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Influence of Curing Accelerators on the Imidization of Polyamic Acids and Properties of Polyimide Films

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Abstract: In order to lower the imidization temperature of polyamic acids (PAA), the catalytic activities of the curing agents p-hydroxybenzoic acid (PHA), quinoline (QL), benzimidazole (BI), benzotriazole (BTA), triethylamine (Et_3N) and 1, 8-diazabicyclo [5.4.0]undec-7-ene (DBU) were investigated in the process of thermal imidization of PAA. In addition, the effect of these various curing agents on the thermal stabilities and mechanical properties of the resultant polyimide (PI) films was determined. Quinoline was found to be an effective curing accelerator in the use of two-step method for synthesizing PI. Due to its moderate base strength, low steric crowding effect and moderate boiling point, quinoline could not only accelerate PAA to achieve imidization completely at 180 ℃, but also maintain the mechanical properties and thermal stability of the ordinary PI film. Any residual quinoline could be removed from PI films by heating at 250 ℃ for 4 h.

Key words: polyimide film; curing accelerator; quinoline; low temperature imidization

1 Introduction

Aromatic polyimides have attracted wide attention since they are used in many industrial fields because of their outstanding properties, such as thermal stability, chemical resistance, solvent resistance and excellent mechanical properties[1-4]. Essentially there are two methods used to obtain aromatic polyimides[5]: the one-pot solution synthesis and the two-step process. For method 1, polycondensation and cyclodehydration reactions are carried out without isolation of the precursor in solution at a temperature 140-180 ℃ for about 5 hours or more. It is used basically to obtain soluble and thermoplastic polyimides. For this reason, flexible diamines and dianhydrides are required as initiators. Method 2 is a two-step process which includes the synthesization of polyamic acid (PAA, polyimide precursor) from the condensation of diamines and dianhydride in an organic solvent and imidization of polyamic acid followed by casting or spin coating onto smooth plates and then ultimately a thermal treatment to complete the cyclodehydration reaction[6].

The disadvantages of method 1 are the limited choices of diamine and dianhydride and the long duration of the process, so that method 2 is more widespread. To fully imidize the PAA, it is necessary to treat it at an elevated temperature (up to 330 ℃). However, this high temperature treatment may lead to partial destruction of the polymer during the transformation of PAA to the final PI and the process is expensive. Most importantly, the components may be damaged when the polyimides are used in the electronics industry. For example, when polyimides are used as alignment films in colored liquid crystal displays with TFTs (thin film transistors), the color filters will be decolorized and the TFT will lose its functional ability if the PAAs cannot be imidized at temperatures lower than 200 ℃[7]. When polyimides are used in the areas of optics, the optical character of the polyimide film will deteriorate if the curing process cannot be accomplished at a lower temperature[8]. Therefore, lowering the imidization temperature in the two-step PI synthesis process is highly desirable.

Previous researchers have considered ways for lowering the imidization temperatures in the two-step synthesizing PI process. For example, Nelson *et al* observed the catalytic activity of benzimidazole (BI) on the imidization reactions, and found that BI could increase the degree of imidization at a relatively

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low temperature (80 ℃) [9]. Oba M investigated the degree of imidization of PAA in the presence of new additives such as p-hydroxyphenylacetic acid and p-hydroxybenzoic acid (PHA), and found that the PAA could completely imidize at 140-200 ℃ in the presence of curing accelerators[7]. Ding *et al* synthesized a series of new poly (amic acid) salt polymers and found that complete imidization of the poly (amic acid) tertiary amine salts can be achieved after being heated at 150 ℃ for 24 h[10]. Ahn *et al* reported that polyimide films imidized at a temperature of 200 ℃ when an organic base catalyst (1, 8-diazabicyclo [5.4.0] undec-7-ene, DBU) was employed. The degree of imidization increased to almost 100% after a thermal treatment at 200 ℃ for 40 min in the presence of DBU[11]. These additives are applicable for lowering the imidization temperature. However, most of these additives possess either a high melting point or strong base strength, which may impact the final properties of PI films[12]. Therefore, in this study, we focused our efforts on investigating the opportunity of using a new additive in the two-step process for accelerating the imidization of PAA.

In the previous studies, many researchers synthesized polyimide in single step polycondensation reaction in the presence of quinoline/isoquinoline, using m-cresol as a solvent at 160-200 ℃. These efforts employed quinoline (QL) /isoquinoline as an accelerator for the formation of PI in solution[13-16]. However, to date there have been few reports about the use of quinoline as a catalyst for lowering the curing temperature of PAA in the two-step process in spite of its potential industrial and academic values.

In the present work, we used QL as a catalyst in the two-step method for synthesizing polyimide and investigated its catalytic activity with PHA, BI, benzotriazole (BTA), triethylamine (Et_3N) and DBU. The basic information about these curing accelerators is shown in Table 1. To the best of our knowledge, this effort is the first for that quinoline has been used as a catalyst to lower the curing temperature of PAA in the two-step method for synthesizing polyimide. Since all of these additives can accelerate the curing process of PAA at lower temperature, we regard them as curing accelerators. To select the most suitable curing accelerator, the influence of curing accelerators on the mechanical properties and thermal stabilities of PI films was studied and compared in detail.

2 Experimental

2.1 Materials and reagents

3,3’,4,4’-biphenyltetracarboxylic dianhydride (BPDA), pyromellitic dianhydride (PMDA), 3,3’,4,4’-benzophenonetetracarboxylic dianhydride(BTDA) and 4,4’-oxydianiline(ODA) were purchased from Sinopharm Chemical Reagent Co., Ltd. BPDA, PMDA and BTDA were dried at 160 ℃ for 3 h prior to use. ODA was recrystallized from ethanol and dried under N_2 atmosphere before use. N-methyl-2-pyrrolidinone (NMP, Sinopharm Chemical Reagent Co., Ltd) was distilled under reduced pressure over phosphorous pentoxide. Other reagents, such as BI, QL, PHA, BTA, Et_3N and DBU, purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd, were used without further purification.

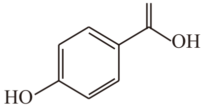
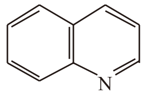
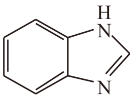
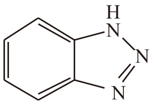
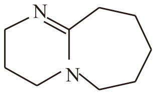
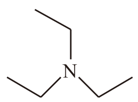
2.2 Preparation of PAA

Copoly(amic acid) was prepared from BPDA, PMDA, BTDA and ODA as follows: Nitrogen gas was introduced into a reaction flask fitted with a stirrer. ODA (20.02 g, 100 mmol) and NMP (300 g) were added. The mixture was stirred until ODA was dissolved. BTDA (7.90 g, 25 mmol), BPDA (16.79 g, 57 mmol) and PMDA (4.45 g 20 mmol) were added into the solution in several portions and an additional part of NMP (150 g) was added to adjust the solid content to 10 wt%. The solution was then stirred for 4 h at 8.0 ℃.

2.3 Imidization of PAA

The obtained viscous PAA solution was then

Table 1 Basic information of various curing accelerators

Curing accelerator	PHA	QL	BI	BTA	DBU	Et_3N
Melting point /℃	213-214	-16	171-174	98-99	-70	-115
Boiling point/℃	>400	238	360	204	261	90
Pk_b	–	9.15	8.20	(PH=5-6)	2.50	3.28
Chemical structure						

divided equally into 7 of 100 mL flasks fitted with stirrers. Curing accelerators (PHA, QL, BI, BTA, Et_3N, DBU) were added into the PAA solutions respectively. Two molecules of curing accelerator were added for one molecule of repeating structure unit of the PAA. One hour later, viscous and homogeneous PAA/curing accelerator solutions were obtained. Then the solutions were cast onto glass plates which were thermally baked in a vacuum oven at 80 ℃ for 1 h, 120 ℃ for 1 h, 150 ℃ for 1 h, 180 ℃ for 1 h, successively. In addition, the pure PAA solution was subjected to an additional heat treatment at 250 ℃ for 1 h and 330 ℃ for 1 h to get pure PI. All of the resultant films were stripped from the glass substrate through immersing in hot water. And then the films obtained from PAA/curing accelerator solutions would be heated at 60 ℃ for 48 h in vacuum oven to remove the residual solvents.

2.4 Measurements

Fourier transform infrared (FT-IR) spectra were measured on a SHIMADZU FTIR-8400s Fourier transform infrared spectrophotometer, the scanning range was 4 000-700 cm^{-1}. We determined the degree of imidization (ID) of dried PAA-PI films by a reported method[17,18], in which the aromatic band at 1 516 cm^{-1} was selected as the internal standard, and the band at 1 361cm^{-1} was selected for quantifying ID. ID was calculated using the following equation:

$$\mathrm{ID}\% = \frac{(S_{1361}/S_{1516})_T}{(S_{1361}/S_{1516})_{T=330}} \tag{1}$$

where *S* is the area of absorption band, *T* is the cured temperature of the films differently, *T*=330 is taken as the temperature (330 ℃) of completely imidized PI. Differential scanning calorimetry (DSC) data were recorded with a TA Q20 instrument under nitrogen atmosphere. The heating rates were 10 ℃/min. The ^{1}H NMR spectra were measured on a Bruker DRX300 (300-MHz) NMR spectrometer in concentrated sulfuric acid with hexamethyl disiloxane (HMDSO) as an internal standard. Thermogravimetric analysis (TGA) data were recorded with a Shimadzu DTG-60 thermal analysis system under nitrogen atmosphere at a heating rate of 20 ℃/min. Mechanical tensile properties were measured on a SUNS CMT-4254 electron omnipotence experimental machine (Shenzhen New Sans Corp., China) at room temperature with film specimens at the rate of 20 mm/min and the sample size was 12.5×80×0.025 mm, average values of more than five measurements were taken for each sample.

3 Results and discussion

3.1 Effect of various curing accelerators on the imidization of polyamic acids

In general, lowering the imidization temperature required a number of studies using many kinds of curing accelerators such as BI, PHA, DBU, Et_3N, *etc*. In the present study, the catalytic activities of these curing accelerators were compared and the use of QL and BTA in the two-step method was investigated for the first time.

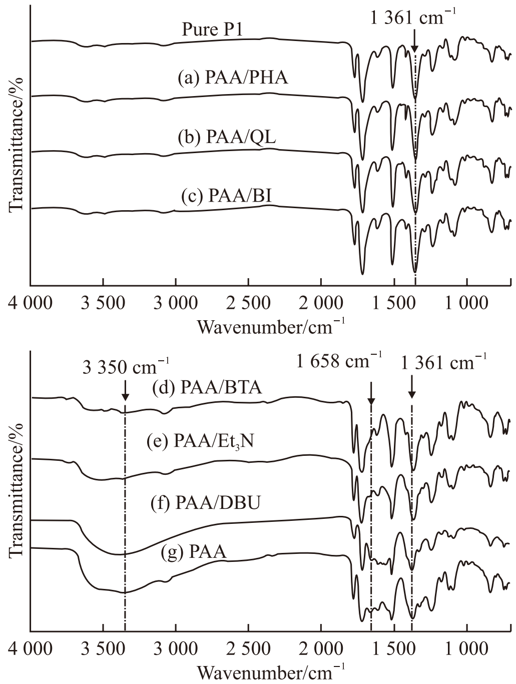


Fig.1 FT-IR spectra of pure PI, and samples derived from PAA and PAA/curing accelerators hybrids after heating treatment at 180 ℃

The imidization degree of the samples at each stage of curing was monitored using FT-IR. Fig.1 shows the FT-IR spectra of each film cured at 180 ℃. It can be seen from spectra a, b and c that the shape of the characteristic absorption peaks of imide ring (1 774, 1 720 and 1 361cm^{-1}) is considerably sharp and the characteristic absorption peaks of PAA(1 658 cm^{-1}, carbonyl in -COOH, and 3 350 cm^{-1} hydroxy in -COOH) have completely disappeared. At the same time, the characteristic absorption peaks for PAA still exist in spectra d, e, f, g. This can be explained by considering that higher degrees of imidization occurred in the films derived from PAA/PHA, PAA/QL and PAA/BI, suggesting that the PHA, QL and BI have more effective catalytic activities than DBU, Et_3N and BTA. Moreover, the spectra of the samples derived from PAA/PHA, PAA/QL and PAA/BI are similar to the spectrum of pure PI which may indicate that the samples derived from PAA/PHA, PAA/QL and PAA/BI have imidized completely after being cured at 180 ℃.

To validate this conclusion, all of the samples were subjected to a DSC heating scan (heating rate of 10 ℃/min, Fig.2) after the solvent was removed at 60 ℃. Beginning at about 150 ℃, all the samples derived from PAA/BTA, PAA/Et_3N and PAA/DBU show an apparent endothermic peak corresponding to the imidization reaction. However, with the exception of a slight endothermic peak from about 230 to 300 ℃, the samples derived from PAA/PHA, PAA/QL and PAA/BI do not show a strong endothermic peak until the temperature reached 350 ℃. These small peaks are probably due to the volatilization of residual solvents and small amounts of curing accelerators which is well accordant with the following TGA results (Fig.4). Therefore, we may conclude that the samples derived from PAA/PHA, PAA/QL and PAA/BI have achieved complete imidization after a 180 ℃ heating treatment.

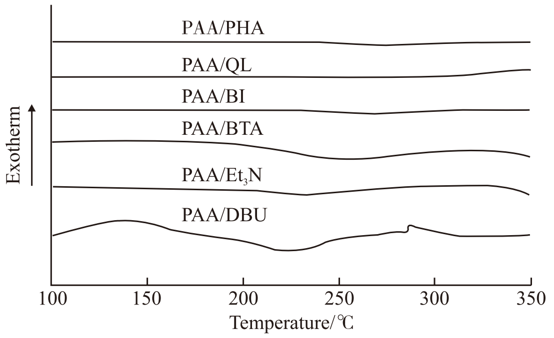


Fig.2 DSC results of samples derived from PAA/curing accelerators hybrids after heating treatment at 180 ℃ and solvent removal at 60 ℃

The degree of imidization (ID) of these samples cured after each stage was calculated according to Eq.(1) and the results are summarized in Fig.3. All the films containing curing accelerators possess a higher ID than the films containing no curing accelerator after each cure stage, which indicates that all of these additives show catalysis of imidization of the PAA. It is noteworthy that complete imidization can be achieved at 180 ℃ by the addition of BI, PHA or QL. The degree of imidization of samples derived from PAA/BTA, PAA/Et_3N and PAA/DBU was only 65.41%, 75.84% and 50.71%, respectively. Moreover, the ID of PAA/BI at 150°C was 97.93%. This may result from the efficient catalytic activity of BI which has been reported in a previous study[9]. Therefore, we classify the catalytic activities of these curing accelerators according to the results of Fig.3 as: BI> PHA> QL> Et_3N> BTA> DBU. Catalytic imidization appears to proceed by the nucleophilic attack of the catalysts on the PAA. Under acidic conditions, the oxygen atoms of the carbonyl groups are easier to protonize, which makes the carbon nuclei more susceptible. This facilitates nucleophilic attack by the catalysts which can accelerate the breakage of the C-O bonds. In other words, an acylium cation can be formed at a lower temperature and then the acylium cation reacts with the imide group to yield the final products (Scheme 1). For base catalysts, the catalytic activity depends on the base strength and chemical structure of the catalyst[19]. Although both Et_3N and DBU possess strong base strength they are poor catalysts which can be attributed to the inability to form the acylium cation because of the high steric crowding of the catalysts molecular structure. However, BI and QL are effective catalysts in spite of their moderate base strength, but the low steric crowding effect in these molecules improves their ability to form the acylium cation. The poor catalytic activity of BTA may result from its weak acidity.

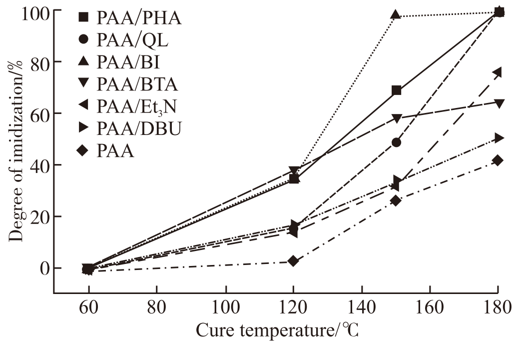
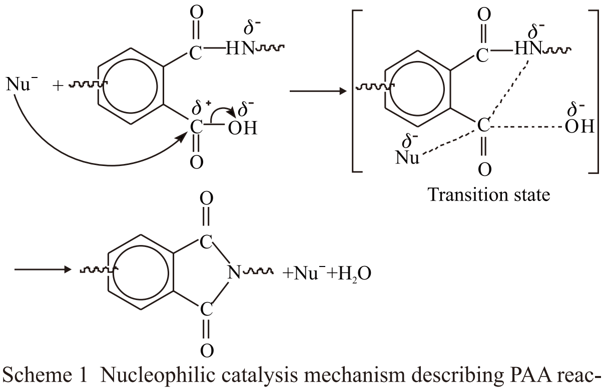


Fig.3 Degree of imidization after each cure stage of samples derived from PAA and PAA/curing accelerators hybrids



Scheme 1 Nucleophilic catalysis mechanism describing PAA reaction to PI in the presence of curing accelerators

3.2 Influence of curing accelerators on the mechanical properties of PI films

In order to objectively investigate the influence of curing accelerators on the mechanical properties, the samples which did not completely imidize at 180 ℃ were subjected to an additional thermal treatment (200

℃/1 h). The mechanical properties of each film are summarized in Table 2. For samples a and c, owing to the high boiling points of PHA and BI, too much of the additive remained in the final films and the mechanical properties were adversely affected. For samples e and f, owing to the strong base of DBU and Et_3N which may attack and weaken the molecular chain of the PI, the tensile strength and elongation at break were considerably low. By contrast the tensile strength and tensile modulus of sample b (154.20 MPa, 2.43 GPa) were close to the values for pure PI (169.92 MPa, 2.63 GPa). This may result from the moderate base strength and lower boiling point of QL. Sample b's elongation at break (11.16%) was higher than pure PI's (4.48%), which may be due to the residual solvents in films causing a plasticization effect[20] providing higher PI flexibility. These results suggest that QL can lower the imidization temperature by more than 100 ℃ and modestly improve the mechanical properties of PI.

Table 2 Mechanical properties of pure PI and PI/curing accelerators after heating treatment at 180 ℃/200 ℃ and solvent removal at 60 ℃

Sample	Curing accelerators	Cure temperature /℃	Tensile strength /MPa	Elongation to break /%	Tensile modulus /GPa
a	PHA	180	87.53	3.69	2.37
b	QL	180	154.20	10.16	2.43
c	BI	180	133.23	4.01	3.32
d	BTA	200	108.46	5.52	1.96
e	DBU	200	26.37	1.26	1.09
f	Et_3N	200	35.56	1.39	0.94
g	–	330	169.92	6.48	2.62

3.3 Influence of curing accelerators on the thermal stability of PI films

Because PI films may potentially be used as high performance heat-resistant engineering plastics, thermal stability is an important consideration for PI films. However, the thermal stabilities of PI films derived from PAA/curing accelerators were rarely investigated in the previous studies[8,9,11,21]. Fig.4 shows the TGA results of PI/curing accelerators hybrids after heating treatment at 180 ℃ and solvent removal at 60 ℃.

All the PI/curing accelerators hybrids show two thermal decompositions. The thermal decomposition beginning temperatures ($T_{d,\ st}$) of each sample are summarized in Table 3. For PI/Et_3N, PI/BTA and PI/DBU hybrids, the first thermal decomposition beginning temperatures ($T_{d,\ 1st}$) were 206.54, 200.17 and 185.19 ℃, respectively. These results may be due to the decomposition of the PAA which did not imidize at 180 ℃, and the volatilization of residual solvents and curing accelerators in the films. For PI/PHA, PI/QL and PI/BI hybrids, the $T_{d,\ 1st}$ was 227.58, 227.15 and 221.73 ℃ which may result from the volatilization of residual solvents and curing accelerators in films. The PI/PHA and PI/BI hybrids possess a lower second thermal decomposition beginning temperature ($T_{d,\ 2st}$), which may be due to the higher boiling point of PHA and BI. The weight loss percent of each sample is also summarized in Table 3, from which it can be seen that the PI/QL hybrid shows the lowest weight-loss percent (2.44%) during the first thermal decomposition process among all these PI/curing accelerators hybrids. It is assumed that the PI/QL hybrid possesses a higher degree of imidization than the PI/BTA, PI/Et_3N and PI/DBU hybrids in which less PAA is decomposed, meanwhile, the boiling point of QL is lower than that of PHA and BI which means that less QL remains in the films.

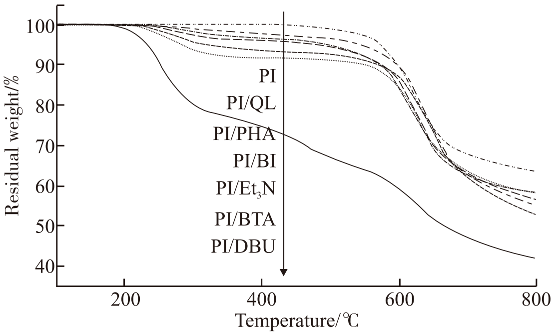


Fig.4 TGA thermograms of pure PI and PI/curing accelerators hybrids after heating treatment at 180 ℃ and solvent removal at 60 ℃

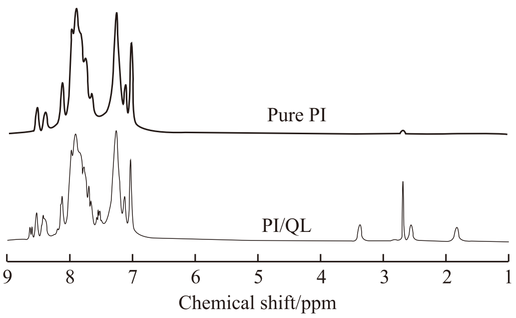


Fig.5 ^1H NMR spectra of pure polyimide cured at 330 ℃ and PI/QL hybrid cured at 180 ℃

Fig. 5 illustrates the ^1H NMR spectra of the pure polyimide heated at 330 ℃ and the PI/QL hybrid after heating treatment at 180 ℃ and solvent removal at 60 ℃. When compared with the pure PI heated at 330 ℃, the PI/QL hybrid shows new peaks at 3.4-0.8 ppm, 7.5 and 8.6 ppm. The chemical shifts of 7.5 and 8.6 ppm are in the range of the characteristic peaks of QL protons, which may result from the residual QL in the films. The peaks at 3.4-0.8 ppm correspond to the six protons of

Table 3 Thermal stability of pure PI and PI/curing accelerators hybrids after heating treatment at 180 ℃ and solvent removal at 60 ℃

PI/curing accelerators	PI/DBU	PI/BTA	PI/Et_3N	PI/BI	PI/PHA	PI/QL	PI
$T_{d,\ 1st}$/℃[a]	185.19	200.17	206.54	227.15	227.58	221.73	-
$T_{d,\ 2st}$/℃[b]	-	511.26	522.46	470.18	453.95	513.26	508.62
Weight loss-1/%[c]	25.53	8.33	6.43	4.12	3.49	2.44	-
Weight loss-2/%[d]	58.45	41.88	47.52	43.72	42.29	45.23	37.3

[a] The first thermal decomposition beginning temperature from TGA measurement.
[b] The second thermal decomposition beginning temperature from TGA measurement.
[c] Weight loss percent after the first thermal decomposition process from TGA measurement.
[d] Weight loss percent after the second thermal decomposition process from TGA measurement.

NMP, which indicates that the solvent is still present in the PI/QL hybrid after the solvent removal. This is in agreement with the TGA results as mentioned above. Meanwhile, the peaks of PI/QL hybrid at 8.5-7.0 ppm which correspond to the aromatic protons of PMDA, BPDA, BTDA and ODA are similar to those of pure PI. It can be deduced from this that PI/QL hybrid imidized completely after being heated at 180 ℃.

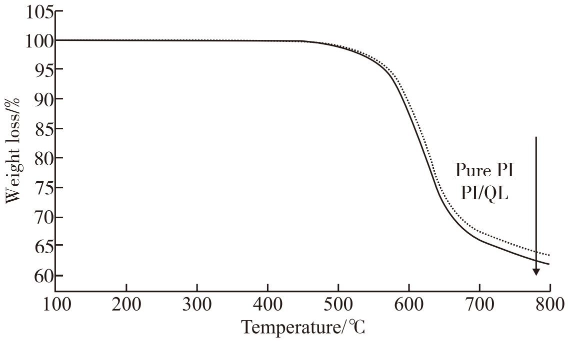


Fig.6 TGA thermograms of pure polyimide cured at 330 ℃ and PI/QL hybrid cured at 250 ℃

In order to remove the residual NMP and QL in PI films, the PI/QL hybrid was subjected to a further heat treatment at 250 ℃ for 4 h. The TGA curve for this sample is shown in Fig.6. It can be seen that the thermal decomposition beginning temperatures ($T_{d,st}$) and the 5% weight loss temperature ($T_{5\%}$) of PI/QL hybrid are almost the same as those of pure PI which may indicate that the residual NMP and QL were removed after the subsequent heating at 250 ℃ for 4 h.

4 Conclusions

Quinoline was found to be an effective curing accelerator that can lower the curing temperature of PAA in the two step synthesis of PI. Due to its moderate base strength and low steric crowding, the catalytic activity of quinoline is more effective than that of BTA, Et_3N and DBU, which makes it possible to achieve complete imidization of PAA at 180 ℃. In addition, the lower boiling point of quinoline facilitated its removal in comparison to BI and PHA and the moderate base strength of quinolone did not compromise the integrity of the PI chain in the sample films. These results indicate that the mechanical properties and thermal stability of PI films can be maintained during the low temperature curing process. Quinoline could be removed from PI films after being heated at 250 ℃ for 4 h. In addition, curing accelerators with strong base strength, such as Et_3N and DBU, adversely affected the mechanical properties of PI.

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