factor. Regardless of band area or height, the value of  $p$  is 2.5 and 0.33 for the 1780 and 730  $\text{cm}^{-1}$  bands, respectively, and 0 for the 1350  $\text{cm}^{-1}$  band<sup>[11]</sup>. Finally, the ID was calculated as follows:

$$I = \frac{A}{A'} \times 100\% \quad (5)$$

where  $A'$  is the normalized and corrected area or height of a certain absorption band of “completely imidized” fibers, which were obtained by PAA fibers treated from room temperature to 400 °C in nitrogen.

## RESULTS AND DISCUSSION

### The Process of Thermal Imidization

Figure 4 shows the TGA-MS results of raw PAA fibers obtained from the production line. In Fig. 4(a), three maxima were found on the DTG curve at about 100 °C, 240 °C, and 330 °C, indicating a three-step weight loss in the entire measurement. From the signals of the mass spectrum detector, the first step of weight loss in the region 50 °C – 150 °C derives only from water ( $m/z = 18$ ). And the second weight loss in the region 150 °C – 300 °C also only originated from the evaporated water but released during imidization reaction. As for the last step of weight loss from 300 °C to 400 °C, it was in accordance with the increasing carbon dioxide signal ( $m/z = 44$ ) as shown in Fig. 4(d). As reported in literature, carbon dioxide may be produced from the degradation

of certain unreacted amic acid groups<sup>[23–26]</sup>. In our study, the production of carbon dioxide indicated the occurrence of degradation reactions.

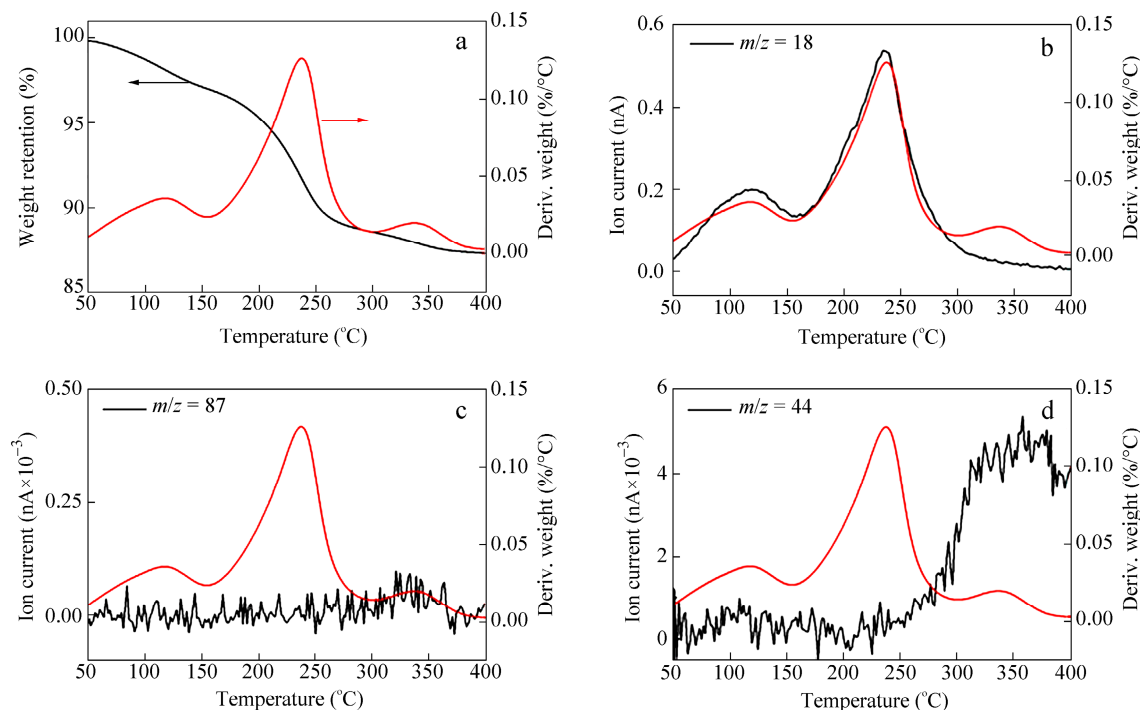


**Fig. 4** TGA-MS curves: (a) TGA and DTG curves of PAA fiber after washing and drying in production, (b) signal of water ( $m/z = 18$ ), (c) signal of DMAc ( $m/z = 87$ ) and (d) signal of carbon dioxide ( $m/z = 44$ )

Furthermore, the signal of DMAc ( $m/z = 87$ ) showed no evident increase during the whole measurement in Fig. 4(c). Unlike in literature<sup>[27]</sup>, this proves a negligible content of residual DMAc even in the PAA fibers just obtained from the production line. A consistent result was also obtained by the  $^1\text{H}$ -NMR spectra, as shown in Fig. 5(a). The content of DMAc was evaluated from the integration of the related peaks. The molar ratio between PAA and DMAc was about 1/0.0878 and the weight percent of DMAc is only about 1.86%. It is believed that the processes of washing by deionized water and the final drying in PAA fiber fabrication can eliminate the DMAc

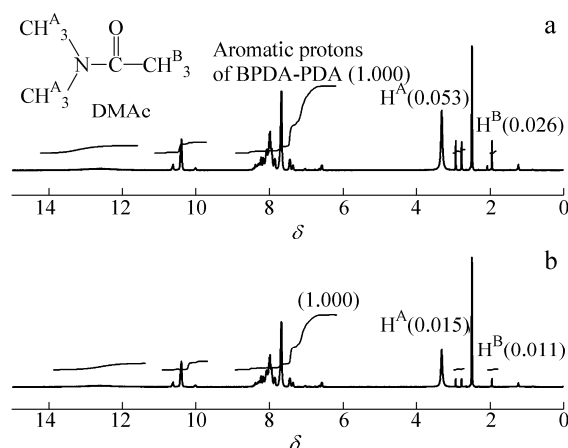


**Fig. 5**  $^1\text{H}$ -NMR spectra of (a) raw PAA fibers after washing and drying at 80 °C for 12 h in fabrication and (b) PAA fibers in (a) pre-dried before the TGA or DSC measurement

notably. In addition, as shown in Fig. 5(b), after PAA fiber experienced the drying process before TGA or DSC measurement, a further reduction of DMAc can be observed. The molar ratio between PAA and DMAc is only 1/0.0289 and the weight percent of DMAc is only 0.62%. So, DMAc in PAA fiber was really in a small amount. Its influence on the ID measurement is negligible.

### ID from TGA Measurement

According to the TGA-MS result discussed above, the imidization process is ended at about 300 °C and the succeeding weight loss is due to degradation of the fiber. So the end point chosen at about 300 °C seems more reasonable than that chosen at about 400 °C. The ID results calculated by these two end points are shown in Fig. 6 for comparison.

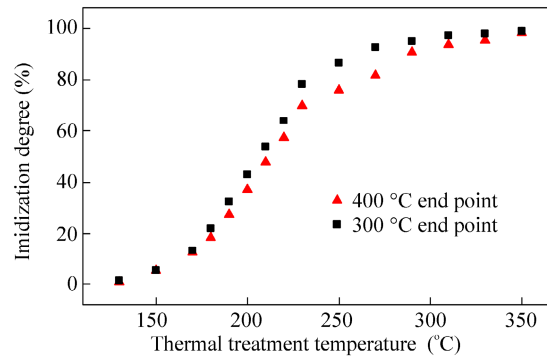


Fig. 6 Imidization degree of PI fibers calculated with different end points in TGA curves

When the treatment temperature was lower than 180 °C, the results calculated by the two end points were almost the same. For PI-130, PI-150, and PI-170, the IDs were 1.15%, 4.72%, and 11.94% for the 300 °C end point, and 0.57%, 4.60%, and 11.21% for the 400 °C end point, respectively. As the treatment temperature increased from 180 °C to 270 °C, the deviation between the two results increased. For PI-180, the IDs were 16.75% and 20.50% for the two end points, and the deviation was 3.76%. However, for PI-270, the IDs were 80.07% and 92.11%, and the deviation was as large as 12.04%. When the temperature exceeded 270 °C, this deviation between two results began to decrease. For example, as the treatment temperature increased from 270 °C to 350 °C, the IDs of the two end points changed to 98.14% and 99.02%, and the deviation was only 0.88%.

The difference in the above results was mainly caused by the weight loss of degradation  $\Delta w (= w_1 - w_2)$ . To study its influence on the ID results, we assumed that all PI and PAA samples had the same amount of degradation during TGA measurement, *i.e.*,  $\Delta w = \Delta W$ . Thus, the difference in ID,  $\Delta I$ , between two obtained results was predicted using Eq. (6).

$$\begin{aligned}
 \Delta I &= I_1 - I_2 = \left( \frac{W_1 - w_1}{W_1} - \frac{W_2 - w_2}{W_2} \right) \times 100\% \\
 &= \left[ \frac{W_1 - w_1}{W_1} - \frac{(W_1 + \Delta W) - (w_1 + \Delta w)}{W_1 + \Delta W} \right] \times 100\% \\
 &= \frac{\Delta W (W_1 - w_1)}{W_1 (W_1 + \Delta W)} \times 100\%
 \end{aligned} \tag{6}$$

As shown in Fig. 7, the determined ID differences were in good agreement with the calculated results when the temperature ranged from 130 °C to 270 °C. When the treatment temperature was higher than 270 °C, a significant deviation was observed because of thermal degradation in the fibers, which made  $\Delta w$  smaller than

$\Delta W$ . Therefore, the weight loss caused by thermal degradation was independent of the imidization process, and the weight loss was not needed to be considered during evaluating ID. Consequently, choosing the minimum of the DTG curve near 300 °C as the end point of imidization can really obtain more reasonable results than choosing 400 °C.

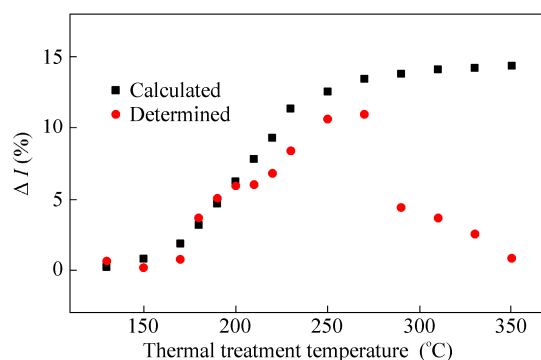


**Fig. 7** Calculated and determined differences of imidization degrees from TGA data

### ID from DSC Measurement

Figure 8 shows the IDs obtained by DSC with a comparison of TGA results (end point at 300 °C). Considering that the temperature was lower than 180 °C or higher than 270 °C, the results obtained by these two methods were nearly the same. However, when PAA fibers were treated at temperatures between 180 °C and 270 °C, the ID obtained by DSC exceeded that obtained by TGA. The differences in IDs between DSC and TGA,  $\Delta I$ , are plotted in Fig. 9, which shows a peak value at about 210 °C.

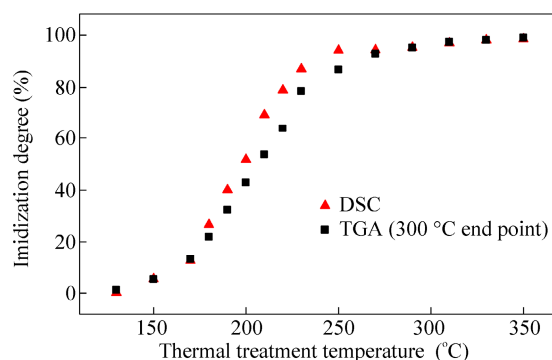


**Fig. 8** Imidization degrees of PI fibers calculated by DSC and TGA (300 °C end point)

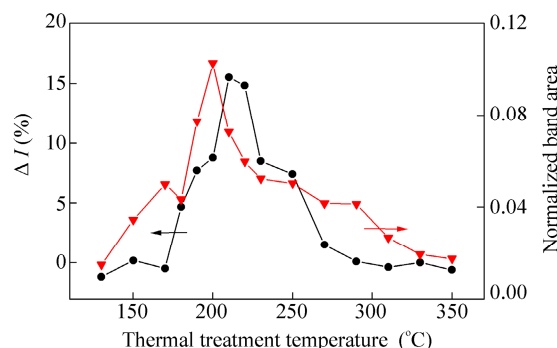


**Fig. 9** Differences of imidization degrees obtained by DSC and TGA methods, and the normalized area of 1850  $\text{cm}^{-1}$  absorption band by FTIR method

As reported in literature<sup>[28]</sup>, PAA may undergo considerable degradation to produce the anhydride and amine groups during treatment under low temperatures. However, with increasing temperature, the produced anhydride and amine groups may be converted into PAA again and finally cyclized into PI. In theory, this process exerts no influence on the sample mass but has a significant effect on heat flow. The re-formation of PAA is an exothermal reaction and will highly reduce the endothermal peak ( $A_{PI}$ ), which leads to higher ID values based on Eq. (3). The  $1850\text{ cm}^{-1}$  band on the FTIR spectrum corresponded to the vibration of carbonyl groups of anhydride. The normalized  $1850\text{ cm}^{-1}$  band areas were also plotted (Fig. 9), and a peak was observed at about  $200\text{ }^{\circ}\text{C}$  close to the peak temperature of  $210\text{ }^{\circ}\text{C}$  from the  $\Delta I-T$  curve. The above results proved that differences in IDs were related to the anhydride contents as expected.

Compared with TGA, the results evaluated by DSC demonstrated positive deviations, especially when the sample contained a large amount of anhydride. Besides, as the treatment temperature exceeded  $250\text{ }^{\circ}\text{C}$ , the endothermal peak of the samples became too low for precise measurements or identification. Thus, the ID of the samples at high treatment temperatures may be less reliable. Table 1 lists the normalized weight and endothermal peak area of the same batch of PAA fibers characterized by these two methods for five times. The data showed that all relative standard deviations were less than 1.5%, indicating good data reproducibility for both TGA and DSC.

**Table 1.** Calculated values of PAA fibers by TGA and DSC methods

| Samples                     | TGA       |           | DSC             |
|-----------------------------|-----------|-----------|-----------------|
|                             | $W_1$ (%) | $W_2$ (%) | $A_{PAA}$ (J/g) |
| PAA-1                       | 10.23     | 11.90     | 156.0           |
| PAA-2                       | 10.20     | 11.88     | 153.7           |
| PAA-3                       | 10.11     | 11.91     | 157.7           |
| PAA-4                       | 10.08     | 11.72     | 152.7           |
| PAA-5                       | 10.00     | 11.82     | 151.8           |
| Average                     | 10.12     | 11.84     | 154.4           |
| Standard deviation          | 0.08063   | 0.06895   | 2.172           |
| Relative standard deviation | 0.80%     | 0.58%     | 1.41%           |

### ID from FTIR Measurement

Three absorption bands at  $1780$ ,  $1350$ , and  $730\text{ cm}^{-1}$  were applied to calculate the ID, and the results were compared with the TGA data. Figure 10 shows the ID calculated by the  $730\text{ cm}^{-1}$  band and TGA results obtained with  $300\text{ }^{\circ}\text{C}$  as the end point. At lower treatment temperatures, the IDs from FTIR were less than 40% and showed an acceptable deviation from the TGA result. As the treatment temperature exceeded  $210\text{ }^{\circ}\text{C}$ , the IDs from the FTIR band exhibited very poor regularities caused by the dichroic effect, because the  $730\text{ cm}^{-1}$  band is highly sensitive to dichroic absorption of the IR beam<sup>[11]</sup>. As the treatment temperature increased, more imide chains were formed and oriented along with the same direction. Thus, the intensity of the absorption band was highly dependent on the experimental conditions. Slight changes in the measurement conditions resulted in notable data deviations. The IDs from the  $730\text{ cm}^{-1}$  band did not show a reliable result at high treatment temperatures.

The ID results calculated by the  $1780\text{ cm}^{-1}$  absorption band are shown in Fig. 11. These IDs were similar to the TGA plot, except for a notable deviation below  $200\text{ }^{\circ}\text{C}$ , because the  $1780\text{ cm}^{-1}$  band was highly influenced by the overlap of anhydride and carbonyl groups of imide. For samples treated at lower temperatures, the obtained band height and area may have substantial positive errors because the absorption band of imide was too low to determine. Although the height and area have been calibrated by the  $1850\text{ cm}^{-1}$  anhydride band<sup>[11]</sup>, the measured band may still include the contribution of the anhydride band.

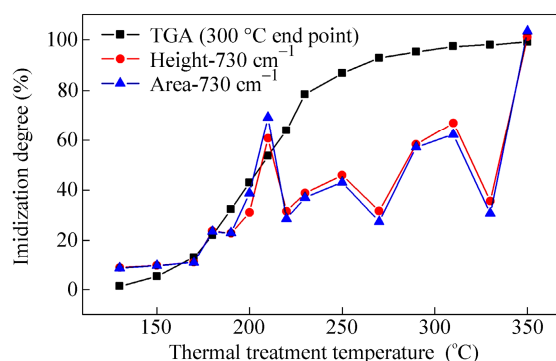


**Fig. 10** Imidization degrees of PI fibers calculated from  $730\text{ cm}^{-1}$  band and from TGA data (end point at  $300\text{ }^{\circ}\text{C}$ )

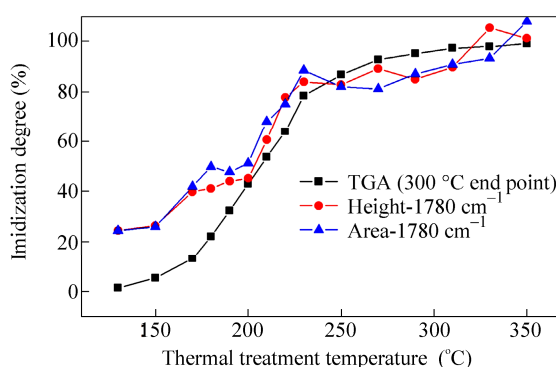


**Fig. 11** Imidization degrees of PI fibers calculated from  $1780\text{ cm}^{-1}$  band and from TGA (end point at  $300^{\circ}\text{C}$ ) data

Compared with the results calculated by the  $730\text{ cm}^{-1}$  and  $1780\text{ cm}^{-1}$  bands, the IDs calculated by the  $1350\text{ cm}^{-1}$  band exhibited better agreement with the TGA results, as shown in Fig. 12, because this band is rarely influenced by the dichroic effect<sup>[11, 12]</sup>. Generally, the results from the band area showed smaller deviations than those from the band height. As the treatment temperature increased from  $200\text{ }^{\circ}\text{C}$  to  $220\text{ }^{\circ}\text{C}$ , a remarkable jump in the ID from the band area was observed. This phenomenon was due to the error from measurements. As shown in Fig. 13, the band at  $1320\text{ cm}^{-1}$  from the C—OH stretching band of carboxylic group was more independent when the temperature was lower than  $200\text{ }^{\circ}\text{C}$ . As the temperature increased, this band gradually overlapped with the imide band at about  $1350\text{ cm}^{-1}$ . Thus, a considerably positive error was found while a baseline was decided. However, the band height was also influenced by this case but only to a certain degree.

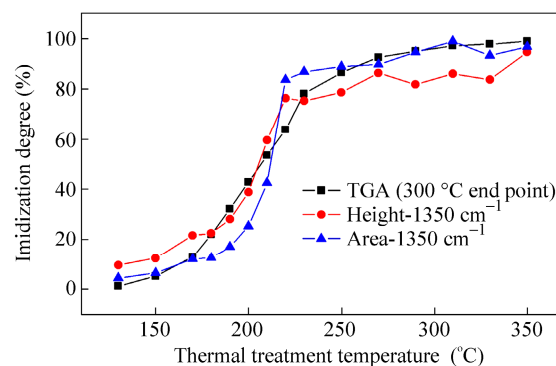


**Fig. 12** Imidization degrees of PI fibers calculated from  $1350\text{ cm}^{-1}$  band and from TGA data (end point at  $300\text{ }^{\circ}\text{C}$ )

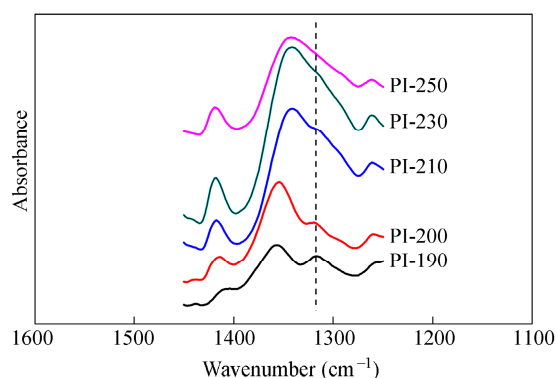


Fig. 13 1350  $\text{cm}^{-1}$  band overlaps with 1320  $\text{cm}^{-1}$  band at different treatment temperature

### Comparison of Three Methods

In brief, the ID obtained by the 1350  $\text{cm}^{-1}$  band area appeared more reasonable than that obtained by the other bands and showed better agreement with the TGA results. However, FTIR still exhibited lower regularities than TGA, which was possibly related to the following reasons. First, the ID estimated by FTIR needs a “completely imidized” sample as a standard, which may possess the highest normalized band area and height. The standard is often, but not always, the one with the highest treatment temperature or, as we did, selecting fibers of the same batch separately and treating with a much more severe conditions. In this case, the disadvantage is obvious; for the same sample, choosing different standards may yield different results. Second, compared with the PI film, which is easy to stably characterize, the FTIR spectra of the PI fiber exhibited relatively larger errors during measurements. Table 2 lists the peak area and height of the standard samples that were measured for five times. Compared with the data obtained by TGA and DSC in Table 1, FTIR measurements showed larger relative standard deviations, especially for the data from the 730  $\text{cm}^{-1}$  band.

Table 2. Calculated values based on “completely imidized” PI fibers by FTIR method

| Samples                     | Normalized band area |                       |                       | Normalized band height |                       |                       |
|-----------------------------|----------------------|-----------------------|-----------------------|------------------------|-----------------------|-----------------------|
|                             | 730 $\text{cm}^{-1}$ | 1350 $\text{cm}^{-1}$ | 1780 $\text{cm}^{-1}$ | 730 $\text{cm}^{-1}$   | 1350 $\text{cm}^{-1}$ | 1780 $\text{cm}^{-1}$ |
| 1                           | 1.248                | 3.061                 | 0.532                 | 1.753                  | 1.252                 | 0.617                 |
| 2                           | 1.367                | 3.259                 | 0.538                 | 1.807                  | 1.274                 | 0.618                 |
| 3                           | 1.499                | 3.260                 | 0.552                 | 2.001                  | 1.278                 | 0.631                 |
| 4                           | 1.176                | 3.040                 | 0.552                 | 1.590                  | 1.209                 | 0.637                 |
| 5                           | 1.014                | 2.870                 | 0.536                 | 1.395                  | 1.166                 | 0.632                 |
| Average                     | 1.261                | 3.098                 | 0.542                 | 1.709                  | 1.236                 | 0.627                 |
| Standard deviation          | 0.1652               | 0.1476                | 0.00837               | 0.2047                 | 0.04241               | 0.00781               |
| Relative standard deviation | 13.1%                | 4.77%                 | 1.54%                 | 12.0%                  | 3.43%                 | 1.25%                 |

### CONCLUSIONS

The PAA fibers of BPDA-PDA were prepared and treated from room temperature to different temperatures to obtain a series of PI fibers at different stages of imidization. The results are summarized as follows.

- The TGA-MS technique indicated three stages of weight loss: the first two stages of weight loss were due to the evaporation of residual water in fiber and release during imidization reaction, respectively; the third one resulted from the degradation reaction in the fiber. The DMAc solvent in PAA fiber is few and has negligible effect on the ID measurement.
- In TGA, two end points (at about 300  $^{\circ}\text{C}$  or 400  $^{\circ}\text{C}$ ) were chosen on the TGA curve to calculate the ID. Based on comparison and analysis, the temperature at which the DTG curve exhibited a minimum near 300  $^{\circ}\text{C}$  was more appropriate to be the end point of imidization. The ID evaluated by this end point was much more reliable than that obtained by the other methods.
- DSC yielded a higher ID in the treatment temperature region of 170 – 250  $^{\circ}\text{C}$ , because anhydride in fiber

- reduced the endothermal peak of imidization and led to a deviation to higher values.
- iv. For FTIR, only the data calculated from the  $1350\text{ cm}^{-1}$  band showed better regularities than those from the  $1780\text{ cm}^{-1}$  or  $730\text{ cm}^{-1}$  band, and they were in good agreement with the TGA results.
  - v. Among these three methods, the TGA method was the optimal technique to determine the ID of PI fibers.

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